Engineering Informed by Research: Practical Applications for Stormwater Management Design and Education

A Dissertation

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by

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AUTHORIZATION TO SUBMIT DISSERTATION

This dissertation of Aimee S. Navickis-Brasch, submitted for the degree of Doctorate of Philosophy with a Major in Civil Engineering and titled "Engineering Informed by Research: Practical Applications for Stormwater Management Design and Education," has been reviewed in final form. Permission, as indicated by the signatures and dates below, is now granted to submit final copies to the College of Graduate Studies for approval.

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ABSTRACT

This three-paper dissertation attempts to address research gaps amongst stormwater management design and engineering education research. The common linkage between the three papers was to conduct research that meets academic standards and results in research findings that could be applied by practitioners to develop practical design and educational solutions to practical problems. In addition, each study incorporated a collaborative approach with different communities to assist with developing and conducting studies that result in recommendations for practical applications. The abstract for each paper is included in this section.

Chapter 2 Abstract

Paper Title: Culturally Relevant Engineering Education (CR-EE): Exploring the Impact on Native American Elementary Students

Native Americans were the original engineers in the United States; however, they are now the most underrepresented ethnic group in the engineering profession. Recommendations for increasing their representation start with the ability to deliver culturally relevant K12 engineering education. However, relevant research is limited to theoretical strategies that lack empirical evidence. This paper describes a case study that involves the collaborative development and implementation of culturally relevant engineering educational (CR-EE) curricular activities with a Tribal Community, Tribal Teachers, and University Researchers. The following research questions guided this study: *What factors engage students in the activity? How are Native American students' perceptions of engineering influenced by participating in a culturally relevant engineering design activity? How did the Tribal community and other group's involvement influence the students' responses?* The case study includes two separate 3-hour events with 122 elementary students from a public school located on a Tribal reservation. Both qualitative and quantitative analysis methods were employed to evaluate questionnaires completed by students after the first event and before and after the second event. The results indicate the students' were most engaged in learning about cultural traditions from the Tribal community, the "*building and testing*" portion of the engineering activity, and collaborative learning. After participating in the CR-EE activities students were more likely to perceive engineering as relevant to their Tribe and the degree of Tribal community involvement had a significant influence on the students' responses. Findings from this study provide the preliminary steps in understanding and validating theoretical strategies, which can support approaches for representing CR-EE in K12 classrooms that serve Native American students.

Chapter 3 Abstract

Paper Title: Identifying the Essential Properties of Biochar for Stormwater Treatment

The goal of this research was to provide a comprehensive evaluation of two different biochars for providing treatment of stormwater pollutants and to develop recommendations for the field application of a bioretention soil media (BSM) amended with biochar (BSM-Biochar mix). The pollutants include total suspended solids (TSS), dissolved Copper (Cu) and Zinc (Zn), Total Phosphorus (TP), Total Nitrogen (TN), Ammonia (NH_3), and Nitrate-

Nitrite (NO_3-NO_2). These goals were achieved by conducting an extensive literature search to identify a list of proposed Essential Properties. Specifically, those biochar physiochemical properties that indicate if a biochar is suitable for stormwater applications and may be useful in stormwater treatment design. Two biochars were selected for this study, one derived from wood (W) and the other from Kentucky blue grass feedstocks (KB), because they provide a range of Essential Properties to evaluate and compare. A laboratory study was conducted to evaluate the treatment performance of the biochars, which included: 1) jar testing and 2) flow through column testing. The results from the laboratory testing indicate: both biochars reduced TSS, Zn and Pb by >90%; the Cu removal efficiency was significantly higher for the W biochar (88% to 96%) compared to the KB biochar (47% to 78%); the NH_3 removal efficiency (56% to 77%) was statistically insignificant between the biochars; the NO_3-NO_2 effluent concentration was only significantly higher than the influent for the columns with a larger quantity of biochar in which the NO_3-NO_2 was reduced by 3% to 12%; and the W biochar reduced (24.2%) significantly more TN compared to the KB biochar (14%). Neither biochar reduced TP. The KB biochar leached TP (-150% to -341%) compared to the W biochar in which the effluent concentration was statistically insignificant compared to the influent concentration. The results from this study may have been influenced by the stormwater influent hardness concentration (277 mg/L total and 227 mg/L dissolved) as well as hydrophobic characteristics observed by the biochars. Results from the laboratory testing were used to refine the list of Essential Properties, which include organic carbon, hydrogen to organic carbon ratio, cation exchange capacity, total surface area, calcium, pH, phosphorus, and nitrogen.

Chapter 4 Abstract

Paper Title: Development a Specification for Bioretention Soil Media Amended with Biochar for Stormwater Treatment

The goal of this research was to develop a specification for a bioretention soil media (BSM) amended with biochar (BSM-Biochar) that provides treatment of regional pollutants of concern (POC) and could be used by practitioners to design and construct bioretention best management practices (BMPs) in the field. The POCs evaluated in this study include total suspended solids (TSS), copper (Cu), zinc (Zn), total phosphorus (TP), total nitrogen (TN), ammonia (NH_3), and nitrate-nitrite (NO_3-NO_2). This study is an extension of the previous study, where the key finding from the study detailed in Chapter 3 were combined with frequent citations from bioretention literature, and the Washington State Department of Ecology requirements for custom BSM to develop a draft BSM-Biochar specification. The two biochars selected for this study were developed from wood (W) and Kentucky blue grass (KB) source materials. A flow through column testing method was used to evaluate the treatment performance of the draft specifications using different BSM-Biochar mixes. The evaluation consisted of comparing the change in pollutant concentrations between influent and effluent samples as well as comparing changes in the pollutant concentrations in the BSM-Biochar mix from the top, middle, and base layer of the columns. The experimental design consisted of creating conditions that are representative of those expected in the field including using a natural stormwater solution to simulate rainfall conditions that are expected in eastern Washington where the study was conducted. The results from the water quality testing indicate: a reduction in TSS, Zn and Pb by >96% in all

BSM-Biochar mixes; a reduction of Cu and NH_3 concentration by >86%; NO_3-NO_2 leached from all the columns ranging from -53% to -48% and -48% to -33% for the columns that contained the KB and W biochars respectively. The columns that contained only the W biochar reduced TP concentrations by 21% to 26% compared the columns that contained only the KB biochar which leached TP by -77% to -110%. The trend in the treatment performances indicate that TP leaching from the KB columns declines over time while the efficacy of the W columns to reduce TP also declines over time. Results from the BSM-Biochar testing indicate that Ca and Mg cations are preferentially sorbed by the W biochar whereas Na cations are preferentially sorbed by the KB biochar. Overall, the majority of the heavy metals were retained in the top 6-inches of the BSM-Biochar mixes that contained both the W and KB biochar. The results of the column testing evaluation were used to confirm and refine the proposed specification and develop recommendations for field applications. A proposed BSM-Biochar specification is included in the Appendix.

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Thank you to Gonzaga University for providing me the laboratory space to conduct the bioretention-biochar research. Being able to conduct my research close to home (rather than driving 4-hours round trip to the UI Moscow campus everyday) provided me with valuable time to spend with my family. To the Technical Advisory Group who met with me monthly to discuss the bioretention-biochar research. Your insight and professional opinions were invaluable to developing a research study that resulted in practical solutions. I would especially like to thank Marcia Davis, Mike Peterson, Mark Maurer, Larry Schaffner, Mark Fuchs, Dave Duncan, and Renel Anderson for their support throughout the research project.

Lastly, thank you to the organizations that provided the funds to conduct this research including the National Science Foundation (NSF, Project# 1139657), the City of Spokane, and the University of Idaho.

DEDICATION

This dissertation is dedicated to my husband Thomas Brasch, our children Annabelle, William, and Samuel, and my parents, Ken and Cheryl Navickis. Their combined support, understanding, and patience were essential to the completion of this project.

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CHAPTER 1. DISSERTATION INTRODUCTION

OVERVIEW OF CHAPTER

This dissertation follows a three-paper format which includes multidisciplinary research in the fields of engineering education (Chapter 2) and stormwater best management practice (BMP) design (Chapters 3 and 4). This chapter is laid out as follows; first, I describe my motivation for the research approach. Next, the linkage between the three chapters (studies) is described followed by an overview of each of the three chapters.

PERSONAL MOTIVATION FOR DISSERTATION

During the first twenty years of my professional life, I was an engineering practitioner and part of my job responsibilities included developing stormwater management design manuals. This demanded that I be able to translate relevant stormwater research findings to a BMP design criterion that could be used by other practitioners to meet the requirements of the National Pollutant Discharge Elimination System (NPDES) permit for projects conducted for operators of municipal separate storm sewer systems (MS4s). For me this endeavor was often challenging because the information typically provided by the researchers in their report was either insufficient to guide the development of a constructible design or the variables required to apply the research findings were not readily available to practitioners during the design process. For example, stormwater practitioners size BMPs and conveyance systems using precipitation depth at the proposed project location and the contributing basin area. The precipitation depth is determined using historical rainfall records and the probability that a particular depth of rainfall will occur. However, research on climate change indicates that rainfall patterns are changing, which could affect the precipitation depths needed to develop a design that meets NPDES permit requirements. In an effort to understand how to apply these climate change findings, I met with a climate change researcher so that I could learn how to apply their work. At the of end of the meeting I asked the researcher to recommend ways in which I could apply their findings to the design of stormwater BMPs. Unfortunately, their response to me was, *'How would I know, I am the researcher and applying my research to design is for practitioners to figure out'*. I walked away from this meeting understanding that climate change was affecting rainfall patterns, but not understanding how to apply these research findings to estimate representative precipitation depths for design.

This disconnect between research and practice is well documented in many fields of study, including education and engineering (Cross, 1999; Muller, 2005; Viadero, 2003). One reason cited for this is the conflict between goals and expectations of researchers and practitioners (Buckley, Ferris, Bernardin, & Harvey, 1998; Muller, 2005). Recommendations for "bridging the gap" (Muller, 2005) include collaborative research that encourages practitioners and researchers to provide equal expertise and attention to the goals for research and the application of the research findings (Buckley et al., 1998). To address this disconnect, it is imperative that researchers expand their goals beyond pure scientific inquiry and learn to translate the new knowledge or information that results from the research study to a useable form that can be applied to solve actual problems (Viadero, 2003).

LINKAGE BETWEEN PAPERS

My experiences as a practitioner, in particular the challenges in applying research findings to design applications, inspired my interest to pursue a Ph.D. The tipping point to pursue a PhD emerged as a result of a very uninformative meeting with the climate change researcher that I previously described. During my state of frustration it occurred to me that with the combination of my design experience and a PhD, I could become a researcher with the skills needed to bridge the gap between research and practice. As such, the goal throughout my graduate research and presented in the studies in this dissertation was to conduct research that meets academic standards (i.e., those required to earn a PhD and publish papers) and which would results in research findings that could be applied by practitioners to develop practical solutions to practical problems.

In the first year of my doctoral program, I was given the opportunity to take part in a community based participatory research (CBPR) project. The CBPR methodology engages community partners to collaborate in the research to achieve shared goals (Christopher, 2005; Hacker; 2013; Thomas et al, 2011). Motives for employing a CBPR approach are to integrate the knowledge and experiences of the collaborators in the research process which leads to an increased understanding of the problem, to develop studies designed to evaluate solutions to the problem, and to provide collaborators with solutions that would meet their needs (Wilmesen et al, 2012). My experiences during that first year enabled me to gain an understanding of CBPR and identify ways to collaborate on research projects with a common interest.

The three research studies, described in Chapters 2, 3, and 4 of this dissertation, are connected in that they incorporated a collaborative approach that resulted in recommendations for practical applications. I do not employ a true, full CBPR approach in any of these research projects, since the partnerships among the collaborators was not equal with respect to the process and implementation of the studies. I did, however, conduct all my research in collaboration with a community and I believe the community and I always shared goals for the research, and their collaboration throughout the projects supported the development of projects that result in practical solutions to practical problems. In the context of my research, I define *community* as people who are most affected by the research findings. In the research studies described in this dissertation, the community varies depending on the study. A summary of each research study as well as the collaborative approach that was employed with the community, is included in the subsequent overview of each chapter.

CHAPTER 2 OVERVIEW

Chapter Title: Culturally Relevant Engineering Education (CR-EE): Exploring the Impact on Native American Elementary Students

Prologue

This research starts with a prologue, which describes the history of Tribal cultural activities that revolved around water. The prologue is presented in the form of a story to honor the Tribes tradition of sharing knowledge with the next generation in the form of oral stories. The content in the prologue is intended to help the reader understand why the research problem is important to the Tribal community. The story in the prologue describes three distinct time periods:

- *How it once was:* Native Americans were the first engineers who applied Indigenous Knowledge to design and build things that the Tribe needed such as fish weirs and fish smokers
- *How it is today:* Land use changes and western engineering practices degraded Tribal water bodies and stopped many cultural activities
- *The Tribes desire for the future:* restoring native land and water bodies is a priority so that salmon may return, and cultural traditions can be restored

Research Problem Statement and Importance of the Problem

Native Americans are the most underrepresented ethnic group in the engineering profession and their representation has remained unchanged for decades.

Once my research problem was identified, the next question I had to satisfy for myself, before continuing with this research was: *'why is this a problem that needs to be solved?'*. The answer I found that motivated me to pursue this research topic was:

- Increasing the representation of Native Americans in the engineering profession is essential for Tribal communities to restore native water bodies. This is because Native Americans are in a unique position of understanding the Tribes ways of knowing which combined with knowledge of Western engineering practices, could inform restoration practices that restore both water bodies and cultural traditions.

The recommendations I found in the literature for increasing the representation of Native Americans in engineering emphasize incorporating cultural relevance and engineering education into K12 classrooms. The challenge I faced with solving this research problem is that few studies focus on this combined approach and of those studies, most emphasize theoretical strategies that lack empirical evidence or strategies for implementation were often unclear or too complex to readily apply in a classroom setting.

Overview of Relevant Literature

The theoretical strategies from the literature were combined to define a conceptual pathway for increasing the representation of Native Americans' in the engineering profession. These strategies include:

- Incorporate culturally relevant engineering education (CR-EE) early in elementary school, before students lose interest in math and science
- Early exposure to CR-EE has the potential to motivate students to engage in learning STEM
- Students who are engaged in learning are more likely to develop the content knowledge necessary to prepare them for postsecondary STEM education

- Engineering education can demonstrate the relevance and benefit of engineering to the Tribal community, which may increase Native American students' interest in pursuing engineering careers

This research focuses on the initial steps of the conceptual pathway: incorporate culturally relevant engineering education (CR-EE) in elementary school and determine whether this approach motivates students to engage in learning STEM. Before starting the research study, I had to define CR-EE. This was done by first defining K12 engineering education and then culturally relevant education using on frequent citations in the literature. The two were combined to into a single approach, which is referred to as the CR-EE Curricular Framework.

Research Questions

The following research questions guided the experimental design of this study:

- What factors engaged students in the activity?
- How are Native American students'perceptions of engineering influenced by participating in the activity?
- How did the Tribal community and other groups involvement influenced the students' responses?

Research Community and Approach

The lesson plans for the CR-EE activities were developed using the curricular framework and in collaboration with community. For this study, the community is defined as the Tribal members and teachers from the Tribal school. They were selected as the community because they are most impacted by the research. Specifically:

- Tribal members are vested in improving STEM education for their youth and their representation in engineering. In addition, the Tribal members identify their cultural priorities for their youth to learn which becomes part of the lesson plans.
- Teachers at the Tribal school will be the one to implement the lesson plans in their class rooms

The Case Study and Methods

A case study methodology was selected which includes two three-hour events where students participated in two different engineering activities that were developed using the CR-EE curricular framework. Participants were all students enrolled in grades 3-6 at a school located on a Tribal Reservation. Both qualitative and quantitative methods were used to evaluate questionnaires completed by the students after the first event and before and after the second event. The questionnaire included three components: drawings, open ended questions, and multiple-choice questions.

Unique Contribution to K12 CR-EE Field

- I drew from theoretical strategies to define the conceptual pathway for increasing the representation of Native American's in engineering

- The findings from this study provided validation of the theoretical strategies that define the initial steps of the conceptual pathway for increasing the representation of Native American students in engineering and identify specific aspects of the activity which engaged the students
- A CR-EE curricular framework was developed from common citations in the literature and my experiences as an engineering practitioner. This framework presents a single approach for combining K12 engineering education and culturally relevant education.
- The framework is intended to provide teachers with guidance so they could use it to guide the development of engineering educational lessons that are aligned with K12 science standards and to identify where and how the culturally relevant elements can be integrated into the lesson

Paper Publication Plans

The paper has been submitted to the Journal of American Engineering Education and at the time this dissertation was published, the paper is under review by the editors for publication.

CHAPTER 3 OVERVIEW

Chapter Title: Identifing the Essential Properties of Biochar for Stormwater Treatment

Research Problem Statement

Biochar is a carbon rich material produced by thermally modifying a biomass (i.e., wood, grass, etc.) at elevated temperatures with little or no oxygen. The documented sorptive characteristics of biochar amendments in soils have attracted attention from the stormwater community because these characteristics are desirable for bioretention BMPs. However, the bulk of research conducted on biochar was not done using conditions that are representative of a bioretention BMP function. Specifically, evaluate the changes in the stormwater pollutant concentration before and after infiltrating through a bioretention soil media (BMS) amended with biochar. As such, there are many unanswered questions related to the application of biochar in BSM mixes such as the necessary quantity to add to the BSM, what types of biochar should be used for this application, and the effectiveness of the biochar for reducing stormwater pollutants.

Research Questions

The goal of this research is to provide a comprehensive evaluation of biochar for providing treatment of stormwater pollutants of concern (POC) and to develop recommendations for the field application of a biochar as an amendment in BSM (BSM-Biochar mix). These research goals were achieved by answering the following questions:

- Do the selected biochars leach nutrients (N and P) or metals (Cu, Zn, Pb, Ca, and Mg)?
- What is the short-term effectiveness of the selected biochars for reducing the POC pollutants?
- How does the hydraulic performance of the selected biochars change over the duration of testing?
- What is the estimated lifespan of the biochars for reducing pollutants?

- Which biochar physiochemical properties (or range of properties) appear to indicate the treatment performance for stormwater applications?

Overview of Relevant Literature

This study started with identifying the Essential Properties of biochar based on common citations in the literature. Essential Properties in the context of this study are biochar physiochemical properties, which appear to indicate whether a biochar is suitable for stormwater applications. In other words, properties, which may enhance or inhibit the effectiveness of the treatment mechanisms provided by the biochar or increase or decrease the likelihood of pollutant leaching. The biochar properties identified include organic carbon, hydrogen to organic carbon ratio, cation exchange capacity, calcium, phosphorus content, and nitrogen content.

Methodology

The research questions for this study were answered by conducting a two part laboratory study which included:

- <u>Jar Testing</u> – was conducted for the purpose of determing the time required for metals (copper, zinc, and lead) to sorb to biochar and the soprtion capacity of the biochar. Jar testing included placing varying masses of biochar in 250 mL jars with a stormwater solution on a shaker table for 1, 3, 6, 9, and 18-hours. Then the data was fit to Isotherms and the biochars metals sorption capacity was estimated.
- <u>Flow Through Column Testing</u> of two different types of biochar (wood and grass) was conducted using different quantities of each biochar (4- and 8-inch depth). The purpose of this testing was to estimating the quantity of biochar to add to the BSM. Testing included simulating 12 rainfall events averaging 20-hours each for a total of 18-inches of rainfall where the column area was equivalent to 2% of the contributing basin area. Rainfall events were simulated using natural stormwater and regulated pollutants of concern including: TSS, Cu, Zn, Pb, nutrients (phosphorus and nitrogen), and hardness. The treatment performance was analyzed by comparing the reduction in the pollutant concentration from the influent and effluent as well as comparing the effluent concentration from the 4- and 8-inch columns.

Research Community

The chapter 3 and 4 research community is the same: regulators, NPDES MS4 permittees, and designers. This community combined was referred to as the technical advisory group (TAG) and they met once a month for two hours to discuss the research status. I established the TAG for the purpose of receiving professional opinions from those who were most impacted by the research. For example, the designers will apply my research to design bioretention systems, regulatory are interested in verifying that new BMP will meet the NPDES permit requirements, and permittees are looking for cost effective BMP options that meet their NPDES permit requirements. By working together throughout the study, I was able to design and conduct an experiment that met multiple goals for all community members.

Unique Contribution to Bioretention BMP Research Field

- I defined a list of essential properties of biochar for stormwater applications using on common citations in the literature. Results from flow through column testing were used to confirm these properties.
- I evaulated and report the finding for the treatment performance of two biochars under conditions that are representative of those expected in the field
- I developed recommendations for the applying research findings to develop a BSM-Biochar specification

Paper Publication Plans

The paper will be submitted to the American Society of Civil Engineering (ASCE) Journal for publication.

CHAPTER 4 OVERVIEW

Chapter 4 Title: Development a Specification for Bioretention Soil Media Amended with Biochar for Stormwater Treatment

Research Problem Statement

While research indicates that biochar as an amendment in BSM (BSM-Biochar) is promising for achieving NPDES MS4 requirements for reducing regulated pollutants, no research has been identified that evaluated the treatment performance of BSM-Biochar under conditions that are representative of a bioretention BMP function. Specifically, evaluate the changes in the stormwater pollutant concentration before and after infiltrating through a BSM-biochar. While recent studies have focused on the evaluating biochar in stormwater applications, most studies occur in a laboratory using a synthetic stormwater solution made from deionized or tap water with limited pollutants. Since natural stormwater has a complex chemistry and consists of multiple types of pollutants, which can influence the media treatment performance, results from these studies may limit an understanding of biochars treatment performance in field applications. The research described in Chapter 3 provides the first known study that evaluated biochar in in flow through columns using natural stormwater however; this study only evaluated two different types of biochar. Thus, there are many unanswered questions related to the treatment performance of BSM-biochar mixes such as the optimum composition and configuration of the mix, the effectiveness of the mix for reducing stormwater pollutants, and whether the mix can achieve NPDES MS4 regulatory performance requirements for stormwater treatment.

Research Questions

The goal of this research is to develop a specification for a BSM amended with biochar (BSM-Biochar) that provides treatment of regulated pollutants of concern (POC) and can be used by practitioners to design and construction bioretention BMPs in the field. An additional goal of this research is to assess whether the BSM-Biochar specification could meet the Washington State Department of Ecology (Ecology) treatment performance criteria for reducing regulated POC. The research goals were achieved by answering the following questions:

1. Do the selected BSM-Biochar mixes leach nutrients (N and P) or metals (Cu, Zn, Pb, Ca, and Mg)?
2. What is the short-term effectiveness of the BSM-biochar mixes for reducing the POC?
3. How does the hydraulic performance of the BSM-biochar mixes change over the duration of testing?
4. How do the physiochemical properties of the BSM-biochar change over the testing period?
5. What is the estimated lifespan of the biochar for reducing pollutants when amended in a BSM mix?
6. Which biochar physiochemical properties (or range of properties) appear to indicate treatment performance for stormwater applications?

Overview of Relevant Literature

This study started with developing a specification for BSM-Biochar using common citations found in the literature and results from Chapter 3. The literature search focused on identifying the composition and configuration of a BSM-Biochar mix. Since no research was identified relevant to BSM-Biochar, the literature review focused on bioretention studies (without biochar) to identify the bioretention characteristics that appear to optimize treatment performance. Key findings from Chapter 3, specifically the recommended quantity of biochar for a BSM and the Essential Properties of biochar, were also used to develop the specification.

Methodology

The research questions for this study were answered by conducting Flow Through Column Testing on 8 different types of BSM-Biochar mixes using two different types of biochar (wood and grass). The recommendations for the BSM-Biochar specification were used to develop the composition and configuration of the BSM-Biochar mix in each column. The purpose of this testing was to evaluate the BSM-Biochar specification and identify the best mix based on the treatment performance. Testing included simulating 14 rainfall events averaging 24-hours each for a total of 20-inches of rainfall where the column area was equivalent to 2% of the contributing basin area. Rainfall events were simulated using natural stormwater and regulated pollutants of concern including: TSS, Cu, Zn, Pb, nutrients (phosphorus and nitrogen), and hardness. The treatment performance was analyzed by comparing the reduction in the pollutant concentration from the influent and effluent as well as comparing the effluent concentration from the columns. In addition, the changes in the physiochemical properties of the BSM-Biochar were also compared.

Research Community

The research community was the same as defined for Chapter 3.

Unique Contribution to Bioretention BMP Research Field

- I developed a proposed BSM-Biochar Specification using common citations in the literature and recommendation from Chapter 3. Results from flow through column testing were used to refine the specificiation.

- I evaulated and reported the finding for the treatment performance of BSM-Biochar mixes using a multicomponent, natural stormwater solution
- I conducted a comprehensive analysis on the BSM-Biochar physiochemical properties by comparing changes between baseline and post samples. These results provide an understanding an of pollutant treatment process that occurs in the BSM-Biochar mix.

Paper Publication Plans

The paper will be submitted to the American Society of Civil Engineering (ASCE) Journal for publication.

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CHAPTER 2. CULTURALLY RELEVANT ENGINEERING EDUCATION (CR-EE): EXPLORING THE IMPACT ON NATIVE AMERICAN ELEMENTARY STUDENTS

Submitted to the Journal of American Engineering Education

ABSTRACT

Native Americans were the original engineers in the United States; however, they are now the most underrepresented ethnic group in the engineering profession. Recommendations for increasing their representation start with the ability to deliver culturally relevant K12 engineering education. However, relevant research is limited to theoretical strategies that lack empirical evidence. This paper describes a case study that involves the collaborative development and implementation of culturally relevant engineering educational (CR-EE) curricular activities with a Tribal Community, Tribal Teachers, and University Researchers. The following research questions guided this study: *What factors engage students in the activity? How are Native American students' perceptions of engineering influenced by participating in a culturally relevant engineering design activity? How did the Tribal community and other group's involvement influence the students' responses?* The case study includes two separate 3-hour events with 122 elementary students from a public school located on a Tribal reservation. Both qualitative and quantitative analysis methods were employed to evaluate questionnaires completed by students after the first event and before and after the second event. The results indicate the students' were most engaged in learning about cultural traditions from the Tribal community, the "*building and testing*" portion of the engineering activity, and collaborative learning. After participating in the CR-EE activities students were more likely to perceive engineering as relevant to their Tribe and the degree of Tribal community involvement had a significant influence on the students' responses. Findings from this study provide the preliminary steps in understanding and validating theoretical strategies, which can support approaches for representing CR-EE in K12 classrooms that serve Native American students.

Keywords*:* engineering education, K-12, elementary school, underrepresentation, culturally relevant, Native American

PROLOGUE

Imagine a river so crowded with salmon that "…a person could cross a stream by walking across their backs" (Wilkinson, 1993, p. 184). This dramatic sight occurred once a year in the Pacific Northwest during historical salmon runs, as they migrated from the ocean to their natal rivers to spawn. For Tribal communities, who relied upon salmon as a primary source of subsistence, salmon and fishing for salmon were an integral part of life and cultural identity. The return of salmon to the place their ancestors had lived for thousands of years was a much-anticipated event; it was a time to celebrate the renewal of life and pass traditions to the next generation.

The entire community shared in the work of preparing for, harvesting, and preserving salmon. A significant part of the process was in the engineering of fish weirs and fish smokers by applying traditional knowledge. Fish weirs are a trap, designed to span across flowing rivers and obstruct fish passage. Most were constructed of rocks or wooden posts held together using sinew from plant fibers. Tribal members would capture the trapped salmon using nets and spears. The fish weirs were dismantled when enough salmon had been harvested to feed the Tribe for one year. Community efforts then shifted to fish smoking, a preservation technique used to cure fish using air movement, smoke and heat from a smoldering fire. Traditional smokers were constructed in the shape of a tipi or A-frame using lodge poles and sinew. These structures were designed to support wooden racks that contained large quantities of salmon high above the ground so that animals could not eat the salmon during the smoking process.

Traditional ways of life changed when Europeans arrived in the Pacific Northwest. The migration of westerners caused significant land use changes and sprawling construction. During this period, western engineering practices often attempted to dominate nature by diverting and controlling stream flows. Heavy metals from mining sites and sediment from bare land polluted water bodies and reduced fish habitat suitability. The cumulative impact on the natural environment was severe and still affects the beneficial uses of the water bodies throughout the Pacific Northwest.

The consequences were dire for Tribal communities. Dam construction prohibited fish migration resulting in the extirpation of most salmon runs. Without salmon, many cultural traditions ceased. Tribes believe salmon are a gift to them from their creator, in return, they believe they are accountable for the stewardship of the natural resources on their land. Today restoring native land and water bodies is a priority so that salmon may return, and cultural traditions can be restored.

As stated by Barry Dana, Chief if the Penobscot Nation, "Words may not describe what this restoration project means to me and my people.... We are inextricably tied to the… River through a cultural, physical, and spiritual relationship that runs in our veins as the original inhabitants of this region**....** It is time that we, as a society, begin to repay the River for all that she has provided for such a long time". (As cited in McCool, 2007, p. 544)

(Boyd, 2012; Haida-Legend, n.d..; Harrison, 2008; Idaho State Historical Society, 2004; Kimmerer, 2012; Lowan, 2009; McCool, 2007; Montgomery, 2004; National Research Council, 2006; Palmer, 2001; Pierotti, 2011; Pitzer, 1994; Ross, 2011; Wilkinson, 1993)

INTRODUCTION

Native Americans were the original engineers in the United States (National Research Council, 2006). Now they are the most underrepresented ethnic group in the engineering profession, accounting for just 0.3% of the work force (Finamore et al., 2013; Jarosz, 2003; National Science Board, 2014) and 0.4% of students earning engineering degrees (National Action Council for Minorities in Engineering, 2014). Despite consistent national reform efforts focused on improving STEM education (Jarosz, 2003; Kuenzi, 2008), these statistics have remained relatively consistent for the last three decades (National Science Board, 2014). Furthermore, trends in K12 math and science scores suggest this status will not be changing anytime soon. Results from national assessments indicate stagnant progress between 2005 and 2015 for Native American students in 4^{th} and 8^{th} grade (National Center for Education Statistics, 2015; National Science Board, 2014) and less than 20% of 12^{th} graders achieved college–ready bench marks on the 2017 American College Testing (American College Testing, 2017). Without these essential math and science skills, Native American students' pathways to engineering careers are limited before they finish high school (Cajete, 1988a; Cajete, 1988b; National Research Council, 2006).

The "one size fits all" model for K12 Science Technology Engineering and Math (STEM) education likely contributed to this deficit is the (Katehi, Pearson, & Feder, 2009; Lynch, 2001; National Center for Education Statistics, 2015). This model represents a primarily Western view of STEM education that neglects alternative ways of knowing (Klug, 2003; Lynch, 2001). Since Tribal or Indigenous Knowledge is often derived from cultural perspectives and values that are central to their identity (Faircloth, 2009), for Native American students what they learn in school is disconnected from what they learn at home. Compounded by non-native teachers teaching in the community who are unfamiliar with the Tribe or Native Americans unique ways of knowing, many students are forced to choose between their cultural identity and academic achievement (Aikenhead & Michell, 2011; Klug, 2003). Thus, STEM educational experiences are irrelevant to Native American student's lives, leaving many unmotivated to learn or confused as to how to combine these disparate world views (Aikenhead & Michell, 2011; Cajete, 1999; National Research Council, 2006).

Recommendations for making STEM education more accessible for Native American students focus on incorporating cultural relevance and engineering education into K12 classrooms (Aikenhead & Michell, 2011; Cajete, 1988a; Corbett, 2002; Jarosz, 2003; Pember, 2005). Few studies have focused on this combined approach, and of those, most emphasize theoretical strategies that lack empirical evidence or strategies for implementation are often unclear and complex. As a result, many questions remain unanswered including: how to develop culturally relevant engineering lessons, how to align lessons with academic standards, and will these strategies work to increase student engagement in learning and improve STEM literacy (Malcom-Piqueux & Malcom, 2013).

The goal of this study was to develop and implement culturally relevant engineering activities and report on their effectiveness. The following research questions guided this study: *What factors engage students in the activity? How are Native American students' perceptions of engineering influenced by participating in a culturally relevant engineering design activity? How did the Tribal community and other group's involvement influence the students' responses?*

WHAT IS INDIGENOUS KNOWLEDGE?

A basic understanding of Indigenous Knowledge is essential to develop cultural relevance in engineering education. Indigenous Knowledge is wisdom that developed through the direct and practical experiences of Tribal members. It is both dynamic and cumulative, building on the wisdom of generations which is passed down to the next generation orally in the form of a story that relates to everyday life (De Beer & Whitlock, 2009; Demmert, 2001). Indigenous Knowledge is rooted in and inseparable from tribal culture, values, language, and traditions (Cochran & Geller, 2002). It is a philosophy and value system for living that emphasizes respect, sharing, and sustainability (National Research Council, 2006). Science is also a component of Indigenous Knowledge, often referred to as Traditional Ecological Knowledge (TEK) (Pierotti, 2011). TEK is an understanding of a Tribe's aboriginal land and the relationship between the land and biological entities (Kimmerer, 2000; Pierotti, 2011) which developed from the observations of Tribal members made over many generations (De Beer & Whitlock, 2009). For example, Tribal members were able to predict when the salmon run would occur based on subtle changes they observed in animal behavior (Haida-Legend; Ojibwa, 2010).

LITERATURE REVIEW

The goal of culturally relevant education for Native American students is to make education more accessible to students by creating connections between the Indigenous Knowledge students learn at home with what they learn at school (Demmert, 2001; Holdren, Lander, & Varmus, 2010; Kana'iaupuni & Ledward, 2013; Lee, 2003; Lynch, 2001; Titone, Plummer, & Kielar, 2012). This involves designing learning environments, pedagogies, and instructional materials that support the Tribal community's unique ways of knowing and students' learning styles (Foster & Jordan, 2014; Titone et al., 2012). By building educational experiences around topics which students are already familiar with, they are more likely to retain new knowledge by making connections with prior knowledge (Castagno & Brayboy, 2008; Ladson-Billings, 1995; Lee, 2003; Nussbaum & Daggett, 2008). In other words, for Tribal students' cultural relevance is "…the cognitive glue that makes learning stick" (Kana'iaupuni & Ledward, 2013, p. 155).

Integrating cultural relevance into K12 classroom as a strategy for improving the quality of education for Native American students is not a new concept (Pewewardy & Hammer, 2003). Researchers that have explored the impact of these strategies reported a positive correlation between culturally relevant education and students' motivation to learn, academic achievement, and self-esteem (Brophy, 2013; Demmert, 2001; Titone et al., 2012). However, the bulk of the research focuses on non-STEM subjects, such as traditional languages and cultural programs (Demmert, 2001). Research on culturally relevant science represent a small but growing area especially in subjects related to ecology and environmental sciences (Demmert, 2001; Ngai & Koehn, 2010; Roehrig, Campbell, Dalbotten, & Varma, 2012). One reason is because the Western perspectives of these sciences are thought to be more culturally compatible with TEK (Cajete, 1999; Kimmerer, 2012).

Despite the documented benefits of culturally relevant education, the 2015 National Indian Education Study reported the majority of K12 schools fail to integrate these strategies in the classroom (National Center for Education Statistics, 2015). Common reasons cited by teachers include being unfamiliar with Tribal communities' ways of knowing, feeling unable to deviate from teaching anything except state standards (Nam, Roehrig, Kern, & Reynolds, 2012), and that strategies for implementation are complex and unclear (Lewthwaite, McMillan, Renaud, Hainnu, & MacDonald, 2010). These results are not surprising because that the majority of Native American students have non-native teachers trained to teach Western science (Klug, 2003). Furthermore, there is generally a lack of written resources on Indigenous Knowledge since tribal communities traditionally pass knowledge onto the next generation through oral storytelling (Pierotti, 2011). For culturally relevant education to be successfully integrated into K12 classrooms, it is essential for Tribal members to become actively involved in their youths' education (Titone et al., 2012).

A report from the Committee on K12 Engineering Education identified reasons why some ethnic groups are underrepresented in engineering, that "...curricular materials do not portray engineering in ways that seem likely to excite the interest of students from a variety of ethnic and cultural backgrounds" (Katehi et al., 2009). Considering that Western engineering practices have degraded Tribal water bodies, it is easy to imagine why a Native American student would not be excited about engineering if the primary examples of engineering in their community highlight Western achievements such as dams. The reality is that many Native American students perceive engineering as "…repressive and intrusive…" (Jarosz, 2003, p. 54) to their community (Cajete, 1999). Strategies for promoting engineering to Native American students focus on providing students with examples of their ancestors as natural engineers (Herrington, 2014; Jarosz, 2003) and highlighting the relevance and benefit of engineering as it relates to students and their community (1988b; Jarosz, 2003; Pember, 2005). One reason for these findings is that K12 engineering education demonstrates the practical application of science and math by providing a 'real world' context for solving problems (Schweingruber, Quinn, Keller, & Pearson, 2013).

CONCEPTUAL FRAMEWORK

Increasing the representation of Native Americans in the engineering profession begins with incorporating culturally relevant engineering education (CR-EE) early in elementary school, before students lose interest in math and science (Brickhouse, 2001). Early exposure to CR-EE has the potential to motivate students to engage in learning STEM (Brophy, 2013; Demmert, 2001; Herrington, 2014) and since engagement is essential for students to learn, they are more likely to develop the content knowledge necessary to prepare them for postsecondary STEM education (Brophy, 2013; Demmert, 2001; Herrington, 2014). Furthermore, engineering education can demonstrate the relevance and benefit of engineering to the Tribal community, which may increase Native American students' interest in pursuing engineering careers (Cajete, 1988b; Jarosz, 2003; Pember, 2005). Figure 2.1 provides illustration of the theoretical strategies described in this paper, combined to define a conceptual pathway for increasing Native American students' representation in engineering.

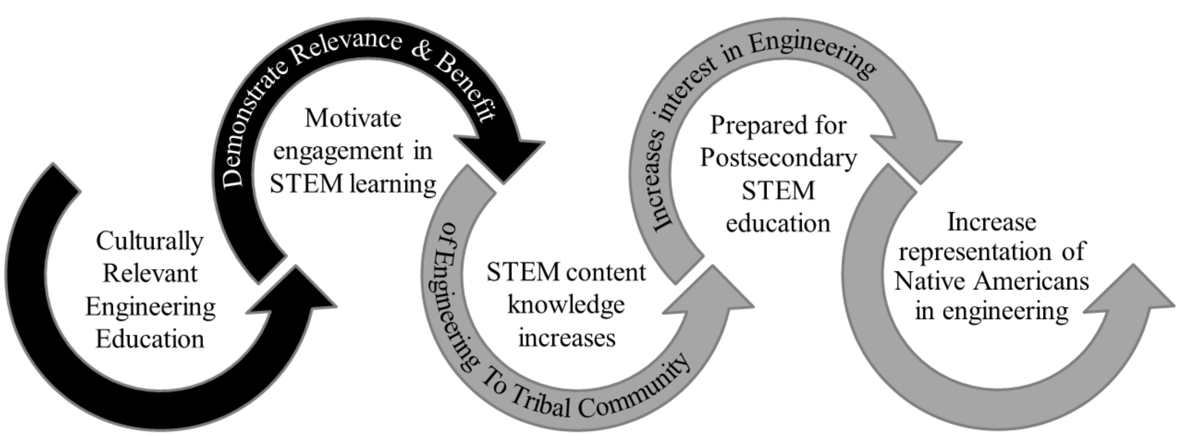


Figure 2.1 Conceptual Pathway for Increasing Native American Students Representation in Engineering

The initial steps of the conceptual framework are the focus of this study (in black), that is to define culturally relevant engineering education (CR-EE) and to develop an understanding of whether CR-EE activities engage Native American students in learning and if so identify what aspects of the activity engaged them. To achieve this goal, culturally relevant education and K12 engineering education are first defined. Then an integrated curricular framework is proposed (Figure 2.2), which combines the K12 engineering and culturally relevant education into a single approach. The focus of this section is to define culturally relevant education and K12 engineering education as well as the integrated framework which was used to guide curriculum development and implementation of the two activities presented in this case study.

Culturally Relevant Education

Culturally relevant education is defined as ways of knowing that are common to a community which can be integrated into the curriculum (Kanaʻiaupuni & Ledward, 2013). Based on common citations, four essential components emerge as characteristics of culturally relevant education: content, context, community involvement, and culturally relevant assessments (Demmert, 2005; Kana'iaupuni & Kawai'ae'a, 2008; López, Schram, & Heilig, 2013; Titone et al., 2012). These components are summarized in the top half of Table 2.1.

K12 Engineering Education

K12 engineering education is defined here by combining recommendations from the Committee on K12 Engineering Education (National Academy of Engineering and National Research Council of the National Academies, 2009), Moore et al. (2014), and core ideas from the NGSS (National Research Council, 2012). The result is four primary principles: introduction to engineers and engineering, the engineering design process, integrate math, science, and technology, and promote essential skills. These principals are defined in Table 2.1.

Table 2.1 Essential Components of Culturally Relevant Education and Principles of K12 Engineering Education

Essential Components of Culturally Relevant Education	
Essential Component	Description
Content	Curriculum is based on content that emphasizes Tribal history, language, and Indigenous Knowledge (Demmert, 2001; W. G. Demmert, 2005; Kana'iaupuni & Kawai'ae'a, 2008; National Research Council, 2006).
Community Involvement	Tribal involvement is essential to develop and implement the culturally relevant aspects of the curriculum and support the younger Tribal members' academic success (Jarosz, 2003; Pember, 2005; Roehrig et al., 2012).
Cultural Context	Pedagogy that supports traditional Tribal teaching styles includes learning by seeing and listening to older community members who share Tribal knowledge through stories, art, ritual, and practical examples (Cajete, 1988b; López et al., 2013).
Assessments	Assessment methods that are traditionally and culturally appropriate for students are essential (Demmert, 2005; Kana'iaupuni & Kawai'ae'a, 2008). Demmert (2015) recommends that assessments for Native American students be developed with consideration for the students' home language, the community's values, using vocabulary that the student understands, and that the questions be compatible with the students' background knowledge. Kana'iaupuni & Kawai'ae'a (2008) acknowledge it is difficult to gauge this for each student, instead they emphasize using diverse methods for assessing student learning.

Principles of K12 Engineering Education	
Principle	Description
Introduction to Engineers and Engineering	This principle focuses on teaching students about 1) what engineers do, 2) the different types of engineers, and the 3) educational pathway to becoming an engineer (Moore et al., 2014).
K12 Engineering Design Process	The engineering design process consists of multiple steps where students actively engage in developing solutions to open ended problems (National Academy of Engineering and National Research Council of the National Academies, 2009). It includes: Define the Challenge – Teachers clearly define the challenge or problem that students will solve and the design constraints that limit the extent of possible solutions. Develop Background Knowledge – Students learn the background knowledge and skills needed to complete the challenge. Design, Build, Test, and Evaluate - The iterative design phase includes brainstorming solutions, evaluating the pros and cons of possible solutions, and developing a design plan or drawing. Guided by their drawing, students build a prototype or model. Then they test their models to verify the design constraints are met. If the constraints are not met, students evaluate their design, identifying the weaknesses of their design, modifying the model to meet the constraints, and retest. The process is repeated until the design constraints are met.
Integrating Math, Science, and Technology	A central component of the engineering design process is that students develop informed engineering solutions by applying knowledge to solve problems as opposed to trial-and-error methods (Burghardt & Hacker, 2004). By integrating standards-based math, science, and technology concepts into the engineering lesson, this principle is achieved (Burghardt, 2013; Burghardt & Hacker, 2004; Katehi et al., 2009; Moore et al., 2014; National Research Council, 2012).
Promote Essential Skills	Essential skills are the values, attitudes, and abilities which are considered traits of an engineer. When students participate in K12 engineering they engage in thinking and reasoning in an engineering context (National Research Council, 2012) and have an opportunity to develop these skills which include: systems thinking, creativity, optimism, collaboration, communication, ethical considerations (Katehi et al., 2009), learning from failure, and reflective thinking (Moore et al., 2014).

Culturally Relevant Engineering Education (CR-EE) – Integrated Curricular Framework

Figure 2.2 provides an illustration of the "Integrated Culturally Relevant Engineering Education (CR-EE) Curriculum Framework" used in this study. The development of the CR-EE Framework was created based on a review of literature and the experiences of the primary author who has been a practicing engineer for more than 20-years. This section describes the theoretical concepts that guided the development of the framework and how the components integrate to create a curricular framework. The "Case Study" section of this paper provides an example of how the framework was applied to create the Fish Weir and Fish Smoker curricular activities.

The engineering principles, in particular the design process, was selected as the primary structure for the framework (shown in boxes in Figure 2.2). This is because the process of developing a design generally includes the same steps: define the challenge; develop background knowledge; design, build, test, and evaluate (Moore et al., 2014). In addition, the NGSS standards provide teachers with guidance for applying the engineering design process. Since most public school K12 teachers draw on the NGSS standards for curricular design and science content evaluation, aligning the structure of the CR-EE Framework with teaching standards will support teachers in developing lesson plans that will meet academic standards.

Engineering provides a natural catalyst for STEM integration, as such it has the potential to serve as a vehicle for integrating culturally relevant strategies into STEM curriculum. The arrows on Figure 2.2 indicate the suggested flow of cultural information within the framework. For example, the CR-EE Framework starts with an introduction to engineers and engineering. By integrating examples of Tribal engineering achievements into the lesson, students learn about the relevance and benefit of engineering in their community which is a suggested strategy for promoting engineering careers to Native American students (Cajete, 1988b; Jarosz, 2003; Pember, 2005).

Developing and implementing lessons that support CR-EE goals requires a partnership and collaboration between Tribal community members and teachers. Tribal community members can help to identify the lesson content and assist teachers in the development and implementation of cultural relevance for the lesson (Kanaʻiaupuni & Ledward, 2013). For the CR-EE curriculum, the engineering content is the focus of the engineering activity, ideally based on authentic Tribal engineering projects. Community members should provide the culturally relevant background knowledge in a traditional pedagogical style, such as oral storytelling and pictures to teach students the relevant history and needs of the community, so students may develop solutions that support those needs and values (Cajete, 1988b). This includes teaching students about the Indigenous Knowledge that is relevant to their engineering feats. Kern, et al. (2015) provides a detailed description regarding how the CR-EE Framework was applied to develop "The Fish Weir Engineering Challenge", an integrated culturally relevant K12 STEM lesson plan that aligns with the NGSS (Kern, Howard, Navickis-Brasch, Fiedler, & Cadwell, 2015). This is also the same lesson plan that was implemented in this case study.

Both the engineering design process and the essential skills that students learn when they engage in K12 engineering education are consistent with some traditional Native American ways of learning. Specifically, systems thinking is similar to the holistic approach of tribal teaching that starts with students learning about the "big picture" (Varma, 2009) and the interconnectedness of everything before they learn about the individual parts (Pierotti, 2011). The engineering design process also aligns with traditional ways of learning, that is oriented toward visual, holistic, and active orientations learning styles (Cajete, 1999); all of which are naturally embedded in the engineering design process (Felder & Silverman, 1988).

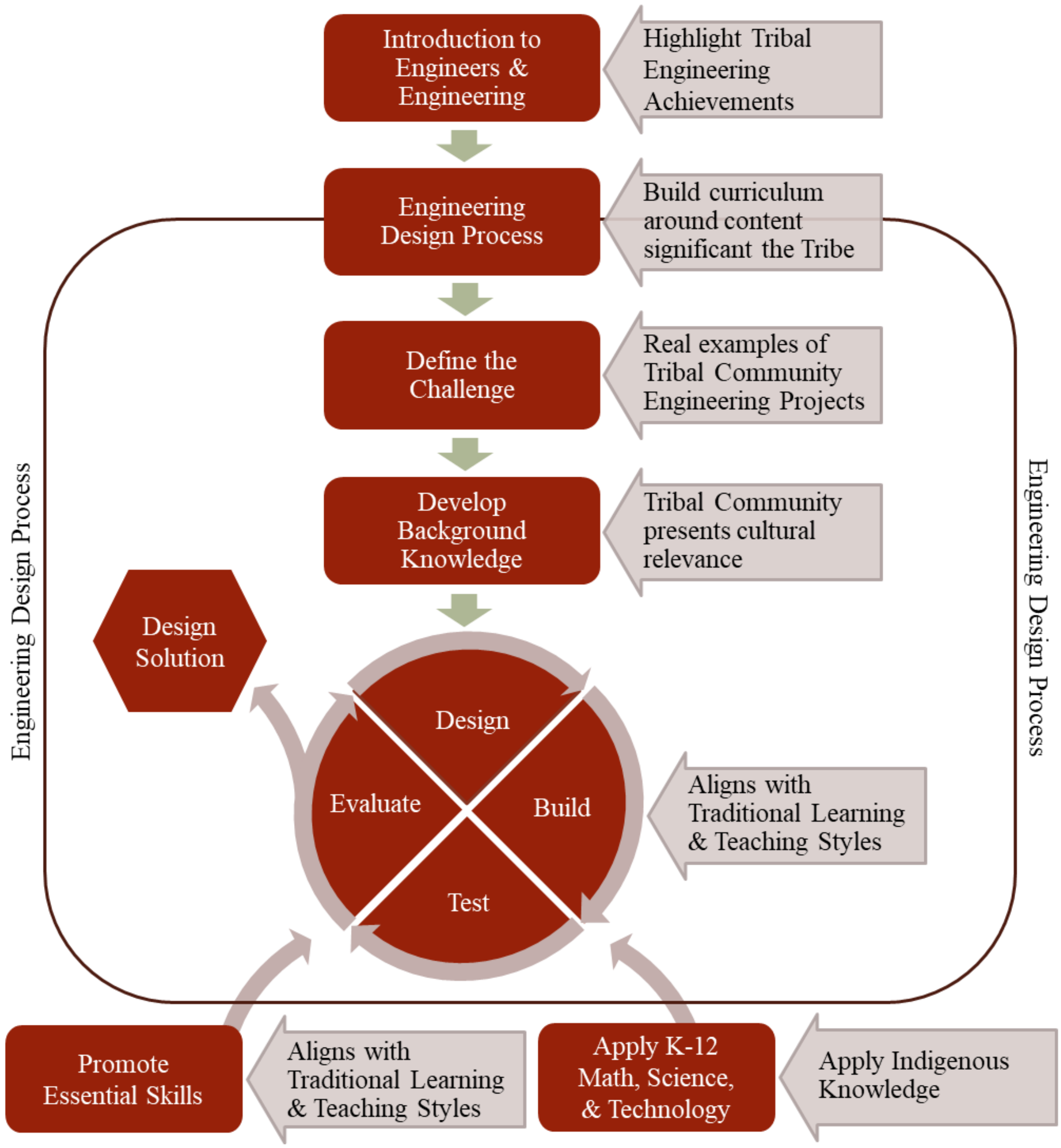


Figure 2.1 Culturally Relevant Engineering Education (CR-EE) Curricular Framework

THE CASE STUDY

This study is part of a three-year National Science Foundation (NSF) funded project titled "Back to the Earth (BTTE)." BTTE is a community-based youth educational partnership between the University of Idaho and two Tribal Communities located in the Pacific Northwest. The goal of the BTTE project is to develop and implement STEM activities for Tribal students in grades 3-6 that merges indigenous knowledge, place, and cultural and historical significance with western approaches.

A case study methodology was selected because the research questions seek to understand the experiences and perceptions of students who participated in a specific activity (Yin, 2017). The case study is bound by two three-hour events where students participated in two different engineering activities that were developed using the CR-EE curricular framework. The events occurred one year apart in the spring semesters during the regular school hours at a public elementary school located on a Tribal reservation. Participants were all 3-6 grade students enrolled in the school. Each year the event was divided into four three-hour work sessions where the activity was repeated for each session. The sessions included an average of 20 students who were all enrolled in the same class.

The first year (Fish Weir Activity) approximately 75 students from grades 3-6 participated. No pre-activity assessment was administered during year one and only 41 students completed the post assessment (Fish Weir-Post). The second year (Fish Smoker Activity) 81 students from grades 3-5 participated with 73 and 72 students completing the Fish Smoker-Pre and Fish Smoker-Post activity assessments respectively. Of the 75 students who participated in the fish weir activity during year one, 32 of them also participated in the year two fish smoker activity. The school's demographic records indicate that approximately 95% of the students are Native American with the remaining 5% mostly Caucasian and a smaller but an equal mix of Asian, Hispanic, and Black students. Table 2.2 provides a summary of the participant demographic information for those students who completed the assessments.

Table 2.2. Demographic Information for Students Who Completed Assessments

	Year 1 – Fish Weir	Year 2 – Fish Smoker		Students that Participated Year 1 & 2
Grade	Post	Pre	Post	
3rd	-	34	33	0
4th	7	18	18	14
5th	25	21	21	18
6th	9	-	-	0
Total	41	73	72	32

Curriculum Development

A working group composed of individuals from the University, Tribe, community school (teachers), and technical specialists from the Tribe's Fish and Wildlife department developed and implemented the curriculum. The University team consisted of one professor and two doctoral students from the Department of Curriculum and Instruction and two professors and one doctoral student from the Department of Civil Engineering. The Tribal Community consisted of approximately one dozen individuals who were members of the Tribe. The Community teachers consisted of 4-5 teachers who taught grades 3-6 at the public school only one of whom was Tribal. Two biologists from the Tribal Fish and Wildlife department were involved in the working group during year one and none were involved for year two. None of the University team or biologists were Native American.

Curriculum development occurred over the course of 3-4 meetings with approximately twelve members of the working group attending each meeting. Both years the process started with Tribal members selecting the focus of the engineering challenge which was fish weirs in year one (Kern et al., 2015) and fish smokers in year two. The

University defined the CR-EE curricular framework and collaborated with members of the working group to develop the curriculum content and create the curricular documents. The Tribe defined and provided the cultural aspects of the curriculum. The teachers recommended grade appropriate math and science content. All working group members had the opportunity to provide input on the draft activities, which were revised prior to implementation.

The University team facilitated the engineering activity which included providing formal instruction and assisting students during the activity. A teacher from each class helped their students as needed. None of the teachers provided formal instruction during the activity. The role of the biologist for the fish weir was to provide formal instruction regarding examples of tribal projects that were relevant to the curriculum. The Tribal members provided cultural background knowledge both years, but their involvement varied from the fish weir to the fish smoker. For the fish weir, approximately two to four Tribal members were present during the entire activity either formally presenting, observing, or assisting and interacting with students. For the fish smoker, up to two Tribal members were present during the activity, which included one member who provided a formal presentation at the beginning of the working session and then returned to work.

Curriculum Implementation - Two Culturally Relevant Engineering Activities

A summary of the curriculum implementation for year one and two is summarized in Table 2.3. Examples of the artifacts created by students during both years is shown in Figure 2.3.

Table 2.3 Summary of Curriculum Implementation for the Fish Weir and Fish Smoker Activities

Fish Weir – Year One	Fish Smoker – Year Two
Introduction to Engineers and Engineering	
Each year the engineering activity started with the University Team providing students with a short introduction to engineers and engineering. Students were told that engineers apply knowledge, such as math and science, to develop solutions that address human needs. The Tribal members told students that their ancestors were engineers who designed and built fish weirs and fish smokers.	
Define the Engineering Challenge – The University Team	
The challenge was to engineer a model fish weir that can fit into a stream activity table, stand upright while a pump circulates water through a stream, and catch all the toy fish. The University team showed the students the toy fish and demonstrated how the fish "swim" in the stream table and can be captured by a fish weir.	The challenge was to engineer a model fish smoker that can hold 24 toy fish without stacking or overlapping. In addition, the fish smoker needed to be designed so the fish can be cured evenly, and the distribution of heat should be similar (less than 2° Fahrenheit difference) at every location in the fish smoker. The heat source was a light bulb (no actual smoke was generated). The University team then showed the students the toy fish and demonstrated that a light bulb generates heat energy with a thermometer.
Students were asked to think about what types of things they might need to know to design their model. The University team brainstormed with the students until they were able to identify all items. For the fish weir, students needed to know the width of the fish (½-inch), the width of the stream (12-inches), and the depth of water in the stream (2-inches). For the fish smoker, students needed to know the toy fish length (3-inches) and width (½-inch) and the light bulb height (6-inches) and width (3-inches). Students were then encouraged to measure these to determine the remainder of their design constraints.	

<table>
<tr><th colspan="2">Background Knowledge – Tribal Community</th></tr>
<tr><td colspan="2">Both years, a Tribal member provided a 20-30-minute-long presentation about the Tribal history that is relevant to the activities. This included showing the students pictures of traditional fish weirs and fish smokers as well as discussion and stories like the Prologue section of this paper. Many of the traditional fish weir pictures students saw were taken on the Tribe's reservation, however most of the traditional fish smoker pictures were from other communities (both tribal and nontribal).</td></tr>
<tr><td>The presentation emphasized cultural activities associated with harvesting fish trapped by the fish weir and the Tribal member brought Tribal tools that their ancestors used to make spears and catch fish. Students learned Indigenous Knowledge that was relevant to engineering a fish weir. For example, "take only what you need" is Indigenous Knowledge that guided community's decisions for when to dismantle and remove the fish weir. Specifically, once Tribal members collected enough salmon to meet the food supply for a year, then the remaining salmon were allowed to "…go upstream and lay their eggs so that there would be a supply of fish for the future years" (Ross, 2011). The Tribal speaker described how their ancestors would apply this knowledge to their designs by constructing a hole in the fish weir. The presenter also brought a model size stream and fish weir they had built with figurines of Indians standing on top of the fish weir holding a bow and arrow.</td><td>The fish smoker presentation included stories about how their ancestors designed fish smokers to hold the fish high above the ground to prevent animals from eating them during the smoking process, a low flame fire is needed to dry the fish, and smoke from the fish smoker gives the fish flavor. Unlike the fish weir presentation during year one, no artifacts or models were included in the Tribes presentation.</td></tr>
<tr><th colspan="2">Background Knowledge – Biologist</th></tr>
<tr><td>The Biologists provided a 15-minute presentation that focused on the modern-day application of fish weirs on the reservation. Students learned that modern fish weirs made of metal and shaped like large square cages with gates are used to capture fish which are tagged and released. Tagged fish are tracked to study and manage fish populations on the reservation. The biologist also explained that fish become trapped in a fish weir is because they cannot swim backwards.</td><td>The biologist did not present during year two.</td></tr>
<tr><th colspan="2">Background Knowledge – University Team</th></tr>
<tr><td>The University Team did not provide any of the background knowledge during year one.</td><td>The University team provided a 15-minute presentation about fish smoker function related to heat and temperature. The students were told that heat energy from the fire preserves (or cooks) the fish and that temperature measures heat energy at a specific location.</td></tr>
<tr><th colspan="2">Engineering Design Process – The University Team</th></tr>
<tr><td colspan="2"><u>Design and Build</u> – Students worked in teams of 3 or 4 to develop their fish weir/fish smoker design, drawing multiple views and create a legend to identify the various parts. Next, teams were provided with kits that contained all the materials needed including various sizes of wood craft sticks, pipe cleaners, and toy fish. The student teams were then encouraged to follow their plans to construct their models.</td></tr>
<tr><td colspan="2"><u>Test and Evaluate</u> – Once the models were complete, the teams tested their models. The first-year students placed their fish weir model into the stream table and the second-year teams placed 24 fish on the fish smoker model and placed it near a light bulb and measured temperature. If the model failed to meet the design constraints, students were asked to collaboratively evaluate and rebuild their model. Most teams repeated the test and evaluate portion of the design process one to two times before their model met the design constraints.</td></tr>
</table>

Figure 2.3 Example of a Fish Weir (left) and Fish Smoker (right) Constructed by Students

METHODS

Given the study questions and literature recommending diverse approaches for culturally relevant assessments (Demmert, 2005), a mixed methods research design was selected for this study using both qualitative and quantitative data. The data sources collected during the activities were questionnaires. The questionnaires were designed to explore four main concepts: 1) the change in student's understanding of fish weir and fish smoker, 2) factors that engaged students in the activity, 3) student's perceptions of engineering, and 4) to understand how the Tribal community and other groups involvement influenced the student's response.

The questionnaires were two pages long with three components: drawings, open-ended questions, and multiple-choice questions. The drawing component included a large framed area for students to draw their fish weir/fish smoker with a smaller framed box for students to describe their drawing. Table 2.4 provides a summary of the questionnaire questions. The drawing instructions were modified slightly and expanded from year one to year two to improve the reseachers' ability to intepret the students responses. For example, the questionnaire for the fish weir only included open ended questions. Since some of the student responses were too general to easily answer the research questions, multiple choice questions were added to the fish smoker questionnaire to direct the students' responses. Students were not interviewed out of respect for the Tribal community's concerns regarding over researching the students.

Teachers administered the questionnaires during the normal school hours and students completed them individually a few days prior to (Fish Smoker-Pre) and a few days after the activity (Fish Weir-Post and Fish Smoker-Post). Teachers were asked to administer the questionnaire without coaching the students and only provide instructions regarding how to complete the questionnaire. If students expressed that they did not know what to draw or write, teachers were asked to respond with "use your best guess" or write "I don't know."

Qualitative Analysis

Student Drawings and Drawing Responses

A checklist was the primary instrument used to evaluate the drawings and drawing descriptions. The checklist was developed using a naturalistic approach (Patton, 2014) which included reviewing the questionnaires and developing a comprehensive list of items drawn or described that. The list was condensed to include items that appear frequently or relate to concepts from the fish weir or fish smoker activity. Then the data was grouped by like-items into codes which were organized into the four major categories: General Information, Fish Weir or Fish Smoker Characteristics, People, Influence, and Miscellaneous. The codes were evaluated as described in the Reliability section of this paper and a copy of the checklist is in the Appendix.

Open Ended Questions

Qualitative analysis for the open-ended questions followed these steps: 1) transcribing the data sources, 2) compiling the responses by data source and question, and 3) reviewing and coding the responses into themes. Prior to reviewing the data, a concept-driven approach was followed to identify the codes and categories (Gibbs, 2008). This approach was selected since the study questions focus on understanding what engaged the students, identify which groups influenced their responses, and their perceptions. After initial review of student data, an open coding approach was followed to refine the codes and themes based on unexpected student responses that emerged from the data (Gibbs, 2008). For data that fit into two or more codes, the data was assigned all applicable codes.

The two primary categories that emerged were student's perceptions and factors that motivated their engagement. Students' perceptions were separated into three sub-groups: 1) perceptions of themselves during the activity and the skills needed to become an engineer; 2) perceptions of the fish weir or fish smoker in relation to society, the tribe, and engineering; and 3) perception of the relevance or benefit of engineers or engineering to society or the Tribe. The engagement category included each of the components that make up the CR-EE curricular framework.

Quantitative Analysis

All multiple-choice responses were quantitatively analyzed using Likert scale and statistical analysis of significance. The frequency of student responses was measured using a three-point Likert scale (-1, disagree; 0, not sure; and 1, agree). The data was then analyzed to determine the mean score for each questionnaire question using simple descriptive statistics. Scores closer to 1 indicate a higher frequency of students who "agree" compared to scores closer to -1 which indicates a higher frequency of students who "disagree." The mean score for Fish Smoker-Pre and Fish Smoker-Post questions were compared to assess changes because students participated in the activity. A nonparametric Mann-Whitney U-test was used to assess the statistical significance of the pre and post responses. This test was selected because the analysis is not based on the assumption of normal distribution and the test assumes only an ordinal measurement of the data based on the ranking scale selected (Takona, 2002). The significance level is identified as follows: $p < 0.05$, statically significant; $0.05 > p < 0.10$, weakly significant; and $p \geq 0.10$, not statically significant. Table 2.6 provides a summary of the students' scores for each response along with the statistical significances of the findings.

Reliability

The first author of this paper, a Civil Engineering PhD candidate, initially developed the instruments used to evaluate the qualitative data. A peer debriefing process was followed to improve the validity of the instruments using two separate reviews by three different evaluators (Barber & Walczak, 2009). The evaluators were all from the Civil Engineering Departing including a graduate student and two professors. These three researchers separately coded 30% of the data. The researchers compared their results and where they did not have similar responses, they discussed their interpretation of the instruments until they mutually agreed on any modifications or additions to the codes, themes, and/or descriptions relative to the study content.

Table 2.4. Summary of Pre and Post Questionnaire Questions

Fish Weir-Post	1. Draw a picture of a fish weir. Describe how the fish weir is used. 2. The best part of the fish weir activity was.... 3. Name something new you learned from the fish weir activity. 4. What did you learn about engineering?
Fish Smoker-Pre	1. Draw a picture of a fish smoker. Please label your drawing. Describe what a fish smoker does and how it is used. 2. I think engineering is fun. (circle one): Disagree Not Sure Agree 3. I like learning about my culture. (circle one): Disagree Not Sure Agree 4. My tribe has been doing engineering for a long time. (circle one): Disagree Not Sure Agree
Fish Smoker-Post	1. Draw a picture of a fish smoker. Please label your drawing. Describe what a fish smoker does and how it is used. 2. The best part of the fish smoker activity was.... 3. Name something new that you learned during the fish smoker activity. 4. What did you learn about engineering? 5. I think engineering is fun. (circle one) Disagree Not Sure Agree 6. I liked learning about my tribe and culture by engineering (making) a fish smoker. (circle one) Disagree Not Sure Agree 7. My tribe has been doing engineering for a long time. (circle one) Disagree Not Sure Agree

RESULTS

This section is organized in the following order: Drawings and Drawing Responses, Open Ended Questions, and Multiple-Choice Questions. The Drawing and Drawing Responses were designed to answer the following research question: *How did the Tribal community and other groups influence the student responses?* The Open Ended and Multiple-Choice Questions were designed to answer the other two research questions: *What factors engaged students in the activity?* and *How are student's perceptions of engineering influenced by participating in the activity?*

Drawings and Drawing Responses

The results provided represent the drawing representations and responses most frequently provided by students'. A complete list of the percentage of students who provided representations for all codes is in the Appendix. Table 2.5 includes examples of student drawings and descriptions along with examples of how the drawings were coded.

General Information

The general information category focused on students understanding and perceptions of fish weirs and fish smokers. Students' understanding of the purpose of a fish weir (pre=10% to post=90.2%) and fish smoker (pre=38% to post=90%) increased through participation in the CR-EE activities. Students were assumed to understand the purpose of a fish weir or fish smoker if they drew or described a fish weir capturing fish or a fish smoker preserving or cooking fish, respectively. Students' prior knowledge of fish weirs was assessed by asking students to raise their hand if they knew what a fish weir was or had ever seen one before prior to the start of the year one fish weir activity. A common misconception about fish smokers depicted in the Pre-questionnaire was fish smoking a cigarette or a person smoking a fish like it was a cigarette (12.3%). This misconception was not present in the Fish Smoker-Post questionnaires.

More students provided written responses that they perceived the fish smoker as beneficial to their Tribe after the activity, (Fish Smoker-Pre=0% to Fish Smoker-Post =18%). The Fish Smoker-post results are similar to the fish weir post results (Fish Weir-Post=24%). "*When fish swim into the fish weir and people could eat them or tag them*, is an example of a student's response that was coded as perceiving fish weirs as beneficial to the Tribe.

Fish Weir/Fish Smoker Characteristics

The fish weir and fish smoker characteristics focused on the materials used for construction and the style (i.e., traditional, modern, or a combination of the two) described or drawn by the student. Fish weirs were represented in 90% of the Fish Weir-Post drawings, primarily in the traditional style their ancestors made (78.0%), followed by a significantly lower occurrence (2.4%) of the modern style that biologists use (i.e., cage, square shape, or with a gate) and a combination of the two (7.3%). Fish smokers were represented in 94% of the Fish Smoker-Post questionnaires, a significant increase from the 49% present in the Fish Smoker Pre-Questionnaires. The fish smoker characteristics depicted in the Fish Smoker Pre-Questionnaires were most commonly a camp fire under a metal grate or a rotisserie-style spit grille (36%) with a significantly lower occurrence of students depicting the traditional style that their ancestors made (5.5%). The occurrence of these styles switched in the Fish Smoker-Post responses, with most students depicting a traditional fish smoker (57%) compared to a campfire grill or rotisserie style (11%) and fewer students depicting a box shaped fish smoker (10%) that the students designed during the engineering activity specifically to go around the light bulb from the CR-EE activity.

The materials students used to build their models during the CR-EE activity, (Fish Weir-Post=22% and Fish Smoker-Post=12.5%), consistently appeared more often than the materials the Tribe described during their presentation, (Fish Weir-Post=15% and Fish Smoker-Post=6%). Other materials from the activity also appeared in the Fish Smoker-Post responses. For example, the University installed a paper clip in the shape of a hook into the mouth of the toy fish, so students could create a fish smoker design that would accommodate either a fish lying or hanging. Many students depicted a fish with this hook in their mouth in their drawings (Fish Smoker-Post=36%).

People

The occurrence of people declined significantly from the Fish Weir-Post (32%), to Fish Smoker-Pre (18%), with the lowest occurrence documented in the Fish Smoker-Post (7%). Most of the people in the Fish Weir-Post (25%) were standing on a fish weir harvesting fish using Tribal tools (e.g., bows and arrows, spears, nets, and baskets) and a few students identified their person as Native Americans (10%). Students identified themselves in some Fish Smoker-Pre-drawings (10%) as well as Native Americans (1%). In comparison, the Fish Smoker-Post responses included slightly fewer self-portraits (7%) but the occurrences of Native Americans (1%) was consistent. Native Americans were identified when students labeled the person "*Indian*" or because they were wearing Native American clothing.

Miscellaneous Items

Miscellaneous items included those depicted in the drawing that did not fit into other categories. Fish were included in the majority of all three questionnaires (Fish Weir-Post=78%, Fish Smoker-Pre=58%, and Fish Smoker-Post=94%). Background scenery (i.e., water, landscape, or the sky) was most commonly depicted in the Fish Weir-Post (68%), followed by the Fish Smoker-Pre (25%), and a few in the Fish Smoker-Post (10%). Representations of fire, smoke, or chopped wood were only included in the fish smoker questionnaires (Fish Smoker-Pre=43% to Fish Smoker-Post=71%). Other types of objects depicted on the fish smoker questionnaires, (Fish Smoker-Pre=21% to Fish Smoker-Post=7%), included boats, tent, tables, an axe, fishing poles, and cooking instruments.

Influence

The influence category focused on identifying items in the student's responses that were specific to the Tribes presentation compared to the western influence of the Biologist or University contributions during the activity. The most significant influence observed in the Fish Weir-Post drawings was the Tribe (90%) followed by the University (46%) and the Biologist (27%). The Tribal influence was documented when the students included representations of items that were from the Tribe's presentation including: Indigenous Knowledge (i.e., take only what you need); native objects used to harvest fish (i.e., spears, bows and arrows, baskets, and nets); a hole in the fish weir, and activities associated with harvesting fish after they were trapped by the fish weir. The University influence was documented when students included elements from the engineering activity including drawing details (i.e., dimension, legend, and cross- sectional views), and references to the design constraints (i.e., catch all the fish) and design process (i.e., design, build, test, evaluate). The Biologist influence was documented when students indicated that the purpose of a fish weir was to monitor fish populations, the fish weir was represented as a modern style, or when students described how the fish weir functions (i.e., fish cannot swim backward).

Items specific to both the Tribe and University were observed in the Fish Smoker-Post. The influence of these two groups was similar with items from the University (59%) represented nearly as often as items from the Tribe (51%). The University influence was documented when students included elements from the engineering activity including: drawing details, any part of the engineering design process, references to the design constraints (i.e., light bulb, 24 fish, catch all fish, cook fish evenly), and/or items used to test and evaluate the fish smoker (temperature, thermometer, or heat energy). The Tribal influence was documented when students included items from their background presentation: smoke gives fish flavor, putting fish up high so animals don't eat them, Native American objects associated with fish smoker, and using a low fire to dry fish. In the Fish Smoker-Post questionnaires, few Native objects were observed (1%) and no references to Indigenous Knowledge were included.

Open Ended Questions

The results from the open ended questionss are organized by the order inwhich they appeared on the questionaire. Table 2.6 provides a summary of highest percentage of student responses to each question along with examplesof student responses. A complete list of the codes along with the definitions and the percentage of all student's responses is located in the Appendix.

Q2. The best part of the fish weir/fish smoker activity was…: Most students indicated that the best part of the fish weir activity was building (56%) and testing (37%) their model with the remainder of the responses split between multiple categories. For the fish smoker, building (54%) and collaboration (28%) were the top two responses.

Q3. Name something new you learned from the fish weir or fish smoker activity: Student responses indicate the 'something' new that they learned both years was from the Tribes background presentation (Fish Weir-Post=51% and Fish Smoker-Post=49%).

Q4. What did you learn about engineering? Most student responses related to their perceptions about the CR-EE activity or engineering. This was different than responses to the other questions which emphasized specific aspects of the CR-EE activity. In the Fish Weir-Post, many students described themselves as being challenged by the activity (20%), while others described positive perceptions of their engineering identity (17%) with responses focusing on being capable, interested, or having fun during the activity. Another prominent Fish Weir-Post response focused on the essential skill learning from failure (22%). In Fish Smoker-Post, the most prominent response related to positive perceptions of an engineering identity (27%).

Responses Related Perceptions

Understanding student perceptions is critical to answer the research questions. However, except for Q4, less than 10% of students' responses related to perceptions. The only negative perceptions students provided focused on the engineering activity. For example, when asked "*what did you learn about engineering,*" the following response was coded into this category "*not that much.*" Students only provided responses related to their perceptions of the relevance and benefit of engineering in the Fish Weir-Post questions which were either neutral or positive with respect to society (less than 6%) and very few (less than 2%) indicated they perceived a connection between engineering and the Tribe. Similarly, the students who provided responses related to their perceptions of the fish weir or fish smoker were primarily in relation to the general benefit to society (less than 11%), some mentioned the benefit to the tribe (less than 7%), and a few indicating they perceived a connection between engineering and fish weir or fish smoker (less than 5%). None of the student responses indicated they had a negative perception of engineering.

Multiple Choice Questions

The results from the multiple-choice questionss are organized by the order inwhich they appeared on the questionaire. Multiple-choice questions are only included for the fish smoker because they were not included in the fish weir post questionaire. Table 2.7 provides a summary of the results.

Q. I think Engineering is fun: Many students agreed that engineering was fun before the activity (Fish Smoker-Pre=0.46). After the activity, there was a statistically significant increase in agree responses with most the students' indicating that they perceived engineering as fun (Fish Smoker-Post=0.90).

Q. I like learning about my culture (pre) and Tribe by engineering a fish smoker (post): Most students agreed that they liked learning about their culture as much before the activity (Fish Smoker-Pre =0.84), as they did after (Fish Smoker-Post=0.90). The differences between the Fish Smoker-Pre and Fish Smoker-Post responses were statistically insignificant.

Q. My Tribe has been doing engineering for a long time: While most of the students agreed with this statement prior to the activity (Fish Smoker-Pre=0.25), there was a statistically significant increase in agree responses after the activity (Fish Smoker-Post=0.53). These results indicate that students' perceptions regarding engineering as relevant to their tribe increased because of participating in the activity.

Table 2.5 Examples of Drawing and Drawing Response Categories and Coding

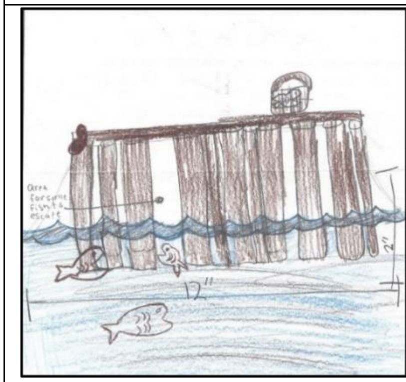
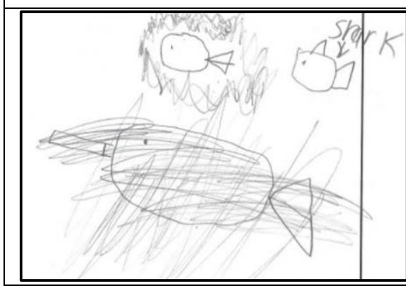
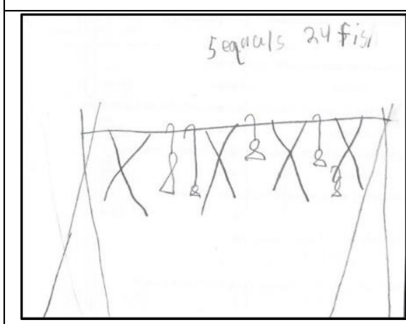
Student Drawings	Student Description Response	Coding Example
	Post Fish Weir	
	*A fish weir is used to capture fish to feed the whole tribe but not to capture all the fish but to at least have enough fish to last for the entire year*	• **Understands fish weir purpose:** Yes • **Objects:** water, basket • **Species:** fish • **Material:** unidentifiable • **University Influence (CR-EE activity**): dimensions on the drawing • **Fish Weir Style:** traditional • **Tribal Influence:** hole for fish to pass, catching fish after trapped by weir, benefit of fish weir to the Tribe, written comments from regarding take only what you need
	Pre Fish Smoker	
	*When Scared covers itself with smoke*	• **Understands fish smoker purpose:** No • **Species:** fish smoking • **Objects:** smoke
	Post Fish Smoker	
	*You put it above the fire and the animals that try to get it will be burned because there is a fire under the fish smoker*	• **Understands fish smoker purpose:** Yes • **Materials:** unidentified • **Fish Smoker Style:** traditional • **University Influence (CR-EE activity):** includes 24 fish as noted in the engineering challenge, fish are drawn with hooks in mouth for hanging on fish smoker • **Tribal Influence:** fish are located up high • **Species:** fish

Table 2.6 Fish Weir-Post & Fish Smoker-Post Comparison of the Highest Percentage of Student Responses

Q	Post Questionnaire	% of Student Responses	Codes Applied: Example Responses
2	Fish Weir	(56%) Build (37%) Test	Build, Test: "putting it together and testing it"
	Fish Smoker	(54%) Build (28%) Collaboration	Collaboration: "working together and learning other people's ideas"
3	Fish Weir	(51%) Tribal	Tribal: "I learned they didn't just go in and grab fished they had a fish weir to catch their fish but they had to get the fish!"
	Fish Smoker	(49%) Tribal	Tribal: "about how the rivers were back in the day" and "now I know how the Indians made fish smokers back then"
4	Fish Weir	(37%) Perceptions of the Engineering Activity (22%) Learning from Failure	Learning from Failure, PEA-Positive: "it's not a bad thing to fail just try again until it is right" PEA-Challenged: "engineering is hard work"
	Fish Smoker	(27%) Perceptions of the Engineering Activity	PEA-Positive: "that it is fun"

PEA-Perceptions of the CR-EE Activity

Table 2.7 Fish Smoker-Pre and Fish Smoker-Post Comparison of Responses to Multiple Choice Questions

Question	Likert Scale Mean[1] Pre	Likert Scale Mean[1] Post	p-value	Statistically Significant
I think engineering is fun.	0.46	0.90	0.01	Y
Fish Smoker-Pre: I like learning about my culture Fish Smoker-Post: I like learnined about my culture by engineering a fish smoker	0.84	0.90	0.36	N
My Tribe has been doing engineering for a long time	0.25	0.53	0.01	Y

Scores closer to 1 indicate a higher frequency of students who "agreed" with a question compared to -1 which indicates a higher frequency of students who "disagreed."

DISCUSSION

What factors engage students in the activity?

The primary factors that engaged students in the CR-EE activity were building and testing the model fish weir or fish smoker, collaborating with their team, and learning about their culture from the Tribal community. Most students identified these factors as the best part of the CR-EE activity or identified them as something new they learned during the activity. These findings are consistent with other culturally relevant studies which report that the Tribal community involvement as well as hands-on experiential and collaborative learning are essential to engage Native American students in STEM education (Herrington, 2014). Furthermore, student responses from both years suggest that they had fun during the CR-EE activity and responses to the Fish Weir-Post questionnaire suggest they were challenged. For example, one student provided the following response to the question What did you learn about engineering "*That it could be hard, but it could also be FUN!*". Educational research indicates that when students are having fun and are challenged in an educational environment, they are generally motivated to engage in learning (Cash, 2010). This finding is significant to this study because it supports the conceptual framework assumption that CR-EE activities can motivate students to engage in learning.

One reason why students' may have been more engaged by these parts of the CR-EE activity is because they align with traditional tribal learning styles. Native American students learn through "...freedom of movement, direct experience, and hands-on and activity-oriented learning..." (Cajete, 1999, p. 153) which is oriented toward visual, holistic, and active learning (Cajete, 1999). Similarly, building and testing are an aspect of the design process which is associated with active learning (Felder & Silverman, 1988). In addition, engaging in the engineering design process promotes essential skills of an engineer, specifically systems thinking and collaboration. Systems thinking is an understanding of the interconnectedness between STEM and society.

"In the old days we learned everything at once, then had to take it apart to understand it. When I went to white school, I had to learn everything in little parts, then try to put it together again. I thought that was backwards. I still do." Lakota Tribal Elder quoted by Kent Nerburn (Pierotti, 2011, p. 7).

In addition, students collaborate with their teams during the activity which provides multiple perspectives while they develop solutions to engineering challenges (Katehi et al., 2009). Since adapting the curriculum to align with traditional Tribal teaching and learning styles is an essential aspect of culturally relevant education, K12 engineering education appears to be naturally compatible with achieving this goal.

Both years the students' most prominent response to the '*something new they learned*' was learning about their culture from the Tribal community. This is further supported by student's response to the multiple-choice question '*I like learning about my culture (Pre)*' and *I like learning about my culture by engineering a fish smoker (Post)*'. While the multiple choice pre and post response were not statistically different, these results indicate students liked learning about their culture just as much before the activity as they did when it was integrated into the CR-EE activity. The Tribal members primary involvement in the CR-EE was their background knowledge presentation when students learned about the history and cultural activities related to fish weir and fish smoker by listening. This approach is different than the NGSS which recommends students conduct research to learn how they should develop their solutions (National Research Council, 2012). The primary reason for this change in the CR-EE is because the background knowledge was presented similar to the oral storytelling and pictures that Tribes traditionally use to pass knowledge down from generation to generation (Pierotti, 2011).

How did the Tribal community and other group's involvement influence the students' responses?

The observed influence of the Tribal community compared to other groups varied from year one to year two. The Tribal community was more involved during the fish weir activity and provided substantially more cultural content that was specific to the students' Tribe compared to the fish smoker activity. Based on the students' drawings, a relationship was also observed between the degree of community involvement and students' cultural representations in their drawings. Specifically, in the Fish Weir-Post drawings the most significant items represented in the students' drawing were from the Tribe (90%) followed by the University (46%) and the Biologist (27%). In comparison to the Fish Smoker-Post drawings, the students' provided more representations of items from the University Team (59%) compared to the observed the Tribe (51%).

The impact of the Tribe's involvement was observed in the students Post questionnaires. Specifically, there was a higher occurrence of the traditional style fish weirs (78%) and fish smokers (57%) from the Tribe presentation compared to the Fish Smoker-Pre (5.5%). In addition, the Fish Weir-Post had significantly more occurrences compared to the Fish Smoker-Post of the following items: Native objects (26.8%, 1.4%), people (31.7%, 6.9%), and background scenery (68%, 10%) respectively. Fralick et al (2009) suggests that when students' do not include items in their drawings it indicates a lack of perception related to those items from the activity (Fralick, Kearn, Thompson, & Lyons, 2009). In the context of this study, the absence of these items suggests that students were less able to draw personal connections or cultural relevance from the fish smoker activity compared to the fish weir activity. These finding are consistent with prior studies which suggestion Tribal involvement is essential to support the initiatives of culturally relevant education (Cajete, 1988a; Demmert, 2001; Herrington, 2014).

The Tribe's influence compared to the University Team was also noted in the students' approach to engineering. Many students incorporated content from the Tribe's background presentation into their engineering designs even though it conflicted with the design constraints defined by the University team. For example, the University team challenged the students to capture all their fish for the fish weir activity, however many students included a hole in their fish weir which prevent them from capturing all the fish during testing. They learned about this during the Tribe's background knowledge presentation which focused on how their ancestors put a hole in the fish weir that allowed a few fish to pass so there would be enough fish for next year. Some students even provided references to Indigenous Knowledge as a justification for the hole, explaining that the Tribe "*only takes what they need*". The Tribe's fish smoker presentation did not include Indigenous Knowledge specific to the CR-EE activity. However, similar occurrences of content from the Tribes presentation were observed in the students' Fish Smoker-Post questionnaires. For example, many of the students designed their fish smoker to hold fish up high, so the animals won't eat the fish during the smoking process. Locating the fish up high was not a University defined design constraint, rather it was included in the Tribes background knowledge presentation.

Most of the student's drawings include representations from both the Tribe as well as the University and Biologist. These results suggest that students found their own way to integrate the Tribal perspective with the Western perspective to develop their engineering designs. The CR-EE curricular framework appears to align with theoretical goals for Native American students to become multicultural: for Native American students to function in the dominant culture while remaining connected to their own community (Ngai & Koehn, 2010; Roehrig et al., 2012). Tribal stream restoration provides an example of an engineer design that could benefit for a multi-cultural approach. Western science and TEK are two distinct knowledge systems. TEK is specific to a "place" and uses diachronic data and intuitive qualitative analysis to diagnose and understand problems. In comparison, Western science can be applied globally by invoking rational synchronic data and quantitative analysis (Kimmerer, 2012). An emerging approach in stream restoration blends these two knowledge systems so they complement one another (Bowers, 2012). For example, Indigenous Knowledge identifies the sources of degradation and knowledge of pre-developed conditions, while Western science is applied to design stream restoration solutions (Kimmerer, 2012). Supporters of this blended approach believe the thoughtful integration of Indigenous Knowledge and Western Science could support successful solutions to stream restoration (Bowers, 2012).

Comparing these results to other studies is challenging because no other CR-EE studies were found in the literature. Results from a culturally relevant education study focused on American Indian and Alaskan Native students found that the influence on students' academic success appears to be related to each student's prior understanding and personal value of their culture (López et al., 2013). While the students in this study were not explicitly asked if they value their culture or Tribal identity, they most likely do since the majority indicated that they like learning about the culture. One reason why the relationship between the Tribal involvement and students' responses were significant in this study is because the CR-EE approach included the Tribal background presentation which provided them with an introduction to the history and cultural activities related to fish weir and fish smoker. Therefore, even though the students indicated they did not understand the purpose of the fish weir and fish smoker before the activity, they appeared to enjoy learning about it as part of the activity.

How are Native American students' perceptions of engineering influenced by participating in a culturally relevant engineering design activity?

Student responses to open ended questions related to their perceptions of the relevance and benefit of engineering to their Tribal community were less than 10%. However, when explicitly asked if they agreed with the statement '*my tribe has been going engineering for a long time*' the increase between the Fish Smoker-Pre and Fish Smoker-Post suggests that perceptions changed because of participating in the activity. These findings are important because an assumption of the conceptual framework is if Native American students perceive engineering as beneficial to their own community, they are more likely to be interested in engineering (Cajete, 1988b; Jarosz, 2003; Pember, 2005).

Just as important are the perceptions students did not provide. None of the students provided a response that indicated they had a negative perception of engineering. This was surprising because negative perceptions were expected as many Native Americans relate engineering to the practices that dominate nature and resulted in significant damage to their water bodies. One reason why students did not provide a negative response may be because elementary age students do not fully understand the history of engineering as well as the impacts it had on the tribe. Another is that participating in engineering activities has been identified by other researchers as method for fostering positive perceptions of the engineering profession (Abaid, Kopman, & Porfiri, 2013). These findings suggest that early exposure to CR-EE activities, like the fish weir or fish smoker, has the potential to support the development of positive perceptions of engineering that are relevant to the Tribe.

CR-EE CURRICULAR FRAMEWORK - RECOMMANDATIONS FOR PRACTICE

When used in collaboration with teachers and Tribal members, the CR-EE curriculum framework (Figure 2.2) provides an approach to integrate western and Tribal perspectives into one curriculum that can align with educational standards. Based on the findings from this study, the following modifications to the CR-EE activity are recommended to enhance the culturally relevant aspects of the activity and further support student learning outcomes related to STEM educational standards.

- Integrate Indigenous Knowledge with Math, Science, and Technology - Since the application of knowledge is an integral part of the engineering design process, it makes sense for Native American students to apply Indigenous Knowledge to develop their engineering solutions. Therefore, include Indigenous Knowledge with math, science, and technology as knowledge students will apply to develop their engineering solutions.
- Be flexible with the design constraints – Students consistently modified the engineering design based on the content from the Tribe's presentation. Teachers should be prepared for this to occur and adapt their lessons as needed.
- Use Native Materials – Since the students were more likely to describe the materials they used during the activity rather than traditional materials the Tribe described, the cultural relevance of this activity could be enhanced by using traditional native materials to build the models.

CONCLUSION, LIMITATIONS, AND FUTURE WORK

This paper essentially describes three very distinct time periods:

- *How it once was:* This is the focus of the prologue, that Native Americans were the first engineers who applied Indigenous Knowledge to design and build things that the Tribe needed such as fish weirs and fish smokers.
- *How it is today:* Land use changes and western engineering practices degraded Tribal waterbodies and stopped many cultural activities. The status of Native American students in K12 STEM education and their low representation in engineering.
- *How it could be:* The questionnaire responses provide a glimpse of the future, specifically how a combination of western and Indigenous perspectives could influence the practice of engineering for Native Americans.

The findings from this study help to understand and validate the theoretical strategies that define the conceptual pathway for increasing the representation of Native American students in engineering. In particular, the initial steps shown in Figure 2.2: culturally relevant engineering education can engage students in learning and demonstrate the relevance and benefit of engineering to the tribal community. These findings are based on lesson plans for the fish weir and fish smoker activities that were developed using the CR-EE Curricular Framework shown in Figure 2.2. The primary instruments used in this study were questionnaires, designed to understand the factors that engaged students in the activity, how the Tribe and other groups influenced student's responses, and track the changes in student's perceptions of engineering as a result of participating in the activity.

Results from this study suggest that the majority of students were engaged in the CR-EE activity. Three primary factors were observed to engage students in the engineering activities: 1) building and testing their model fish weir or fish smoker; 2) opportunities for collaborative learning, and 3) learning about their culture from the Tribal community. Students provided limited but promising responses regarding their perceptions of engineering. Their responses suggest participating in the CR-EE activity can demonstrate the relevance of engineering to their Tribe. The Tribal community's involvement appeared to have a significant influence on students' responses: students applied information they learned from the Tribe's presentation to their engineering designs and the more involved the Tribe was during the activity the higher the occurrences of cultural representations in the students' responses.

Although the findings from this study show promise with respect to the impact CR-EE activities can have on Native American students' attitudes and motivation to participate in Engineering education, the youth in this study is limited to a single Tribal community. There are over 500 Tribes located in the United States, and while similarities exist between communities, each has unique ways of knowing (Kana'iaupuni & Kawai'ae'a, 2008; National Research Council, 2006). Future applications of the CR-EE curricular framework should be adapted to reflect each Tribal community's perspectives and priorities for their youth. Additional studies are needed to investigate whether CR-EE will have a similar impact on students from other Tribal communities. In addition, more research is needed to evaluate how other aspects of the conceptual pathway to increasing Native American students' representation in engineering (2.1) will impact Native American students' including whether the conceptual pathway will ultimately result in a higher representation of Native Americans' in the engineering work force.

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APPENDIX

Table 2.8 Fish Weir-Post and Fish Smoker-Post Checklist for Assessing Students Drawings

FISH WEIR/FISH SMOKER CHARACTERISTICS

MATERIALS

- ☐ Tribe: Sinew, wood, or logs
- ☐ Engineering Activity: Pipe cleaners, popsicle sticks, glue
- ☐ Other: Sticks, metals

FISH WEIR STYLE

- ☐ Tribe: Traditional
- ☐ Biologist: Modern: cage, square shape, gate
- ☐ Tribe/Biologist: Combination

FISH SMOKER STYLE

- ☐ Campfire under grate or stick spit grille
- ☐ Modern Day fish smoker - similar to BBQ
- ☐ Culturally Relevant: Traditional fish smoker - wood frame
- ☐ Smoke House
- ☐ Engineering Activity: Tall Square Box

MISCELLANEOUS

SPECIES

- ☐ People
- ☐ Native American
- ☐ Standing on fish weir
- ☐ Student drew self
- ☐ Animals (other than fish)
- ☐ Fish
- ☐ Smoking or people smoking fish
- ☐ Fish on stick: held over camp fire
- ☐ Engineering Activity: Hook in mouth - hanging on fish smoker

OBJECTS

- ☐ Pot, Bucket
- ☐ Boat, Fishing Pole
- ☐ Tent, Table, Axe
- ☐ Cooking Instruments – i.e., BBQ flipper
- ☐ Smoke, Fire, and/or Chopped Wood

BACKGROUND SCENERY

- ☐ Water – i.e., river, stream, lake
- ☐ Sky - i.e., clouds, stars, sun, moon
- ☐ Landscape - i.e., trees, cliff, grass, rocks

GENERAL INFORMATION

FISH WEIR/FISH SMOKER PERCEPTIONS

- ☐ Understand fish weir/fish smoker purpose
- ☐ Benefit of fish weir/fish smoker to the Tribe
- ☐ Tribe using fish smoker/fish weir for a long time

INFLUENCE

BIOLOGIST (FISH WEIR ONLY)

- ☐ Student response references: research, study, tag fish, or fish cannot swim backward

UNIVERSITY (ENGINEERING ACTIVITY)

- ☐ Design, build, test, evaluate
- ☐ Model, model stability
- ☐ Legend, cross sectional views
- ☐ Fish Weir/Fish Smoker dimensions
- ☐ Fish Weir ONLY
- ☐ Catch All Fish
- ☐ Fish Smoker ONLY
- ☐ Cook Evenly
- ☐ Thermometer, temperature
- ☐ Light bulb

TRIBE

- ☐ Indigenous Knowledge
- ☐ Take only what you need, leave some for next time
- ☐ Native Objects: teepee, spear, bow and arrow, net and/or baskets
- ☐ fish weir ONLY
- ☐ Hole for Fish to Pass
- ☐ Catching fish after trapped by fish weir
- ☐ fish smoker ONLY
- ☐ Smoke gives fish flavor
- ☐ Reference to low/small fire
- ☐ Put fish up high so animals don't eat

Table 2.9 Drawing Instrument Categories of Student Responses and Representations

Check List Category	Category Definition
General Information	Students understanding and perceptions of fish weir/fish smoker including: • Understands Fish Weir/Fish Smoker purpose: Students were assumed to understand the purpose of a fish weir or fish smoker if they drew or described a fish weir capturing fish or a fish smoker preserving or cooking fish • Relevance and/or Benefit of Fish Weir/Fish Smoker to the Tribe: described in the students response
Fish Weir/Fish Smoker Characteristics	Fish Weir/Fish Smoker characteristics identified by the student included: • Materials – used to build the Fish Weir/Fish Smoker were described or drawn (with enough detail) to be identified. The two primary groups included: traditional (Tribal) or materials used during the engineering activity • Style – or type of Fish Weir/Fish Smoker depicted in the drawing included traditional (used by ancestors), modern (i.e., fish weir used by biologists), or a combination of the two. For example, fish weir styles were coded as modern (biologist influenced) if they were depicted as a cage, square shape, or gate.
Miscellaneous Items	The miscellaneous category includes all other items represented in the drawings including: • Species - The two types of species were represented in the questionnaires included: fish or people. If the characteristics or actions of the people were inferred, these were also documented. For example, Native Americans were identified when students labeled people as “Indian” or because they were wearing native clothing such as a headdresses • Objects - All items not previously listed were included in this category. A subcategory of this group included fire, smoke, or chopped wood • Background Scenery -draw in the pictures included: water bodies (i.e., rivers or streams), landscape (i.e., trees, cliff, grass, rocks, etc), or sky (i.e., clouds, stars, sun, moon, etc).
Influence	The influence was identified by locating items in the student’s responses that were specific to the working group’s contribution during the activity, specifically: • CR: Tribal Presentation - a hole in the fish weir, activities associated with harvesting fish after trapped by fish weir; smoke gives fish flavor; put fish up high so animals don't eat; use low fire to dry fish • Native Objects – included in the Tribes presentation: teepees, spears, bows and arrows, nets, baskets • Indigenous Knowledge - take only what you need (fish weir Only) • Engineering Activity: The engineering design process (i.e., design, build, test, evaluate), drawing details (i.e., dimension, legend, cross sectional views), design constraints (i.e., light bulb, 24 fish, catch all fish, cook fish evenly), temperature, thermometer, or heat energy. • Biologist (B): Modern fish weir purpose is to monitor fish populations (i.e., research or tag fish) and fish weir function (i.e., fish cannot swim backward)

Table 2.10 Summary of Student Responses for all Drawing Questionnaires

General	Fish Weir Post	Fish Smoker Pre	Fish Smoker Post
No Response	2.4%	17.8%	2.8%
Understands fish weir (Y1) or fish smoker (Y2) Purpose	90.2%	38.4%	84.7%
Tribal Benefit of fish weir or fish smoker	24.4%	0%	17.8%
Tribe has been using fish weir or fish smoker for a long time	7.3%	0%	4.2%
Fish Weir and Fish Smoker Characteristics			
Fish weir (represented in drawing)	90.2%	-	-
Traditional	78.0%	-	-
Combination	7.3%	-	-
Modern	2.4%	-	-
Fish Smoker (represented in drawing)	-	49.3%	94.4%
Campfire under metal grate or stick spit grille	-	35.6%	11.1%
Campfire (person holding fish on stick over)	-	5.5%	0%
Modern (represented as similar to BBQ)	-	11.0%	1.4%
Tribal: Traditional or Smoke House	-	5.5%	63.8%
Engineering Activity: Tall Box (fit around light bulb)	-	-	9.7%
Materials (identified)	36.6%	11.0%	22.3%
Tribal: Traditional Native (rocks, sinew, wood)	14.6%	-	5.6%
Engineering Activity: pipe cleaners, popsicle sticks, clay, glue gun	22.0%	-	12.5%
Other: sticks or metal	0%	11.0%	4.2%
Species			
People	31.7%	17.8%	6.9%
Standing on the Fish weir	29.3%	-	-
Native Americans	9.8%	1.4%	1.4%
Student (drew self in picture)	0%	9.6%	0%
Fish	78.0%	57.5%	94.4%
Fish Smoking or people smoking fish	-	12.3%	2.8%
Engineering Activity: Fish hooks (for hanging on fish smoker)	-	-	35.7%
Animals	2.4%	1.4%	4.2%
Objects			
Water (including water body)	56.1%	9.6%	4.2%
Landscape or Sky	12.2%	15.1%	5.6%
Fire, smoke, and/or chopped wood	-	42.5%	70.8%
Boat, tent, table, axe, cooking instruments, pot, bucket, fishing pole	-	20.6%	7.0%
Engineering Activity Items-University Influence	46.3%	6.8%	58.5%
Biologist Influence	26.8%	-	-
Tribal Influence	90.2%	-	51.4%
Indigenous Knowledge	17.1%	-	0%
Native American Tools or Objects (i.e., spears, teepee, bow, arrow)	26.8%	-	1.4%
Tribal Background Knowledge Presentation	46.3%	-	50.5%

Table 2.11 Summary of Categories and Codes for All Students Responses to Open Ended Questions

Category Title (Abbr.) - Description	Codes for Student Responses
Students Perceptions	
Engineering Activity - Students perceptions of themselves during the CR-EE activity or the skills needed to be an engineer	**Positive** - Identifies self as being capable, interested, or having fun
	Challenged - Identifies self as being challenged or that engineering is "hard work"
	Negative - Identifies self as not being capable or interested
Fish weir or Fish Smoker - Students perceptions of fish weir or fish smoker in relation to society, the tribe, or engineering	**General Positive** - Represents Fish Weir/Fish Smoker as beneficial to society
	Tribe Positive - Represents Fish Weir/Fish Smoker as beneficial to tribal community
	Engineering - Student connects making/building Fish Weir/Fish Smoker to engineering
Engineering Relevance/Benefit - Students perception of the relevance or benefit of engineers or engineering to society or the Tribe	**Neutral** - comments about engineering focus on function without reference to benefit
	General Positive - Represents engineering as beneficial to society
	Tribe Positive - Represents as beneficial to the Tribe, identifies tribal members as engineers
Motivate-Engagement	
Engineering Design Process - Students response references an element of the EDP: either explicitly stating the element or implicitly by describing something that occurred during that element	**Intro to Engineers**: learning about engineering
	Background Knowledge: general comment regarding learning about Fish Weir/Fish Smoker
	Culturally Relevant - response reflects Tribal influence: i.e., history, activities, traditions or native tools associated with harvesting and preserving fish.
	Biologist - (fish weir ONLY) response reflects biologist influence: i.e., fish cannot swim backward, cage, square shape, gate, research, study or tag fish.
	Design or design constraints - describes activities associated with design (i.e., developing a plan or drawings before building) or how the constraints affected their Fish Weir/Fish Smoker design (i.e., fish weir needed to be as wide as the stream or the fish smoker needed to hold 24 fish)
	Build - student describes building or making the model
	Test - student describes testing model
	Evaluate - student describes evaluating or fixing the model
Materials - Materials the student references	**Engineering Activity** - popsicle sticks, pipe cleaners, fake fish
	Culturally Relevant - traditional materials i.e., logs, wood, or sinew
Essential Skills - Connection to values, skills, and attitudes considered traits of an engineer	**Team work** - student mentions or describes working as a team
	Learning from failure - if you don't get it right the first time, try again, or don't give up
Knowledge Applied - by the student to make the fish weir or fish smoker	**K12 Science** - Concepts represented related to the fish life cycle or heat energy
	K12 Math - Concepts applied to design constraints: dimensions, measuring, temperature
	Indigenous Knowledge - Concepts related to take only what you need

Table 2.12 Fish Weir and Fish Smoker Post Questions 2-4: Percentage of Student Responses to All Open-Ended Questions

Themes	Codes	Q2		Q3		Q4	
		Y1 fish weir	Y2 fish smoker	Y1 fish weir	Y2 fish smoker	Y1 fish weir	Y2 fish smoker
	Response: None or "I forgot"	4.7	5.6	9.7	9.7	17.1	27.8
Student Perceptions							
Engineering Activity (PEA)	Positive	2.4	9.7	1.8	4.2	17.1	23.6
	Challenging	-	-			19.5	2.8
	Negative	-	2.8	-	2.8	2.4	-
Fish Weir or Fish Smoker	General Positive	-	-	10.7	1.4		4.9
	Tribal Positive	2.4	-	5.4	-		1.4
	Engineering	-	-	-	-	2.4	4.2
Engineering Relevance or Benefit	Neutral	-	-	-	-	4.9	-
	General Positive	-	-	-	-	5.6	-
	Tribal Positive	-	-	1.8%	-	-	-
Motivate Engagement							
Engineering Design Process	Introduction to Engineering	-	-	-	-	-	6.9
	Background Knowledge	2.4	1.4	14.6	8.3	-	5.6
	Culturally Relevant	4.9	1.4	51.2	48.6	4.9	5.6
	Biologist	-	-	14.6	-	2.4	-
	Design Criteria & Design	-	-	2.4	-	7.3	9.7
	Build	56.1	54.2	4.9	15.3	14.6	16.7
	Test	36.6	11.1	4.9	5.6	2.4	2.8
	Evaluate	2.4	2.8	2.4	-	2.4	1.4
Materials	Engineering Activity	-	5.6	--	-	-	1.4
	Culturally Relevant	-	-	9.8	2.8	-	-
Essential Skills	Collaboration	2.4	27.8	-	2.8	-	1.4
	Learning from Failure	-	2.8	-	-	22.0	4.2
Knowledge Applied	K12 Science	-	-	-	-	-	9.7
	K12 Math	-	-	-	-	2.4	8.3
	Indigenous Knowledge	-	-	7.3	-	-	-

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CHAPTER 3. IDENTIFYING THE ESSENTIAL PROPERTIES OF BIOCHAR FOR STORMWATER TREATMENT

ABSTRACT

The goal of this research was to provide a comprehensive evaluation of two different biochars for providing treatment of stormwater pollutants and to develop recommendations for the field application of a bioretention soil media (BSM) amended with biochar (BSM-Biochar mix). The pollutants include total suspended solids (TSS), dissolved Copper (Cu) and Zinc (Zn), Total Phosphorus (TP), Total Nitrogen (TN), Ammonia (NH_3), and Nitrate-Nitrite (NO_3-NO_2). These goals were achieved by conducting an extensive literature search to identify a list of proposed Essential Properties. Specifically, those biochar physiochemical properties that indicate if a biochar is suitable for stormwater applications and may be useful in stormwater treatment design. Two biochars were selected for this study, one derived from wood (W) and the other from Kentucky blue grass feedstocks (KB), because they provide a range of Essential Properties to evaluate and compare. A laboratory study was conducted to evaluate the treatment performance of the biochars, which included: 1) jar testing and 2) flow through column testing. The results from the laboratory testing indicate: both biochars reduced TSS, Zn and Pb by >90%; the Cu removal efficiency was significantly higher for the W biochar (88% to 96%) compared to the KB biochar (47% to 78%); the NH_3 removal efficiency (56% to 77%) was statistically insignificant between the biochars; the NO_3-NO_2 effluent concentration was only significantly higher than the influent for the columns with a larger quantity of biochar in which the NO_3-NO_2 was reduced by 3% to 12%; and the W biochar reduced (24.2%) significantly more TN compared to the KB biochar (14%). Neither biochar reduced TP. The KB biochar leached TP (-150% to -341%) compared to the W biochar in which the effluent concentration was statistically insignificant compared to the influent concentration. The results from this study may have been influenced by the stormwater influent hardness concentration (277 mg/L total and 227 mg/L dissolved) as well as hydrophobic characteristics observed by the biochars. Results from the laboratory testing were used to refine the list of Essential Properties, which include organic carbon, hydrogen to organic carbon ratio, cation exchange capacity, total surface area, calcium, pH, phosphorus, and nitrogen.

INTRODUCTION

Bioretention cells are a common stormwater best management practice (BMP) in urban areas. These BMPs are characterized as shallow landscaped depressions which are designed to capture and store stormwater runoff from small catchment areas followed by infiltration through engineered soils commonly referred to as bioretention soil media (BSM) (Hatt, 2008). Pollutant removal primarily occurs as runoff infiltrates into and through the BSM. Treated stormwater then infiltrates into the existing soils beneath the bioretention cell or is collected in an underdrain and conveyed to a storm drain network (AHBL & HDR, 2013).

The composition of BSM mixes varies nationally, however most are composed of a mix of topsoil, sand, and organic materials (Carpenter & Hallam, 2010; Hunt & Lord, 2006; Janoch & Liu, 2012). Recent studies indicate that the natural humic content found in organic materials, which is primarily responsible for sorption of metals, can be a source of pollutants specifically phosphorus and nitrogen (California Department of Transportation, 2009; Clark & Pitt, 1999; Washington State Department of Ecology, 2013). Regulatory agencies, concerned over impacts to receiving water bodies, have placed restrictions on the use of bioretention BMPs until the pollutant leaching concerns are resolved (Ecology, 2016; Washington State Department of Ecology, 2013). This presents a challenge for Municipal Separate Storm Sewer (MS4) operators regulated under a National Pollutant Discharge Elimination System (NPDES) stormwater permit, particularly since bioretention cells are a popular option for achieving permit requirements in ultra-urban areas.

Biochar may provide an alternative to the traditional organic materials that have been used in BSM. Biochar is a carbon rich material produced by thermally modifying a biomass (source feedstocks) at elevated temperatures with little or no oxygen. The result is a cellular structure that resembles the original biomass except the pore structure is more complex, which increases the total surface area of the material (Beck, Johnson, & Spolek, 2011; Beesley, Moreno-Jimenez, Gomez-Eyles, & Harris, 2011; McLaughlin, Anderson, Shields, & Reed, 2009). The thermal modification allows biochar to persist in soils longer than traditional BSM organic materials which require more frequent replacement to maintain the full benefits due to decomposition (California Department of Transportation, 2009). Studies suggest that biochar has sorption characteristics similar to activated carbon for immobilizing and reducing contaminants (Erickson, Gulliver, & Weiss, 2007; Gomez-Eyles, Yupanqui, Beckingham, Riedel, & Gilmour, 2013; Patil & Kulkarni, 2012). Since source materials are limited to biomass waste, biochar provides an inexpensive and more environmentally sustainable option compared to activated carbon, which has had limited application in stormwater due to expensive production costs (Bridgwater, 2003; Clark & Pitt, 1999; Gomez-Eyles et al., 2013; Patil & Kulkarni, 2012).

Biochar has been widely studied as a soil amendment for agricultural applications and environmental remediation. In agricultural applications, researchers have reported that biochar improves soil quality and function by increasing the water and nutrient retention capacity of the soils (Beck et al., 2011; Denyes, Langlois, Rutter, & Zeeb, 2012; Griffith, Banowetz, & Gady, 2013; Lehmann & Joseph, 2015; H. McLaughlin et al., 2009). In environmental remediation, contaminated soils amended with biochar were found to immobilized both inorganic and organic constituents thus preventing their subsurface transport to groundwater (L. Beesley et al., 2011; Lehmann & Joseph, 2015). The documented benefits of biochar amendments in soils have attracted notice from the stormwater community, particularly since these benefits are desirable characteristics of BSM (Beesley et al., 2011; Cao, 2010; Gomez-Eyles et al., 2013; Yaoa, 2011; Zheng, 2013). However, the bulk of these studies evaluated biochar under conditions not representative of a bioretention BMP function, that is when pollutants are removed from a solution while the solution flows through the media (Beesley et al., 2011). While more recent studies have focused on the evaluating biochar in stormwater applications, most studies occur in a laboratory using a synthetic stormwater solution made from deionized or tap water with limited pollutants (Leach, 2015; Mohanty & Boehm, 2015; Mohanty, Cantrell, Nelson, & Boehm, 2014; Reddy, Xie, & Dastgheibi, 2014; Tian et al., 2014; Ulrich, Im, Werner, & Higgins, 2015). Since natural stormwater has a complex chemistry and consists of multiple types of pollutants which can influence the media treatment performance, results from these studies may limit an understanding of biochars treatment performance in field applications (Stahnke & Poor, 2017). Thus, there are many unanswered questions related to the application of biochar in BSM mixes such as the necessary quantity to add to the BSM, what types of biochar should be used for this application, and the effectiveness of the biochar for reducing stormwater pollutants.

The goal of this research is to provide a comprehensive evaluation of biochar for providing treatment of stormwater pollutants of concern (POC) and to develop recommendations for the field application of a biochar as an amendment in BSM (BSM-Biochar mix). This study was conducted for the City of Spokane which is a MS4 operator in eastern Washington that is regulated under the NPDES permit. As such, the POCs identified for this research include those regulated under the Washington MS4 NPDES permit or identified as POC for impaired water bodies in the Spokane area. These POCs include: total suspended solids (TSS), dissolved copper (Cu) and zinc (Zn), total phosphorus (TP), pH, total nitrogen (TN), ammonia (NH_3), and nitrate-nitrite (NO_3-NO_2).

The research goals were achieved by answering the following questions:

7. Do the selected biochars leach nutrients (N and P) or metals (Cu, Zn, Pb, Ca, and Mg)?
8. What is the short-term effectiveness of the selected biochars for reducing the POC pollutants?
9. How does the hydraulic performance of the selected biochars change over the duration of testing?
10. What is the estimated lifespan of the biochars for reducing pollutants?
11. Which biochar physiochemical properties (or range of properties) appear to indicate the treatment performance for stormwater applications?

OVERVIEW OF THE RESEARCH PROJECT

The research questions were answered by conducting an extensive literature search and a comprehensive laboratory study. The literature search was conducted to identify a list of proposed Essential Properties that is biochar physiochemical properties which appear to indicate if a biochar is suitable for stormwater applications. The two biochars selected for this study were selected because they provide a range of Essential Properties to evaluate and compare. The laboratory study was conducted to evaluate the treatment performance of the biochars as a filter media for future application in bioretention BMPs. The experimental design focused on creating conditions that are representative of those expected in the field including using a natural stormwater solution for all testing. The laboratory study had two parts: 1) jar testing biochar and 2) flow through column testing biochar only. The results from the laboratory testing along with the physiochemical properties of the biochars evaluated during this study were used to refine the proposed list of Essential Properties and develop recommendations for a design specification for a BSM-Biochar mix.

LITERATURE SEARCH

Essential Properties of Biochar for Stormwater Applications

The performance and subsequent suitability of biochar for a particular application is a function of the physiochemical properties which are influenced by the biomass source material and the processing conditions (Bolan et al., 2014). Considering that biochar can be produced from many types of biomass (e.g., wood, grass, nutshells) using different processing conditions (e.g., method, duration, and temperature), there is a large variation in the biochar physiochemical properties (Lehmann & Joseph, 2015; McLaughlin, Anderson., Shields, Reed, 2009, p. L3476). Understanding how biochar properties influence the performance of biochar has been and continues to be a focus of research, especially for stormwater since biochar has only recently been considered for this application. Based on the literature available, there appears to be no "one size fits all" biochar (Abiven, Schmidt, & Lehmann, 2014; Mukherjee, Zimmerman, & Harris, 2011) meaning some biochars appear be more suitable for certain applications compared to others.

For this research Essential Properties are defined as biochar physiochemical properties which appear to indicate whether a biochar is suitable for stormwater applications. In other words, properties which may enhance or inhibit the effectiveness of the treatment mechanisms provided by the biochar or increase or decrease the likelihood of pollutant leaching. Table 1 provides a summary of the Essential Properties which are discussed in detail in this section. One notable omission from the discussion that is common in biochar literature is the influence source materials and processing conditions have on the treatment performance. The end goal of this study was to develop a BSM-Biochar specification that identifies suitable biochar properties measured after production. As such, evaluating how source materials and production conditions influence those properties was considered outside the scope of this study.

Table 3.1 Essential Properties of Biochar for Stormwater Applications Based on Literature Search

Property	Criteria	Description
Organic Carbon (C_{org})	Class 1: ≥ 60%	Class 1 Corg content indicates a high carbon content which is associated with higher adsorption capacities (Lehmann & Joseph, 2015; McLaughlin, Anderson., Shields, Reed, 2009)
Hydrogen to Organic Carbon ratio ($H:C_{org}$)	0.7 max	H:Corg < 0.7 is associated with a higher adsorption capacities (Lehmann & Joseph, 2015)
Cation Exchange Capacity (CEC)	high	The higher the CEC of a biochar the greater ability to exchange ions (International Biochar Initiative, 2013)
Total Surface Area (SA)	high	The higher the SA, the more available sites for adsorption (Lehmann & Joseph, 2015; Minton, 2012)
Mineral Ions: Calcium (Ca)	high	Higher Ca content may enhance P removal (Erickson et al., 2007)
Phosphorous (P)	low (less than 0.04%)	Organic materials with lower P content are less likely to leach (Erickson et al., 2007; Payne et al, 2015; Janoch & Liu, 2012).
Nitrogen (N)	low (less than 0.10%)	Organic materials with lower N content are less likely to leach (Payne et al, 2015).

Total carbon is the portion of biochar that includes carbon along with the non-volatile and solid fuel remaining after the volatile matter is driven off during the thermal conversion process (Lehmann & Joseph, 2015; McLaughlin, Anderson, Shields, Reed, 2009). Comparatively, the Organic Carbon (C_{org}) content represent the carbonized portion of biochar that has condensed into fused aromatic ring structures. As the fused ring structure form, the C_{org} content porosity increase. More carbonized biochars are expected to persist longer in soils because more fused ring structures have formed making the biochar more resistant to biological and chemical degradation (Lehmann & Joseph, 2015).

The hydrogen to organic carbon ratio $H:C_{org}$ ratio is the degree to which a biochar has been carbonized. IBI recommends a maximum limit for $H:C_{org}$ of 0.7 to distinguish biochars from biomass. A ratio $H:C_{org}$ less than 0.7 indicates the biomass is thermally converted to biochar (International Biochar Initiative, 2013). A $H:C_{org}$ ratio greater than 0.7 indicates the biomass is thermally altered but not converted to biochar and elastic properties from the original biomass are still present (McLaughlin, Shields, Jagiello, & Thiele, 2012).

The primary sorption processes exhibited by biochar are cation exchange and adsorption. Cation exchange capacity (CEC) is the measure of the total negative charge (meq/100g) of the sorbent (biochar). Cation exchange occurs when cations on the media (biochar) are replaced with cations in the stormwater solution. The higher the CEC, the more cations a media can exchange compared to media with a lower CEC (Lehmann & Joseph, 2015; Minton, 2012). Surface Area is a measure of the external and internal sites available for cations to adhere to and a high surface area indicates more adsorptive capacity (Lehmann & Joseph, 2015; Minton, 2012). With adsorption, there is no exchange of ions. Instead, forces at the surface of a media (biochar) attract and hold dissolved cations in the stormwater solution onto the biochar surface (Minton, 2012). At the time this paper was written, no analytical methods had been developed to measure the adsorption capacity of biochar, therefore it is not possible to distinguish between which pollutants are removed through adsorption compared to cation exchange (McLaughlin et al., 2012).

Researchers have reported inconsistent findings regarding biochars capacity to retain or leach nutrients in a soil column (Beesley et al., 2011; Beesley, Moreno-Jiménez, & Gomez-Eyles, 2010; Lehmann & Joseph, 2015; Taghizadeh-Toosi, Clough, Sherlock, & Condron, 2012; Yao, Gao, Zhang, Inyang, & Zimmerman, 2012). The majority of these studies focused on agriculture applications where it is desireable for biochar to retain nutrients that were added to the soils for the purpose of increasing crop productivity. In contrast, nutrients are distributed to bioretention cells as stormwater runoff is conveyed through the cell. While it is desirable for a BSM to retain nutrients to support plant growth in bioretention cells, it is essential that nutrients do not leach from the BSM. Biochar properties that appear to influence nutrient retention and leaching include:

- The nutrient content of the biochar appears to be the most dominant predictor of nutrient leaching. The nutrient content is the portion of nutrients from the original biomass that are retained in the biochar after thermal modification or conversion (Lehmann & Joseph, 2015). No biochar studies where located that recommend a biochar nutrient content with respect to reducing the potential for nutrient leaching. Instead, recommendations from bioretention literature were reviewed which include: a TN content of less than 1000 mg/kg (0.1%) (Payne et al, 2015; Janoch, Liu, 2012) and a TP content of 400 mg/kg (0.04%) (Payne et al, 2015; Hunt & Lord, 2006).

- The ash content of biochar consists of inorganic mineral ions (i.e Na, K, Ca, Mg, S, Si) from the source material which are incombustible and preserved in biochar at increasing concentrations as the volatile matter is released during processing. In particular, calcium (Ca) is known to contribute to the formation of particulate phosphorus (P) depending on the solution pH. When P is in a particulate form, it can be readily removed in a bioretention cell through filtration (Erickson et al., 2007).

MATERIALS

Biochar Material Selection and Material Characterization

The two biochars shown in Figure 3.1 were evaluated during this study. The source materials and processing conditions for these biochars were: 1) Kentucky Blue KB (KB) seed mill screenings processed using a small-scale gasification unit operated at 625°C for 1-minute (Griffith et al., 2013) and 2) Wood (W) waste from a sustainable forest processed using a modified gasification process at 900°C for approximately 10 minutes.

Figure 3.1 Close-up Photo of Wood Biochar (left) and Grass Biochar (right)

Samples of each biochar were collected directly from the sealed 5-gallon buckets they were received in from the vendor and homogenized following the cone and quarter technique (Schumacher, Shines, Burton, & Papp, 1991). A laboratory analyzed the biochar physiochemical properties using the standard methods recommended by IBI for *Biochar That Is Used in Soils* (International Biochar Initiative, 2013). Table 3.2 provides a summary of the results for just the Essential Properties of each biochar. Appendix A includes a complete list of the parameters tested, standard testing methods, and biochar characterization results.

Table 3.2 Biochar Material Characterization Results - Essential Properties

Property	Acronym	KB	W	Units
Organic Carbon	C_{org}	38.5	83.8	% of total dry mass
Hydrogen to Organic Carbon Ratio	$H:C_{org}$	1.6	0.42	% of total dry mass
Cation Exchange Capacity	CEC	29	19	m_{eq}/100g
Total Surface Area	SA	209	482	m^2/g dry
Calcium	Ca	1.36	1.28	% of total dry mass
Magnesium	Mg	0.57	0.10	% of total dry mass
Phosphorous Total/Available (TP percent of biochar content)	P	12,600/7900 (1.26%)	603/574 (0.06%)	mg/kg
Total Nitrogen	N	15,000 (1.5%)	6,000 (0.6%)	mg/kg

Expected Treatment Behavior of Selected Biochars

This section describes the expected treatment behavior of the selected biochars in stormwater applications based on the Essential Properties previously described along with the measured properties of the W and KB biochar presented in Table 3.2. The higher surface area, and organic carbon properties of the W biochar indicate a higher adsorptive capacity compared to the KB biochar. Comparatively, the higher CEC of the KB biochar indicates a higher capacity for cation exchange. The W biochar has a $H:C_{org}$ ratio of less than 0.7, which means the W biochar has been thermally converted to and is classified as biochar. Comparatively, the $H:C_{org}$ ratio is greater than 0.7 for the KB biochar, which indicates that while the KB biomass was thermally modified it was not thermally converted to biochar. As such the KB biochar has a larger portion of the original biomass present (compared to the W biochar) which may react in soils more like traditional bioretention organic matter where CEC is a dominant process (L. Beesley et al., 2011). Since neither biochar is fully carbonized (C_{org}=100%), both adsorption and cation exchange processes will likely occur simultaneously (Beesley, Moreno-Jimenez, Gomez-Eyles, Harris., 2011; McLaughlin et al., 2012). Considering the balance of a higher surface area and lower CEC provided by the W biochar and the lower surface area and higher CEC provided by the KB biochar, both biochars are expected to have an excellent sorption capacity for immobilizing dissolved metals.

The nutrient content of the W and KB biochars, may have the most significant influence on the suitability of the two biochars for stormwater applications. The substantially higher nutrient content in the KB biochar indicates it has a higher potential to leach nutrients compared to the W biochar. However, Ca content of the biochars is similar as such both biochars are expected to have a similar potential for forming particulate forms of calcium phosphates that can enhance phosphorus removal. Considering the differences in the nutrient content of the biochars, the W biochar is expected to be more suitable for stormwater applications because the nutrient content is lower compared to the KB biochar, therefore the nutrient leaching potential is lower.

METHODOLOGY

Stormwater Solution

A multi-component stormwater solution was used in this study. The solution was composed of natural stormwater, with chemical additions to meet the target stormwater influent (SSW) characteristics. The targets were based on measurements made at the Cochran Basin stormwater outfall in Spokane. The stormwater characteristics from this outfall were selected because this is the largest outfall in Spokane with mixed residential and commercial land use which is the land use where the BSM-Biochar mix is intended to be used. The SSW characteristics are summarized in Table 3.3. Because the pollutant background concentrations in the collected stormwater were lower than the target concentrations, chemical standards were added to achieve the target concentrations. The jar testing concentrations were increased above the target concentrations to adequately quantify removal and complete the experiment in a timely manner.

The original stormwater was harvested from a roof top catchment which included a portion that had passed through a green roof. Multiple batches of natural stormwater were collected a few days before starting the jar and column testing and again midway through for the column testing only. All batches were stored in a HPDE tanks in the lab. On the day of each testing event, a portion of the natural stormwater was diverted to a second HDPE tank and chemical standards were mixed in by manual shaking. For jar testing, the stormwater solution was continuously mixed throughout the testing. For the column testing, the influent tanks were manually mixed by shaking to re-suspend settled solids every 4 hours during each rainfall event.

Table 3.3 Stormwater Influent (SSW) Characteristics and Testing Methods

Pollutant	Standard Testing Methods	Target (mg/L)	Background (mg/L)	Jar Testing (mg/L)	Column Testing (mg/L)	Chemical Standards
pH	EPA 150.2	-	7.58	7.6	7.6	none
TSS	SM2540D-97	100	3.5	NT	172	Sil-Co-Sil 106
Copper Total/Dissolved	EPA 200.8	0.040/0.010	0.046/0.021	3.48/1.96	0.042/0.032	Copper Sulfate $CuSO_4$
Zinc Total/Dissolved		0.280/0.020	0.058/0.030	8.22/6.00	0.208/0.105	Zinc Chloride $ZnCl_2$
Lead Total/Dissolved		0.030/0.030	0.030/0.030	31.00/12.30	0.038/0.008	Lead Nitrate $Pb(NO_3)_2$
Arsenic Total/Dissolved		-	NT	ND	NT	none
Cadmium Total/Dissolved		-	NT	ND	NT	none
Chromium Total/Dissolved		-	NT	ND	NT	none
Nickel Total/Dissolved		-	NT	ND	NT	none
Phosphorus	SM 4500PE	1.000	0.47	117	1.039	Potassium Phosphate Monobasic KH_2PO_4
Ammonia	SM4500-NH_3	0.360	0.09	27.3	0.330	Ammonium Chloride NH_3Cl
Nitrate-Nitrite	SM4500-NO_3	-	0.99	8.26	1.309	none
TKN	EPA 351.2	-	0.60	30.1	1.133	none
Hardness Total/Dissolved	SM2340-B97	-	232.7/228.0	130/100	230.5/226.3	none
Calcium Total/Dissolved	EPA 200.7	-	NT	29.3/22.5	54.39/53.44	none
Magnesium Total/Dissolved		-	NT	13.9/10.8	23.49/23.19	none

a. NT – Not Tested, ND – Not Detected

Experimental Design – Part 1 Jar Testing

Three jar test experiments were conducted which included:

- Desorption Testing – conducted to assess the potential of each biochar for leaching dissolved metals (Ca, Mg, Zn, Cu, and Pb) into a stormwater solution
- Kinetics Testing – conducted to assess the time required for each biochar to sorb metals (Zn, Cu, and Pb) from the stormwater solution and determine an appropriate run time for the sorption equilibrium testing
- Sorption Capacity Equilibrium Testing – conducted to assess the biochar sorption performance for dissolved metals (Zn, Cu, and Pb) and estimate the total sorption capacity

For each test, varying masses of biochar, between 2-mm to 0.42-mm in diameter, were placed in 250 mL bottles of a solution. Blank bottles were also tested that contained the solution without biochar. The bottles were placed on an Orbit Shaker table (Figure 3.2) at 100 RPMs for varying durations of time. The time intervals in hours for the desorption and kinetics testing were as follows: 1, 3, 6, 9, 18, and 36 (desorption only). These intervals were selected based on the lower range of national values for BSM permeability rates (1-in/hr) and BSM depth (18-inches) (Carpenter & Hallam, 2010). The mass of biochar in grams added to the solution was: 0.25 for desorption testing, 1.0 for kinetics testing, and 0.05, 0.10, 0.25, 0.5, and 1.0 for sorption equilibrium capacity testing.

Figure 3.2 Jar Testing Set-Up

The solution was deionized water for the desorption testing and the multi-component stormwater solution (Table 3.3) for the equilibrium capacity and kinetics testing. Samples of the solution and blanks were collected by sacrificially removing bottles at each time interval to test the pH and concentrations of dissolved metals (Cu, Zn, Pb, Ca, and Mg) using the standard testing methods Table 3.3. The SSW solution was tested for additional parameters that could influence the sorption capacity including nutrients (TP, TN, NH_3-N, NO_3-NO_2-N) and metals (As, Cd, Ni, Cr). As shown in Table 3.3, none of the four metals were detected in the SSW.

Experimental Design – Column Testing

The purpose of testing biochar in flow through columns was to: 1) evaluate and compare the short-term effectiveness of two different biochars for reducing pollutants, 2) evaluate the treatment performance of different quantities of the same biochar to determine the appropriate quantity of biochar to recommend for a BSM-Biochar mix, and 3) compare the treatment performance predicted in the Essential Properties section to the actual treatment performance of the biochars. The column testing set-up is shown in Figure 3.3.

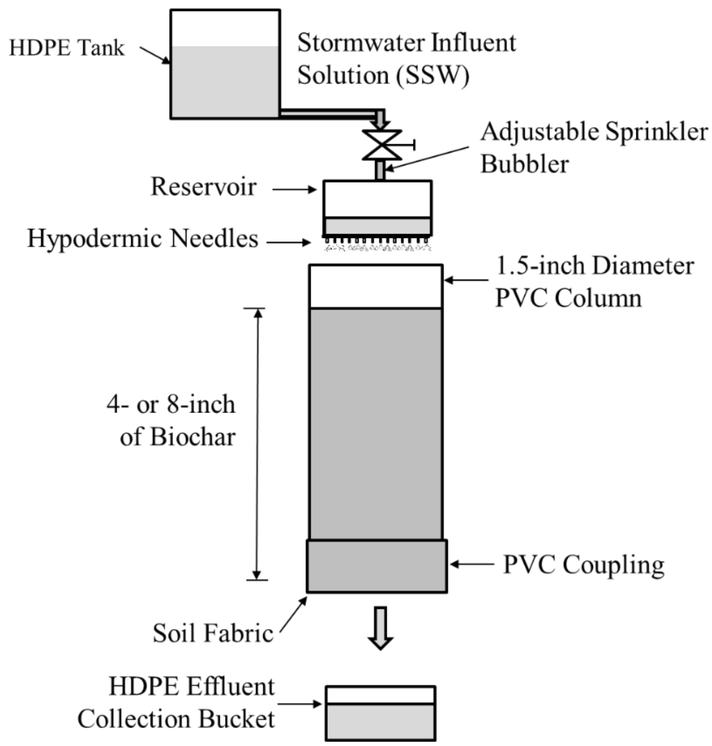

Figure 3.3 Flow Through Column Test Set-up

The column setup was designed to be representative of a bioretention cell constructed in the field. For example, the surface area of the column was assumed equivalent to the surface area from the same diameter section in a bioretention cell. The depth of stormwater distributed to the columns during each of the 12 rainfall events was equivalent to 1.5-in for a total of 18-inches which is equivalent to the mean annual precipitation in Spokane Washington. The total volume of stormwater distributed to each column was determined by assuming the column area was 2% the size of the contributing impervious basin area. This bioretention cell sizing ratio is consistent with the national average which varies between 2% to 20% (Carpenter & Hallam, 2010; Davis, Hunt, Traver, & Clar, 2009; Hunt, Davis, Traver, 2012; Minnesota Pollution Control Agency, 2014).

Four 1.5-inch diameter schedule 40 plexiglass columns were used for this study. A 150 mesh (0.105 mm) soil fabric was secured on the bottom of each column using a schedule 40 PVC coupling to prevent loss of the biochar material during testing. The biochars were received from the suppliers in sealed 19-liter buckets and placed in the columns without any modification to the material. To obtain representative and equivalent biochar in each column, the biochar was homogenized using the cone and quarter technique. Then the biochar was collected by "spooning" from each of the four quadrants and the contents of each scoop was equivalently divided between the four columns (Schumacher et al., 1991).

At the time of this study, no previous studies were identified that provided recommendations for quantity of biochar to include in BSM mixes. Instead, the assumptions described in this paragraph were made to determine the column configurations. Two columns were packed with W biochar and two with KB biochar, each to a depth of 4-inches

(W4 and KB4) and 8-inches (W8 and KB8). These quantities are equivalent to the volume of organic matter used nationally in BSM which ranges from 10% to 40% of the total volume of the BSM (Minnesota Pollution Control Agency, 2014; Carpenter, Hallam, 2010; Hinman, 2009; Hunt & Lord, 2006). For example, if the bioretention cell contains an 18-inch depth of BSM, the 4- and 8-inch depth of biochar placed in the columns is equivalent to 22% and 44% of the BSM by volume. These biochar quantities are also equivalent to 2% and 4% of the total BSM dry weight which is the amount recommended for agricultural applications (Beesley et al., 2011). The reason two different quantities of each biochar were selected for column testing was to assess the influence on the treatment performance, particularly the nutrient leaching and to recommend a quantity of biochar for the field application in BSM. The density of the biochar in each column along with the column coding and gradation information is summarized in Table 3.4.

Table 3.4 Column Coding and Physical Characteristics

Column Code	Biochar Type	Depth (in)	Bulk Density (g/cc)	Particle Size Distribution (% passing)					D10 (mm)	D50 (mm)
				#4	#8	#40	#100	#200		
KB8	Kentucky Blue Grass (KB)	8	0.085	100	99.3	98.2	65.8	24	0.08	0.12
KB4		4								
W8	Wood (W)	8	0.081	100	87.3	11.2	1.9	0.9	0.04	1.42
W4		4								

Stormwater Solution and Rainfall Simulations

Rainfall simulations for the column testing were conducted every 2 to 5 days for a total of twelve events with each event averaging 20 hours. This duration was selected because is representative of long duration rainfall events that are common in eastern Washington (WSDOT, 2016) which are used to design bioretention cells (AHBL & HDR, 2013). The rainfall frequency was selected to allow a dry period between storms however the actual duration between storm events was selected based on constraints in the project schedule.

For each rainfall event, 8-Liters of the SSW solution was distributed equally to four HDPE tanks which were elevated above the columns (Figure 3.3). The tank discharge connection included a manually operated valve that remained open during the rain simulations allowing stormwater to gravity flow through tubing to the 250-mL reservoir. Each tube then discharged into a 250-mL reservoir through an adjustable sprinkler bubbler which was adjusted to maintain a target flow rate of approximately 1.40 mL per minute. Flow from the reservoir was distributed over the top of each column through seven equally spaced 22-gauge hypodermic needles. Stormwater then gravity drained through each column and discharged into an HDPE effluent collection bucket.

Composite water quality samples were collected from 12 rainfall events which included one influent and four effluent samples. The influent sample was collected immediately before the rainfall event from the combined discharge of all four bubblers. Effluent samples were collected from cleaned HDPE buckets located under each of the four columns after discharge from the columns ceased (typically an hour after the event). All samples were collected and analyzed following the standard methods shown in Table 3.3.

Data Analysis Procedures – Part 1 Jar Testing

Desorption

Desorption testing was conducted to assess whether the biochars release (leach) metals, specifically Cu, Zn, Pb, Ca, and Mg, into the stormwater solution. This included calculating the density of the metals desorbed (Equation 1) for both biochars at each of the testing time interval.

$$q_d = \frac{(C_i - C_e)V}{M} \qquad \text{Equation 1}$$

Where:

q_d	=	density of desorbed (mg/g)
C_i	=	initial dissolved concentrations (mg/L)
C_e	=	residual dissolved concentrations (mg/L)
V	=	volume of solution (L)
M	=	dry mass of biochar (mg)

Kinetics

The sorption kinetics reaction order was determined by graphing the measured C_e/C_i vs. time (interval when bottles were removed) and fitting the data to zero, first, and second order reaction equations (Equations 2-4). This included using the hydraulic retention time (HRT) equations (Equations 5-7) along with the measured data to calculate the average reaction rate constant (k) for each mass of biochar. Then the zero, first, and second order reaction equations (Equations 2-4) were used to solve for C_e/C_i using the constant (k). The determination of whether the reaction was zero, first, or second order was evaluated using a Chi Goodness of Fit test (X^2). For the best fit, the HRT needed to achieve 30%, 60%, and 90% pollutant reduction was predicted using the respective zero, first, or second order reaction equation (Equations 2-4).

Zero Order Reaction $$\frac{C_e}{C_i} = \left(1 - \frac{kt}{C_i}\right) \qquad \text{Equation 2}$$

First Order Reaction $$\frac{C_e}{C_i} = e^{-kt} \qquad \text{Equation 3}$$

Second Order Reaction $$\frac{C_e}{C_i} = (1 - C_e^{kt}) \qquad \text{Equation 4}$$

Zero Order HRT $$H_{RT} = \frac{(C_i - C_e)}{k} \qquad \text{Equation 5}$$

First Order HRT $$H_{RT} = \frac{ln\left(\frac{C_i}{C_e}\right)}{k} \qquad \text{Equation 6}$$

Second Order HRT $$H_{RT} = \frac{(C_i - C_e)}{kC_iC_e} \qquad \text{Equation 7}$$

Where:

k	=	reaction rate constant
t	=	time

Sorption Capacity Equilibrium

The actual density of the metals sorbed to the biochar was calculated for each metal (Equation 8). Then the data was fit to the Langmuir and Freundlich isotherm models (Equations 9-10) to assess the treatment performance and estimate the total sorption capacity. This included fitting the data to linear forms of the isotherm models to determine the model constants and then using the constants to develop non-linear plots of the isotherm models (Metcalf, Eddy, & Tchobanoglous, 2004; Minton, 2012). The goodness of fit was evaluated using the r-squared value (R^2) for the linear plots and the Chi Goodness of Fit test (X^2) for the non-linear plots. The isotherm model with the overall best fit to the data was determined for each metal (Cu, Zn, and Pb) based on the higher r-squared value (where R^2=1 indicates a perfect fit) and the lowest X^2 (Bolster & Hornberger, 2007). Specifically, Cohen's rule of thumb suggests that r values of 0.1, 0.3, and 0.5 represent a small, medium, and large effect size (Cohen, 1970). For example, an r≥0.5 a large association or relationship between the two values.

Density Sorbed $$q_e = \frac{(C_i - C_e)V}{M}$$ Equation 8

Freundlich $$q_e = K_F C_e^{\frac{1}{n}}$$ Equation 9

Langmuir $$q_e = \frac{Q_{max} K_L C_e}{(1 + K_L C_e)}$$ Equation 10

Where:

q_e	=	density of metals sorbed (mg/g)
K_F	=	sorption capacity constant $(L/g)^{1/n}$
1/n	=	strength of sorption constant
Q_{max}	=	maximum sorption capacity constant (mg/g)
K_L	=	binding strength coefficient constant (L/mg)

Data Analysis Procedures – Part 2 Column Testing

Hypothesis Testing

A statistical comparison was conducted to determine whether there was a significant difference between: 1) the influent (SSW) and the effluent concentration from each column and 2) the treatment performance of different types of biochars and different quantities of the same biochar. This included evaluating whether the data was normally distributed using the Ryan-Joiner test (similar to Shapiro-Wilk test) (Helsel, 2002). Normality was assumed if the tests produced a p-value greater than 0.05 (Ecology, 2008). If the data was normally distributed, a paired two-sample t-test was used to determine if there was a significant difference between the influent and effluent concentrations. If the data was non-normally distributed, a Wilcoxon rank sum test was used instead;

which is a nonparametric analogue to the paired t-test. The statistical comparison was based on a confidence level of 95% (α=0.05). The specific null hypothesis (H_o) and alternative hypothesis (H_a) evaluated are as follows:

Hypothesis 1:

- H_o: Effluent pollutant concentration from each column is equal to the influent (SSW) concentration
- H_a: Effluent concentrations is not equal to the influent concentration

Hypothesis 2:

- H_o: Effluent pollutant concentration from a column is equal to the effluent concentration of another column: KB4 to W4, KB8 to W8, KB4 to KB8, and W4 to W8
- H_a: Effluent concentration from a column is not equal to the effluent concentration from another column: KB4 to W4, KB8 to W8, KB4 to KB8, and W4 to W8

Short Term Effectiveness

The short-term effectiveness was assessed based on the mean removal efficiency for each pollutant over all 12 rainfall events. This included calculating the removal efficiency for each pollutant from each individual rainfall events using Equation 11. Then the bootstrapping method was used to compute the 95% confidence interval for the mean removal efficiency from all rainfall events. The boot strapping method assumes the dataset is not normally distributed (*Technical Guidance Manual for Evaluationg Emerging Stormwater Treatment Technologies*, 2011). In a few instances, analytical results provided by the lab included values that were non-detectable. When this occurred, ND values were replaced with the reporting limit for the respective parameter as defined by the standard testing method noted in Table 3.3.

$$\Delta C_{SW} = 100x\frac{C_{in}-C_{eff}}{C_{in}} \qquad \text{Equation 11}$$

Where:

C_{in} = influent concentration (mg/L)

C_{eff} = effluent concentration (mg/L)

Cation Exchange Capacity (CEC)

The change in the CEC over the testing period was evaluated to estimate the life-cycle of the biochars. This included measuring the CEC of each biochar after column testing (post sample) using standard testing method 2320B and then multiplying the mass of biochar contained in a column by the respective baseline and final CEC (meq/100g). Then the baseline and final CEC were averaged from the two W columns (W4 and W8) and the two columns (KB4 and KB8) and the percent change in CEC for each biochar was calculated using Equation 12.

$$\Delta C = 100x\frac{CEC_{baseline} - CEC_{final}}{C_{baseline}}$$ Equation 12

Where:

$CEC_{baseline}$	=	Average baseline CEC (meq)
CEC_{final}	=	Average final CEC (meq)

Saturated Hydraulic Conductivity (K_{sat})

The changes in the hydraulic conductivity over the course of the simulated rainfall events was determined for each column media using a falling head test. Four tests were conducted immediately before the first rainfall simulation and then after every four rainfall simulations. This included filling each column with 12-inches of deionized water and recording the time required for water to drop every 1-inch. Then the hydraulic conductivity was calculated using Equation 13. Testing continued until the hydraulic conductivity was stable which is defined as when the values did not change more than 10% for 3 increments.

$$K_{sat} = \frac{L}{t}\ln\frac{h_1}{h_2}$$ Equation 13

Where:

k	=	hydraulic conductivity (in/hr)
L	=	length of flow through soil depth in column (in)
t	=	time (hour)
h_1 & h_2	=	initial head and final head (in)

RESULTS AND DISCUSSION

Part 1 Jar Testing - Desorption

The only metals detected in the effluent solution Ca and Mg. Both Ca and Mg are mineral ions that make up part of the ash content of biochar. As shown in the Figure 3.4 graphs, complete desorption of Ca and Mg was not observed for either biochar since none of the trend lines reached a plateau. The results indicate that the W biochar desorbed more Ca (2.5 mg/g) over time compared to the KB biochar (0.8 mg/g) however, the KB desorbed more Mg (0.72 mg/g) compared to the W (0.35 mg/g).

Biochar studies have documented the leaching of mineral ions (Tian et al., 2014) with higher leaching rates attributed to a higher content of that mineral ion within the biochar (Lehmann & Joseph, 2015). The relationship between a higher mineral content and leaching of mineral ions could explain why the KB biochar, which is composed of 0.57% Mg, desorbed more Mg compared to the W biochar, which is composed of 0.1% Mg. However, it does not explain why the W biochar (1.28%) desorbed more Ca than the KB biochar (1.36%). Based on the total content of these minerals measured in each biochar, the amount leached represents only 20% Ca and 35% Mg contained in the W and 6% Ca and 13% Mg contained in the KB biochar.

Since both biochars release Ca and Mg over time, this may enhance phosphorus reduction (Erickson et al., 2007). Specifically, these mineral ions are known to contribute to the formation of particulate phosphorus (P). When P is in a particulate form, it can be readily removed in a bioretention cell through filtration (Erickson et al., 2007).

Part 1 Jar Testing - Kinetics

The results from the sorption kinetics testing indicate a first order reaction best fit the data for both biochars and all three metals (Figures 3.5-3.7). First order reactions initially remove pollutants quickly and then more gradually over time (Minton, 2012). As shown in the graphs, the pollutant reduction ratio (C_e/C_i) for all three metals reached 0.2 for the W biochar within 9 hours. Comparatively the KB biochar only reached a C_e/C_i ratio of between 0.6 and 0.7 for all metals within 9 hours. These results suggest that the rate of the sorption is faster for the W biochar compared to the KB biochar.

The hydraulic residence time (HRT) was calculated for each biochars to achieve 30%, 60%, and 90% pollutant removal of Cu, Pb, and Zn. The results (Table 3.4), indicate that 90% reduction of these pollutants will occur within 7-13 hours for the W biochar and 44-57 hours for the KB biochar. Since the BSM permeability rate is limited to a minimum of 1-in/hr (AHBL & HDR, 2013; Carpenter & Hallam, 2010) and the minimum BSM depth is 18-inches, a run time duration of 18-hours was selected for the equilibrium testing. As such, the equilibrium capacity results for the KB biochar are expected to be less than the total capacity of the biochar, but potentially more representative of the conditions expected in the field. Based on the results, it appears the W biochar can achieve a 90% reduction of all metals within an 18-hour HRT required for stormwater to infiltrate through a BSM 18-inch in depth at the same time the KB biochar is only expected to achieve 60% (Cu) or less (Zn and Pb) reduction.

The results from the Chi Goodness of Fit test indicate that the KB biochar for all metals and the W biochar for Pb had the best overall fit to the HRT equations based on the lower X^2 values.

Table 3.5 Jar Testing – Sorption Kinetics Results (first order, best fit)

Parameter	W - Biochar			KB - Biochar		
	k	HRT (hrs) 30%/60%/90%	X2	k	HRT (hrs) 30%/60%/90%	X2
Cu	0.264	1/3/7	0.328	0.052	7/18/44	0.124
Zn	0.212	2/4/11	0.590	0.046	8/20/50	0.118
Pb	0.183	2/5/13	0.145	0.040	9/23/57	0.133

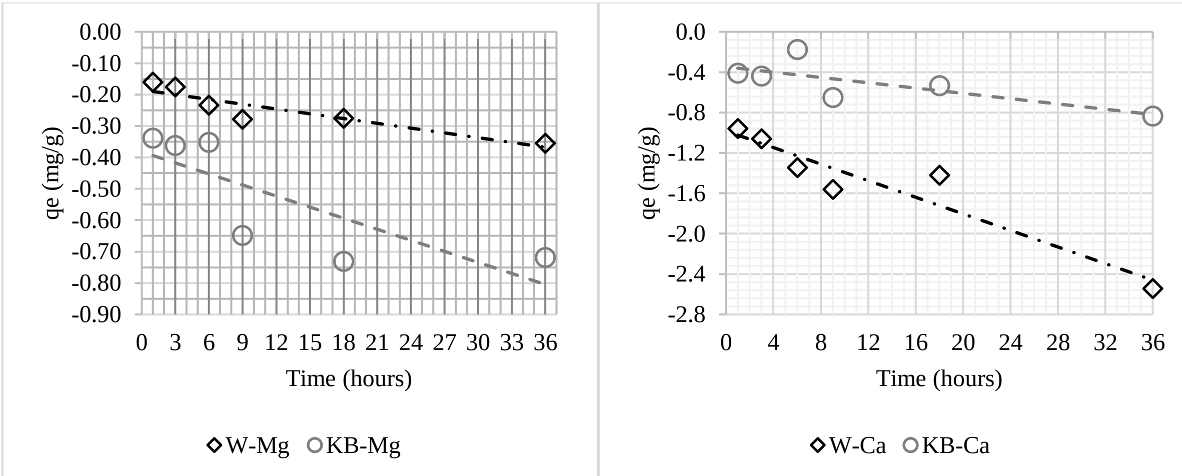

Figure 3.4 Desorption Results – Release of a) Mg (left) and b) Ca (right) Over Time

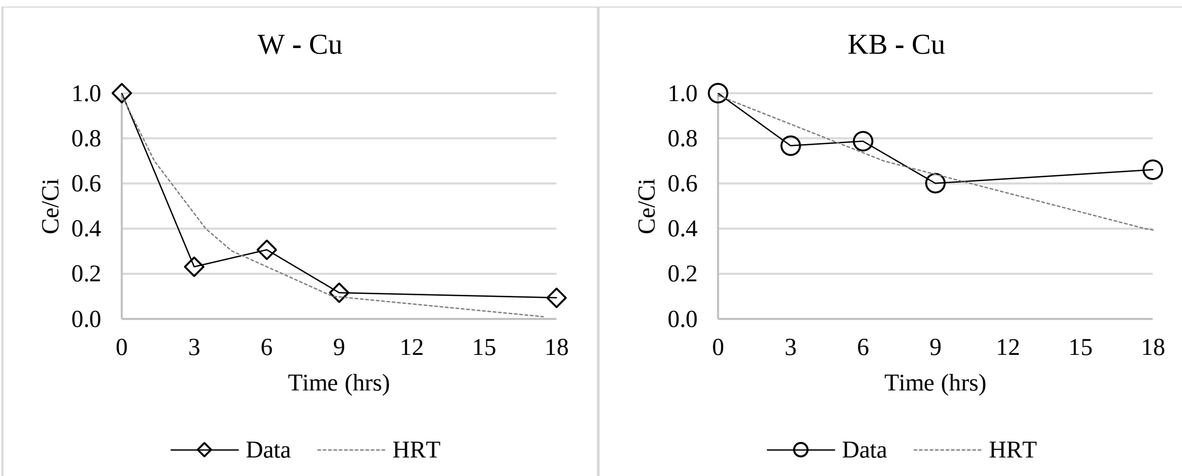

Figure 3.5 Cu Kinetics Results a) W Biochar (left) and b) KB Biochar (right)

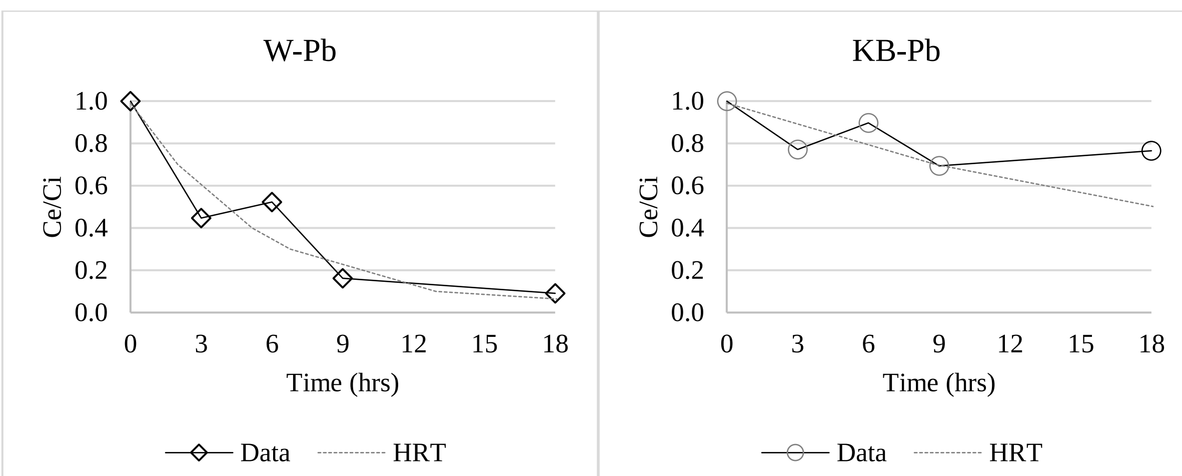

Figure 3.6 Pb Kinetics Results a) W Biochar (left) and b) KB Biochar (right)

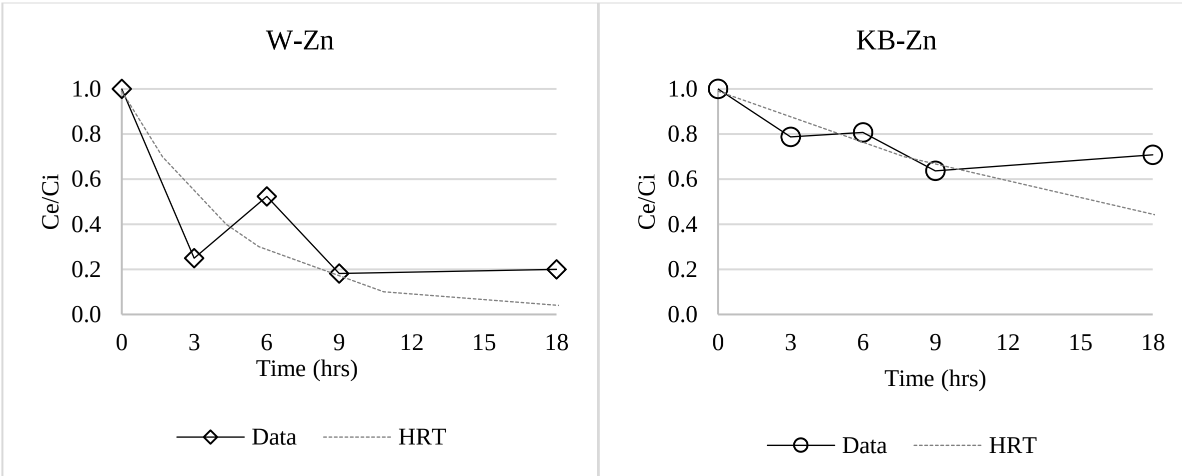

Figure 3.7 Zn Kinetics Results a) W Biochar (left) and b) KB Biochar (right)

Part 1 Jar Testing - Sorption Equilibrium

The data from the sorption equilibrium testing was fit to the Freundlich and Langmuir isotherms models for Cu, Pb, and Zn. Table 3.5 provides a summary of the results and the Isotherm graphs are shown in Figures 3.8-3.10.

Table 3.6 Summary of Isotherm Results

	Langmuir				Freundlich				Largest Observed Metal
	K_L	Q_{max} (mg/g)	R^2	r	K_F (mg/g)	1/n	R^2	r	Uptake (mg/g)
Copper									
KB	3.70	0.52	0.15	0.39	**0.05**	**0.12**	**0.30**	**0.55**	2.30
W	0.47	4.90	0.74	0.86	**1.52**	**0.74**	**0.98**	**0.99**	2.20
Lead									
KB									11.70
W	**0.36**	**3.43**	**0.90**	**0.95**	2.84	0.36	0.74	0.86	8.90
Zinc									
KB									0.90
W					**2.04**	**1.34**	**0.98**	**0.99**	0.70

b. Note: Gray shading indicates the best overall fit to the Isotherms models.

The data from the equilibrium testing was fit to the Langmuir and Freundlich isotherm models. A comparison of the goodness of fit measures between the two different isotherm models (shown in gray cells in Table 3.5), indicates that the best overall fit was the Freundlich model for Cu and the Langmuir model for the W biochar with Pb. No coefficients are reported for either model with the KB biochar for Pb or Zn or the Langmuir model for the W biochar with Zn. This is because the scatter in the data yielded negative coefficients for the model to fit the data.

Total sorption capacity is observed when the isotherm curves reach a plateau. Based on sorption isotherm plots (Figures 3.8-3.10), the capacity was not exhausted for either biochar during testing. Since the total capacity of the biochars was not achieved, the largest metal uptake observed in the data for each biochar was added to Table 3.5. The KB biochar had the largest uptake for all metals. The trend in the KB biochar isotherm plots generated from the actual data indicates that the metals uptake was high when mass of biochar was the smallest (0.05- and 0.10-grams) however the equivalent uptake was not observed with the larger masses of biochar (0.25-, 0.50-, and 1.0-grams). This trend can be observed by the multiple inflection points in the isotherm plots that form an 'S" shape. This isotherm shape is considered "unfavorable" because it indicates that while a sorptive media is effective at removing metals when the concentration in a solution is high, the media is less effective when the solution metals concentration is low (LeVan, 2007). Comparatively the trend in the W biochar plots indicates the uptake of metals was consistent for all the masses of biochar tested (0.05, 0.10, 0.25, 0.50, and 1.00). This relationship can be observed by the concave down shape of the isotherm plot. This shape is considered "favorable" because it indicates that the sorptive media is effective for removing metals over a range of concentrations (LeVan, 2007).

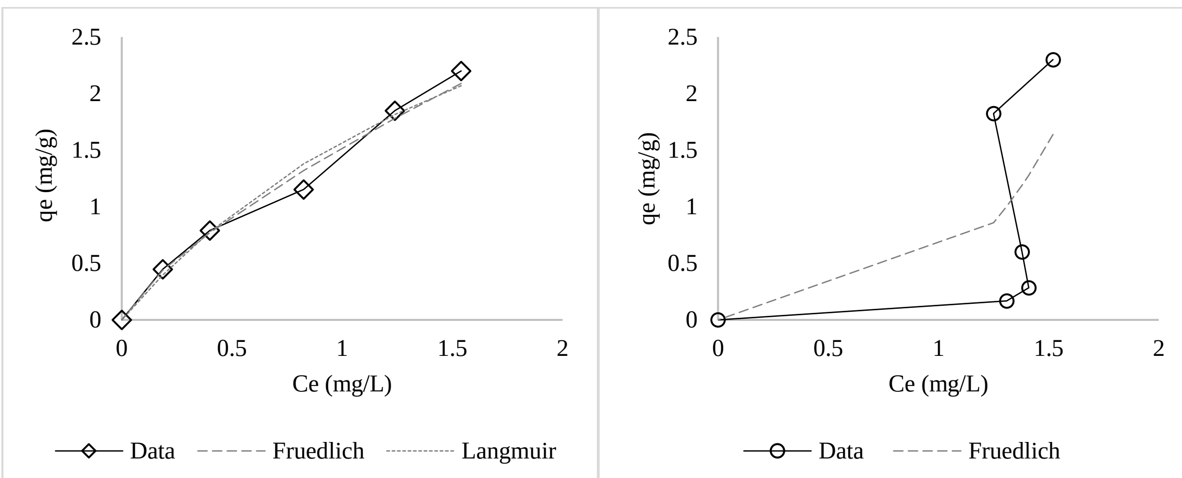

Figure 3.8 Cu Sorption Isotherms Plots a) W Biochar (left) and b) KB Biochar (right)

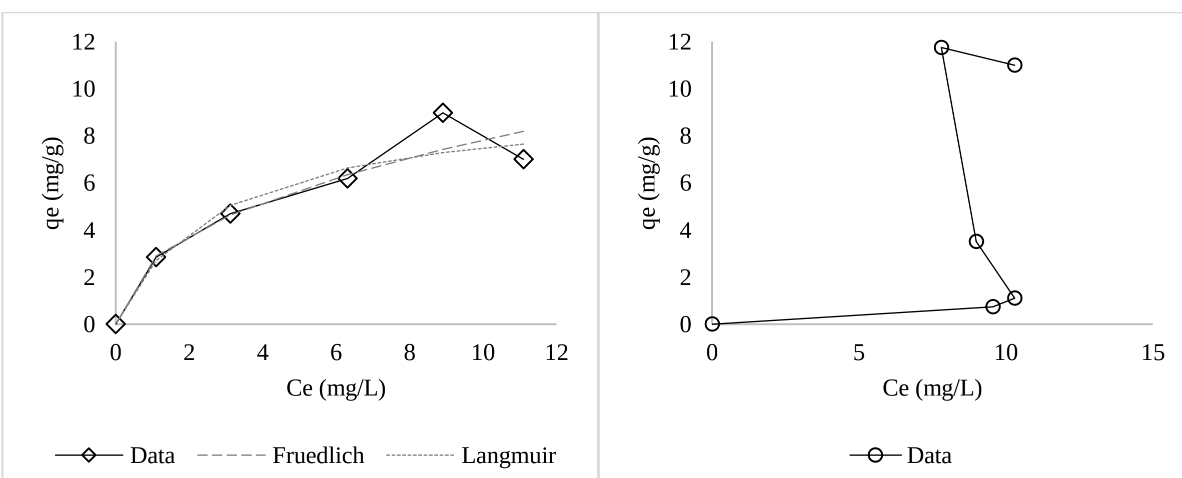

Figure 3.9 Pb Sorption Isotherms Plots a) W Biochar (left) and b) KB Biochar (right)

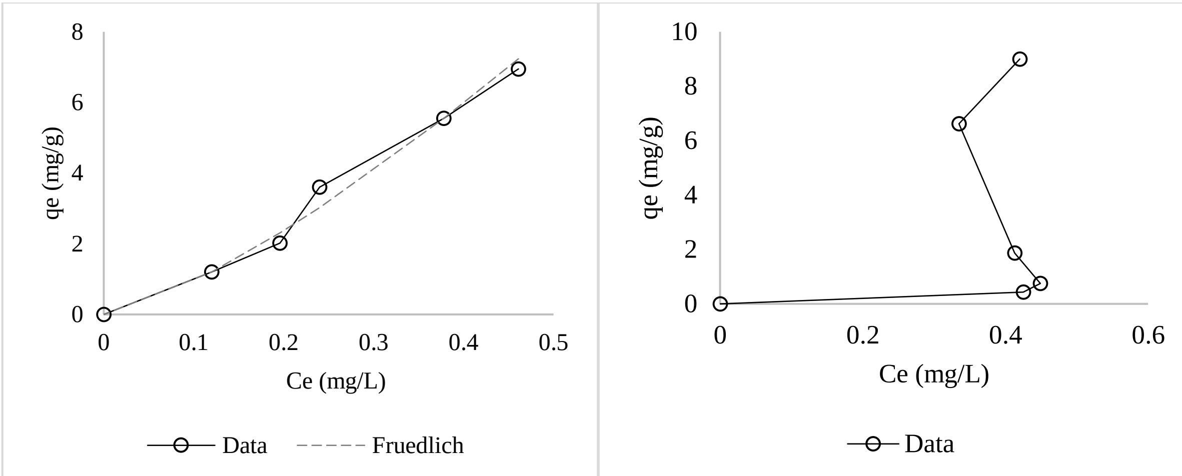

Figure 3.10 Zn Sorption Isotherms Plots a) W Biochar (left) and b) KB Biochar (right)

One reason why the data from the W biochar had a better fit compared to the KB biochar may relate to the dominant sorption process. The isotherm models describe the relationship between the sorbent and the amount of sorbate adsorbed. Because the KB biochar had a $H:C_{org}$ ratio greater than 0.7 and a higher CEC value compared to the W biochar, cation exchange may be a more dominant sorption process for KB (Foo & Hameed, 2010). Another reason may relate to an increase in the stormwater solution pH that occurred during testing (Figure 3.11). The pH measured in the blank sample was 7.6 at the end of testing compared to the pH of the other samples which increased as a function of the biochar mass with the highest pH measured in the samples with 1.0 gram at 8.1 and 8.5 for the W and KB biochar respectively. The increase in pH was not surprising since the pH of the biochars ranged from 9.45 for the KB biochar to 10.32 for the W biochar (Appendix A). A change in the stormwater solution pH can influence the speciation of the metals (Minton, 2012) thereby changing the amount of dissolved metal ions in the stormwater solution available for adsorption during testing.

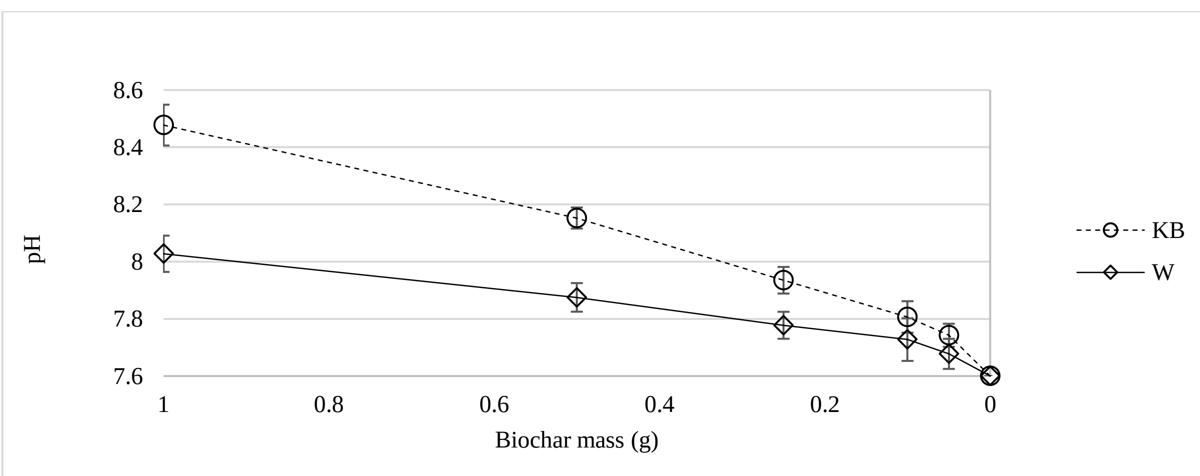

Figure 3.11 Sorption Equilibrium Testing – Mean pH vs biochar mass

Hydrophobic tendencies exhibited by both biochars during testing likely contributed to the large variance in the data particularly for the KB biochar. The biochar particles initially floated at the top of the solution during testing.

After 18-hours, most of the W biochar had settled at the bottom of the jar compared to about half of the KB which was still floating on the surface (Figure 3.12). This behavior is likely due to negative capillary forces which held air in the biochar micro-pores inhibiting the uptake of water preventing the biochar from becoming saturated (Gray, Johnson, Dragila, & Kleber, 2014; Jeffery et al., 2015). The degree of saturation can also influence the biochar sorption capacity since the total surface area, which includes the micropores and macropores, is inaccessible to the stormwater solution. Researchers have reported that the hydrophobic characteristics tend to diminish once the biochar becomes saturated which presumably would increase the accessibility of the micropores (total surface area available) to the stormwater solution (Gray et al., 2014).

Figure 3.12 Batch Testing Observations: W biochar at 1 hour (far left) and 18 hours (2nd from left); KB biochar at 1 hour (3rd from left) and 18 hours (4th from left).

The observed hydrophobic tendencies may explain why the pollutant reduction ratio (C_e/C_i) for the KB biochar was higher (0.6 to 0.7) compared to the W biochar (0.2) during the kinetics testing. Specifically, the W biochar was more saturated so more of the surface area sites on the biochar were available for adsorption. Potentially the treatment performance of the KB (indicated by the C_e/C_i) may improve as the KB biochar saturation increases. Considering the 18-hour run time for the equilibrium testing was selected based on the actual time required for stormwater to infiltrate through a bioretention cell as well as the dry periods expected between rainfall events, it is possible that the biochars selected for this study may not become fully saturated in a typical field application. However, it is anticipated that the BSM will remain moist between rainfall events which may influence the degree of saturation of the biochar and subsequently the adsorptive capacity. Researchers have theorized that due to the water repellency characteristic of biochar, the micropores may never be fully accessible (Morrow, 2013). Based on the results of this study it is not possible to determine the total sorption capacity of the biochars instead the results provide an indication of how the hydrophobic characteristics of biochar may influence the treatment performance.

Part 2 Column Testing - Water Quality Performance

This section presents the water quality results, organized by parameter and presented in the following order: pH, TSS, heavy metals, phosphorus, nitrogen, and hardness. Graphs of the results are embedded for in each parameter section. The graphs include box plots which illustrate the mean SSW concentration compared to the mean effluent concentration for each column. In addition, scatter plots for each parameter are also include that illustrate the change in the pollutant reduction ratio (C_e/C_i) from each column over the duration of the simulated rainfall events. Tables of the water quality results are included in each section.

pH

The pH increased from the influent 7.58 to the effluent 8.26 for the KB4 and KB8 columns and 8.35 to 8.39 for the W4 and W8 columns respectively (Table 3.6 and Figure 3.12). There is a statistically significant difference between the influent and effluent pH for all columns (p=0.001). These results are consistent with the pH increase observed during the Part 1 testing which is attributed to the higher pH of the biochars (KB=9.45 and W=10.32) compared to the stormwater solution (pH=7.58). The differences in the column effluent concentrations was statistically insignificant between the columns of the same biochar (W4 to W8 and KB4 to KB8) however the difference was a moderately significant (p=0.076) when comparing the columns with different biochars with the same quantity (KB4 to W4 and KB8 to W8). These results suggest that the type of biochar influenced the effluent pH: the KB columns had a slightly lower pH compared to the effluent from the W columns.

Table 3.7 pH Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Mean Concentration (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
SSW	11	7.58 (±0.24)	-	-	-
KB4	10	8.26 (±0.39)	-7.9%	0.001	KB4 to W4: 0.076
KB8	10	8.26 (±0.49)	-6.7%	0.001	KB8 to KB4: 0.734
W4	10	8.35 (±0.26)	-9.2%	0.001	W4 to W8: 1.000
W8	10	8.39 (±0.33)	-9.5%	0.001	W8 to KB8: 0.076

The reduction ratio (C_e/C_i) was graphed to assess the trend in the pH values over the duration of the rainfall events (Figure 3.13). The effluent pH values were highest during the initial rainfall event (C_e/C_i=1.30 to 1.2) and then gradually declined to between 1.1 to 1.0 for the final rainfall event.

These results are consistent with other studies which have reported an increase in the effluent pH (compared to influent) after a solution is combined with biochar (Iqbal, Garcia-Perez, & Flury, 2015; Tian et al., 2014). Some researchers have reported that after the initial rainfall events, the pH difference was insignificant (Reddy et al., 2014) while other researchers reported an increase in the effluent pH was sustained beyond the initial events (Iqbal et al., 2015). Based on the studies reviewed, variations in the effluent pH (compared to the influent) appear to be dependent upon the biochar pH and the stormwater influent pH: biochars with a higher pH (compared to influent pH) appear to result in a higher pH that is sustained longer (Iqbal et al., 2015; Reddy et al., 2014; Tian et al., 2014). Potential variations in the effluent pH are important to consider because the parameter speciation is pH dependent which may influence the treatment performance of the biochars.

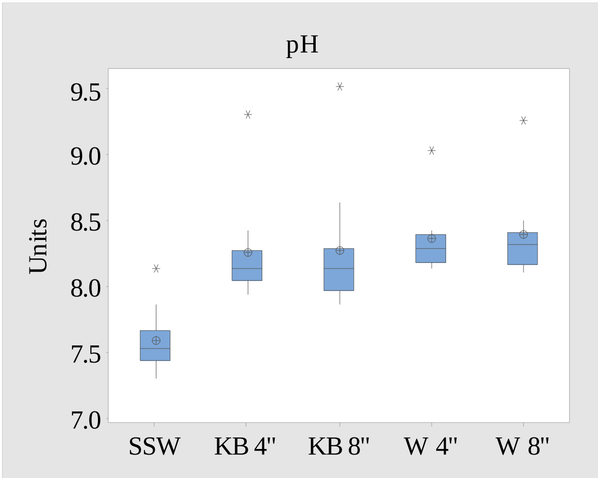

Figure 3.12 pH Box Plots: Comparison of Mean Influent & Effluent Concentrations

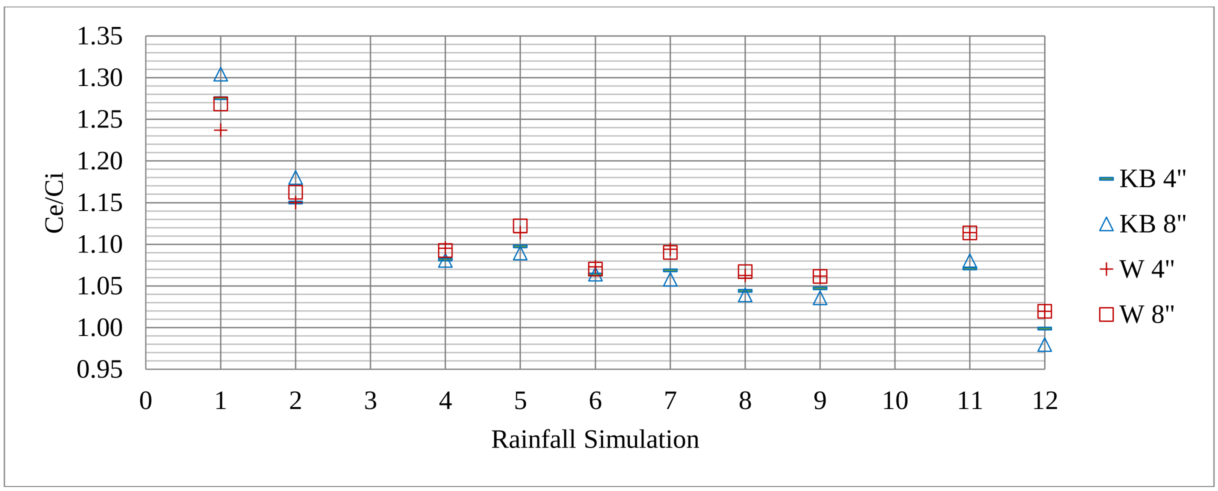

Figure 3.13 pH Reduction Ratio (C_e/C_i) vs. Time

TSS

The average TSS removal efficiency ranged between 89.3%-96.1% for all four columns (Table 3.7 and Figure 3.14) which exceeds the 80% reduction required by most NPDES MS4 permits (EPA, 2016). The difference in the effluent concentrations between the columns was only statistically significant when comparing columns W8 to KB8 (0.024). These results suggest that removal efficiency maybe influenced by the type of biochar (W biochar removal efficiency was higher) in larger quantities.

The pollutant reduction ratio (C_e/C_i) graphs show that over the duration of the rainfall events, the pollutant reduction was generally higher for the W columns compared to the KB columns (Figure 3.15). In addition, the pollutant reduction trend for both the KB and W columns indicates that the effluent contained a higher concentration of TSS during the initial rainfall events and was then relatively consistent ($C_e/C_i \leq 0.01$) for the remaining events. Other biochar column studies have documented similar trends in TSS concentrations during the initial rainfall events (Iqbal et al., 2015) which were attributed to a "flushing period" in which finer particles are flushed from the media (Rheaume, 2015). This initial flushing could explain the differences in the treatment performance between the biochars: the KB biochar contained more fines (24%) compared to the W biochar (0.9%) (Table 3.4) as such more fines were likely flushed from the KB columns during the initial rainfall events.

Table 3.8 TSS Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Average Concentration (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
SSW	12	171.0 (±193.26)	-	-	-
KB4	12	2.64 (±4.26)	92%	0.001	KB4 to W4: 0.175
KB8	12	2.39 (±3.36)	89%	0.001	KB8 to KB4: 0.908
W4	12	1.39 (±1.96)	96%	0.001	W4 to W8: 0.453
W8	12	1.12 (±1.69)	95%	0.001	W8 to KB8: 0.024

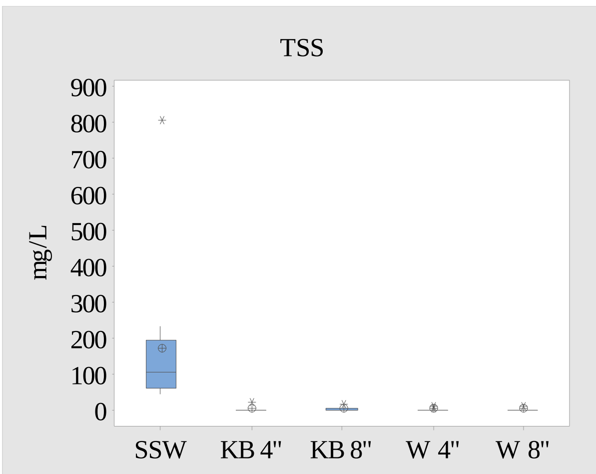

Figure 3.14 TSS Box Plots: Comparison of Mean Influent & Effluent Concentrations

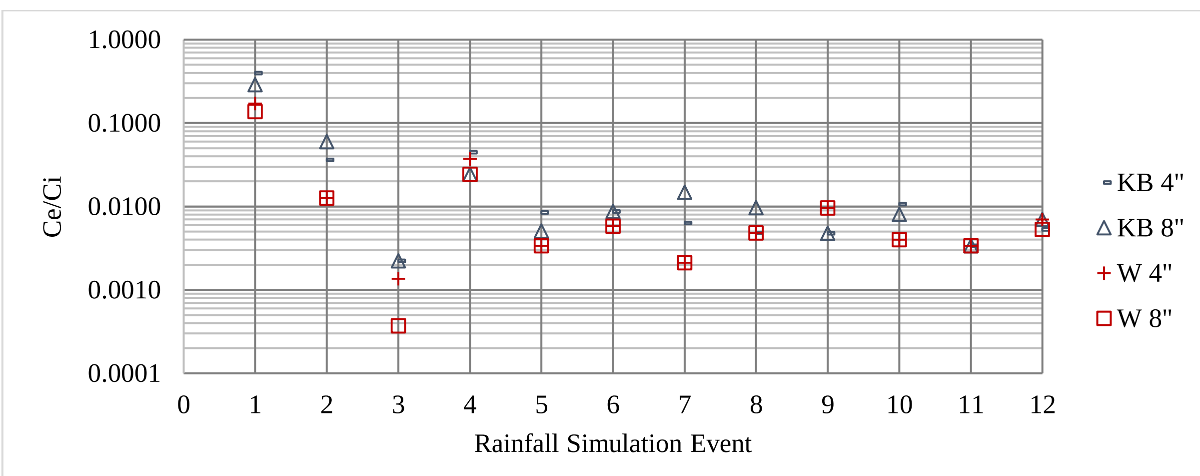

Figure 3.15 TSS Pollutant Reduction Ratio (C_e/C_i logarithmic scale) vs. Time

Heavy Metals (Zn, Pb, and Cu)

The Zn removal efficiency was the highest for all columns, compared to the other metals, ranging from 91% to 98% and 94% to 97% for total and dissolved respectively (Table 3.8 and Figure 3.16). The difference between the influent and effluent concentrations are statistically significant for all columns (p=0.001). The differences in the effluent concentrations between the columns were only statistically significant (total, dissolved) when comparing the following columns: W4 to W8 (0.005, 0.023) and KB8 to W8 (0.002, 0.014). These results suggest that the Zn removal efficiency was influenced by the type of biochar in larger quantities (with the W8 outperforming the W4 and KB8).

Table 3.9 Zn Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

Column ID	n	Average Concentration (µg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to other Columns
Total Zn					
SSW	12	207.70 (±64.3)	-	-	-
KB4	12	7.64 (±6.45)	96%	0.001	KB4 to W4: 0.708
KB8	12	12.53 (±18.92)	91%	0.001	KB8 to KB4: 0.419
W4	12	10.03 (±8.11)	92%	0.001	W4 to W8: 0.005
W8	12	3.52 (±5.39)	98%	0.001	W8 to KB8: 0.002
Dissolved Zn					
SSW	12	105.15 (±30.61)	-	-	-
KB4	12	5.67 (±4.68)	94%	0.001	KB4 to W4: 0.544
KB8	12	6.31 (±5.02)	94%	0.001	KB8 to KB4: 1.000
W4	12	5.66 (±4.79)	94%	0.001	W4 to W8: 0.023
W8	12	3.76 (±5.31)	97%	0.001	W8 to KB8: 0.014

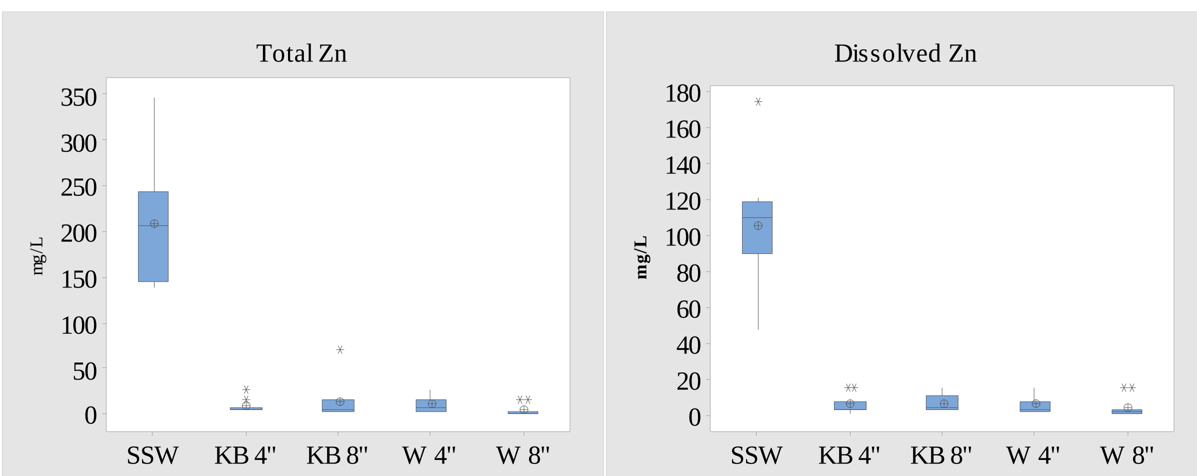

Figure 3.16 Zn Box Plots: Comparison of Mean Influent & Effluent Total (a) & Dissolved (b)

The Pb removal efficiency of all the columns ranged from 97% to 99% and 91% to 98% for total and dissolved respectively Table 3.9 and Figure 3.17). The difference between the influent and effluent concentrations are statistically significant for all columns (p=0.001). The differences in the effluent concentrations between the columns are statistically significant (total, dissolved) when comparing the following columns: KB4 to W4 (0.007, 0.021) and KB8 to W8 (0.041, 0.014). These results suggest that the Pb removal efficiency was influenced by the type of biochar (with the W biochar outperforming the KB biochar).

Table 3.10 Pb Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Mean Concentration (µg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to other Columns
Total					
SSW	12	37.59 (±12.72)	-	-	-
KB4	12	3.37 (±8.40)	97%	0.001	KB4 to W4: 0.007
KB8	12	3.13 (±8.50)	97%	0.001	KB8 to KB4: 0.168
W4	12	2.76 (±8.58)	99%	0.001	W4 to W8: 0.428
W8	12	2.67 (±8.61)	99%	0.001	W8 to KB8: 0.041
Dissolved					
SSW	12	8.392 (±3.253)	-	-	-
KB4	12	0.429 (±0.322)	91%	0.001	KB4 to W4: 0.021
KB8	12	0.394 (±0.432)	92%	0.001	KB8 to KB4: 0.717
W4	12	0.137 (±0.077)	98%	0.001	W4 to W8: 0.442
W8	12	0.091 (±0.164)	97%	0.001	W8 to KB8: 0.014

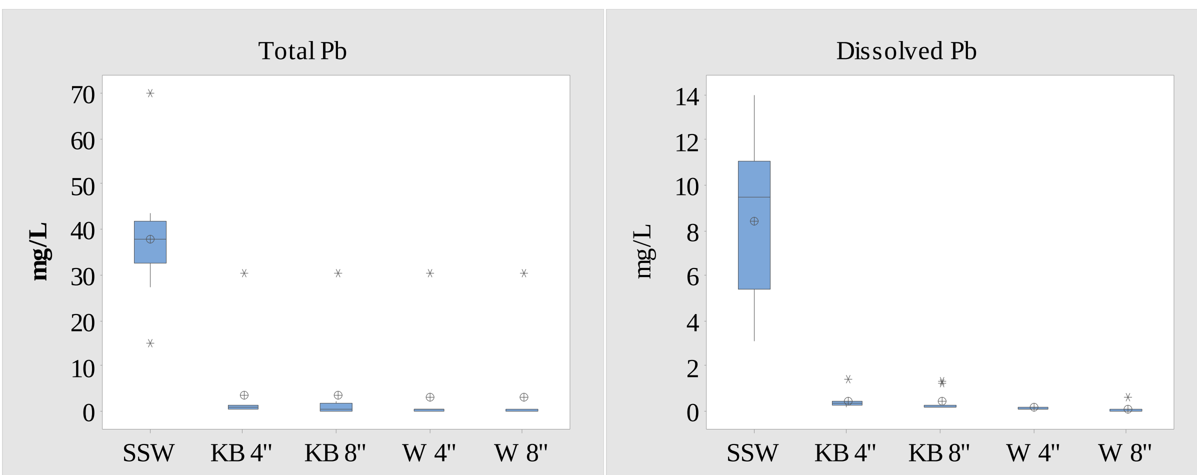

Figure 3.17 Pb Box Plots: Comparison of Mean Influent & Effluent Total (a) & Dissolved (b)

The Cu removal efficiency of all the columns ranged from 72% to 96% and 47% to 89% for total and dissolved respectively (Table 3.10 and Figure 3.18). The removal efficiency from the W columns was higher for both total and dissolved (93% to 96% and 88% to 89%) compared to the KB columns (72% to 75% and 47% to 62%). The difference in the effluent concentrations are statistically significant (total and dissolved) when comparing the W4 to KB4 (0.001, 0.001) and W8 to KB8 (0.001, 0.003). These results suggest that the Cu removal efficiency was influenced by the type of biochar (with the W biochar outperforming the KB biochar).

The KB8 column has one less sample (n=11) compared to the other columns (n=12). With a sample size of n=12, the KB8 column removal efficiency was only 25% which was the result of one rainfall simulation when the measured Cu effluent concentration was double the influent concentration. The KB8 data set was evaluated using the Grubb's test and this one data point was identified as an outlier (α=0.001). As such, the data point was removed from the data set and the data set was re-analyzed. The results indicate that the KB8 column reduced dissolved Cu by 47%. It is worth noting that the lab was contacted and asked to verify the one data point however, the remaining sample had been disposed of, so it was not possible to re-run the analytical testing and rule-out whether the value reported was an error. Since the dissolved Cu value reported for this one data point (0.084 mg/L) was ten times higher than the value reported for the respective total Cu (0.056 mg/L), the value is presumed to be an error. This is because the total Cu represents the sum of the faction of Cu that is solid plus dissolved in a solution as such dissolved Cu should be equal to or less than the total Cu value.

Table 3.11 Cu Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Average Concentration (µg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total					
SSW	12	41.52 (±28.03)	-	-	-
KB4	12	9.17 (±4.97)	72%	0.001	KB4 to W4: 0.001
KB8	12	8.74 (±6.81)	75%	0.001	KB8 to KB4: 0.586
W4	12	1.94 (±1.34)	93%	0.001	W4 to W8: 0.224
W8	12	1.26 (±1.26)	96%	0.001	W8 to KB8: 0.001
Dissolved					
SSW	12	31.57 (±10.65)	-	-	-
KB4	12	10.42 (±4.43)	62%	0.001	KB4 to W4: 0.001
KB8	12 11[a]	15.55 (±6.46) 9.29 (±5.84)[a]	25% 47%[a]	0.001[a]	KB8 to KB4: 0.378[a]
W4	12	2.36 (±1.36)	88%	0.001	W4 to W8: 0.623
W8	12	2.21 (±1.80)	89%	0.001	W8 to KB8: 0.003

c. *The values reported reflect the results of the data set analysis without the outlier.*
d.

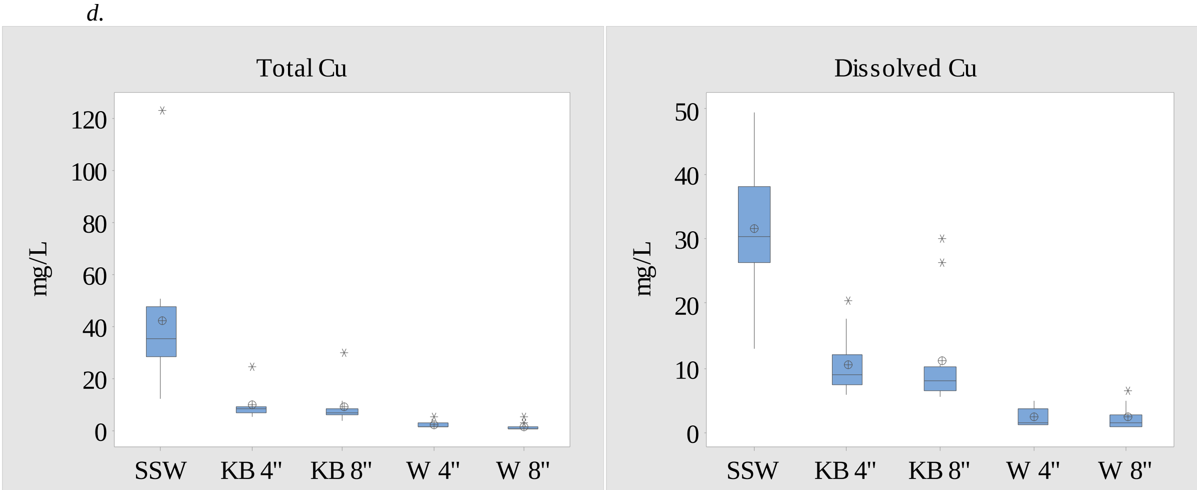

Figure 3.18 Cu Box Plots: Comparison of Mean Influent & Effluent Total (a) & Dissolved (b)

The pollutant reduction ratio of effluent to influent concentrations (C_e/C_i) for dissolved metals was graphed to assess the trend in the treatment performance over the testing period. As shown Figures 3.19 and 3.20, the pollutant reduction ratio for Zn and Pb was consistently ≤ 0.1 for all columns except for Pb during two events for the KB4 column and one event for the KB8 column. No change was observed in the trend of the pollutant reduction ratio for any of the columns that would indicate that the treatment performance was declining or reaching capacity.

The trend in the Cu pollutant reduction ratio differed from the other metals in that for both biochars the pollutant reduction ratio (C_e/C_i) was larger which indicates less reduction of Cu compared to Zn and Pb (Figure 3.21). For the KB biochars the treatment performance gradually increased which is shown as a decline in the C_e/C_i over the testing period ranging from 0.54 to 0.16 and 0.41 to 0.24 for the KB8 and KB4 columns respectively. For the W columns, the pollutant reduction was overall lower compared to the KB columns ranging from 0.21 to 0.02 and 0.24 to 0.03 over the testing period for the W8 and W4 columns. The trend in the W columns indicates the treatment performance gradually improved during first half of the events (shown as a decline in C_e/C_i) and then gradually decreased over the second half (shown as an increase in C_e/C_i). The increase in the pollutant reduction ratio for the W columns may indicate that the biochar was reaching capacity.

These results are similar to the jar testing results in that the pollutant reduction ratio (C_e/C_i) was consistently lower for the W biochar compared to the KB biochar for all metals. The results are different than the jar testing in that rate of the reaction was expected to take longer (HRT) to achieve this level of pollutant reduction: 7-, 11- and 13-hours and 44-, 50-, and 57-hours for the W biochar and KB biochar to achieve 90% reduction of Cu, Zn, and Pb respectively (Table 3.4). Based on the mean column infiltration rates (Table 3.21) which ranged from 12.33- to 39.14-inches/hour, the contact time (HRT) between the stormwater solution and the biochar was 0.1- to 0.3-hours. One justification for the differences is that the weight of the biochar layers packed into the columns prevented most of the biochar from floating compared to the Part 1 testing when most of the KB and W biochar were floating during parts of the testing period. (See the Empirical Observations discussion and Figure 3.36 at the end of this section for more information). Thus, the biochar may have become saturated making the internal surface area more accessible to the stormwater solution, increasing the potential for adsorption of dissolved metals to occur.

These results are consistent with the expected treatment performance based on the Essential Properties in that both biochars were expected to have an excellent sorption capacity for immobilizing dissolved metals. This is because the biochars have a balance of a higher surface area (482 m^2/g) and lower CEC (19 meq/100g) provided by the W biochar and the lower surface area (209 m^2/g) and higher CEC (29 meq/100g) provided by the KB biochar. Since neither biochar is fully carbonized (C_{org}=100%), both adsorption and cation exchange processes are expected to occur simultaneously (Beesley et al., 2011; McLaughlin et al., 2012).

The results from this study are consistent with other studies in that researchers have reported that biochar is effective for removing metals from stormwater solutions. The average removal varies between studies which researchers have attributed to the physiochemical properties of the biochar, the solution pH, speciation of the metals in solution, as well as the types on concentrations of metals competing for sorption sites (Reddy et al., 2014). *Reference the Influent of Stormwater Chemistry on Treatment Process for additional discussion on this topic.*

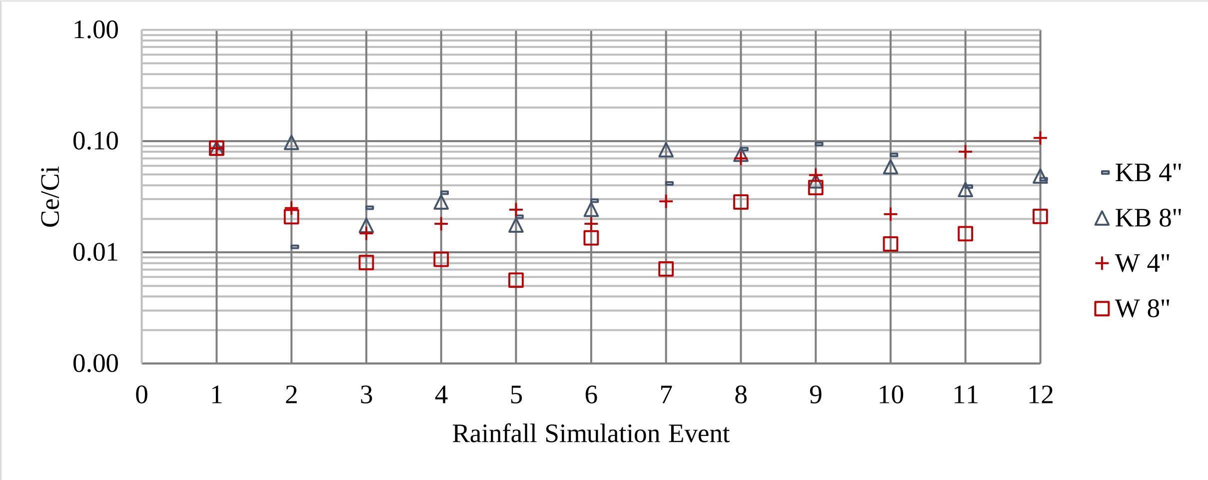

Figure 3.19 Zn Dissolved Pollutant Reduction Ratio (C_e/C_i logarithmic scale) vs. Time

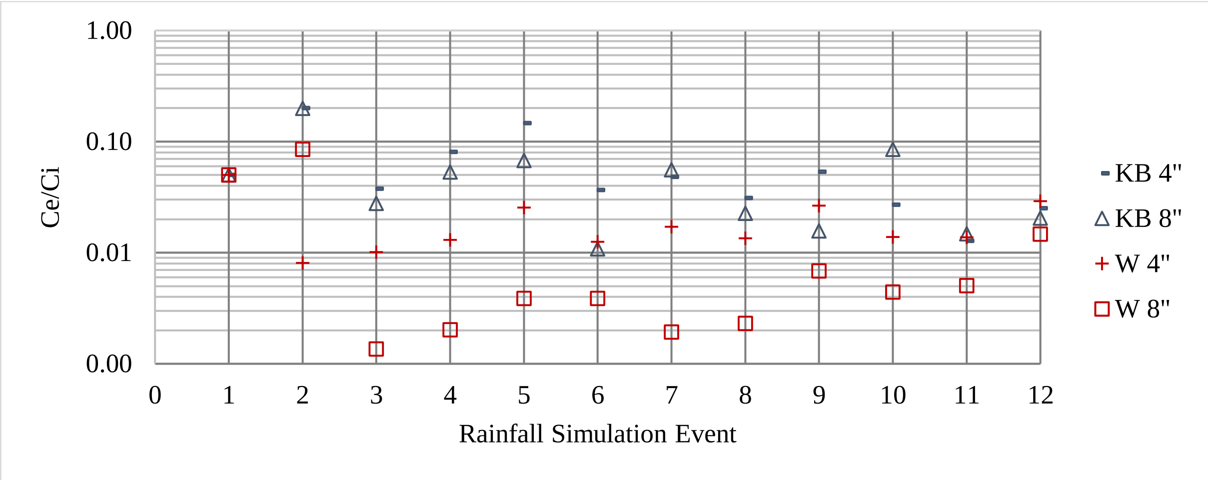

Figure 3.20 Pb Dissolved Pollutant Reduction Ratio (C_e/C_i logarithmic scale) vs. Time

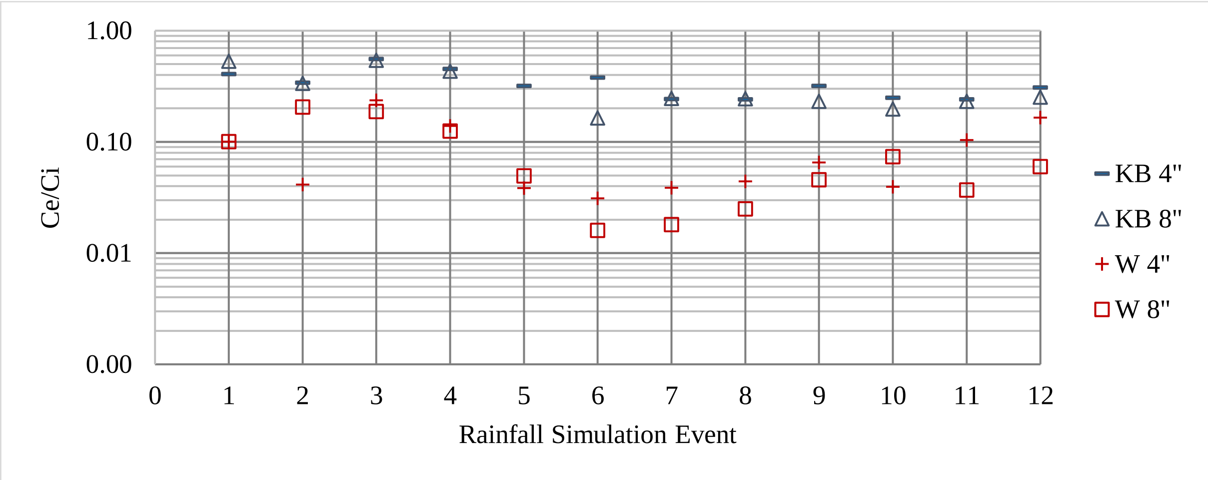

Figure 3.21 Cu Dissolved Pollutant Reduction Ratio (C_e/C_i logarithmic scale) vs. Time

Total Phosphorus (TP)

Neither biochar was effective for removing TP (Table 3.11 and Figure 3.22). The treatment performance of the W columns ranged from 1.1% reduction to -5.7% leaching for the W4 and W8 columns respectively. In comparison, the KB columns leached between -150% to -341% for the KB4 and KB8 columns respectively. The difference between the influent and effluent concentrations is statistically significant for the KB columns (p=0.001) and statistically insignificant for the W4 and W8 columns (0.081, 0.826). The difference in the effluent concentrations between the columns was only statistically insignificant when comparing the W4 to W8 (p=0.0.227). These results suggest that the TP removal efficiency is influenced by: the type of biochar (with W outperforming KB) and for the KB biochar the quantity of biochar (TP leaching increased as the quantity of the KB biochar increased).

Table 3.12 TP Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Average Concentration (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
SSW	12	1.039 (±0.072)	-	-	-
KB4	12	2.240 (±0.636)	-150%	0.001	KB4 to W4: 0.001
KB8	12	3.796 (±1.428)	-341%	0.001	KB8 to KB4: 0.004
W4	12	0.989 (±0.069)	1.1%	0.081	W4 to W8: 0.227
W8	12	1.031 (±0.096)	-5.7%	0.826	W8 to KB8: 0.001

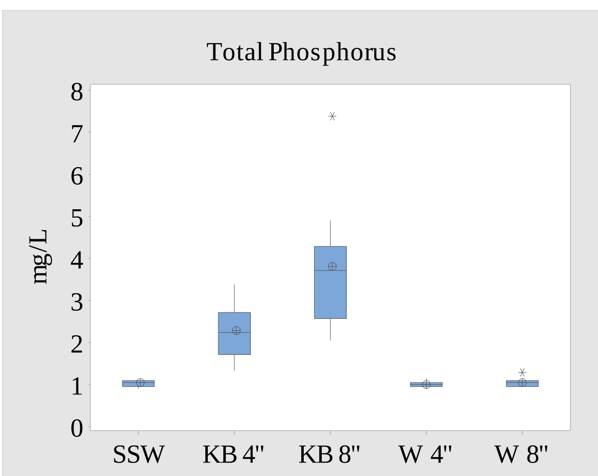

Figure 3.22 TP Box Plots: Comparison of Mean Influent & Effluent

The Essential Properties section predicted that both biochars would leach TP since the composition of the biochars contains a higher phosphorus content than recommended (less than 0.04%). As expected, the KB columns leached TP however the difference between the TP effluent and influent concentration from the W columns was insignificantly despite a higher biochar phosphorus content (0.06%) than recommended. The treatment performance may have been influenced by the hardness concentration in the SSW, specifically the amount of leaching from both biochars may have been reduced. Additional discussion on this topic is included subsequent section titled the *Influence of Stormwater Chemistry on the Treatment Process.*

As predicted in the Essential Properties, the KB biochar, which contained a significantly higher phosphorus content (1.26%) compared to the W biochar (0.06%), leached more TP. These results are consistent with bioretention research which indicates that TP leaching is a function of the quantity of organic matter as such limiting the quantity of OM in the BSM can reduce the leaching potential (Hunt, Davis., Traver, 2012).

The pollutant reduction ratio (C_e/C_i) was graphed to assess the trend in the treatment performance over the testing period. As shown in Figure 3.23, the TP leaching for the KB biochar was highest during the initial rainfall events, then gradually declined and was approaching 1.0 by the final event. For the W biochar, the C_e/C_i was higher during the initial rain fall event (1.34 and 1.18 for the W8 and W4 columns) and then consistently at 1.0 (no leaching was observed) or just below 1.0 (some reduction of TP was observed) for the remainder of the rainfall events. These results suggest that TP leaching is a function of time and may only be a concern during the initial period after the BSM is installed in the field. Other studies that amend stormwater BMPs with biochar have reported similar trends in which TP leaching declined over the course of testing (Kuoppamäki, Hagner, Lehvävirta, & Setälä, 2016; Kuoppamäki & Lehvävirta, 2016). This trend is reportedly due to the washing away of nutrients during the initial rainfall events (Kuoppamäki et al., 2016).

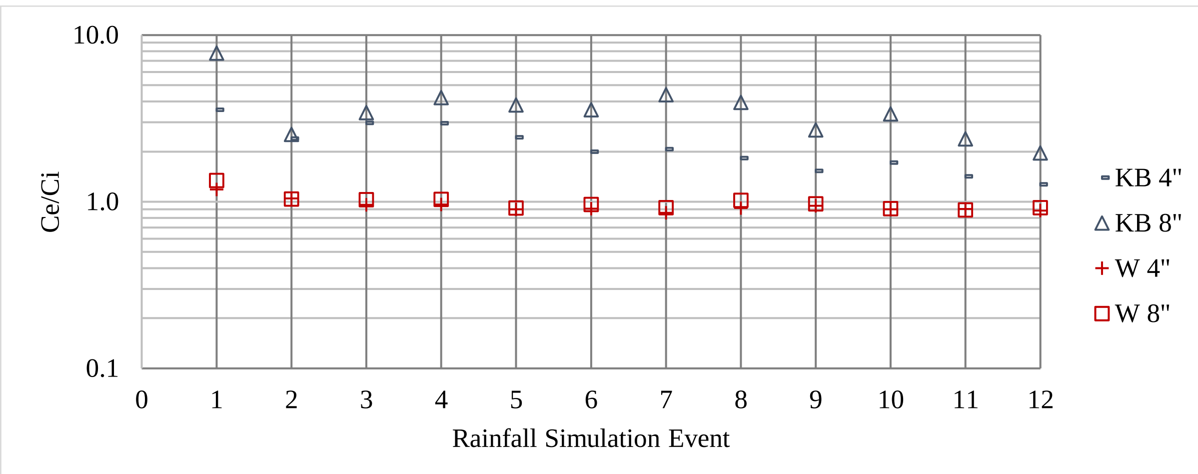

Figure 3.23 TP Pollutant Reduction Ratio (C_e/C_i logarithmic scale) vs. Time

Nitrogen Results & Discussion

Ammonia (NH_3)

The mean NH_3 removal efficiency was 77% and 72% for the KB4 and KB8 columns compared to the 56% and 62% for the W4 and W8 columns, respectively (Table 3.12 and Figure 3.24). The effluent concentration from all four columns was significantly lower compared to the influent concentration (p=0.001). While the mean removal efficiency was higher for the KB columns, the difference between the column effluent concentrations is statistically insignificant (p>0.05). These results suggest that neither the type nor the quantity of biochar significantly influenced the treatment performance.

Table 3.13 NH3 Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Mean Concentration (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison
SSW	12	0.331 (±0.055)	-	-	-
KB4	12	0.056 (±0.043)	77%	0.001	KB4 to W4: 0.195
KB8	12	0.049 (±0.052)	72%	0.001	KB8 to KB4: 0.729
W4	12	0.095 (±0.090)	56%	0.001	W4 to W8: 0.564
W8	12	0.077 (±0.088)	62%	0.001	W8 to KB8: 0.583

The pollutant reduction ratio trend (Figure 3.25) for the KB and W columns indicates that the effluent contained a higher concentration of NH_3 during the initial rainfall simulations (events 1 to 6). For the second half of the rainfall simulations (events 7 to 12), the pollutant reduction was consistent ≤0.02 and all the effluent concentrations were below the detection limit. Based on the consistent trend in the data during events 7 to 12, there is no indication that the treatment performance was not declining or reaching capacity.

Biochar's ability to reduce NH_3 is well documented (Spokas, Novak, & Venterea, 2012; Taghizadeh-Toosi et al., 2012; Tian et al., 2014; Yao et al., 2012). NH_3 reduction occurs first through the transformation of NH_3 to ammonium (NH_4^+) (Spokas et al., 2012; Taghizadeh-Toosi et al., 2012), after which the NH_4^+ cation is available for sorption to the negatively charged surface of the biochars (Spokas et al., 2012). The transformation results from a Brownsted-Lowry reaction (Equation 14). Under ambient conditions, NH_3 in a solution of water acts as a Brownsted-Lowry base (proton acceptor) that accepts hydrogen ions (H^+) from water and acts as the Brownsted-Lowry base (proton donor).

$$H_2O + NH_3 \leftrightarrow OH^- + NH_4^+ \qquad \text{Equation 14}$$

Under ambient conditions there is a balance of NH_3 to NH_4^+ ions in a solution of water and the balance is a function of the solution pH. Specifically, the quantity of NH_4^+ ions available for transformation in a solution (and subsequently available for sorption) increases as the pH decreases while an equivalent quantity of NH_3 decreases (to maintain the balance) (Spokas et al., 2012; Stumm & Morgan, 2012). The differences in the effluent pH are attributed to the biochar pH which is influenced by the processing temperature. As the temperature increases, the ash content increases removing acidic functional groups from the biochar surface, causing the biochar pH to increase and become more basic (Lehmann & Joseph, 2015).

The biochar CEC also appears to influence the removal efficiency of NH_3. Tian et al. conducted jar testing on biochars made from poultry litter and hardwood to determine the NH_3 sorption capacity using a synthetic stormwater solution. The findings reported that the NH_3 sorption capacity correlated to the CEC as opposed to the surface area of biochar indicating that the cation exchange is the primary treatment mechanism for removing NH_3 (Tian et al., 2016).

The mean removal efficiency from the KB columns was 10% to 20% higher compared to the W columns. While the differences between the KB and W columns were statistically insignificant, the influence of CEC and pH is consistent the KB biochar properties as well as the higher removal efficiency observed from KB columns. Specifically, the KB biochar was processed at a lower temperature (625°C) resulting in a lower pH (9.45) compared to the W biochar which was processed at a higher temperature (900°C) resulting in a higher pH (10.32). In addition, the CEC of the KB biochar (29 meq/100g) is higher compared to the W biochar (19 meq/100g). As such it is anticipated that the KB biochar can remove larger quantities of NH_3 from stormwater solutions compared to the W biochar.

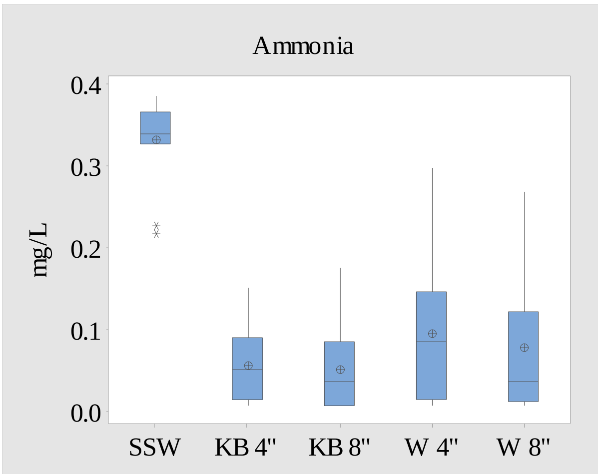

Figure 3.24 NH_3 Box Plots: Comparison of Mean Influent & Effluent

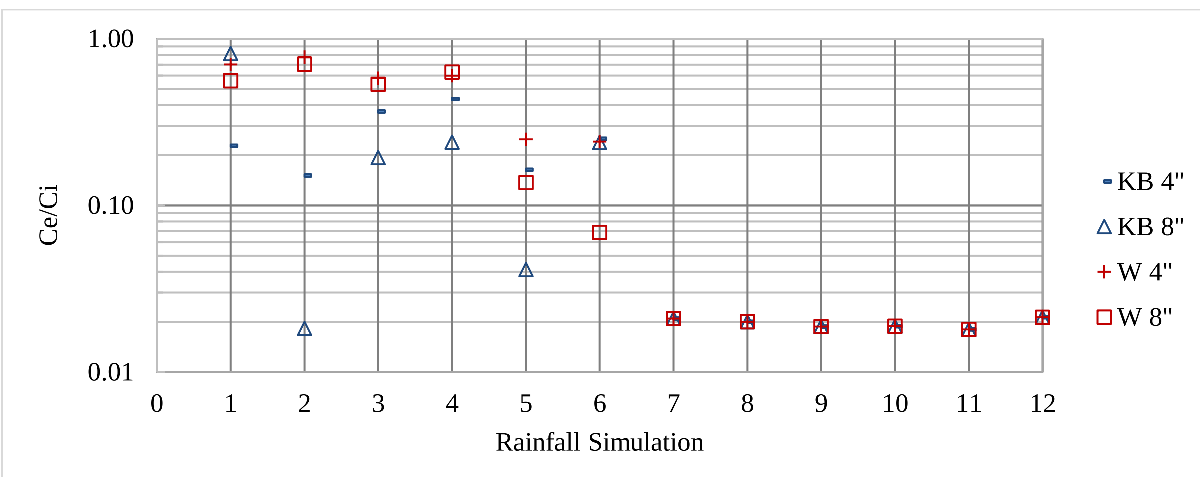

Figure 3.25 NH_3 Pollutant Reduction Ratio (C_e/C_i logarithmic scale) vs. Time

<u>Nitrates-Nitrites (NO_3-NO2)</u>

The NO_3-NO_2 removal efficiency was -5% and 3% for the KB4 and KB8 columns compared to -2% and 12% for the W4 and W8 columns respectively (Table 3.13 and Figure 3.26). The difference between the influent and effluent concentrations was only <u>statistically significant</u> for KB8 ($p=0.028$) and W8 ($p=0.003$) columns. The difference between the column effluent concentrations was <u>statistically significant</u> when comparing the W4 to W8 ($p=0.016$) and moderately significant when comparing the KB4 and KB8 columns ($p=0.078$). These results suggest that the NO_3-NO_2 removal efficiency may be influenced by the quantity of biochar (the treatment performance improved from the 4- to 8-inch columns) but not the type of biochar.

Table 3.14 NO_3-NO_2 Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Average Concentration (mg/L)	% Difference	Effluent p-value Compared to SSW	Effluent p-value Comparison
SSW	12	1.309 (±0.167)	-	-	-
KB4	12	1.346 (±0.186)	-5%	0.465	KB4 to W4: 0.850
KB8	12	1.242 (±0.201)	3%	0.028	KB4 to KB8: 0.078
W4	12	1.391 (±0.240)	-2%	0.517	W4 to W8: 0.016
W8	12	1.133 (±0.226)	12%	0.003	W8 to KB8: 0.230

The trend in the NO_3-NO_2 pollutant reduction between the KB and W biochar over the testing period (Figure 3.27). The KB biochar C_e/C_i declined over the testing period ranging from 1.2 during the initial rainfall event to 0.8 during the last rainfall event. These results suggest that NO_3-NO_2 leaching may only be a concern during the initial rainfall events. The W biochar C_e/C_i fluctuated from 0.5 to 1.1 with no apparent trend in the data.

NO_3-NO_2 is highly soluble and researchers have reported that biochar has a limited ability to sorb NO_3-NO_2 (Lehmann & Joseph, 2015; Yao et al., 2012). The small reduction in NO_3-NO_2 observed from the 8-in columns is likely attributed to the water holding capacity of biochar. Specifically, NO_3-NO_2 removal is associated with longer hydraulic residence times (Hunt, Davis, Traver, R. G., 2012) and thicker media (Hunt, Davis, Traver, 2012). The biochars may have retained stormwater which decreased the quantity of stormwater and thus the quantity of NO_3-NO_2 leaving the columns (Tian et al., 2014). Considering there was a larger quantity of biochar in the 8-in columns, more stormwater would have been retained compared to the 4-in columns.

Researchers have reported mixed results regarding the efficacy of biochar to removal NO_3-NO_2 with some reporting biochar can remove NO_3-NO_2 (Hart, 2012; Yao et al., 2012) while other researchers have reported NO_3-NO_2 leaching (Leach, 2015). These differences suggest that the treatment performance varies based on the type of biochar. Yao et al. conducted sorption capacity testing on 13 different types of biochar and found that the biochar processing temperature appears to be associated with the NO3-NO2 treatment performance. In this research four types of the bicohars (made from sugarcane, bamboo, peanut hull, and Brazilian pepperwood) reportedly sorbed small concentrations of nitrate (3.7-0.12%) from the solution. The researchers attributed the reduction to the high processing temperature (>600°C) of the respective four biochars (Yao et al., 2012). No explanation was provided by the researchers regarding the reactions between the surface of the biochar and solution that may have caused the removal of NO_3-NO_2 from the solution. Both the W and KB biochars used during this study were processed at temperatures greater than 600°C which may also explain why small amount of NO_3-NO_2 was reduced.

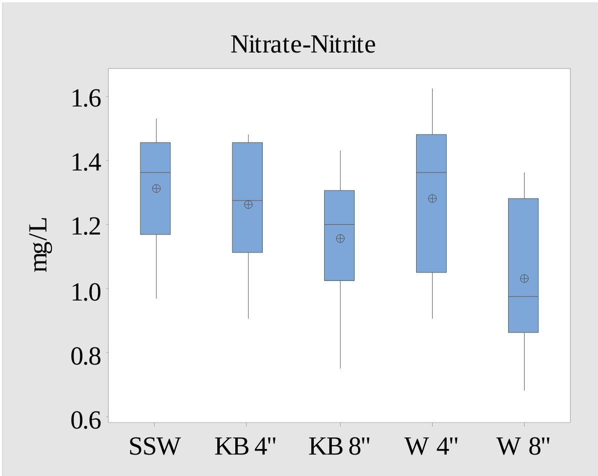

Figure 3.26 NO_3-NO_2 Box Plots: Comparison of Mean Influent & Effluent

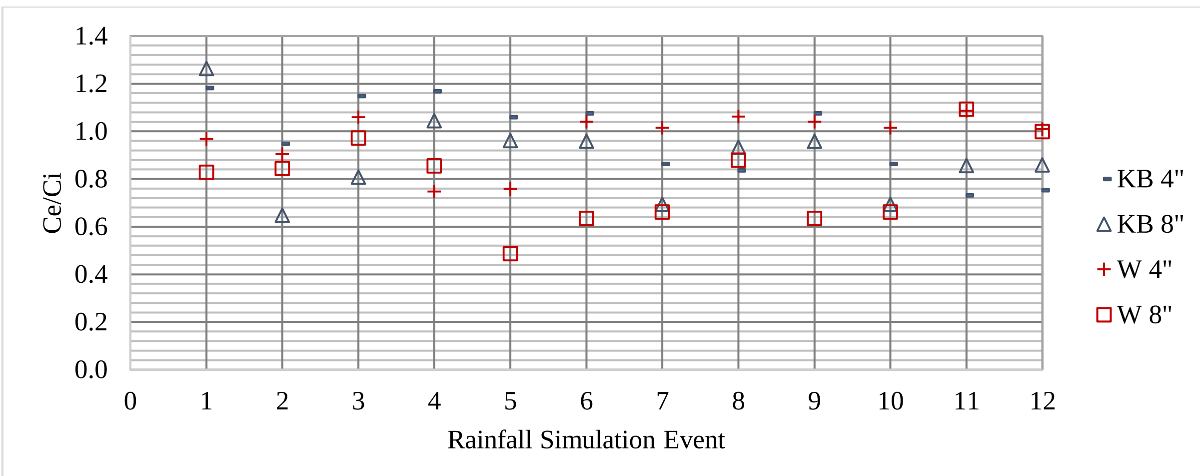

Figure 3.27 NO3-NO2 Pollutant Reduction Ratio (C_e/C_i) vs. Time

The TKN effluent concentrations were statistically significant compared to the influent concentrations for all columns (Table 3.14 and Figure 3.28). The removal efficiency from the W4 and W8 columns ranged from 48% to 51% respectively compared to the leaching observed from the KB4 and KB8 columns which ranged between -46%% to -165% respectively. The trend in the TKN pollutant reduction (C_e/C_i) graph shows that the treatment performance improved was consistently at or below C_e/C_i=1.0 (Figure 3.29). The exception is the effluent concentration from the KB columns during the initial rainfall. During this first event, the effluent concentration for KB8 and KB4 was 6.92 mg/L and 3.20 mg/L respectively. Since high effluent concentration is likely attributed to leaching and inconsistent with the other measured TKN effluent concentrations, the data sets were reanalyzed without the initial rainfall events from the KB columns. The removal efficiency for the KB 4 and KB8 columns (n=11) was 32% and 16% respectively. The differences in the effluent concentrations between the columns were only statistically significant when comparing KB4 to W4 columns (p=0.070) and the W8 to KB8 (p=0.001). These results suggest that the type of biochar influenced the treatment performance with the W biochar reducing significantly more TKN compared to the KB biochar. However, it is not possible to assess the true removal efficiency of the W columns because most of the effluent concentrations were reported as below the detection limit. As such the detection limit was used as the effluent concentration in the analysis.

Table 3.15 TKN Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Average Concentration (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Others
SSW	12	1.133 (±0.193)	-	-	-
KB4	12 11	0.939 (±0.210) 0.734 (±0.085)[b]	-46% 32%[b]	0.002	KB4[b] to W4: 0.070
KB8	12 11	1.332 (±0.510) 0.825 (±0.181)[b]	-165% 16%[b]	0.003	KB8 to KB4: 0.293
W4	12	0.518 (±0.061)	48%	0.001	W4 to W8: 0.339
W8[a]	12	0.500 (±0.000)	51%	0.001	W8 to KB8[b]: 0.001

a. *The W8 effluent values were below the MDL, as such the MDL (0.50 mg/L) was used in the analysis*
b. *Values reflect the results without the effluent concentration from the initial rainfall simulation*

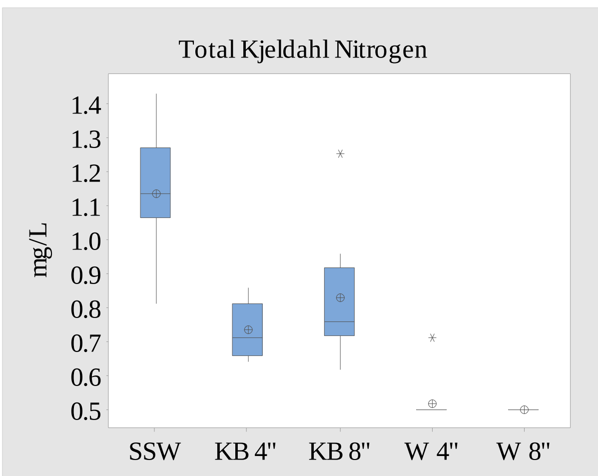

Figure 3.28 TKN Box Plots: Comparison of Mean Influent & Effluent

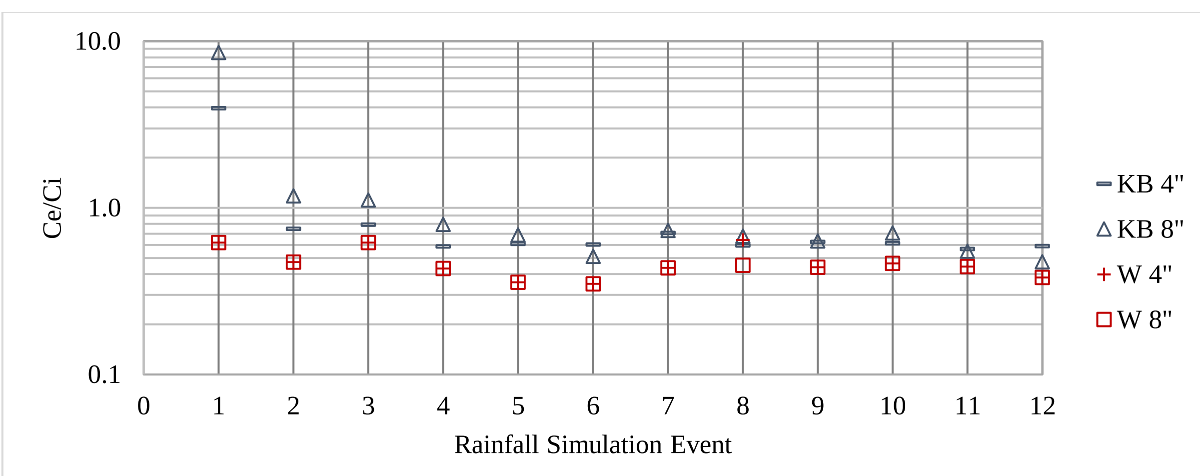

Figure 3.29 TKN Pollutant Reduction Ratio (C_e/C_i logarithmic scale) vs. Time

Total Nitrogen

The total nitrogen (TN) treatment performance varied between the W and KB columns (Table 3.15 and Figure 3.30). The removal efficiency from the W4 and W8 columns ranged from 18% to 24% respectively compared to the leaching observed from the KB4 and KB8 columns which ranged between -25% to -75% respectively. Since the leaching was due to TKN during the first rainfall simulation, those data points were removed, and the data set was reanalyzed. The removal efficiency for the KB 4 and KB8 columns (n=11) was 14% and 16% respectively. The differences in the effluent concentrations between the columns were only statistically significant when comparing the W8 to KB8 (p=0.013). These results suggest that the treatment performance may have been influenced by the type of biochar with the W biochar outperforming the KB biochar. While the differences in the effluent concentrations between the W4 and W8 columns were also statistically significant (p=0.008), since TN for the W columns was calculated using the detection limit for the TKN effluent concentrations it is difficult to draw meaningful conclusions regarding differences in the W columns.

Table 3.16 TN Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Average Concentration (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison
SSW	12	2.364 (±0.380)	-	-	-
KB4	12 11[a]	2.211 (±0.212) 2.168 (±0.308)[a]	-25% 14%[a]	0.021[a]	KB4[a] to W4: 0.228
KB8	12 11[a]	2.499 (±0.517) 2.080 (±0.196)[a]	-75% 16%[a]	0.004[a]	KB8[a] to KB4[a]: 0.630
W4	12	1.934 (±0.254)	18.0%	0.002	W4 to W8: 0.008
W8	12	1.727 (±0.260)	24.2%	0.001	W8 to KB8[a]: 0.013

a. *The values reported reflect the results of the data set analysis without the effluent concentration from the initial rainfall simulation.*

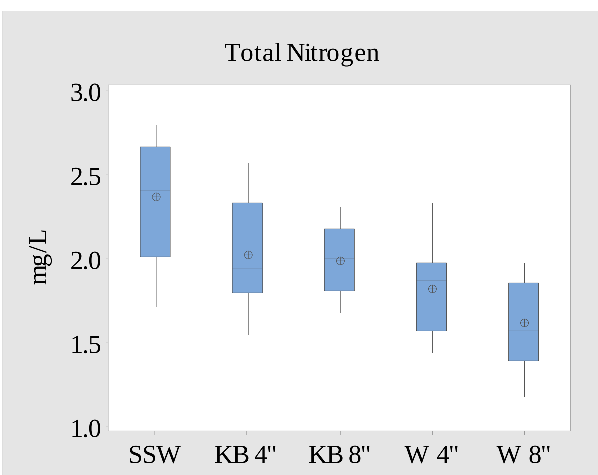

Figure 3.30 TN Box Plots: Comparison of Mean Influent & Effluent

Total nitrogen represents the sum of the concentrations of the different forms of nitrogen measured in the stormwater solution: nitrate-nitrite and total kjeldahl nitrogen or TKN (ammonia, organic and reduced nitrogen)

(Minton, 2012). The Figure 3.31 bar graphs illustrate the mean TN concentration based on the sum of the mean concentration of the different nitrogen forms. These graphs were developed twice: one for all rainfall events n=12 (Figure 3.31.a) and one without the first rainfall event n=11 (Figure 3.31.b), because TKN leaching was reported only during the initial event for the KB biochars. The overall reduction in total nitrogen is primarily due to the reduction of NH_3 for all columns, organic nitrogen for the W columns, and NO_3-NO_2 for the W8 and KB8 columns. Organic nitrogen is typically reduced by nitrogen cycling, that is organic nitrogen is converted to NH_4^+ through ammonification and ultimately NO_3-NO_2 through nitrification (Minton, 2012). The reduction in organic nitrogen in the W columns without an increase in NO_3-NO_2 suggests that organic nitrogen was converted to NH_4^+ and then presumeably sorbed to the biochar however there is no evidence that nitrification occurred.

One justification for the better overall treatment performance of the W compared to the KB biochar is the total nitrogen content in the KB biochars (1.5%) is twice that of the W biochars (0.6%) and 15 times higher than the 0.1% recommended in the Essential Properties section. Subsequently the treatment performance of the KB biochar may be attributed to the higher nitrogen composition of the biochar which is consistent with the predicted performance of the biochars in the Essential Properties section.

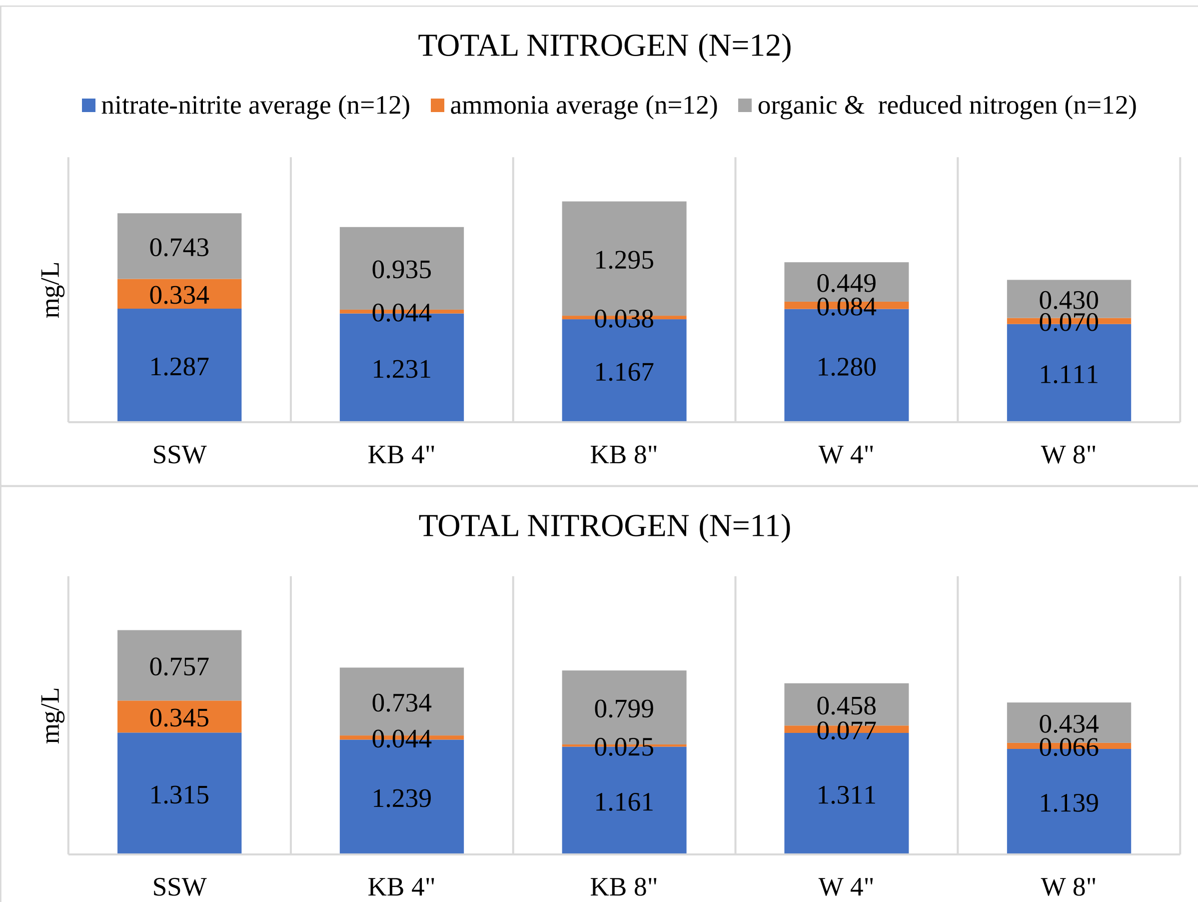

Figure 3.31 Mean TN Bar Graphs with: a) initial rainfall event (n=12) & b) without initial event (n=11)

Hardness

Hardness is a measure of the multivalent cations in water, specifically Ca and Mg. Hardness as well as the concentration of Ca and Mg were measured in the stormwater influent and effluent because they can both influence the stormwater chemistry. When compared to the influent concentrations, the difference between the hardness and Ca (total and dissolved) effluent concentrations were statistically insignificant (Table 3.16 and 3.17). In addition, the difference between the effluent concentrations for all columns were also statistically insignificant for hardness and Ca (total and dissolved). The only statistically significant difference was the total Mg concentrations. Specifically, the influent total Mg concentration was significantly different compared to the KB4 (0.050) and KB8 (0.030) effluent concentrations. The differences in the dissolved Mg influent and effluent concentrations were moderately significant for KB4 (0.100) and KB8 (0.069). In comparing the total effluent concentrations between columns for Mg, differences were significant between KB4 to W4 (0.027) and KB8 to W 8 (0.032). The differences in the dissolved Mg effluent concentrations between columns were moderately significant when comparing KB4 to W4 (0.082) and KB8 to W8 (0.080). These results suggest that neither the type nor quantity of biochar influenced the removal efficiency for hardness or Ca however the type of biochar appears to have influenced the removal efficiency of Mg (with the KB biochar leaching more Mg).

The pollutant reduction ratio (C_e/C_i) for dissolved hardness, Ca, and Mg (Figures 3.32-3.34) ranges from approximately 0.8 to 1.2 for hardness and Ca whereas the ratio for Mg ranges from approximately 0.9 to 1.5. There is no apparent trend in the data that would suggest the C_e/C_i ratios are changing which would indicate an increase or decrease in leaching with time.

Desorption of Ca and Mg was expected based on the results from the jar test (Part 1) of this study. The Mg results are consistent with Part 1 in that the KB biochar desorbed more Mg compared to the W biochar. This was not surprising since the desorption (leaching) of Mg directly related to the biochar Mg content (the higher the biochar Mg content, the higher the expected Mg leaching). This this case, the KB biochar Mg content (0.57%) was over five times higher compared to the W biochar (0.1%). With respect to the Ca leaching, the difference between the influent and effluent concentration was statistically insignificant. It is possible that Ca leached from the biochars and that the leached Ca is fixed in the column (because it precipitated with phosphate) and this is why the Ca concentrations are statistically insignificant. However, it is not possible to draw meaningful results about the behavior of Ca base on these results.

Table 3.17 Hardness Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Mean Concentration (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total					
SSW	12	277.06 (±22.95)	-	-	-
KB4	12	236.93 (±18.01)	-4.9%	0.339	KB4 to W4: 0.312
KB8	12	242.69 (±29.14)	-10.9%	0.378	KB8 to KB4: 0.403
W4	12	233.52 (±25.61)	-2.3%	0.706	W4 to W8: 0.885
W8	12	233.57 (±21.94)	-3.0%	0.754	W8 to KB8: 0.260
Dissolved					
SSW	12	227.06 (±24.16)	-	-	-
KB4	12	234.8 (±19.03)	-7%	0.200	KB4 to W4: 0.520
KB8	12	236.53 (±27.17)	-12%	0.427	KB8 to KB4: 0.858
W4	12	229.13 (±23.22)	-3%	0.452	W4 to W8: 0.794
W8	12	231.7 (±24.43)	-5%	0.271	W8 to KB8: 0.520

Table 3.18 Ca Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Average Concentration (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total					
SSW	12	54.39 (±5.11)	-	-	-
KB4	12	54.17 (±2.95)	-4%	0.992	KB4 to W4: 0.944
KB8	12	54.28 (±8.71)	-9%	0.961	KB8 to KB4: 0.940
W4	12	54.29 (±5.56)	-1%	0.728	W4 to W8: 0.950
W8	12	54.43 (±4.04)	-3%	0.984	W8 to KB8: 0.941
Dissolved					
SSW	12	53.44 (±6.11)	-	-	-
KB4	12	53.07 (±4.44)	-0.5%	0.860	KB4 to W4: 0.714
KB8	12	53.53 (±9.22)	-9.8%	0.982	KB8 to KB4: 0.878
W4	12	53.77 (±4.88)	-2.7%	0.597	W4 to W8: 0.929
W8	12	53.95 (±4.51)	-4.4%	0.655	W8 to KB8: 0.889

Table 3.19 Mg Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Average Concentration (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total					
SSW	12	23.49 (±2.19)	-	-	-
KB4	12	24.69 (±3.25)	-9%	0.050	KB4 to W4: 0.027
KB8	12	26.02 (±4.03)	-18%	0.030	KB8 to KB4: 0.099
W4	12	23.75 (±2.78)	-4%	0.546	W4 to W8: 0.879
W8	12	23.73 (±2.70)	-4%	0.570	W8 to KB8: 0.032
Dissolved					
SSW	12	23.19 (±2.30)	-	-	-
KB4	12	24.88 (±4.09)	-13.9%	0.100	KB4 to W4: 0.082
KB8	12	25.28 (±3.72)	-16.9%	0.069	KB8 to KB4: 0.507
W4	12	23.33 (±2.57)	-3.4%	0.699	W4 to W8: 0.416
W8	12	23.67 (±3.37)	-6.2%	0.454	W8 to KB8: 0.080

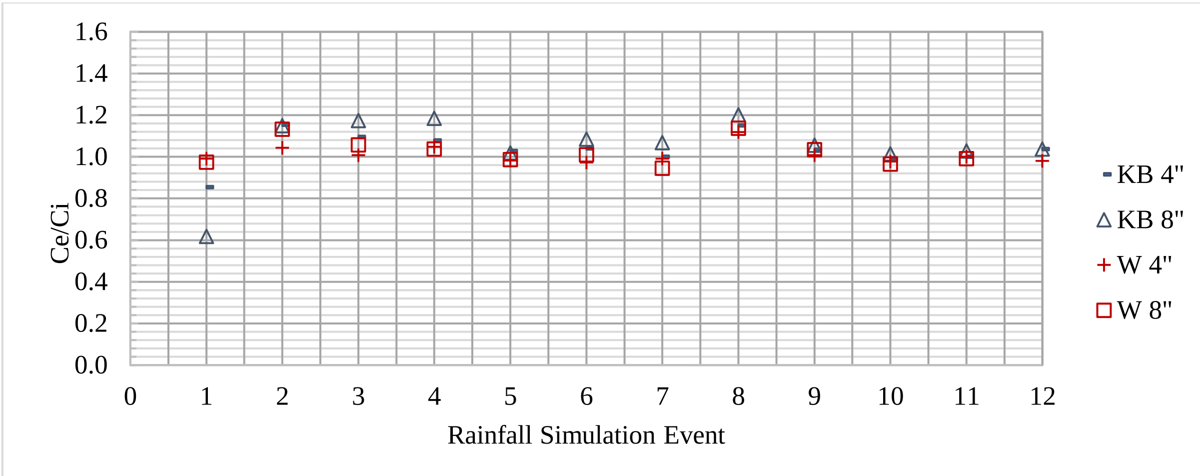

Figure 3.32 Dissolved Hardness Pollutant Reduction Ratio (Ce/Ci) v.s Time

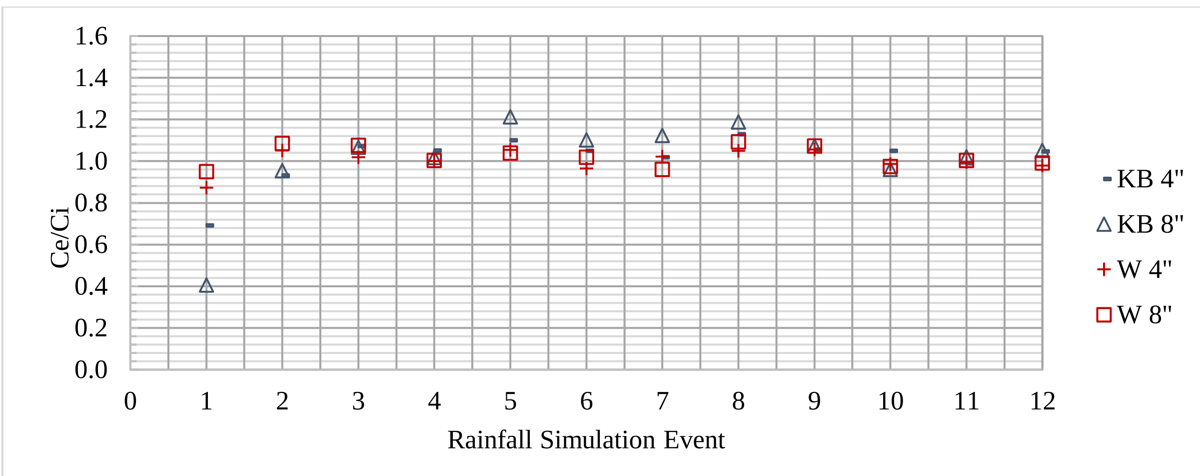

Figure 3.33 Dissolved Ca Pollutant Reduction Ratio (Ce/Ci) vs. Time

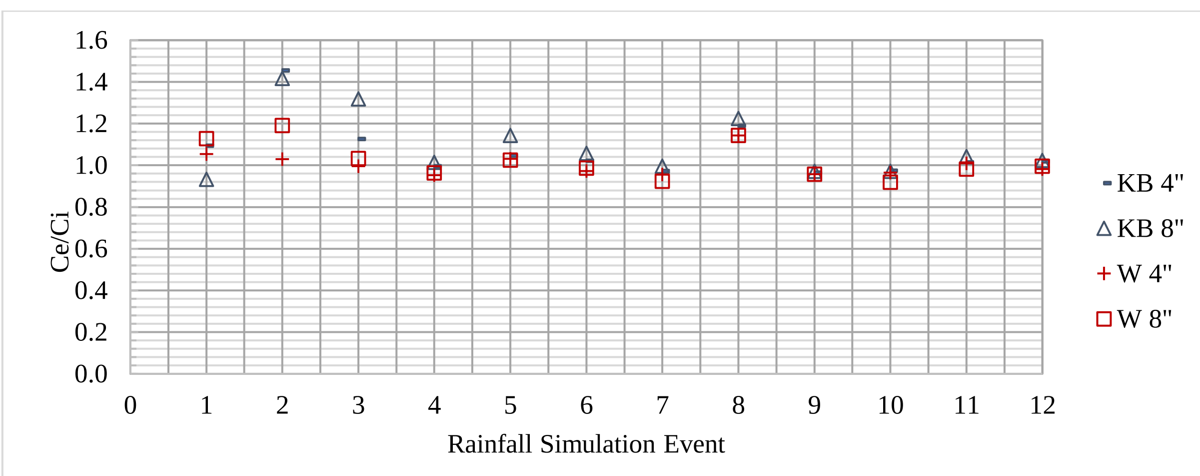

Figure 3.34 Dissolved Mg Pollutant Reduction Ratio (Ce/Ci) vs. Time

The SSW had an average total and dissolved hardness concentration of 230.5 mg/L and 227.1 mg/L respectively. The average stormwater hardness for urban areas is rarely reported in the literature so it is difficult to determine how representative the influent concentration (SSW) in this study is compared to national averages. Instead the SSW average total hardness was compared to the data available which was collected from urban watersheds in New Zealand and Canada with mixed land use (Good, O'Sullivan, Wicke, & Cochrane, 2014; Hall & Anderson, 1988), highway runoff data from California, and influent data reported in the International Stormwater BMP Database for mixed land use (International Stormwater BMP Database, 2017). Table 3.19 provides a summary of the total hardness data from these sources along with the total hardness values from this study (SSW) and the 2013 water year Cochran Basin outfall data which is primarily commercial and residential land use.

The average total hardness for the SSW (230.5 mg/L) is higher than the other sources by a factor of 2 to 4. The maximum total hardness value reported from the Cochran Basins outfall (492 mg/L) was collected in January when the City of Spokane typically experiences the largest amount of snowfall (11 inches on average). During snowfall events deicers that contain Ca and Mg are commonly used on paved surfaces to reduce the build-up of ice. The authors of the other studies did not report when the samples were collected so it is not possible to determine whether the other maximum value reported are temporal due to the weather. Based on this comparison, the average total hardness for the SSW in this study appears higher compared to the other studies however the maximum value is within the range measured in other urban watersheds.

Table 3.20 National Comparison of Mean Total Hardness

	SSW	Cochran Basin 2014	New Zealand (Good et al., 2014)	Canadian Watershed[a] (Hall & Anderson, 1988)	Highway Runoff[b] (Kayhanian et al., 2012)	International Stormwater BMP Database[c] (2017)
Average	230.53	127.10	<30	84.67	49.55	71.7
Maximum	284.90	492.00	ND	327.00	78.90	ND
Minimum	203.00	26.30	ND	12.00	30.30	ND
SD	19.86	204.12	ND	89.66	21.69	128

a. *Twelve samples collected from an urban Canadian watershed with a mixture of commercial, industrial, and residential land use (Hall & Anderson, 1988). The data was analyzed using descriptive statistical methods to determine the mean, maximum, minimum, and standard deviation.*

b. *A literature search conducted by Kayhanian et al. reported on the mean total hardness values from California highways (Kayhanian et al., 2012). The data was analyzed using descriptive statistical methods to determine the mean, maximum, minimum, and standard deviation.*

c. *The International Stormwater BMP database statistical analysis tool was used to determine the mean and standard deviation of total hardness from the 2809 event mean concentrations reported from studies that have been uploaded to the database (International Stormwater BMP Database, 2017)*

Influence of Stormwater Chemistry on Treatment Process

The influent stormwater solution was modeled using MINTEQ to assess how the hardness concentration and change in the stormwater solution pH (from influent to effluent) may have affected the speciation of the parameters and subsequently the treatment performance of the biochars. MINTEQ is a chemical equilibrium model that calculates the metal speciation and solubility in natural waters. The influent solution was modeled three different ways:

- Model 1: Influent solution at the mean influent pH (7.58) to each column
- Model 2: Influent solution at the mean effluent pH (8.26-8.39) from each column
- Model 3: Influent solution at the mean effluent pH for each column (8.26-8.39) with the solution hardness (Mg and Ca concentration) reduced to the match the minimum reported for the Cochran Basin (26.3 mg/L) in Table 3.19

The model calculates the species distribution and the saturation index (difference between Ion Activity Product and the solubility product) which was compared for each run to assess changes in the solubility of the parameters. In comparing the results between model 1, 2, and 3, the results indicate that the primary change was with the solubility of phosphorus. For model 1, using the average influent pH of 7.58, approximately 2% phosphorus exists as particulate calcium phosphate. When the pH is increased to 8.38 for model 2, 28% of the phosphorus exists as particulate calcium phosphate. When the solution hardness was reduced using the mean effluent pH for model 3, only 6% of phosphorus exists as particulate calcium phosphate. These results indicate that the hardness concentration of the stormwater solution resulted in a larger fraction of phosphorus in a particulate form. With respect to bioretention treatment BMPs, parameters in a particulate form are typically removed by filtration as stormwater runoff infiltrates through a media (Erickson et al., 2007; Hunt & Lord, 2006). As such the higher hardness concentration appears to have increased total phosphorus removal above what would occur in a stormwater solution with a lower hardness concentration.

CEC Analysis

The results from the CEC analytical testing conducted before and after the column testing indicate that the biochar CEC was reduced on average by 51% for KB and 69% for W (Table 3.20). To understand what metal cations may have contributed to the change in CEC, the known cations in the stormwater influent were assessed in comparison to the change in CEC. The NH_3 concentration was included since NH_3 is known to transform into ammonium NH_4^+ (Taghizadeh-Toosi et al., 2012) which can then be removed from a solution through cation exchange (Taghizadeh-Toosi et al., 2012; Tian et al., 2014). These values were determined by multiplying the average concentration of the metals measured in the influent (Table 3.3), by the total volume of the stormwater (24-liters) that was distributed to each column over the entire testing period. As shown in Table 3.20, the known influent cation content distributed to each column (Cu, Zn, Pb, Ca, Mg, NH_3) is equivalent to 114.21 meq. However, the known heavy metal cation content (Cu, Zn, and Pb) in the stormwater solution only accounts for 0.11 meq which is substantially less than the reduction of CEC estimated in the KB (2.2-meq) and W (3.9-meq) biochars.

These results are not surprising since lighter weight metals (such as Ca^{2+}, Mg^{2+}, K^+, Na^+) and nutrients (NH^{4+}) are known to complete for sorption sites on biochars (Lehmann & Joseph, 2015; Vijayaraghavan, Teo, Balasubramanian, & Joshi, 2009; Yargicoglu, Sadasivam, Reddy, & Spokas, 2015). Based on the data collected during this study, it is not possible to determine what cations were removed through cation exchange however it appears that both biochars sorbed more cations than just the targeted heavy metals.

Table 3.21 Summary of Part 2 CEC Testing Results

CEC	Column ID				SSW Characteristics	
	KB-4”	KB-8”	W-4”	W-8”	Known Cations[a]	Average Dissolved Concentration[b]
Average Baseline (meq/100g)	29		19		Cu, Pb, Zn	0.11 meq
Average Final (meq/100g)	14		6		Ca, Mg	110.00 meq
Average Reduction (meq)	2.2		3.9		NH^3	4.10 meq
Average Reduction (%)	51%		69%		Total	114.21 meq

a. Represents known metal ions in the stormwater influent solution
b. Represents average concentration of each cation times the total volume of stormwater distributed to each column (24-Liters).

The CEC results are important for estimating the lifespan of the biochar which appears to be 2-years for the KB biochar and 1.7-years for the W biochar. However, researchers have reported that the oxidation of biochar that occurs overtime in the environment, may also influence the CEC (Lehmann & Joseph, 2015, p. 151). As such the actual CEC lifespan in the field has the potential to extend beyond what is estimated from the data collected during this study. This estimate of the lifespan does not consider the adsorption capacity of the biochar which is also expected to sorb cation from the stormwater solution.

Saturated Hydraulic Conductivity (K_{sat})

The results from the falling head testing are summarized in Table 3.21 and Figure 3.35. The K_{sat} values for all columns declined over the 12-rainfall simulation with the last measured K_{sat} approximately half the initial value. These results are consistent with previous bioretention research. The TSS in the stormwater influent is known to settle on the surface of and into the first few inches of the media which over time will clog the media and reduce K_{sat} (Hsieh, Davis, & Needelman, 2007). The results from the KB8 column were the exception in which the measured K_{sat} gradually increased over the first three tests and then declined during the fourth test but was still higher than the initial K_{sat} value. Considering only one column was tested for each biochar (as opposed to duplicate or triplicate columns) is not possible to conclude if the K_{sat} results from the KB8 column are an outlier or possibly due to the hydrophobic properties of the biochar.

The average K_{sat} for the KB4 (12.33-inches/hour) and KB8 (15.88-inches/hour) columns was lower compared to the average K_{sat} for the W4 (39.14-inches/hour) and W8 (25.51-inches/hour) columns. The difference is likely attributed to the higher percentage of fines in the KB biochar (25%) compared to the W biochar (0.9%) which would reduce the pore space of the media and subsequently the permeability. In addition, wood biochars typically have a larger porosity compared to grass biochars and the larger porosities are associated with higher K_{sat} values due to larger flow paths through the media (Jeffery et al., 2015). The K_{sat} value was also lower for the columns which contained more biochar. Similar results have been reported by other researchers which maybe a function of the biochar particles absorbing water which causes the particles to swell reducing the media void spaces and subsequently the K_{sat} value (Brockhoff, Christians, Killorn, Horton, & Davis, 2010).

Table 3.22 Part 2 K_{sat} Falling Head Test Results

Column ID	Baseline[a] (in/hr)	Event 4[a] (in/hr)	Event 8[a] (in/hr)	Event 12[a] (in/hr)	Average (in/hr)
KB 4”	28.14	9.29	4.96	6.91	12.33
KB 8”	11.21	17.59	18.98	15.77	15.88
W 4”	61.44	42.52	32.67	19.92	39.14
W 8”	59.30	20.84	9.10	12.81	25.51

a. *K_{sat} testing occurred prior to the first rainfall simulation (baseline) and then after rainfall simulations 4, 8, and 12.*

b.

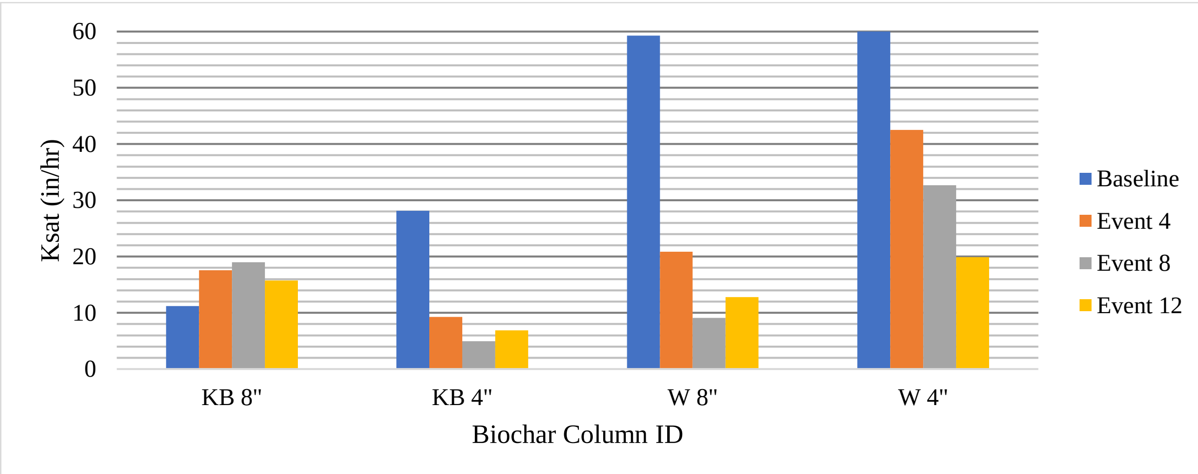

Figure 3.35 Part 2 K_{sat} Falling Head Mean Bar Graphs

Empirical Observations

As noted in the jar testing discussion, biochar has hydrophobic tendencies. This behavior was also noted during the column testing to a lesser degree when the biochar from the top of the columns floated on the water surface during the falling head testing as shown in Figure 3.36. Presumably the differences between the jar to column testing is because more biochar was saturated and held down by the weight of biochar in the column. These results suggest that the hydrophobic tendencies may have less of an influence on the biochar in the field. However, it is anticipated that under ponding conditions, such as immediately following a high intensity rainfall event, some biochar will float on the top of the ponded water in a bioretention cell. To reduce the likelihood of this occurrence, it is recommended that a mulch material, heavier than the typical bark (Hunt & Lord, 2006), be placed on top of the BSM-biochar mixes to hold the biochar down.

Figure 3.36. Falling Head Test: Biochar Floats

BSM-BIOCHAR SPECIFICATION RECOMMENDATIONS

This section provides a summary of the recommendations for the field application of biochar as an amendment in BSM for bioretention cells based on the finding from this research.

- Phosphorus – Based on the findings, neither biochar is effective for reducing TP concentrations. The phosphorus content in the biochar and the quantity of biochar in the columns both had a significant influence on the quantity TP leaching. Recommendations for reducing leaching include using less biochar in a BSM (4-inch instead of 8-inch) and biochars with a lower phosphorus content. Leaching from the W biochar was insignificant however the biochar phosphorus content was 0.06% which exceeded the 0.04% limit recommended in the literature. Since the hardness concentration appears to have influenced the treatment performance, the recommended biochar phosphorus limit will remain at 0.04%.
- Nitrogen – Reduction of total nitrogen was significantly higher with the W biochar compared to the KB in larger quantities (8-inch). These results may be attributed to the nitrogen content of the biochars which was higher for the KB biochar (1.5%) compared to the W biochar (0.6%). However, both biochars have a higher nitrogen content than recommended in the Essential Properties (<0.1%) as such both biochars were expected to leach TN. This difference between the hypothesized results (defined in the Essential Properties) compared to the results of this study, particularly for the W biochar, may be attributed to nitrogen cycling which appeared to be responsible for changes in the different forms of nitrogen. The biochar nitrogen limit (0.1%) is still recommended for the Essential Properties however more research is needed to understand nitrogen reduction using biochar and the biochar physiochemical properties that influence the TN treatment performance.
- Heavy Metals – The heavy metal (Zn, Cu, Pb) results were consistent with the Essential Properties in that both biochars have an excellent sorption capacity for immobilizing dissolved metals. This is because the biochars have a balance of sorptive capabilities (W biochar has a high surface area and low CEC whereas

the KB biochar which has a low surface area and high CEC) and since neither biochar is fully carbonized (C_{org}=100%), both adsorption and cation exchange processes are expected to occur simultaneously. The biochar CEC and surface area limits are recommended to be consistent with the lowest measured values of the biochar: CEC ≥ 19-meq/100g and surface area ≥ 209-m^2/g dry.

- Biochar Quantity – For TSS and NH_3, the differences in the removal efficiency were statistically insignificant for each biochar regardless of the type or quantity of biochar. For metals, the removal efficiency of the 8-inch columns compared to the 4-inch columns was insignificant except for Zn when the W8 column was significantly higher than W4. However, the Zn removal efficiency of all four columns was greater than 90%. Therefore, the primary decision for selecting the quantity of biochar was the TP leaching which appears to be a function of the biochar phosphorus content and the quantity of biochar in the column. As such, a smaller quantity of biochar (equivalent to 4-inches of the total BSM mix depth) is recommended for BSM.
- Biochar has hydrophobic tendencies which causes some of the biochar to float on the water surface during ponding conditions which is expected to occur following a high intensity rainfall event in the field. To reduce the likelihood of this occurrence, it is recommended that a mulch material, heavier than the typical bark (Hunt & Lord, 2006), be placed on top of the BSM-biochar mixes to hold the biochar down.
- Essential Properties: The updated Biochar Essential Properties is summarized in Table 3.22. The results of the column testing were consistent with the Essential Properties (Table 3.2) and predicted treatment performance of each biochar. Some revisions to the table include:
    - Magnesium - This research did not produce evidence that Mg leaching influenced the treatment performance of the biochars. Since this research did not seek to eliminate Mg from the Essential Properties lists, Mg has been left on the list for future research.
    - CEC and pH - Based on the results from the column testing, it was hypothesized that the biochar pH and CEC values may influence the removal efficiency of NH_3. Specifically, the quantity of NH_4^+ ions available for transformation (from NH_3) in a solution and subsequently sorption, increases as the pH decreases and the higher the CEC the higher the capacity for removing NH_4^+ ions from the solution. As such, for applications that target NH_3, biochars with a lower pH and higher CEC are recommended.

Table 3.23 Essential Properties of Biochar for Stormwater Applications - Updated

Property	Criteria	Description
Organic Carbon (C_{org})	Class 1: ≥ 60%	Class 1 C_{org} content indicates a high carbon content which is associated with higher adsorption capacities (Lehmann & Joseph, 2015; McLaughlin, Anderson, Shields, Reed, 2009)
Hydrogen to Organic Carbon ratio ($H:C_{org}$)	0.7 max	$H:C_{org}$ < 0.7 is associated with a higher adsorption capacities (Lehmann & Joseph, 2015)
Cation Exchange Capacity (CEC)	high	The higher the CEC of a biochar the greater ability to exchange ions (International Biochar Initiative, 2013)
Total Surface Area (SA)	high	The higher the SA, the more available sites for adsorption (Lehmann & Joseph, 2015; Minton, 2012)
Mineral Ions: Calcium (Ca)	high	Higher Ca content may enhance P removal (Erickson et al., 2007)
pH	low	For applications that target NH_3 removal, biochars with a low pH are recommended.
Phosphorous (P)	low (less than 0.04%)	Organic materials with lower P content are less likely to leach (Erickson et al., 2007; Payne et al, 2015; Janoch & Liu, 2012).
Nitrogen (N)	low (less than 0.10%)	Organic materials with lower N content are less likely to leach (Payne et al, 2015).

CONCLUSION

The goal of this research is to provide a comprehensive evaluation of biochar for providing treatment of stormwater pollutants of concern (POC) and to develop recommendations for the field application of a biochar as an amendment in BSM (BSM-Biochar mix). This goal was achieved by conducting an extensive literature search identify a list of proposed Essential Properties (biochar physiochemical properties) which appear to indicate if a biochar is suitable for stormwater applications. The two biochars selected for this study were selected because they provide a range of Essential Properties to evaluate and compare. The comprehensive laboratory study was conducted to evaluate the treatment performance of the biochars as a filter media for future application in bioretention BMPs. The laboratory study had two parts: 1) jar testing biochar and 2) flow through column testing biochar only. The results from the laboratory testing along with the physiochemical properties of the biochars evaluated during this study were used to refine the proposed list of Essential Properties and develop recommendations for a design specification for a BSM-Biochar mix. The following is a summary of the specific research questions that were answered during this study:

Does biochar leach nutrients (N and P) or metals (Cu, Zn, Pb, Ca, and Mg)? If so, (how) does the leaching change over the duration of testing?

- Jar Testing - The results from the desorption testing indicate that Cu, Zn, and Pb did not leach from either biochar however Ca and Mg leached from both biochars. Leaching increased with time however complete desorption of Ca and Mg was not observed for either biochar during the 36-hour testing period.

    - No leaching of <u>heavy metals</u> was observed

- While some leaching of NO_3-NO_2, TKN, and TN was observed during rainfall events, on average the difference between the influent and effluent was either insignificant or some reduction was observed

- The TP effluent concentrations from the KB columns were significantly higher compared to the influent concentrations for the KB4 biochar (-150%) and the KB8 biochar (-341%). TP leaching appears to decline over time (rainfall simulations) and was approaching zero by the last rainfall simulation. As such, leaching from the KB biochar may only be a concern during the initial rainfall events.

- The hardness, Ca, and Mg effluent concentrations was only significantly higher than the influent concentration for total and dissolved Mg from the KB4 biochar (-9% and -13.9%) and the KB8 biochar (-18% and -16.9%). Mg leaching is attributed to the higher concentration of Mg in the KB biochar compared to the W biochar. The Mg leaching does not appear to change with time (rainfall simulations).

1. What is the short-term effectiveness of the selected biochars and BSM-Biochar mixes for reducing the following pollutants: TSS, heavy metals (Cu, Zn, Pb), phosphorus, and nitrogen (ammonia, nitrate-nitrite, and TKN)?

- Jar Testing - Results from the sorption kinetics testing indicate that the W biochar removed 90% of dissolved Cu, Zn, and Pb in 7, 11, and 13 hours compared to the KB biochar which requires 44, 50, and 57 hours respectively for the same metals. Hydrophobic tendencies exhibited by both biochars during testing (as indicated by the biochar floating during the initial rainfall events) likely contributed to the longer hydraulic retention times for the KB biochar. Specifically, the biochars were not fully saturated during testing which is essential for the full surface area of the biochar to be accessible (for adsorption) to the stormwater solution.

- TSS - The TSS removal efficiency ranged between 89.3%-96.1% for all four columns. The results of the statistical analysis suggest that the removal efficiency may be influenced by the type of biochar in larger quantities (W8 removal efficiency was significantly higher compared to KB8). The difference is likely attributed to the lower percentage of fines in the W biochar (0.9%) compared to the KB biochar (24%). For all columns, the removal efficiency was lowest during the initial rainfall events which is attributed to a "flushing period" in which finer particles are flushed from the biochar.

- Zn - The total and dissolved Zn removal efficiency for all columns ranged from 91% to 98% and 94% to 97%. The Zn removal efficiency appears to be influenced by the type of biochar in larger quantities (with the W8 outperforming the W4 and KB8 columns).

- Pb - The total and dissolved Pb removal efficiency for all columns ranged from 97% to 99% and 91% to 98% respectively. The Pb removal efficiency was influenced by the type of biochar (with the W biochar outperforming the KB biochar).

- Cu – The total and dissolved Cu removal efficiency ranged from 72% to 78% and 47% to 62% for the KB4 and KB8 columns respectively compared to the W4 and W8 columns which ranged from 93% to 96% and 88% to 89% respectively. The Cu removal efficiency was influenced by the type of biochar (with the W biochar outperforming the KB biochar).

- TP - Neither biochar was effective for removing total phosphorus. The KB4 and KB8 columns leached TP (-150% to -341%) while the difference between the influent and the W columns effluent was insignificant. The trend in the pollutant reduction ratio (C_e/C_i) vs rainfall simulations indicates that the TP leaching for the KB biochar was highest during the initial rainfall events, then gradually declined and was approaching 1.0 (no leaching by the final event). For the W biochar, minor leaching was observed during the initial rainfall event and then consistent at Ce/Ci=1 (no leaching was observed) or just below 1.0 (some reduction of TP was observed). These results suggest that TP leaching is a function of time and appears to only be a concern during the initial rainfall events.

- Ammonia - The mean NH_3 removal efficiency was 77% and 72% for the KB4 and KB8 columns compared to the 56% and 62% for the W4 and W8 columns respectively. These results suggest that neither the type nor the quantity of biochar significantly influenced the treatment performance.
- Nitrate-Nitrite - The NO_3-NO_2 removal efficiency was -5% and 3% for the KB4 and KB8 columns compared to -2% and 12% for the W4 and W8 columns respectively. These results of the statistical analysis suggest that the NO_3-NO_2 removal efficiency may be influenced by the quantity of biochar (the treatment performance improved from the 4- to 8-inch columns) but not the type of biochar.
- TKN – The removal efficiency from the W4 and W8 columns ranged from 48% to 51% respectively compared to the 32% and 16% reduction from the KB4 and KB8 columns respectively. The type of biochar appears to influence the treatment performance: the W biochar reduced significantly more TKN compared to the KB biochar.
- TN - The removal efficiency from the W4 and W8 columns ranged from 18% to 24% respectively compared to 14% to 16% from the KB4 and KB8 columns respectively. The removal efficiency for the KB 4 and KB8 columns (n=11) was 14% and 16% respectively. The results suggest that the treatment performance may have been influenced by the type of biochar in larger quantities with the W8 biochar outperforming the KB8 biochar.

2. How does the hydraulic performance of the selected biochars and BSM-Biochar mixes change over the duration of testing?

- The saturated hydraulic conductivity (K_{sat}) generally declined over the testing period for all columns. This was expected since TSS accumulate in the top of the media which reduces K_{sat} over time.

- The columns that contained the W biochar had a higher K_{sat}. The difference is likely attributed to the higher percentage of fines in the KB biochar (24% fines) compared to the W biochar (0.9% fines). In addition, wood biochars have a larger porosity compared to grass biochars which provides larger flow paths through the media (Jeffery et al., 2015). The 8-inch columns had a lower K_{sat} compared to the 4-inch columns which is likely due to the biochar particles absorbing water which causes the particles to swell reducing the media void spaces as well as the permeability.

3. What is the estimated lifespan of the biochar for reducing pollutants?

- Jar Testing - Total sorption capacity was not exhausted for either biochar during the sorption capacity testing as such it is not possible to estimate the lifespan of the biochars for reducing pollutants using the Part 1 results. However, the sorption equilibrium results indicate that while the KB biochar is effective at removing metals when the concentration in a solution is high, the media is less effective when the solution metals concentration is low. Comparatively the W biochar results indicate that the media is effective for removing metals over a range of concentrations. These results suggest that the adsorptive capacity, and subsequently the life span, of the W biochar is higher compared to the KB biochar.
- Column Testing - It is not possible to use the water quality data to estimate the lifespan of the biochars for reducing pollutants. However, the pollutant reduction ratio (C_e/C_i) vs the rainfall simulations event graphs can be used to assess changes in the treatment performance including whether the biochars appears to be reaching capacity (lifespan) for pollutant removal (as indicated by a consistent increase in C_e/C_i over time). This trend was only observed for the W columns with dissolved Cu when the C_e/C_i gradually increased for the second half of the rainfall simulations (events 7-12).

APPENDIX

Table 3.24 Complete Biochar Characterization Results

Category	Parameter		Kentucky Blue Grass	Wood	Compost Max Threshold	Criteria or Max. Threshold	Unit
Category A	CEC[1]		29	19	N/A	Declaration	meq/100g
	Bulk Density[2]		5.7	5.6		Declaration	lb/cft
	% Moisture[2]		9	45.4		Declaration	% of total dry mass
	C_{org}[3]		38.5	83.8		Class 1: ≥60% Class 2: ≥30%; <60% Class 3: ≥10%; <30%	% of total dry mass
	$H:C_{org}$[4]		1.6	0.42		Maximum: 0.7	Molar Ratio
	Total Nitrogen[4]		1.5	0.6		Declaration	% of total dry mass
	Total Ash[2]		40.5	7.6		Declaration	% of total dry mass
	pH[5]		9.45	10.32		Declaration	pH
	Electrical Conductivity[5]		3.35	1.33		Declaration	dS/m
	Liming[6]		5.1	2.9		Declaration	%CaCo3
	Carbonates[7]		5.6	6.3		Declaration	%CaCo3
	Butane Activity[8]		2.4	11		Declaration	g/100g dry
	Total Surface Area[9] (Correlated to Butane)		209	482		Declaration	m^2/g dry
	Maximum Density						
	Particle Size Distribution[10,11]		% Passing unrinsed(rinsed)	% Passing rinsed		Declaration	%
	#4	4.76 mm	100(100)	100			
	#8	2.38 mm	99.3(100)	87.3			
	#40	0.42 mm	98.2(31)	11.2			
	#100	0.15 mm	65.8(23.7)	1.9			
	#200	0.075 mm	24(15.4)	0.9			
Category C	Ammonia[6]		93	22		Declaration	mg/kg
	Nitrate[6]		< MDL	7.5			
	Phosphorous Total/Available[12]		12634/7900	603/574		Declaration	mg/kg
	Potassium Total/Available[12]		50473/48520	12298/8948		Declaration	mg/kg
	Volatile Matter[2]		60	92.39		Declaration	% of total dry mass
	Magnesium (Mg)[19]		0.57	0.10		Declaration	% of total dry mass
	Calcium (Ca)[19]		1.36	1.28		Declaration	% of total dry mass

	Parameter	Kentucky Blue Grass	Wood	Compost Max Threshold	Criteria or Max. Threshold	Unit
Category B	PCB[13]	ND	ND	N/A	0.2-0.5	mg/kg I-TEQ
	Chloride[13]	640	ND		Declaration	mg/kg dry weight
	Total Metals:[14]					
	As	ND	9.5	20[17]	As: 12-100	mg/kg dry weight
	Cd	ND	ND	10[17]	Cd: 1.4-39	
	Cr	ND	ND	N/A	Cr: 64-100	
	Co	ND	ND		Co: 100-150	
	Cu	44	39	750[17]	Cu: 63-1500	
	Pb	ND	ND	150[17]	Pb: 70-500	
	Hg	ND	ND	8[17]	Hg: 5-75	
	Mo	ND	ND	9[17]	Mo: 1-17	
	Ni	15	ND	210[17]	Ni: 47-600	
	Se	ND	ND	18[17]	Se: 1-100	
	Zn	99	13	1400[17]	Zn: 200-2800	
	B	16	16	N/A	Declaration	
	Na	570	850		Declaration	
	PAH[15]					
	Acenaphthene	0.7	ND	N/A	Max Threshold Allowed: 6-20	mg/kg TM
	Acenaphthylene	6.3	ND			
	Anthracene	1.5	ND			
	Benzo(a) anthracene	1.2	ND			
	Benzo(a) pyrene	2.1	ND			
	Benzo(g,h,i)perylene	2.6	ND			
	Benzo(k)fluoranthene	1.5	ND			
	Benzo(b)fluoranthene	1.7	ND			
	Chrysene	1.3	ND			
	Dibenzo(a,h)anthracene	ND	ND			
	Fluoranthene	3.2	ND			
	Fluorene	1.6	ND			
	Indeno(1,2,3-cd)pyrene	1.6	ND			
	Naphthalene	25	ND			
	Phenanthrene	6.8	ND			
	Pyrene	4.3	ND			

	Parameter	Kentucky Blue Grass	Wood	Compost Max Threshold	Criteria or Max. Threshold	Unit
Category B						
	Dioxins/Furans[16]					
	2378-TCDF	2	3	N/A	Max Threshold Allowed: 6-20	mg/kg TM
	12378-PeCDF	3.9	4.3			
	23478-PeCDF	ND	ND			
	123478-HxCDF	ND	ND			
	123678-HxCDF	4.7	4			
	234678-HxCDF	2.2	ND			
	123789-HxCDF	2.7	ND			
	1234678-HpCDF	5.6	7.5			
	1234789-HpCDF	2.8	ND			
	OCDF	10	13			
	2378-TCDD	1.9	1.5			
	12378-PeCDD	4.9	3.7			
	123478-HxCDD	2.1	ND			
	123678-HxCDD	4.4	4.6			
	123789-HxCDD	ND	ND			
	1234678-HpCDD	7	6.6			
	OCDD	13	13			
	Totals-Tetrafurans	ND	ND			
	Totals-Tetradioxins	ND	ND			
	Totals-Pentafurans	5.3	ND			
	Totals-Pentadioxins	4.9	ND			
	Totals-Hexafurans	11	7.8			
	Totals-Hexadioxins	8.6	8.1			
	Totals-Heptafurans	8.4	10			
	Totals-Heptadioxins	7	ND			
	Toxicity Equivalent (TEQ)	6.56	4.87	9	9 (TEQ)	ng/Kg-dry

c. ***Test Methods:*** *1). SM 2320B, 2). ASTM D1762-84, 3). Dry combustion, ASTM D4373, 4). Dry combustion, Dumas method, 5). Rajkovich, 6). Rayment & Higginson, 7). ASTM D4373, 8). ASTM D5742-95, 9). McLaughlin, Shields, Jagiello, Thiele's, 10&11). ASTM D2862-10, D422, 12). Enders & Lehmann/Wang after Rajan, 13). EPA 9056A, 14). TMECC, 15). EPA 8270C, 16). EPA 8290A, 17). WAC173-350-220 Compost Limits, 18). Ecology BSM, 19). Properties provided by vendor. 20). Simplified Method (Muszynski, 2006)*

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CHAPTER 4 - DEVELOPMENT A SPECIFICATION FOR BIORETENTION SOIL MEDIA AMENDED WITH BIOCHAR FOR STORMWATER TREATMENT

ABSTRACT

The goal of this research was to develop a specification for a bioretention soil media (BSM) amended with biochar (BSM-Biochar) that provides treatment of regional pollutants of concern (POC) and could be used by practitioners to design and construct bioretention best management practices (BMPs) in the field. The POCs evaluated in this study include total suspended solids (TSS), copper (Cu), zinc (Zn), total phosphorus (TP), total nitrogen (TN), ammonia (NH_3), and nitrate-nitrite (NO_3-NO_2). This study is an extension of the previous study, where the key finding from the study detailed in Chapter 3 were combined with frequent citations from bioretention literature, and the Washington State Department of Ecology requirements for custom BSM to develop a draft BSM-Biochar specification. The two biochars selected for this study were developed from wood (W) and Kentucky blue grass (KB) source materials. A flow through column testing method was used to evaluate the treatment performance of the draft specifications using different BSM-Biochar mixes. The evaluation consisted of comparing the change in pollutant concentrations between influent and effluent samples as well as comparing changes in the pollutant concentrations in the BSM-Biochar mix from the top, middle, and base layer of the columns. The experimental design consisted of creating conditions that are representative of those expected in the field including using a natural stormwater solution to simulate rainfall conditions that are expected in eastern Washington where the study was conducted. The results from the water quality testing indicate: a reduction in TSS, Zn and Pb by >96% in all BSM-Biochar mixes; a reduction of Cu and NH_3 concentration by >86%; NO_3-NO_2 leached from all the columns ranging from -53% to -48% and -48% to -33% for the columns that contained the KB and W biochars respectively. The columns that contained only the W biochar reduced TP concentrations by 21% to 26% compared the columns that contained only the KB biochar which leached TP by -77% to -110%. The trend in the treatment performances indicate that TP leaching from the KB columns declines over time while the efficacy of the W columns to reduce TP also declines over time. Results from the BSM-Biochar testing indicate that Ca and Mg cations are preferentially sorbed by the W biochar whereas Na cations are preferentially sorbed by the KB biochar. Overall, the majority of the heavy metals were retained in the top 6-inches of the BSM-Biochar mixes that contained both the W and KB biochar. The results of the column testing evaluation were used to confirm and refine the proposed specification and develop recommendations for field applications. A proposed BSM-Biochar specification is included in the Appendix.

INTRODUCTION

Bioretention cells are a common stormwater best management practice (BMP) in urban areas. These BMPs are characterized as shallow landscaped depressions which are designed to capture and store stormwater runoff from small catchment areas followed by infiltration through engineered soils commonly referred to as bioretention soil media (BSM) (Hatt, 2008). Pollutant removal primarily occurs as runoff infiltrates into and through the BSM.

Treated stormwater then infiltrates into the existing soils beneath the bioretention cell or is collected in an underdrain and conveyed to a storm drain network (AHBL & HDR, 2013).

The composition of BSM mixes varies nationally, however most are composed of topsoil, sand, and organic materials (Carpenter & Hallam, 2010; Hunt & Lord, 2006; Janoch & Liu, 2012). Recent studies indicate that the natural humic content found in organic materials, which is primarily responsible for sorption of metals, can be a source of pollutants specifically phosphorus and nitrogen (California Department of Transportation, 2009; Clark & Pitt, 1999; Washington State Department of Ecology, 2013). Regulatory agencies, concerned over impacts to receiving water bodies, have placed restrictions on the use of bioretention BMPs until the pollutant leaching concerns are resolved (Ecology, 2016; Washington State Department of Ecology, 2013). This presents a challenge for Municipal Separate Storm Sewer (MS4) operators regulated under a National Pollutant Discharge Elimination System (NPDES) stormwater permit, particularly since bioretention cells are a popular option for achieving permit requirements in ultra-urban areas.

Biochar may provide an alternative to the traditional organic materials that have been used in BSM. Biochar is a carbon rich material produced by thermally modifying a biomass (source feedstocks) at elevated temperatures with little or no oxygen. The result is a cellular structure that resembles the original biomass except the pore structure is more complex, which increases the total surface area of the material (Beck, Johnson, & Spolek, 2011; Beesley, Moreno-Jimenez, Gomez-Eyles, & Harris, 2011; McLaughlin, Anderson, Shields, & Reed, 2009). The thermal modification allows biochar to persist in soils longer than traditional BSM organic materials which require more frequent replacement to maintain the full benefits due to decomposition (California Department of Transportation, 2009). Studies suggest that biochar has sorption characteristics similar to activated carbon for immobilizing and reducing contaminants (Erickson, Gulliver, & Weiss, 2007; Gomez-Eyles, Yupanqui, Beckingham, Riedel, & Gilmour, 2013; Patil & Kulkarni, 2012). Since source materials are limited to biomass waste, biochar provides an inexpensive and more environmentally sustainable option compared to activated carbon, which has had limited application in stormwater due to expensive production costs (Bridgwater, 2003; Clark & Pitt, 1999; Gomez-Eyles et al., 2013; Patil & Kulkarni, 2012).

Biochar has been widely studied as a soil amendment for agricultural applications and environmental remediation. In agricultural applications, researchers have reported that biochar improves soil quality and function by increasing the water and nutrient retention capacity of the soils (Beck et al., 2011; Denyes, Langlois, Rutter, & Zeeb, 2012; Griffith, Banowetz, & Gady, 2013; Lehmann & Joseph, 2015; H. McLaughlin et al., 2009). In environmental remediation, contaminated soils amended with biochar were found to immobilize both inorganic and organic constituents thus preventing their subsurface transport to groundwater (L. Beesley et al., 2011; Lehmann & Joseph, 2015). The documented benefits of biochar amendments in soils have attracted notice from the stormwater community, particularly since these benefits are desirable characteristics of BSM (Beesley et al., 2011; Cao, 2010; Gomez-Eyles et al., 2013; Yaoa, 2011; Zheng, 2013). However, the bulk of these studies evaluated biochar under conditions not representative of a bioretention BMP function that is when pollutants are removed from a solution while the solution flows through the media (Beesley et al., 2011). While recent studies have focused on the evaluating biochar in stormwater applications, most studies occur in a laboratory using a synthetic stormwater solution made from deionized or tap water with limited pollutants (Leach, 2015; Mohanty & Boehm, 2015; Mohanty, Cantrell, Nelson, & Boehm, 2014; Reddy, Xie, & Dastgheibi, 2014; Tian et al., 2014; Ulrich, Im, Werner, & Higgins, 2015). Since natural stormwater has a complex chemistry and consists of multiple types of pollutants, which can influence the media treatment performance, results from these studies may limit an understanding of biochars treatment performance in field applications (Stahnke & Poor, 2017). The research described in Chapter 3 provides the first known study that evaluated biochar in in flow through columns using natural stormwater. However, no research has been identified that evaluated the treatment performance of BSM amended with biochar using natural stormwater. Thus, there are many unanswered questions related to the treatment performance of BSM-biochar mixes such as the optimum composition and configuration of the mix, the effectiveness of the mix for reducing stormwater pollutants, or whether mix can achieve NPDES MS4 regulatory performance requirements for stormwater treatment.

The goal of this research is to develop a specification for a BSM amended with biochar (BSM-Biochar) that provides treatment of regional pollutants of concern (POC) and can be used by practitioners to design and construction bioretention BMPs in the field. This study was conducted for the City of Spokane, which is a MS4 operator in eastern Washington that is regulated under the NPDES permit. As such, the POCs identified for this research include those regulated under the Washington MS4 NPDES permit or identified as POC for impaired water bodies in the Spokane area. These POCs include total suspended solids (TSS), dissolved copper (Cu) and zinc (Zn), total phosphorus (TP), pH, total nitrogen (TN), ammonia (NH_3), and nitrate-nitrite (NO_3-NO_2). An additional goal of this research is to assess whether biochar could meet the Washington State Department of Ecology (Ecology) treatment performance criteria for '*general use*' for removing the regulated POC. Specifically, the Ecology performance criteria requires that a new BMP demonstrate the following pollutant reductions to a 95% confidence interval: 80% TSS, 60% dissolved Zn and 30% dissolved Cu, and 50% TP. If the treatment criterion is met, the BSM-Biochar mix could be applied on future projects where BMPs are required to achieve the NPDES MS4 Permit requirements (Ecology, 2012a).

The research goals were achieved by answering the following questions:

1. Do the selected BSM-Biochar mixes leach nutrients (N and P) or metals (Cu, Zn, Pb, Ca, and Mg)?
2. What is the short-term effectiveness of the BSM-biochar mixes for reducing the POC?
3. How does the hydraulic performance of the BSM-biochar mixes change over the duration of testing?
4. How do the physiochemical properties of the BSM-biochar change over the testing period?
5. What is the estimated lifespan of the biochar for reducing pollutants when amended in a BSM mix?
6. Which biochar physiochemical properties (or range of properties) appear to indicate treatment performance for stormwater applications?

OVERVIEW OF THE RESEARCH PROJECT

To achieve the project goals, a proposed specification for BSM-Biochar was developed based on common citations found in the literature. The literature search focused on identifying the composition and configuration of a BSM-Biochar mix. Since no research was identified that evaluated BSM mixes amended with biochar, the literature review focused on bioretention studies (without biochar) to identify the bioretention characteristics that appear to optimize treatment performance. Then key findings from Chapter 3 are summarized, specifically the recommended quantity of biochar for a BSM and the Essential Properties of biochar: the physiochemical properties, which appear to indicate if a biochar is suitable for stormwater applications. Recommendations for the Essential Properties guided the selection of the two biochars for this study, wood (W) and Kentucky blue grass (KB), because they provide a range of Essential Properties to evaluate and compare. The treatment performance of the proposed specification was evaluated using flow through column testing of different BSM-Biochar mixes. The experimental design focused on creating conditions that are representative of those expected in the field including using a natural stormwater solution for all testing and simulating rainfall conditions that are expected Spokane Washington. The results from the column testing were used to refine the proposed specification and develop recommendations for field applications.

LITERATURE SEARCH

Bioretention BMP Stormwater Treatment Performance

Total Suspended Solids (TSS)

TSS refers to all particles suspended in stormwater runoff that are between 1.5 microns and 0.375 inches in diameter (Minton, 2012). Studies have reported that bioretention is a effective for reducing TSS by more than 80% (Barrett, Limouzin, & Lawler, 2012; Hsieh & Davis, 2005; Read, Wevill, Fletcher, & Deletic, 2008), which is the treatment standard specified in all NPDES MS4 permits (EPA, 2016). TSS is primarily removed within the top 3- to 4-inches of the BSM through sedimentation, as particles settle on the surface of the bioretention cell, and filtration, as stormwater infiltrates through the BSM particulates become physically trapped in the media pore spaces (Hatt, 2008; Hunt & Lord, 2006; Li & Davis, 2008). Optimum TSS removal rates appear to correlate with the BSM mix permeability rates between 2- to 6-inches/hour (Hunt & Lord, 2006) and a uniformity coefficient (d_{60}/d_{10}) of less than 4 (Hsieh & Davis, 2005).

Heavy Metals (Copper, Zinc, and Lead)

Heavy metals in stormwater are inorganic pollutants that exist in both dissolved and particulate forms. Particulate metals are typically removed by the same treatment mechanisms as TSS. Dissolved is the fraction of metals small enough to pass through a 1.5-micron filter (Grant et al., 2003) and the form most toxic to aquatic species. The primary bioretention treatment mechanism for dissolved metals is attributed to sorption (Oregon Department of Transportation, 2011) onto the surface of organic materials in the BSM or sediment in the stormwater solution (Carpenter & Hallam, 2010). The non-polar and hydrophobic characteristics of heavy metal cations drive the dissolved fraction to sorb onto organic materials through adsorption or cation ion exchange (Gnecco, Sansalone, & Lanza, 2008; Grant et al., 2003).

Research indicates that bioretention cells are effective for removing both the particulate and dissolved fraction of Zn, Cu, and Pb (Barrett et al., 2012; Hatt, 2008; Le Coustumer, Fletcher, Deletic, & Barraud, 2008; Reddy et al., 2014). However, the actual removal rates vary, particularly for dissolved metals. This is because the treatment performance is dependent on many variables including the type and quantity of organic material included in the BSM (Reddy et al., 2014) as well as the stormwater chemistry (i.e. solution pH, solubility of parameters in the solutions, etc.). Some of the more common organic materials in BSM mixes include peat moss, compost, and mulch (Carpenter & Hallam, 2010).

Researchers have also reported that the dissolved removal rate is rapid (Davis, Shokouhian, Sharma, & Minami, 2001) and most of removal occurs in the top 4-inches to 8-inches of the BSM (Davis et al., 2001; Hatt, 2008; Li & Davis, 2008). Recommendations for optimizing metal removal in bioretention BMPs include preventing the top of the BSM mix from becoming saturated for prolonged periods by maintaining a permeability rate of greater than 2-inches/hour (Hunt, 2003; Hunt & Lord, 2006). Regular maintenance is recommended to sustain the efficacy of the treatment performance and extend the lifespan of the BMP (Hunt, Davis, Traver, 2012) which includes replacing the top few inches of the BSM surface material every 2 to 3-years (Hunt & Lord, 2006).

Nutrients

Phosphorus and Nitrogen are valuable nutrients essential to supporting plant growth however; they are also chemical stressors that can degrade aquatic ecosystems when discharged to receiving water bodies. With respect to forms and behavior in stormwater, phosphorus and nitrogen have a more complicated ‘story’ compared to other pollutants (Davis, Hunt, Traver, & Clar, 2009), as described in the subsequent sections.

<u>Phosphorus</u>

Phosphorus exists as both organic and inorganic species in stormwater where the inorganic species is the form that is bioavailable for plant uptake (EPA, 1983). Total phosphorus (TP) is the form regulated in NPDES MS4 permit, which represent the sum of the particulate, and dissolved fractions of phosphorus (P) found in solution. The dissolved fraction of P is defined as the portion that passes through a 1.5-micron filter (Morgan, 2011).

A challenge with using bioretention cells to remove P from stormwater solutions is that the organic material included BSM often contains P, which can leach causing effluent P concentration to exceed the influent concentration (Mullane et al., 2015). To reduce the likelihood of P leaching researchers recommend using organic materials with a P content less than 100 mg/kg (0.01%) in locations where P is targeted for reduction otherwise the P content should be limited to between less than 400 mg/kg (0.04%) to reduce the likelihood of leaching (Payne et al, 2015; Hunt & Lord, 2006).

The particulate fraction of P is removed by similar treatment mechanisms as TSS, however the dissolved fraction is one of the more challenging pollutants to remove from stormwater (Erickson et al., 2007; Hunt & Lord, 2006).

This is because phosphorus (PO_4^{-3}) is an anion and treatment mechanisms for removing P is anion exchange which is pH dependent and dominant in acidic conditions (Brady & Weil, 1996). Since the pH of urban stormwater varies from 6.5 to 8.4 with the average reported around 7.4 (Minton, 2012; Morgan, 2011; Pitt, Maestre, & Morquecho, 2004; Pitt, Maestre, Morquecho, 2005), anion exchange is not expected to occur under these conditions.

Approaches for targeting P removal from urban stormwater focus on amending BSM with materials that can enhance precipitation and adsorption of P (Erickson, Weiss, Gulliver, & Huser, 2013). In particular, P can adsorb to soils that contain iron or aluminum oxide (Fe and Al) or complex and form a precipitate with materials that contain calcium. These processes are pH dependent specifically, adsorption of P to Fe and Al minerals dominates when the pH<6 compared to precipitation of P with Ca which dominates when the pH>6. Both P adsorption and precipitation are still expected to occur outside the dominant pH range, just to a lesser degree (Arias, Del Bubba, & Brix, 2001; Erickson et al., 2007). Another consideration with amending BSM mixes with Fe, Al, or Ca materials is kinetics (the rate of the reaction) and the hydraulic residence time (HRT). For example, a 2001 study conducted in Denmark found that the optimum P removal occurred when the HRT between the amendment and the solution was greater than 24-hours (Arias et al., 2001). Considering the typical BSM depth is 18-inch to 36-inches (Carpenter & Hallam, 2010) and that permeability range from 1- to 12-inches per hour, the expected HRT in bioretention cells is between 1.5 to 36 hours. Achieving the optimum P removal using Fe, Al, and Ca amendments in a bioretention cells requires a BSM a with the lower permeability and thicker BSM mix depth (Hunt & Lord, 2006).

Nitrogen (N)

Nitrogen exists in many different forms in the natural environment however the most common observed in stormwater include ammonia (NH^3), nitrite-nitrate (NO^{3-}, NO^{2-}), and total kjeldahl nitrogen (TKN). Typically, total nitrogen (TN) is the concentration regulated in NPDES permits, which represents the sum of all forms of nitrogen, found in a solution (EPA, 2013).

Nitrogen removal from stormwater in bioretention cells is primary through biological nitrification-denitrification reactions (Davis, Shokouhian, Sharma, & Minami, 2006). A common approach to target nitrogen removal in bioretention designs is to create conditions for nitrogen cycling to occur which converts toxic forms of nitrogen to less toxic forms or forms that can be removed using treatment mechanisms available within the BMP. For example, bioretention cell designs are modified by moving the underdrain outlet pipe several inches above the bottom of the cell, which creates a saturated zone in the soil column when the cell is lined with an impermeable liner. This modification creates anoxic conditions in which denitrification can occur and nitrate concentrations are reduced through conversion to nitrogen gas (N_2) (Minton, 2012).

Biochars are known to retain nitrogen primarily through sorption (Lehmann & Joseph, 2015). Most of the research on this topic is specific to the role of biochar in agricultural applications. Considering the neutral to basic pH of the stormwater solution, cation ion exchange is expected to be a dominant process compared to anion exchange, as such the cations forms of nitrogen (NH^{4+}) are expected to be retained by biochar. Researchers have reported that ammonia (NH^3) can transform into ammonium (NH^{4+}) (Taghizadeh-Toosi, Clough, Sherlock, & Condron, 2012) which is then removed from a solution through cation exchange (Taghizadeh-Toosi et al., 2012; Tian et al., 2014).

Studies have also documented that organic materials in BSM mixes can leach nitrogen. As such, the recommended nitrogen content of organic materials used in BSM mixes is less than 1000 mg/kg (0.1%) (Payne et al, 2015; Janoch, Liu, 2012).

BSM Aggregate

Nationally the aggregate portion of the BSM varies. The most common types of aggregate include C-33 sand, sandy loam, and loamy sand (Carpenter & Hallam, 2010). The selection of type of aggregate selected for a BSM appears to be based on which aggregate is the readily available in a specification location (Hunt & Lord, 2006; Carpenter & Hallam, 2010).

Influence of Bioretention Configuration on Stormwater Treatment Performance

Most bioretention research has been conducted on homogeneous BSM, which is a well-mixed blend of BSM materials. Some studies have focused on a layered configuration to improve the BSM treatment performance. For example, in a 2007 study conducted by Hsieh et. al., researchers found that placing a high permeability BSM layer over a low permeability layer resulted in higher P removal rates (compared to a single homogeneous BSM) because the contact time between dissolved P and the BSM in the upper layer was increased (Hsieh, Davis, & Needelman, 2007). Research indicates that a layered configuration can reduce the potential for P leaching. Specifically, by locating the organic materials in and above the plant root zone, the overall quantity of organic material is reduced, and subsequently the quantity of P and potential for P leaching from the BSM (Erickson et al., 2007; Minnesota Pollution Control Agency, 2014).

Conclusion Bioretention Characteristics for Optimum Treatment Performance

Based on the literature reviewed, the bioretention cell design and BSM characteristics that appear to optimize treatment performance include:

- A permeability rate of 2 to 6-inches/hour is recommended for TSS and heavy metals removal
- Removal of TSS and heavy metals primarily occurs in the top 4 to 8-inches of the BSM mix
- Nutrient leaching maybe reduced by locating organic materials in the plant root zone
- Nutrient leaching maybe reduced by using materials with low nutrient content: less than 400 mg/kg of phosphorus (0.04%) and 1000 mg/kg of nitrogen (0.10%)
- Using a layered BSM mix configuration may improve the treatment performance: a lower permeability base layer overlaid by a higher permeability layer will increasing contact time between the stormwater solution and the BSM in the upper layer

- Nitrogen removal maybe enhanced by modifying the bioretention cell to include an anaerobic zone in the base layer. However, modifying the cell was not part of the scope of this research project. As such, this option is not considered for this study.
- Selection of the aggregate portion of the BSM should be based on which of the following is more readily available: sandy loam, loamy sand, or construction sand

Chapter 3 Key Findings

Essential Properties of Biochar

In Chapter 3 the Essential Properties of biochar were proposed. For this research, Essential Properties are defined as biochar physiochemical properties, which appear to indicate whether a biochar is suitable for stormwater applications. In other words, properties, which may enhance or inhibit the effectiveness of the treatment mechanisms provided by the biochar or increase or decrease the likelihood of pollutant leaching. The Essential Properties were identified based on common citation biochar and bioretention literature. Two biochars were selected for evaluation. These biochars were selected because they provide a range of Essential Properties to evaluate and compare. A laboratory study was conducted to evaluate the treatment performance of the biochars, which included: 1) jar testing and 2) flow through column testing. The results from the laboratory testing were used to refine the list of Essential Properties summarized in Table 4.1.

Table 4.1 Essential Properties of Biochar for Stormwater Applications

Property	Criteria	Description
Organic Carbon (C_{org})	Class 1: ≥ 60%	Class 1 C_{org} content indicates a high carbon content which is associated with higher adsorption capacities (Lehmann & Joseph, 2015; McLaughlin, Anderson, Shields, Reed, 2009)
Hydrogen to Organic Carbon ratio ($H:C_{org}$)	0.7 max	$H:C_{org}$ < 0.7 is associated with a higher adsorption capacities (Lehmann & Joseph, 2015)
Cation Exchange Capacity (CEC)	high	The higher the CEC of a biochar the greater ability to exchange ions (International Biochar Initiative, 2013)
Total Surface Area (SA)	high	The higher the SA, the more available sites for adsorption (Lehmann & Joseph, 2015; Minton, 2012)
Mineral Ions: Calcium (Ca)	high	Higher Ca content may enhance P removal (Erickson et al., 2007)
pH	low	For applications that target NH_3 removal, biochars with a low pH are recommended.
Phosphorous (P)	low (less than 0.04%)	Organic materials with lower P content are less likely to leach (Erickson et al., 2007; Payne et al, 2015; Janoch & Liu, 2012).
Nitrogen (N)	low (less than 0.10%)	Organic materials with lower N content are less likely to leach (Payne et al, 2015).

Biochar Material Characterization

The two biochars were evaluated during the Chapter 3 study. The source materials and processing conditions for these biochars were: 1) Kentucky Blue KB (KB) seed mill screenings processed using a small-scale gasification unit operated at 625°C for 1-minute (Griffith et al., 2013) and 2) Wood (W) waste from a sustainable forest processed using a modified gasification process at 900°C for approximately 10 minutes. Table 4.2 provides a summary of the physiochemical characteristics of each biochar, which includes the Essential Properties.

Figure 4.1 Close-up Photo of Wood (W) Biochar (left) and Kentucky Blue (KB) Grass Biochar (right)

Table 4.2 Biochar Physiochemical Characterization Results

Property	Acronym	KB	W	Units
Organic Carbon	C_{org}	38.5	83.8	% of total dry mass
Hydrogen to Organic Carbon ratio	$H:C_{org}$	1.6	0.42	% of total dry mass
Cation Exchange Capacity	CEC	29	19	m_{eq}/100g
Total Surface Area	SA	209	482	m^2/g dry
Butane Activity	BA	2.4	11	g/100g dry
Electric Conductivity	EC	3.35	1.33	dS/m
pH	pH	9.45	10.35	units
Ash	Ash	40.5	7.6	% of total dry mass
Calcium	Ca	1.36	1.28	% of total dry mass
Magnesium	Mg	0.57	0.10	% of total dry mass
Phosphorous Total/Available (TP percent of biochar content)	P	12,600/7900 (1.26%)	603/574 (0.06%)	mg/kg
Total Nitrogen	N	15,000 (1.5%)	6,000 (0.6%)	mg/kg
Ammonia	NH_3	93	22	mg/kg
Nitrate	NO_3^-	< MDL	7.5	mg/kg
Physical Contaminants	-	6.56	4.87	ng/Kg-dry
Particle Size Distribution	PSD			
Sieve Sizes	#4	100	100	%
	#8	100	87.3	
	#40	31	11.2	
	#100	23.7	1.9	
	#200	15.4	0.9	

BSM-Biochar Specification Recommendations

This section provides a summary of the recommendations for developing a BSM-Biochar specification based on the findings from the Chapter 3 research.

- Phosphorus – Neither biochar is effective for reducing TP concentrations. The phosphorus content in the biochar and the quantity of biochar in the columns both had a significant influence on the quantity TP leaching. Recommendations for reducing leaching include using less biochar in a BSM (the equivalent of 4-inches of an 18-inch BSM). The TP leaching from the W biochar was insignificant compared to the KB biochar which leached P (>150%). The leaching appears to be attributed to the higher phosphorus content of the KB biochar (1.26%) compared to the W biochar (0.06%). However, TP leaching appears to decline over time (rainfall simulations) and was approaching zero by the last rainfall simulation. As such, leaching from the KB biochar may only be a concern during the initial rainfall events. More research over a longer testing period is recommended to verify these results.

- Nitrogen – The total nitrogen reduction was significantly higher with the W biochar compared to the KB biochar. These results may be attributed to the nitrogen content of the biochars, which was higher for the KB biochar (1.5%) compared to the W biochar (0.6%). However, both biochars have a higher nitrogen content than recommended in the Essential Properties (<0.1%) as such both biochars were expected to leach TN. This difference between the hypothesized results (defined in the Essential Properties) compared to the results of this study may be attributed to nitrogen cycling which appears to be responsible for changes in the different forms of nitrogen. More research is needed to understand nitrogen reduction using biochar and the biochar physiochemical properties that influence the TN treatment performance.
- Heavy Metals – The heavy metal (Zn, Cu, Pb) results were consistent with the Essential Properties in that both biochars have an excellent sorption capacity for immobilizing dissolved metals. This is because the biochars have a balance of sorptive capabilities (W biochar has a high surface area and low CEC whereas the KB biochar which has a low surface area and high CEC) and since neither biochar is fully carbonized (C_{org}=100%), both adsorption and cation exchange processes are expected to occur simultaneously.
- Biochar Quantity – For TSS and NH_3, the differences in the removal efficiency were statistically insignificant for each biochars regardless of the type or quantity of biochar evaluated. The metals removal efficiency of the flow through columns that contained a larger quantity of biochar (the equivalent of 8-inches of an 18-inch BSM) compared to the columns with a smaller quantity (the equivalent of 4-inches of an 18-inch BSM) was insignificant except. Therefore, the primary decision for selecting the quantity of biochar was the TP leaching which appears to be a function of the biochar phosphorus content and the quantity of biochar in the column. As such, a smaller quantity of biochar (equivalent to 4-inches of the total BSM mix depth) is recommended.
- Biochar has hydrophobic tendencies, which causes some of the biochar to float on the water surface during ponding conditions. To reduce the likelihood of this occurrence, it is recommended that a mulch material, heavier than the typical bark (Hunt & Lord, 2006), be placed on top of the BSM-biochar mixes to hold the biochar down.

MATERIALS AND METHODS

Stormwater Solution

A multi-component stormwater solution was used in this study. The solution was composed of natural stormwater and the pollutant types and concentration that are typical in urban runoff (Flint & Davis, 2007). The stormwater influent (SSW) characteristics are summarized in Table 4.3. The target influent concentrations were selected because they represent the higher of either the influent concentration required by Ecology for evaluating a new treatment BMP (Ecology, 2011) or the average 2013 Water Year concentrations measured at the Cochran Basin Stormwater Outfall (Table 4.4). The concentrations from the outfall were considered because the Cochran Basin is the largest in the City of Spokane. This basin is primarily commercial and residential land use, which is representative of the locations where the BSM-Biochar mix will applied in the future. Because the background concentrations in the natural stormwater was lower than the target concentrations, the chemical standards listed in Table 4.3 were added to achieve the target concentrations.

Table 4.3 Stormwater Influent (SSW) Characteristics and Testing Methods

Pollutant	Standard Testing Methods	Target (mg/L)	Background (mg/L)	Column Testing (mg/L)	Chemical Standards
pH	EPA 150.2	-	7.58	7.9	none
TSS	SM2540D-97	100	3.5	153	Sil-Co-Sil 106
Copper Total/Dissolved	EPA 200.8	0.040/0.010	0.046/0.021	0.054/0.049	Copper Sulfate
Zinc Total/Dissolved		0.280/0.020	0.058/0.030	0.277/0.192	Zinc Chloride
Lead Total/Dissolved		0.030/0.030	0.030/0.030	0.082/ND	Lead Nitrate
Arsenic Total/Dissolved		-	NT	NT	none
Cadmium Total/Dissolved		-	NT	NT	none
Chromium Total/Dissolved		-	NT	NT	none
Nickel Total/Dissolved		-	NT	NT	none
Phosphorus	SM 4500PE	1.000	0.47	1.140/1.063	Potassium Phosphate Monobasic
Ammonia	SM4500-NH_3	0.360	0.09	0.410	Ammonium Chloride
Nitrate-Nitrite	SM4500-NO_3	-	0.99	1.124	none
TKN	EPA 351.2	-	0.60	1.204	none
Hardness Total/Dissolved	SM2340-B97	-	232.7/228.0	215.3/209.7	none
Calcium Total/Dissolved	EPA 200.7	-	NT	48.87/47.56	none
Magnesium Total/Dissolved		-	NT	22.63/22.03	none

NT – Not Tested, ND – Not Detected

Table 4.4 Cochran Basin Outfall - 2013 Water Year Concentrations

	Hydrology				Nutrients (mg/L)				Metals (mg/L) Total/Dissolved			
	Gal. at Outfall[1]	Precip (in)	Temp (°C)	pH	TSS	TP	NH_3	NO_3^-	Cu	Pb	Zn	Hardness
Mean	8.45	0.51	15.5	7.03	233	1.00	0.36	0.38	0.04/0.01	0.03/0.00	0.28/0.01	127
SD	7.48	0.35	2.2	0.46	274	0.75	0.38	0.16	0.02/0.01	0.04/0.00	0.20/0.02	137

Values represent 100,000 gallons.

Stormwater was harvested from a roof top catchment (the Saranac Building located in downtown Spokane) which includes a portion that passes through a green roof. Multiple batches of natural stormwater were collected a few days before running the first rainfall simulation and midway through testing (before rainfall simulation 8). All batches were stored in a HPDE tank in the lab. On the day of each testing event, a portion of the natural stormwater was diverted to a second HDPE tank and chemical standards were mixed using a mixer that ran for the entire rainfall simulation to prevent the solids from settling to the bottom of the tank.

Rainfall simulations were run every 2 to 18 days for a total of fourteen events with each event averaging 24-hours. The rainfall duration was selected to mimic the long duration rainfall events that are common during the spring and fall in eastern Washington (Washington State Department of Transportation, 2016). These type of rainfall events are used to design bioretention cells (AHBL & HDR, 2013) because they produce a large volume of runoff (Washington State Department of Transportation, 2016). The rainfall frequency was selected to to mimic single rainfall events that are common in eastern Washington, however the actual days between events were chosen based on constraints in the research schedule.

The SSW solution was mixed in a 775-Liter HDPE tank, 1.52-meters tall with a 0.89-meter diameter. A Sharp Mixer, with a 133-centimeter long metal propeller and two blades, ran continuously for the entire simulated event to prevent any solids in the solution from settling. The SSW solution was distributed to each column through plastic tubing at flow rate of 40-mL/minute using a peristaltic pump with eight cartridges. Composite water quality samples were collected from each of the 14 rainfall events including one influent and eight effluent samples. The influent sample was collected from the combined discharge of all eight tubes immediately before starting the rainfall event. The effluent discharge was collected in large HDPE buckets located under each column. Immediately after the discharge from each column ceased, the effluent was well-mixed using a 15-inch long paint mixer attached to a power drill. All samples were collected and submitted to an Ecology certified laboratory following the standard testing methods shown in Table 4.3.

Experimental Design – Column Testing

The column setup for the flow through testing is shown in Figure 4.2. The column setup was designed to be representative of a bioretention cell constructed in the field. For example, the surface area of the column was assumed equivalent to the surface area from the same diameter section in a bioretention cell. Fourteen rainfall events were simulated and the depth of stormwater distributed to the columns during each event is equivalent to 1.5-inches of rainfall for a total of 21-inches, which is just over the 18-inches mean annual precipitation expected in Spokane Washington. The total volume of stormwater distributed to each column was determined by assuming the column area was 2% the size of the contributing impervious basin area. This bioretention cell sizing ratio is consistent with the national average which varies between 2% to 20% (Carpenter & Hallam, 2010; Davis, Hunt, Traver, & Clar, 2009; Hunt, Davis, Traver, 2012; Minnesota Pollution Control Agency, 2014).

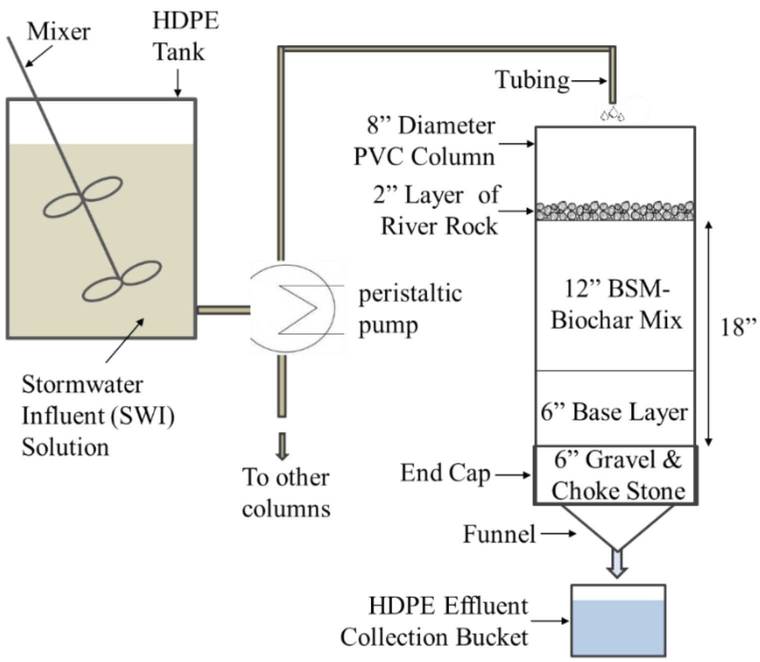

Figure 4.2 Flow Through Column Test Set-Up

Eight flow-through columns were constructed using 8-inch diameter schedule 40 PVC pipe that was cut into 4-foot sections (Figure 4.3). At the bottom of the column, end caps drilled with eleven 0.25-inch diameter holes, were attached to allow effluent to freely discharge. A 6-inch gravel and choke stone layer separated the BSM mix from the bottom of the columns, which was sized to prevent soil particles from migrating into the effluent (Brown & Clyde, 1989). A gravel base layer was selected in lieu of permeable geotechnical fabric due to clogging reports from other studies (Ecology, 2012b; Erickson et al., 2007). The gravel layers consisted of 6-inches of washed #57 stone overlaid by a 2-inch layer of choke stone (washed #89 stone).

The BSM-Biochar composition and configuration was developed based on the recommendations from the literature search and Chapter 3. The W and KB biochar used in Chapter 3 will also be used for this study. These biochars were selected because they provide a range of Essential Properties (Table 4.2) to evaluate and compare. Loamy Sands (LS) was selected as the aggregate for this study because it is a common top soil in the Spokane area and readily available for future projects. The mix depth in each column was 18-inches, the typical depth recommended in Washington State stormwater manuals (Ecology, 2015; AHBL & HDR, 2013). A layered BSM-Biochar configuration was selected which includes 2/3 of the biochar distributed throughout the top 12-inches and the remaining 1/3 tilled into the top 3-inches and no biochar in the base 6-inch layer. This configuration places biochar where most of the heavy metals treatment is expected to occur (Davis et al., 2001; Hatt, 2008; Li & Davis, 2008) and in the plant root zone which is expected to reduce the likelihood of nutrient leaching (Erickson et al., 2007; Minnesota Pollution Control Agency, 2014).

Four columns contained the KB biochar (70% LS:30% KB by volume) and four columns contained the W biochar (70% LS:30% W by volume). The base 6-inches layer of the columns contained four different mixes: one with LS only and the other three contained a 3-inches layer of LS which was placed over the top of a 3-inch layer of either basalt (BS), limestone dolomite (LD), or oyster shells (OS). These materials contain Fe, Al, and Ca, which reportedly can enhance chemical reactions that can immobilize phosphorus in the soil mix (Erickson et al., 2013). The BS, LD, and OS were added to the base layer because neither the KB nor W biochars are effective for removing phosphorus during the Chapter 3 study.

All mixes were overlaid by a 2-inch layer of washed 1½-inch minus river rock. The rock layer was included to allow for even distribution of SSW during the rainfall events and to reduce the potential of biochar floating during ponding events. The BSM-Biochar mix was packed into the columns in 6-inch lifts, except the base layer that contain BS, LD, and OS which was packed in two 3-inch lifts. Each lift was sprayed with tap water and compacted by repeatedly dropping a 7-inch diameter plate attached a rod to mimic "boot packing" as defined in Ecology's field installation requirements for BSM mixes (Ecology, 2014, pp. 7-28, Volume V). Boot packing is recommended (in lieu of using heavy equipment to compact the BSM) to prevent from over compacting which could reduce the permeability of the BSM-Biochar mix.

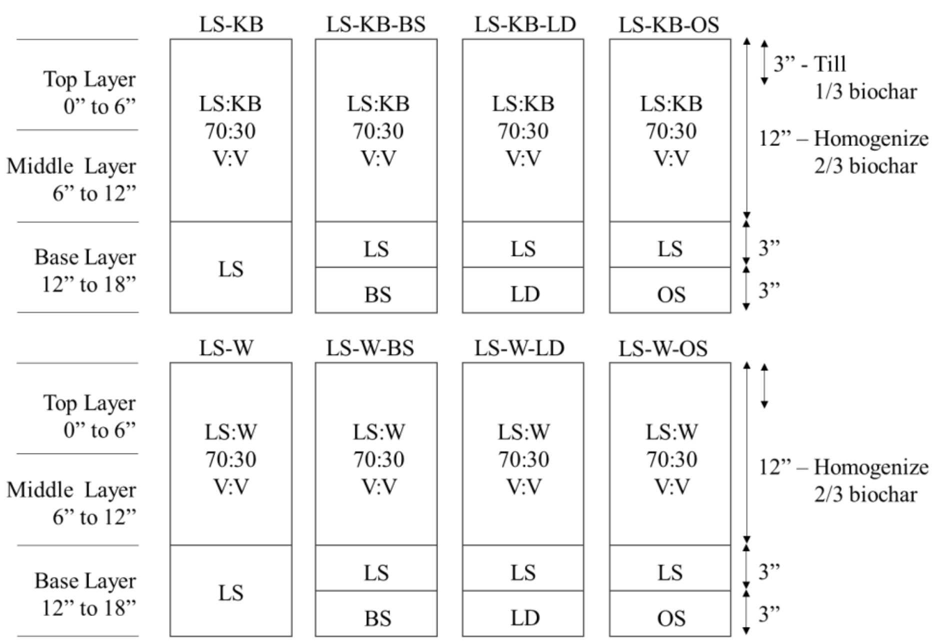

Figure 4.3 Column Coding and BSM-Biochar Mix Composition

Materials Characterization

Samples of the BSM-Biochar were collected from each column prior to the first rainfall simulation (baseline) and again after the last rainfall simulation (post). The physiochemical properties were then measured using the standard testing methods shown in Table 4.5. The purpose of this testing was to 1) evaluate and refine the BSM-Biochar specification for future field testing and 2) assess the influence of the biochar properties on stormwater treatment.

Table 4.5 BSM-Biochar Standard Testing Methods

Parameter	Standard Testing Method	Units
Bulk density @ 80% max density	SWC 50.100.90 (Klute, 1986)	g/cc
K_{sat} @ 80% max density		in/hr
Particle Size Distribution	ASTM D422	%
Saturated Paste pH, Ca, Mg, Na, P	S-1.10, S-1.60 (Klute, 1986)	meq/L
CEC	S-10.10 (Klute, 1986)	meq/100g
Organic Matter (OM)	S-9.20 (Klute, 1986)	%
Total Elements: Zn, Cu, Pb, Fe, Al	EPA 3050A/6010B	mg/kg
NH4-N, NO3-N	S-3.10 (Klute, 1986)	mg/kg
Total Nitrogen	ASTM D5373	mg/kg

BSM-Biochar Samples were collected from every column at the center of the top layer (3-inch horizon) and middle layer (9-inch horizon). For the columns that only contained LS in the base layer, samples were collected at the center of the base layer (15-inch horizon). For columns that contained a base layer with a 3-inch layer of LS overlaying a 3-inch layer of either BS, LD, or OS, samples of LS were not collected instead one sample was collected from each column at the 16.5-inch horizon. The samples from each horizon represent a homogenized composite sample collected from each of the four quadrants and one from the center of the column using a stainless-steel scoop. The samples were then homogenized in a stainless-steel bowl, transferred to the soil bags, and submitted to a laboratory for analysis.

Data Analysis Procedures

Water Quality Hypothesis Testing

The water quality results from the analytical testing included samples (n=14) collected from each column in which the concentrations of each parameter were measured using the standard methods shown in Table 4.3. A statistical comparison was conducted to determine whether there was a significant difference in the concentrations between the parameter datasets. This included evaluating whether the data was normally distributed using the Ryan-Joiner test (similar to Shapiro-Wilk test) (Helsel, 2002). Normality was assumed if the tests produced a p-value greater than 0.05 (Ecology, 2008). If the data was normally distributed, a two-sample t-test was used to determine if there was a significant difference between the influent and effluent concentrations. If the data was non-normally distributed, a Wilcoxon rank sum test (a nonparametric analogue to the paired t-test) was used instead. The specific null hypothesis (H_o) and alternative hypothesis (H_a) were evaluated as defined below. The statistical comparison was based on a confidence level of 95% (α=0.05).

<u>Scenario 1</u> - Statistical comparison between the influent (SSW) concentration for each pollutant and the respective effluent concentration from each of the eight columns.

- H_o: Effluent pollutant concentration from each column is equal to the SSW concentration

- H_a: Effluent concentrations are less than or greater than influent concentrations

<u>Scenario 2</u> - Statistical comparison of the pollutant concentration between the column with LS only in the base layer (control) to columns with the same biochar and different base layer composition: 1) LS-KB to LS-KB-BS, LS-KB-LD, LS-KB-OS and 2) LS-W to LS-W-BS, LS-W-LD, and LS-W-OS.

- H_o: Effluent concentrations from the control column are equal to the effluent concentrations of the other columns
- H_a: Effluent concentrations from the control column are less or greater than effluent concentrations from other columns

Water Quality Short Term Effectiveness

The short-term effectiveness was assessed using on the mean removal efficiency for each pollutant over all 14 rainfall events. This included calculating the removal efficiency for each pollutant from each individual rainfall events using Equation 1. Then the bootstrapping method was used to compute the 95% confidence interval for the mean removal efficiency from all rainfall events. The boot strapping method assumes the dataset is not normally distributed (*Technical Guidance Manual for Evaluationg Emerging Stormwater Treatment Technologies*, 2011). In a few instances, analytical results provided by the lab included values that were non-detectable. When this occurred, ND values were replaced with the reporting limit for the respective parameter as defined by the standard testing method noted in Table 4.3.

$$\Delta C_{SW} = 100x\,\frac{C_{in}-C_{eff}}{C_{in}} \qquad \text{Equation 1}$$

Where:

C_{in} = influent concentration (mg/L)

C_{eff} = effluent concentration (mg/L)

BSM-Biochar Physiochemical Properties

For each parameter measured in Table 4.5 the average and standard deviation was calculated for both the baseline and post samples. The data analysis process for determining these values was as follows:

- Top Layer (0 to 6-inch horizon) – Since the top layer of the four KB columns and the four W columns contained the same BSM-Biochar mix, the results from the analytical testing for each parameter were combined. This included determining the average and standard deviation for the baseline samples from the KB columns (n=2) and the W columns (n=2) as well as the post samples from the KB columns (n=4) and the W columns (n=4).
- Middle Layer (6 to 12-inch horizon) – The middle layer of the four KB columns and the four W columns also contained the same BSM-Biochar mix. As such, the same data analysis process as described for the top layer was followed for the middle layer.

- Base Layer (12 to 18-inch horizon) – The base layers were composed of four different combinations of materials which were replicated for the columns that contained KB biochar and the columns that contained W biochar. While there was a replicate for each base layer, it was overlaid by a BSM mix that contained a different biochar. Subsequently the results from the BSM-Biochar analytical testing could not be combined as they were for the top and middle layers. The only base layer results that were combined were the baseline samples collected from the LS-KB and LS-W columns that contained LS only. For these columns, the analytical testing results were averaged and the standard deviation (n=2) was calculated. The remaining baseline and post sample values measured represent a sample size of one (n=1).

BSM-Biochar Physiochemical Layers Hypothesis Testing

A statistical comparison was conducted to assess whether there was a significant difference in the analytical results between datasets as well as the magnitude of the difference between the datasets. A two-sample t-test was used to determine if there was a significant difference between the baseline and post physiochemical properties in the respective layers of the BSM-Biochar mix. The effect size (d) is a measure of the magnitude of the difference between datasets based on the relationship between the average and standard deviation of two data sets as shown in Equation 2. For unequal and extremely small sample sizes ($n \leq 5$), an effect size of $d \geq 3$ is equivalent to an 80% power when the confidence level is 95% or higher ($\alpha \leq 0.05$) (de Winter, 2013).

$$d = \frac{c_{gr1} - c_{gr2}}{\sqrt{\frac{\sigma_{gr1}^2 - \sigma_{gr2}^2}{2}}} \qquad \text{Equation 2}$$

Where:

c_{gr1}	=	Average concentration from a group of data (mg/kg)
c_{gr2}	=	Average concentration from another group of data (mg/kg)
s_{gr1}	=	standard deviation from a group of data (mg/kg)
s_{gr2}	=	standard deviation from another group of data (mg/kg)

The specific null hypothesis (H_o) and alternative hypothesis (H_a) were evaluated as defined below. The statistical comparison was based on a confidence level of 95% ($\alpha \leq 0.05$) using a t-test and an 80% power ($d \geq 3$). No hypothesis testing was conducted on the samples collected from the base layers due to insufficient sample sizes.

<u>Scenario 3</u> – Statistical comparison of the parameter concentration between the base line and post samples collected from each of the following layers: the top layer of the KB columns, the middle layer of the KB columns, the top layer of the W columns, and the middle layer of the W columns.

- H_o: The base line parameter concentrations are equal to the post parameter concentrations
- H_a: The base line parameter concentrations are less than or greater than the post parameter concentrations

BSM-Biochar Change in Pollutant Concentration

For every parameter tested, the change in concentration was determine using Equation 3. In a few instances, analytical results provided by the lab were non-detectable (ND). When this occurred, ND values were replaced with the reporting limit for the respective parameter as defined by the standard testing method noted in Table 4.5.

$$\Delta C_{BSM} = 100x\,\frac{C_b - C_p}{C_b} \qquad \text{Equation 3}$$

Where:

C_b	=	Average baseline concentration (mg/kg)
C_p	=	Average post concentration (mg/kg)

BSM-Biochar Saturated Hydraulic Conductivity (K_{sat})

The Ksat was measured using two methods. One method was falling head testing which was conducted on the BSM-Biochar mixes in each column using tap water. Testing occurred three times: once prior to starting the rainfall simulations (baseline) and again after completing the fourth and eighth rainfall simulation. This included filling each column with tap water and recording the time required for water to drop in 1-inch intervals. Then the hydraulic conductivity was calculated using Equation 4. Testing continued until the hydraulic conductivity was stable which is defined as when the values did not change more than 10% for three consecutive time increments.

$$K_{sat} = \frac{L}{t}\ln\frac{h_1}{h_2} \qquad \text{Equation 4}$$

Where:

K_{sat}	=	Saturated hydraulic conductivity (in/hr)
L	=	length of flow through soil depth in column (in)
t	=	time (hour)
h_1 & h_2	=	initial head and final head (in)

K_{sat} was also measured in the baseline and post samples using standard method SWC 50.100.90 (Klute, 1968). This included collecting composite samples from the layers noted below and submitting them to the lab for analysis. Then the change between the baseline and the post K_{sat} values were compared using Equation 3.

- the middle of the top layer (3-inch horizon)
- the middle of the middle layer (9-inch horizon)
- the middle of the base layer (15-inch horizon) for the columns that contained LS only
- the middle of the base layer (16.5-inch horizon) for the columns that contained BS, LD, and OS The

RESULTS AND DISCUSSION

Material Physical Characteristics

This section provides a summary of the mean (n=2) baseline physical properties of the BSM-Biochar materials in the top, middle, and base layers. This includes the ratio of biochar to loamy sand (by weight and volume), particle size distribution, and bulk density.

The mean ratio of biochar to LS in both the top and middle layers was 30%:70% (volume) and 2.65:97.35 (weight). The biochar volume and weight were higher in the top layer because of the biochar tilled into the top of the column. The differences in the weights and volumes between the BSM-Biochar columns of the same layer are due to differences in the biochar bulk density (KB=0.085-g/cc and W=0.081-g/cc). However, since most of the BSM-Biochar mix is LS (1.39-g/cc), the bulk density was relatively consistent when comparing the top layers and the middle layers of all columns. The mean particle size distribution (% Sand, Silt, and Clay) varied by ≤1% in the top and middle layers of columns with different biochar (LS-KB to LS-W).

The baseline gradation of the BS, LD, and OS base layers were consistent with ASTM C-33 sand. This gradation was selected because it is the most commonly used in stormwater filtration systems that target TSS removal (Minton, 2012). The actual baseline particle size distribution, bulk density, and K_{sat} for BS and LD were not tested. After these materials were packed into the columns and rinsed with tap water, water remained ponded on the surface for more than 6-hours. Because of this, the BS and LD materials were removed from the columns, rinsed on a #100 screen to remove the finer materials, and placed back in the columns. Since insufficient material remained for baseline testing, only the post samples were analyzed. The values shown in Table 4.6 represent the mean (n=2) of the values measured in the LS-KB and LS-W columns with the same base layer (post samples). Rinsing these materials resulted in a higher sand and lower clay size fraction in the BS (92% and 2.7%) and LD (95% and 2%) base layers compared to OS (86% and 5%) and LS (87.5% and 5.5%) respectively. Rinsing also contributed to higher bulk density for the LD (1.77-grams/cc) and BS (1.67-g/cc) base layers compared to the OS (0.9-grams/cc) and LS (1.39-g/cc) base layers.

Table 4.6 BSM-Biochar Physical Material Characterization

Column ID & Layer	Ratio Biochar to LS (%)		Sand (%)	Silt (%)	Clay (%)	Bulk Density[a] (g/cc)
	W:W	V:V				
LS-KB Top 0-6”	3.1:96.9	35.2:64.8	90.3	6.0	3.7	1.8
LS-KB Middle 6-12”	2.3:97.7	26.8:73.2	90.6	5.9	3.5	1.7
LS-W Top 0-6”	3.0:97.0	34.9:65.1	89.5	7.0	3.5	6.2
LS-W Middle 6-12”	2.2:97.8	26.3:73.7	90.4	6.3	3.3	3.2
LS Base 12”-18”	N/A	N/A	87.5	7.0	5.5	4.7
BS Base 15”-18”	N/A	N/A	92.0[b]	5.3[b]	2.7[b]	17.9[b]
LD Base 15”-18”	N/A	N/A	95.0[b]	3.0[b]	2.0[b]	29.2[b]
OS Base 15”-18”	N/A	N/A	86.0	9.0	5	3.9

a. *Bulk density is measured at 80% maximum compaction.*
b. *Represents the values measured in the post sample*

Saturated Hydraulic Conductivity

The saturated hydraulic conductivity (K_{sat}) was measured using two methods: 1) using baseline and post samples from the top, middle, and base layers of each column (Table 4.7 and Figure 4.4) and 2) using falling head tests conducted in the columns following the rainfall simulations (Table 4.8 and Figure 4.5). This section provides a summary of the results from both tests.

The baseline K_{sat} in the top and middle layers was higher for the LS-W columns (6.2- and 3.2-inches/hour) compared to the LS-KB columns (1.8- and 1.7-inches/hour) by a factor of 3 and 2 respectively. Differences in K_{sat} between the LS-KB columns compared to the LS-W columns are attributed to the higher percentage of fines in the KB-biochar (15.4%) compared to the W-biochar (0.9%) (Table 4.2). In addition, wood biochars typically have a larger porosity compared to grass biochars and biochars with a larger porosities are associated with higher K_{sat} values due to larger flow paths through the media (Jeffery et al., 2015). The higher K_{sat} in the top layer of the LS-W columns compared to the middle layer is attributed to the larger volume of biochar in the top layer (34.9:65.1) compared to the middle layer (26.3:73.7) and the larger volume biochar is expected to increase the porosity. However, the larger volume of KB biochar in the top layer of the LS-KB columns did not significantly increase K_{sat} (1.8-inches/hour) compared to the LS-KB middle layer (1.7-inches/hour).

The baseline K_{sat} values in the base layers varied from 3.9 inches/hour to 29.2-inches/hour. The K_{sat} variations appear to correlate with the percentage of clay and sand, specifically the materials with a higher fraction of sand and lower fraction of clay had a higher K_{sat}, 29.2-inches/hour (LD) and 17.9-inches/hour (BS), compared to the materials with a lower fraction of sand and higher fraction of clay, 4.7-inches/hour (LS) and 3.9-inches/hour (OS). These differences are not surprising since the mean diameter of sand is larger compared to clay as such a media with a higher fraction of sand is expected to have a higher porosity (Minton, 2012).

The configuration and composition of the column layers was designed such that the permeability would be the highest in the top layer and then gradually decline with the lowest permeability in the base layer. This configuration was selected because researchers have reported that a low permeability base layer will increase the contact time between the BSM and stormwater in the upper layers, which is known to enhance P removal (Hsieh et al., 2007). While higher permeability of the BS and LD base layers was expected due to the removal of fines during rinsing, the permeability of the top and middle layers was expected to be higher than the base layers, particularly compared to LS. This is because researchers have reported that the addition of biochar to soils can increase permeability above that of soil alone (Yaghoubi & Reddy, 2011). However, research published, since this study was conducted, by Jin (2017) provides a potential explanation for these results. Specifically, that amending bioretention soils with biochar will increase porosity above that of soil alone however the increased porosity did not always result in an increase in K_{sat}. Jin attributed larger K_{sat} values to biochars with a larger particle size, which have larger pore spaces and more pore spaces with complete connectivity, which provide more flow pathways for stormwater. Whereas lower or decreases in K_{sat} are attributed to smaller particle size biochars with smaller pore spaces or less connected pore spaces within the biochar (Jin, 2016). Jins findings may also explain why the larger volume of KB biochar in the top layer of the LS-KB columns did not significantly increase K_{sat} compared to the LS-KB middle layer.

The post K_{sat} results indicate a 45% to 85% decline in the top and middle layers as well as the LS base layers. The K_{sat} decline in the top layers was expected based on other bioretention research which have reported that sediment loading (TSS) from the influent creates a clogging layer on the surface and within the top 20% of the BSM reducing the permeability rates over time (Hatt, 2008; Hsieh et al., 2007; Pitt, Clark, Johnson, & Voorhees, 2007). The permeability decline in the top and middle layers may also be attributed to the biochar particles absorbing water which causes the particles to swell, reducing the media void spaces and subsequently the K_{sat} value (Brockhoff, Christians, Killorn, Horton, & Davis, 2010). The decline the LS base layers was not expected. One possible theory for these results is that biochar may have broken apart and migrated through the BSM-Biochar media and into the LS base layer. This theory is based on empirical observations made when the post BSM-biochar samples were collected from the columns. Specifically, prior to the study, there was a visual difference in the size and shape of the two biochar's (Figure 4.1) and the biochar was visually distinguishable from the LS. However, when post BSM-Biochar samples were collected, there was no visual difference between the KB or W biochar columns or between LS and biochar.

The K_{sat} values measured during the falling head tests in the columns, also declined over the 14-rainfall simulations (Table 4.8 and Figure 4.5). The values reported for November 11th were estimated based on the depth of ponding observed in each column after 18 hours of rainfall at a constant inflow rate of 40 mL/minute. Based on these results, the final K_{sat} was estimated at less than 2.93-inches/hour for the all columns except the LS-W-BS, LS-W-LD, and LS-W-OS which are estimated at greater than 2.93 inches/hours. The differences in K_{sat} is attributed to the larger porosity of the W biochar compared to the KB biochar (Jeffery et al., 2015). The higher K_{sat} of the BS and LD base layers (18- and 29-inches/hour) likely influenced these results.

Table 4.7 K_{sat} Laboratory Results for Top, Middle, & Base Layers

Column ID & Layer	Baseline Ksat (in/hr)	Post Ksat (in/hr)	% Difference
LS-KB Top 0-6"	1.8	0.87±0.06	52%
LS-KB Middle 6-12"	1.7	0.93±0.15	45%
LS-W Top 0-6"	6.2	0.95±0.10	85%
LS-W Middle 6-12"	3.2	1.13±0.15	65%
LS Base Layer (12"-18")	4.7	0.9±0.14	80%
BS Base Layer (15"-18")	NT	18±2.97	N/A
LD Base Layer (15"-18")	NT	29±3.68	N/A
OS Base Layer (15"-18")	NT	1.3±0.14	N/A

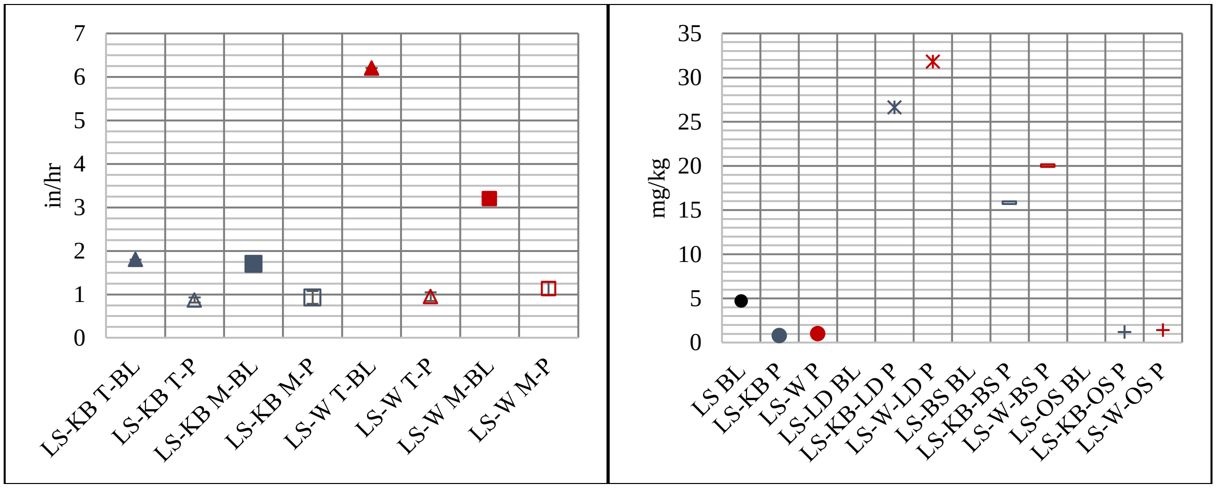

Figure 4.4 Lab Baseline (BL) & Post (P) Ksat Results: Top (T) & Middle (M) (left) & Base Layers (right)

Table 4.8 K_{sat} Falling Head Test Results

Column ID	Testing Date			
	2-Sep	12-Sep	10-Oct	11-Nov[a]
LS-KB	18.55	8.41	5.45	<2.93
LS-W	23.32	9.51	6.39	<2.93
LS-KB-BS	24.36	14.67	7.63	<2.93
LS-W-BS	12.76	12.06	9.3	>2.93
LS-KB-LD	18.75	14.21	13.05	<2.93
LS-W-LD	17.7	12.88	12.01	>2.93
LS-KB-OS	18.29	15.83	12.97	<2.93
LS-W-OS	18.59	13.7	10.41	>2.93

a. The Ksat value is estimated based on ponding depth observed after 18-hours of rainfall at a flow rate of 40 mL/min

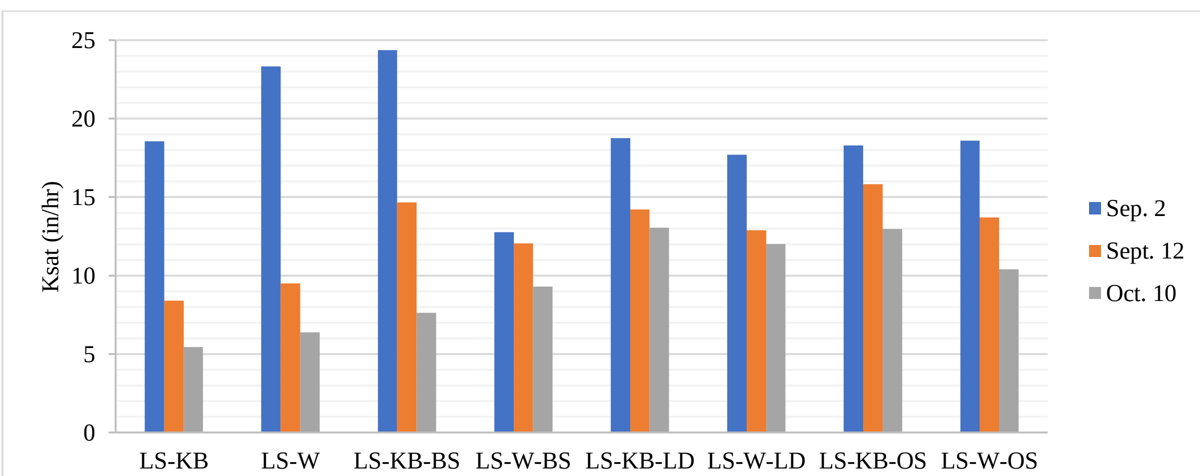

Figure 4.5 K_{sat} Falling Head Test Results

Water Quality Performance and BSM-Biochar Chemical Properties

This section summarizes the testing and analysis results for water quality and BSM-Biochar chemical characterization. The section is organized first by the water quality parameter (pH, TSS, heavy metals, nitrogen, phosphorus, and hardness) with the BSM-Biochar chemical analytical testing and analysis results embedded within the respective water quality parameter section. Each section includes the following elements:

- Water Quality – Results are summarized in tables including: the sample size (n), mean and standard deviation (SD), the removal efficiency at the 95% confidence interval (CI), and the results of the hypothesis testing (scenario 1 and 2). Box plots are included for each parameter to illustrate the mean, interquartile, and outliers for the SSW concentration compared to the effluent concentration from each column. The regulated pollutants (TSS, dissolved Zn and Cu, and TP) are compared to the Ecology treatment performance criteria with a red dashed line, which indicates the minimum performance, needed to meet the criteria. Mean effluent values below the red line indicate that the Ecology treatment performance criteria was achieved. Scatter plots, are included which illustrate the change in pollutant reduction ratio (C_e/C_i) over the course of all the rainfall events.
- BSM-Biochar Chemical Characterization and Layer Analysis - Results include hypothesis testing for scenario 3 (comparison of the base line to the post values in the top and middle layers). The change in the baseline and post values are also included for the top, middle, and base layers. All data are summarized in tables and on interval plots, which illustrate the difference between the base line and post mean parameter concentration as well as the standard deviation.

pH Water Quality

The mean influent pH was 7.67 and the average effluent pH ranged from 7.81 to 8.03 as shown in Table 4.9 and Figure 4.6. The difference between the influent and effluent pH ranged from an increase of -2.0% to -4.8%, this difference is statistically significant for all the columns. These results are consistent with the results from Chapter 3 in that the mean effluent pH increased for both biochars. It is worth noting that the Chapter 3 pH increase was higher (-6.7% to -9.5%) compared to the increase (-2.0% to -4.8%) during this study. The results suggest that when biochar is amended with sand (BSM-Biochar mix) the addition of sand appears to buffer the effluent pH. The higher pH of the influent (compared to the effluent) is attributed to the higher pH biochar (KB=9.45 and W=10.32). This pH buffering effect has been document in similar studies which reported that BSM mixes can buffer fluctuations in influent pH resulting in a smaller range of effluent pH (Davis et al., 2006; Davis, Shokouhian, Sharma, Minami, & Winogradoff, 2003; Muthanna, Viklander, Gjesdahl, & Thorolfsson, 2007).

There was no visible trend in the pH values noted in the reduction ratio (C_e/C_o) (Figure 4.7). The fluctuations in the effluent pH appears to be consistent with the trend in the influent pH (Figure 4.8) except the effluent pH was more stable as indicated by the smaller standard deviation (SD=0.12 to 0.17) compared to the influent (SD=0.30).

The difference between the column effluent pH was only statistically significant when comparing LS-KB to LS-KB-OS (p=0.001) and LS-W to LS-W-OS (p=0.001). These results suggest that the BSM-Biochar effluent pH is influenced by the OS base layer (Table 4.9). This is likely attributed to the pH of the OS base layer which measured 8.27 and 8.4 in the baseline and post samples respectively (Table 4.11).

Table 4.9 pH Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean	SD	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
SSW	14	7.67	0.30	-	-	-
LS-KB	14	7.81	0.12	-2.0%	0.050	0.370
LS-W	14	7.86	0.17	-2.7%	0.017	
LS-KB-BS	14	7.82	0.13	-2.1%	0.042	LS-KB: 0.562
LS-W-BS	14	7.89	0.13	-3.1%	0.007	LS-W: 0.189
LS-KB-LD	14	7.83	0.14	-2.3%	0.025	LS-KB: 0.345
LS-W-LD	14	7.87	0.12	-2.8%	0010	LS-W: 0.728
LS-KB-OS	14	7.94	0.12	-3.7%	0.002	LS-KB: 0.001
LS-W-OS	14	8.03	0.12	-4.8%	0.001	LS-W: 0.001

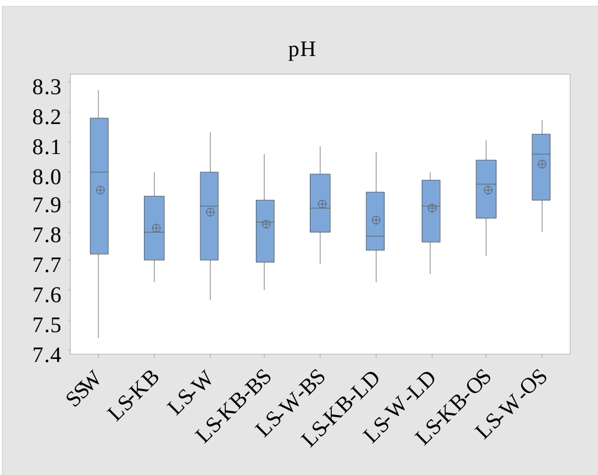

Figure 4.6 pH Box Plots: Comparison of Mean Influent & Effluent

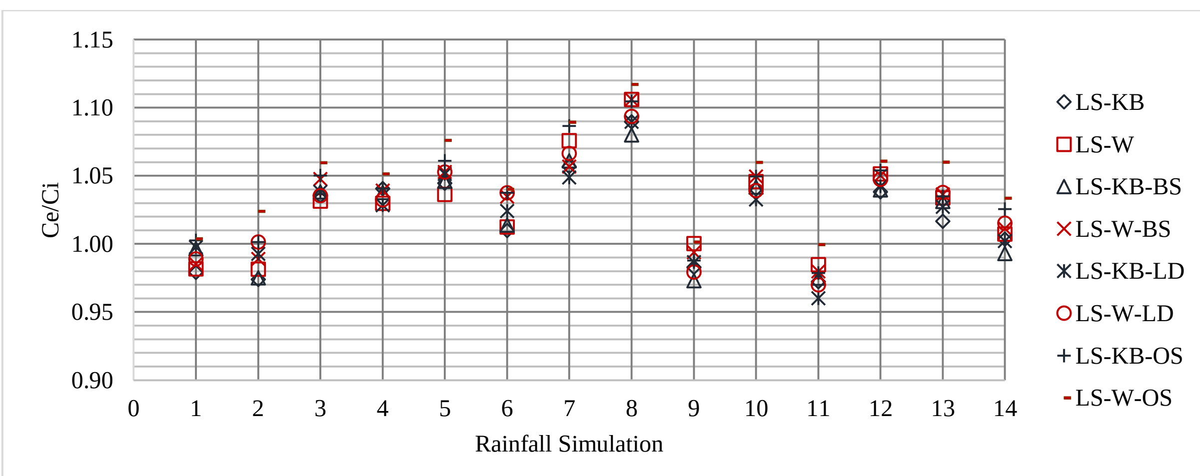

Figure 4.7 pH Reduction Ratio (C_e/C_i) vs. Time

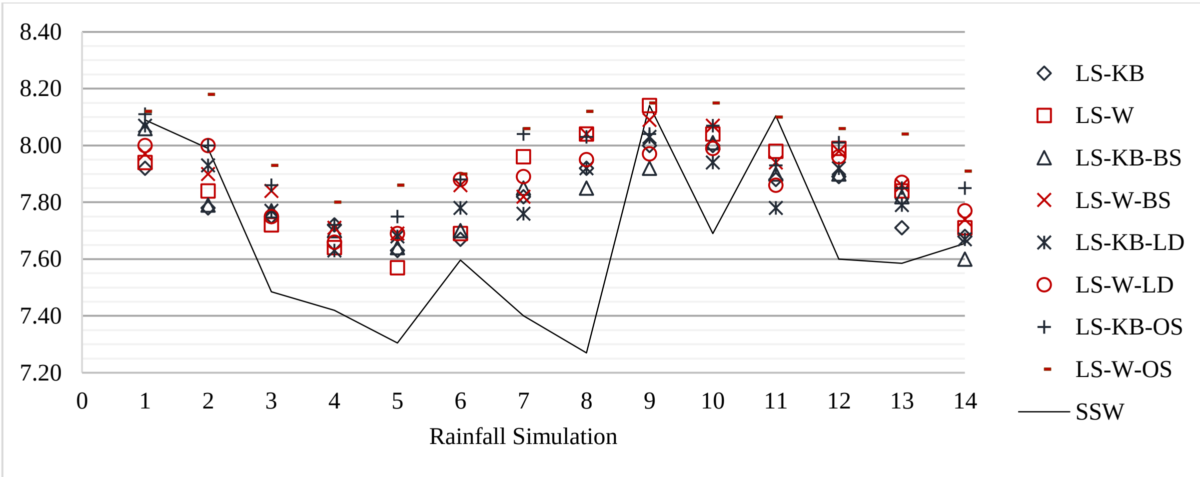

Figure 4.8 pH Influent & Effluent Concentrations vs. Time

pH BSM-Biochar

The baseline pH in the top and middle layers of the BSM-biochar mix ranged from 8.06 to 8.41 and 7.70 to 7.88 respectively (Table 4.10). The baseline pH of the top and middle layers of the columns that contain the KB biochar (8.21 to 8.06) was lower compared to the columns that contain the W biochar (8.41 to 8.34) as shown in Table 4.10 and Figure 4.9. The pH difference is attributed to the lower pH of the KB biochar (9.45) compared to the W biochar (10.32). The pH of both BSM-Biochar mixes declined between the baseline and post samples in the top and middle layers, (6.2% to 4.5% LS-KB and 8.2% to 5.5% LS-W) and these differences were statistically significant for all layers except the middle LS-KB layer. The pH decline in the BSM-biochar top and middle layers between the baseline and post samples suggests that the influence of the biochar pH on the effluent pH may decline over time.

The difference in the base layer pH between the baseline and post samples varied from a -5.0% increase (LS-KB-BS) to a 5.6% reduction (LS-KB-LD). While the effluent pH from the OS columns was significantly higher compared to the LS-KB and LS-W columns, the base layer pH was highest in the LD baseline (8.69) and the post the LS-KB-LD base layer (8.7) compared to the baseline pH of the OS base layer (8.27) and the post pH of the LS-KB-OS and LS-W-OS columns (8.4). One reason the effluent from the LD columns did not result in a statistically significant increase in pH is likely attributed to less contact time between the stormwater and the LD material due to the higher infiltration rate of LD base layer (29-inches/hour) compared to the OS base layer (1.3-inches/hour). The sample size was insufficient to assess the significance of the difference between the baseline and post results.

Table 4.10 pH BSM-Biochar Top & Middle Layers: Mean, SD, Mean Difference, and Hypothesis Testing

	Parameter	Units	Baseline Mean (n=2)	Baseline Stdev	Post Mean (n=4)	Post Stdev	Mean %Diff.	Statistically Significant	t-test	d
Top	pH	-	8.21	0.01	7.70	0.01	6.2%	Y	0.001	58.31
Mid			8.06	0.20	7.70	0.08	4.5%	N	0.245	2.38
	LS-W									
Top	pH	-	8.41	0.07	7.73	0.22	8.2%	Y	0.011	4.16
Mid			8.34	0.02	7.88	0.10	5.5%	Y	0.003	6.63

Table 4.11 BSM-Biochar Base Layer pH Properties

Base Layer Material	Parameter	Units	Baseline	Baseline SD	LS-KB Post n=1	LS-W Post n=1	LS-KB %Diff.	LS-W %Diff.
LS	pH	-	7.65	0.03	7.9	7.9	-3.3%	-3.3%
LD			8.69	N/A	8.2	8.7	5.6%	-0.1%
BS			7.62		8.0	7.9	-5.0%	-3.7%
OS			8.27		8.4	8.4	-1.6%	-1.6%

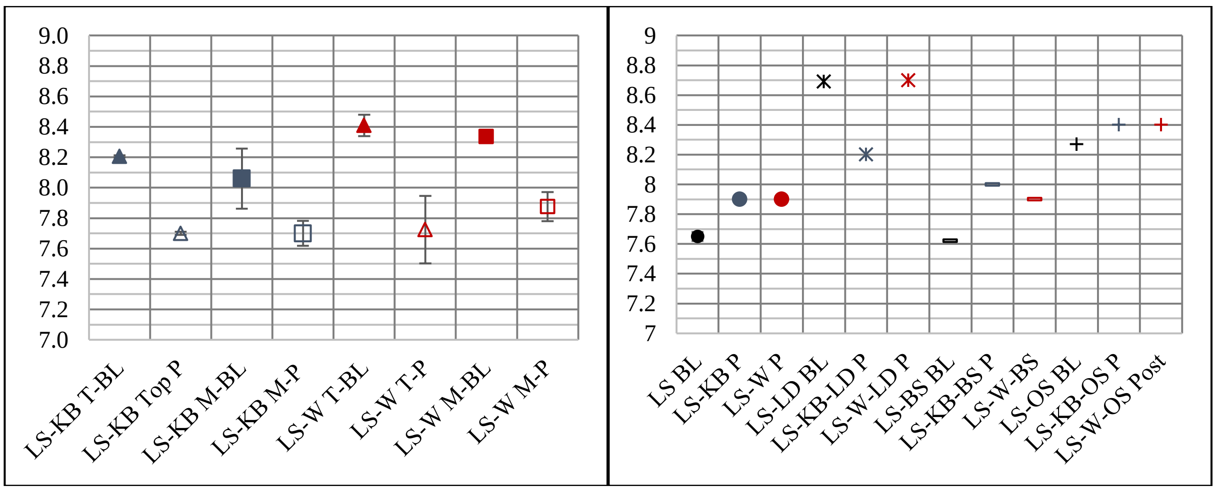

Figure 4.9 pH Baseline (BL) & Post (P) in: Top (T) & Middle (M) Layers (left) & Base Layers (right)

TSS Water Quality

The mean TSS removal efficiency from all eight columns ranged between 96%-98% at a confidence interval of 95%, which exceeds Ecology 80% treatment performance criteria (Table 4.12 and Figure 4.10). The difference was statistically significant between the influent and effluent for all columns however; the difference in the effluent concentrations between the columns was statistically insignificant. These results suggest that the type of biochar or the differences in the base layers did not influence the TSS treatment performance. These results are not surprising since the efficacy of bioretention cells for TSS removal correlates with the BSM mix permeability and gradation (Hsieh & Davis, 2005). These parameters were relatively consistent in the top and middle layers of the BSM-Biochar mix which was composed of an average of 97% (by dry weight) of loamy sand (Table 4.6).

The pollutant reduction ratio (C_e/C_i) over the duration of the rainfall testing was consistently less than 0.1 (removal efficiency greater than 90%) for all columns despite fluctuations in the TSS influent concentration (SD=85.3).

There was no apparent trend in the data that would suggest that the treatment performance was changing (Figure 4.11). These results are consistent with the Chapter 3 results except for the initial rainfall event when flushing of the finer particles was observed from the Chapter 3 columns, particularly the KB columns, which was not observed during this research. The differences in these results are likely attributed to rinsing the KB biochar prior to installing the BSM-Biochar into the columns as such there was less fines in the BSM-Biochar mix to "flush" from the columns. The addition of LS to the columns also provided a thicker layer of media (compared to just biochar in Chapter 3) to filter and trap TSS in the media pore spaces.

Table 4.12 TSS Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean (mg/L)	SD (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
SWI	14	153.50	85.3	-	-	-
LS-KB	14	3.264	4.85	96%	0.001	0.646
LS-W	14	1.300	0.743	98%	0.001	
LS-KB-BS	14	1.248	0.716	97%	0.001	LS-KB: 0.3953
LS-W-BS	14	1.621	2.688	98%	0.001	LS-W: 0.2802
LS-KB-LD	14	1.281	0.889	98%	0.001	LS-KB: 0.4082
LS-W-LD	14	1.109	0.705	98%	0.001	LS-W: 0.5053
LS-KB-OS	14	1.693	0.701	97%	0.001	LS-KB: 0.3462
LS-W-OS	14	1.714	0.869	97%	0.001	LS-W: 0.1870

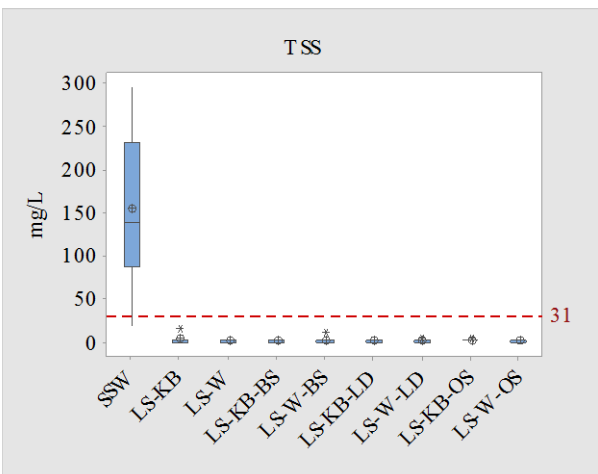

Figure 4.10 TSS Box Plots: Comparison of Mean Influent & Effluent

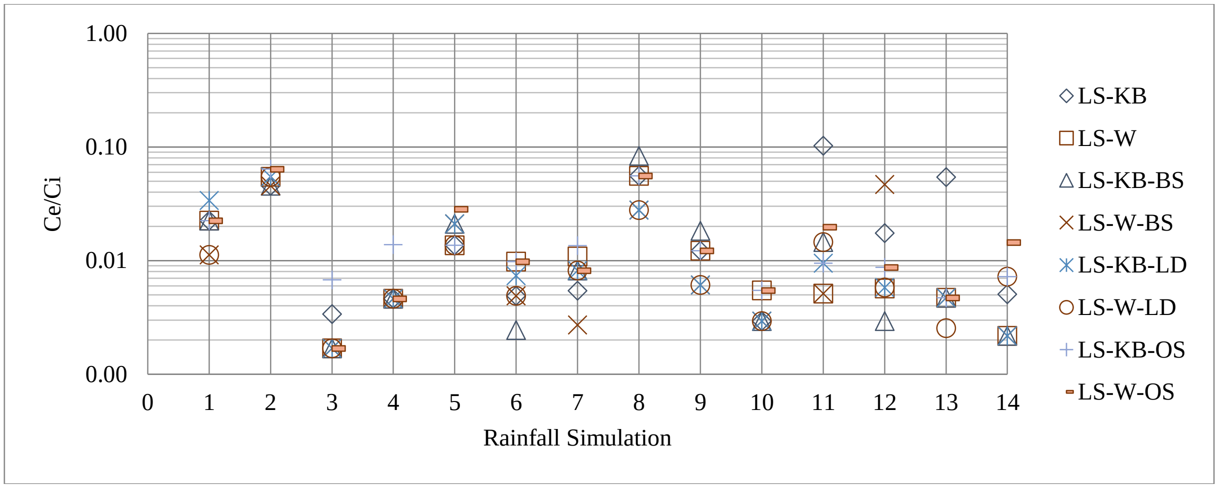

Figure 4.11 TSS Changes (C_e/C_i) vs Time

Heavy Metals (Zn, Cu, Pb) Water Quality

All columns achieved the Ecology performance standards for dissolved metals with the mean removal efficiency exceeding 60% for Zn and 30% for Cu to a confidence interval of 95% (Tables 4.13 and 4.14 and Figures 4.12 and 4.13).

The mean total and dissolved Zn removal efficiency was 97% and 96% respectively for all columns except the LS-W and LS-KB-BS which was slightly lower, ranging from 80%-81% (Table 4.13). The lower mean removal efficiency was due to two separate rainfall events when the effluent removal efficiency was measured at 17% (LS-W) and 24% (LS-KB-BS). The LS-W and LS-KB-BS data sets were evaluated using the Grubb's test and these data points were identified as an outlier (α=0.001). Without the outliers, the removal efficiency was 96%, which is consistent with the other columns. These results are statistically significant when comparing the influent to the effluent however the difference between the column effluent concentrations was statistically insignificant ($p>0.05$). These results suggest that neither the type of biochar nor the differences in the base layer materials influenced the treatment performance.

The Zn pollutant reduction ratio (C_e/C_o) was consistently below 0.1 for all rainfall events (Figure 4.13) and no trend was observed that would suggest a change in the treatment performance.

Table 4.13 Zn Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean (µg/L)	SD (µg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total						
SWI	14	277.214	65.657	-	-	-
LS-KB	14	7.150	3.784	97%	0.001	0.204
LS-W	14	6.256	3.760	97%	0.001	
LS-KB-BS	14	7.650	3.401	97%	0.001	LS-KB: 0.716
LS-W-BS	14	6.529	3.598	97%	0.001	LS-W: 0.846
LS-KB-LD	14	6.429	3.631	97%	0.001	LS-KB: 0.611
LS-W-LD	14	6.429	3.631	97%	0.001	LS-W: 0.903
LS-KB-OS	14	6.429	3.631	97%	0.001	LS-KB: 0.611
LS-W-OS	14	7.093	4.162	97%	0.001	LS-W: 0.581
Dissolved						
SWI	14	191.864	69.185	-	-	-
LS-KB	14	6.457	3.621	96%	0.001	0.223[a]
LS-W	14 13[a]	20.503 5.542[a]	56.052 2.957[a]	80% 96%[a]	0.001[a]	
LS-KB-BS	14 13[a]	12.700 6.720[a]	22.675 3.720[a]	81% 96%[a]	0.001[a]	LS-KB: 0.659[a]
LS-W-BS	14	6.864	3.649	96%	0.001	LS-W: 0.349
LS-KB-LD	14	6.286	3.292	96%	0.001	LS-KB: 0.654
LS-W-LD	14	6.429	3.631	96%	0.001	LS-W: 0.343
LS-KB-OS	14	6.429	3.631	96%	0.001	LS-KB: 0.336
LS-W-OS	14	6.071	4.009	96%	0.001	LS-W: 0.949

a. *The values reflect the results of the data set analysis without the outlier.*

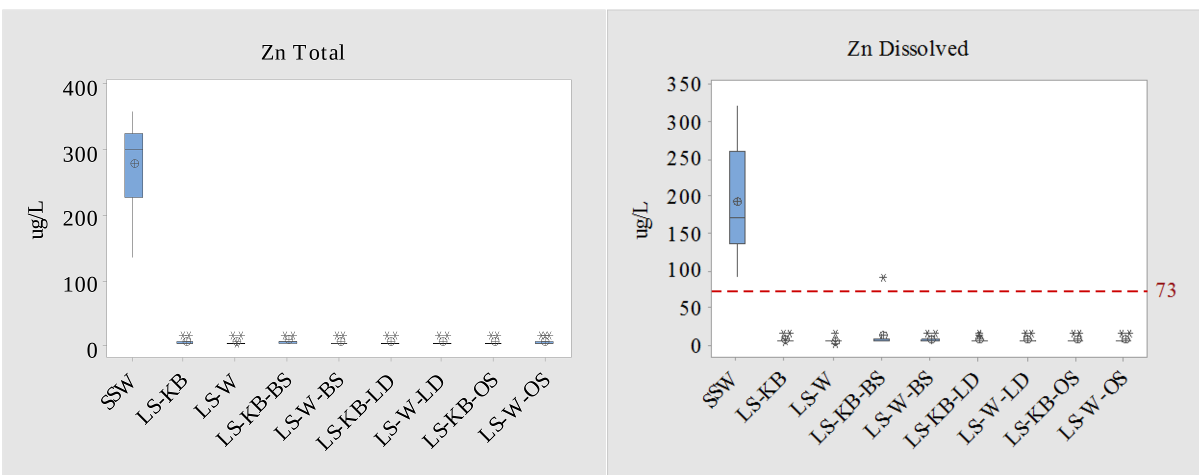

Figure 4.12 Zn Total (a) & Dissolved (b) Box Plots: Comparison of Mean Influent & Effluent

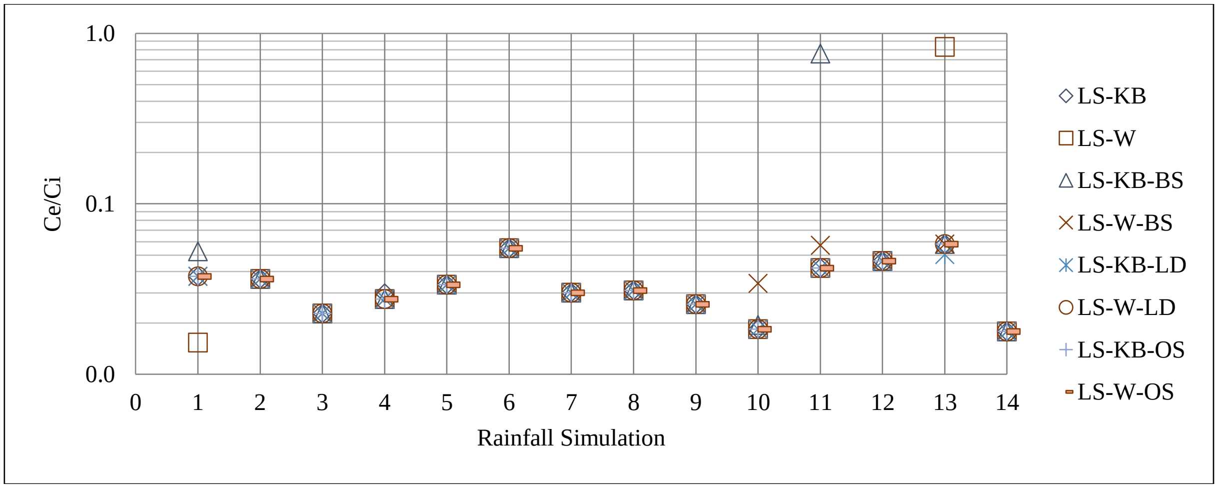

Figure 4.13 Zn Dissolved Reduction Changes (C_e/C_i) vs Time

The mean Cu removal efficiency was consistently higher in the columns that contained W biochar (total 86%-96% and dissolved 83%-94%) compared to the KB columns (total 53%-77% and dissolved 49%-76%) as shown in Table 4.14 and Figure 4.14. These results are statistically significant when comparing the influent to the effluent concentrations and statistically insignificant when comparing the effluent concentration from the LS-W columns and the LS-KB columns to the columns with the same base material. These results suggest that neither the type of biochar nor the base layer materials influenced the treatment performance.

The Cu pollutant reduction ratio (C_e/C_o) over the rainfall events was consistently around 0.10 for the W columns compared to the KB columns in which the C_e/C_o gradually declined from 1.0 and was approaching 0.1 by the last rainfall simulation (Figure 4.15). These results suggest that the treatment performance of the W biochar was higher and consistent over the rainfall events; however, the treatment performance of the KB biochar gradually improved and was approaching the same removal efficiency as the W columns. This time delay in the treatment performance may be attributed to the hydrophobic behavior of the KB biochar that was observed during the Chapter 3 testing. Specifically, the negative capillary forces can hold air in the biochar micro-pores which will inhibit the uptake of SSW preventing the biochar from becoming saturated (Gray et al, 2014; Jeffery et al, 2015). The degree of saturation can also influence the biochar sorption capacity since the total surface area, which includes the micropores and macropores, is inaccessible to the SSW when the biochar is not saturated. The results from this study are consistent with reports from other researchers in that the hydrophobic characteristics appear to diminish once the biochar becomes saturated because more of the micropores become accessible to the SSW (Gray et al, 2014). For this study, the weight of LS and the rock mulch appears to have reduced the quantity of floating biochar and moisture retained in the columns between rainfall simulations which likely influenced (increased) the degree of saturation in the biochar.

Table 4.14 Cu Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean (µg/L)	SD (µg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total						
SWI	14	53.736	8.854	-	-	-
LS-KB	14	10.553	2.309	77%	0.001	0.004
LS-W	14	3.032	1.074	94%	0.001	
LS-KB-BS	14	19.029	12.298	53%	0.001	LS-KB: 0.007
LS-W-BS	14	6.507	3.989	84%	0.001	LS-W: 0.001
LS-KB-LD	14	16.394	6.85	62%	0.001	LS-KB: 0.002
LS-W-LD	14	6.877	1.963	86%	0.001	LS-W: 0.001
LS-KB-OS	14	13.864	3.241	71%	0.001	LS-KB: 0.003
LS-W-OS	14	5.41	4.191	87%	0.001	LS-W: 0.033
Dissolved						
SWI	14	48.729	8.72	-	-	-
LS-KB	14	10.109	2.352	76%	0.001	0.001
LS-W	14	2.73	1.339	94%	0.001	
LS-KB-BS	14	18.113	12.068	49%	0.001	LS-KB: 0.008
LS-W-BS	14	6.658	4.21	83%	0.001	LS-W: 0.002
LS-KB-LD	14	15.914	7.103	59%	0.001	LS-KB: 0.002
LS-W-LD	14	6.137	2.247	86%	0.001	LS-W: 0.002
LS-KB-OS	14	13.224	3.174	69%	0.001	LS-KB: 0.005
LS-W-OS	14	5.719	3.759	85%	0.001	LS-W: 0.005

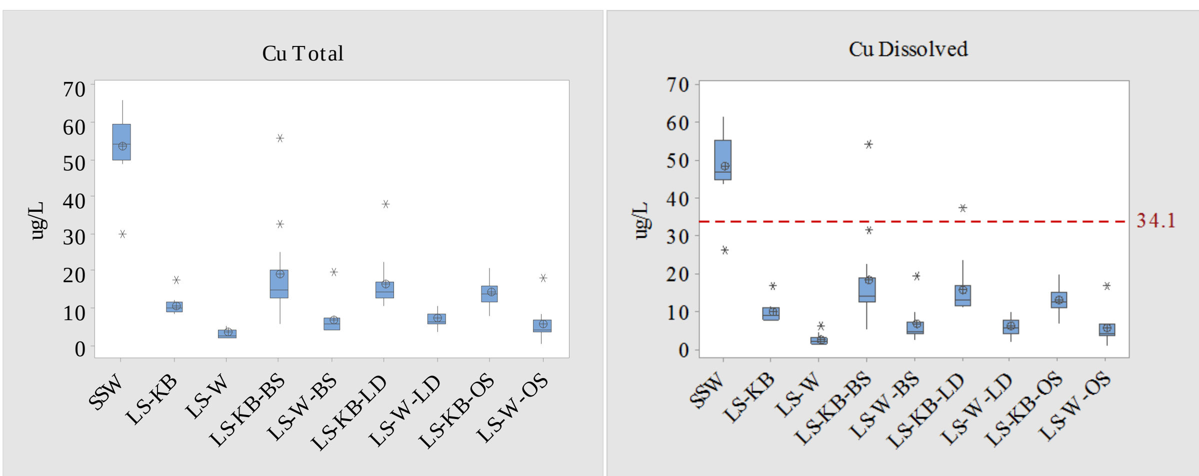

Figure 4.14 Cu Total (a) & Dissolved (b) Box Plots: Comparison of Mean Influent & Effluent

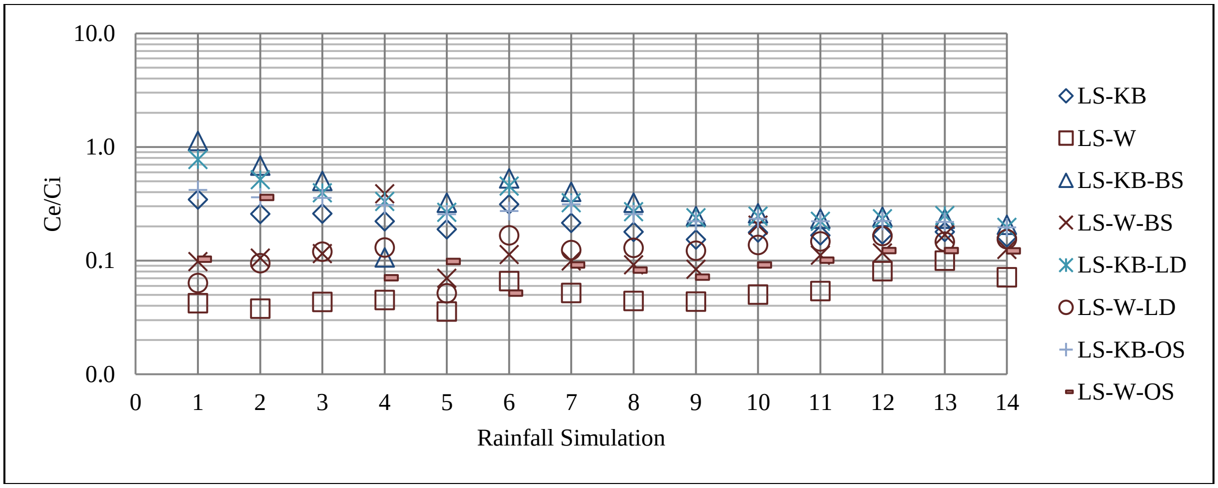

Figure 4.15 Cu Dissolved Reduction Changes (C_e/C_i) vs Time

The Pb removal efficiency for all columns ranged between 96%-99% for total (Table 4.15 and Figure 4.16). These results are statistically significant when comparing the influent to the effluent however, the difference between the column effluent concentrations was statistically insignificant. These results suggest that neither the type of biochar nor the differences in the base layer materials influenced the treatment performance. The mean dissolved fraction of Pb in the SSW was below the detection limit despite consistently mixing increasing concentrations of the lead nitrate chemical standard into the SSW solution to achieve a desired concentration of 0.080 mg/L. This is not surprising since the solubility of Pb tends to decrease above a pH of 7.0 and most likely, the chemical standards were converted to Pb precipitates.

Table 4.15 Pb Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean (µg/L)	SD (µg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total						
SWI	14	82.38	45.772	-	-	-
LS-KB	14	0.293	0.111	97%	0.001	0.388
LS-W	14	0.262	0.031	99%	0.001	
LS-KB-BS	14	0.260	0.028	99%	0.001	LS-KB: 0.388
LS-W-BS	14	0.655	1.515	96%	0.001	LS-W: 0.638
LS-KB-LD	14	0.262	0.030	99%	0.001	LS-KB: 0.388
LS-W-LD	14	0.297	0.176	99%	0.001	LS-W: 0.638
LS-KB-OS	14	0.254	0.014	99%	0.001	LS-KB: 0.346
LS-W-OS	14	0.250	0.000	99%	0.001	LS-W: 1.000
Dissolved						
Most of the SSW influent and column effluent concentrations were below the detection limit.						

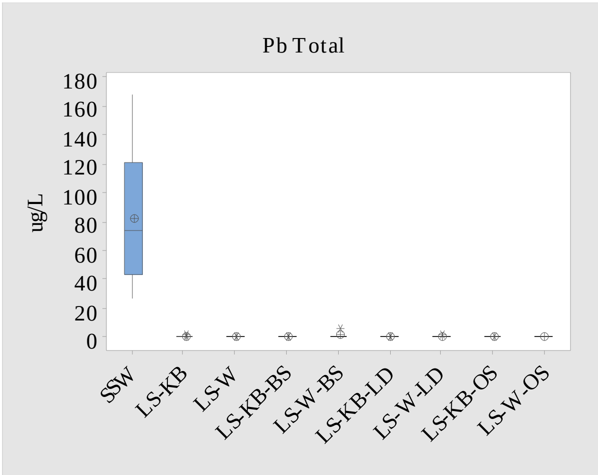

Figure 4.16 Pb Total Box Plot: Influent Stormwater vs. Effluent

Heavy Metals (Zn, Cu, Pb) BSM-Biochar

The Zn, Cu, and Pb content in the top layers of the columns significantly increased for both the LS-KB and LS-W columns for all three metals, Zn (-93% and -101%), Cu (-46% and -51%), and Pb (-36% and -43%), as shown in Table 4.16 and Figures 4.17 to 4.19. Whereas the difference between the baseline and post samples from the middle layers were statistically insignificant for all columns. These results are consistent with other bioretention research, which suggest that most of heavy metal removal occurs in the top 4-inches to 8-inches of the BSM (Hatt, 2008; EPA, 2016; Le Coustumer, 2008).

Except for the LS base line sample (n=2), only one sample was collected per column for the base layers as such it is not possible to draw meaningful conclusions. Instead, the results for the base layers focus on patterns that were observed or large differences in the results.

- The metals concentration from the LS base layer declined for both the LS-KB and LS-W columns, which suggests that metals, leached from the LS material
- The OS base layer retained more Zn (-37.3% and -47.69%) and Pb (-729% and -659%) from both LS-KB and LS-W columns respectively than any other base layer. These results suggest that OS as a BSM amendment has potential for enhancing both Zn and Pb removal.
- No apparent pattern was observed in the Cu base layer results that would suggest why the LS-W columns removed more Cu. These results support the findings reported in the Cu water quality section, specifically that the base layer materials did not significantly influence the treatment performance of the columns.

Table 4.16 BSM-Biochar Top & Middle Layer Zn, Cu, & Pb Properties

	Parameter	Units	Baseline Mean (n=2)	Baseline Stdev	Post Mean (n=4)	Post Stdev	Mean %Diff.	Statistically Significant	t-test	d
	LS-KB									
Top	Zn	mg/kg	40.5	1.3	78.1	14.9	-92.8%	Y	0.016	3.56
Mid			39.35	0.78	41.27	3.52	-4.9%	N	0.459	0.75
	LS-W									
Top	Zn	mg/kg	38.75	0.49	77.73	12.35	-101%	Y	0.008	4.46
Mid			38.05	0.21	36.73	3.16	3.5%	N	0.468	0.59
	LS-KB									
Top	Cu	mg/kg	11.5	0.0	16.7	2.0	-45.5%	Y	0.013	3.74
Mid			11.85	1.06	12.05	1.04	-1.7%	N	0.845	0.19
	LS-W									
Top	Cu	mg/kg	12.65	0.07	19.06	3.14	-50.7%	Y	0.027	2.88
Mid			10.55	0.07	12.63	1.43	-19.7%	N	0.128	2.05
	LS-KB									
Top	Pb	mg/kg	11.35	0.07	15.44	1.04	-36.0%	Y	0.004	5.52
Mid			11.65	0.64	10.79	1.08	7.4%	N	0.307	0.97
	LS-W									
Top	Pb	mg/kg	11.75	0.49	16.79	2.35	-42.9%	Y	0.026	2.97
Mid			11.85	0.78	10.76	0.65	9.2%	N	0.338	1.52

Table 4.17 BSM-Biochar Base Layer Zn, Cu, & Pb Properties

Base Layer Material	Parameter	Units	Baseline	Baseline Stdev	LS-KB Post n=1	LS-W Post n=1	LS-KB %Diff.	LS-W %Diff.
LS	Zn	mg/kg	39.15	1.48	30.56	34.11	21.9%	12.9%
LD			13.30	N/A	17.12	14.04	-28.7%	-5.6%
BS			51.00		52.77	47.81	-3.5%	6.3%
OS			11.30		15.52	16.71	-37.3%	-47.9%
LS	Cu	mg/kg	11.3	0.57	10.61	10.02	6.1%	11.3%
LD			28.6	N/A	24.47	27.05	14.4%	5.4%
BS			8.8		11.83	8.79	-34.4%	0.1%
OS			6.0		4.56	5.64	24.0%	6.0%
LS	Pb	mg/kg	11.65	0.07	9.55	9.88	18.0%	15.2%
LD			1.10	N/A	2.63	1.06	-139%	3.6%
BS			8.20		5.94	5.15	27.6%	37.2%
OS			ND[a]		7.46	6.83	-729%	-659%

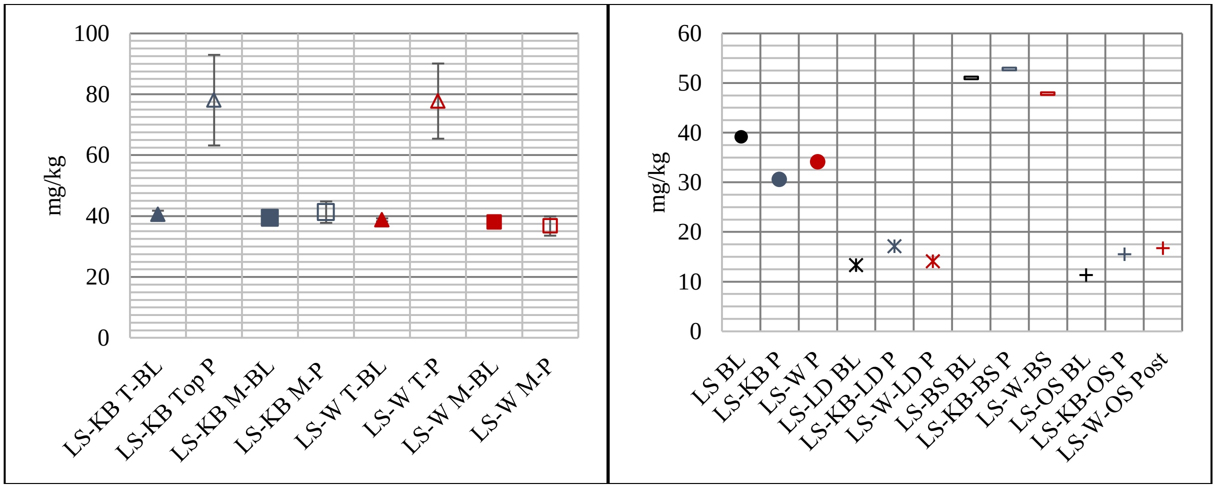

Figure 4.17 Zn Baseline (BL) & Post (P) in: Top (T) & Middle (M) Layers (left) & Base Layers (right)

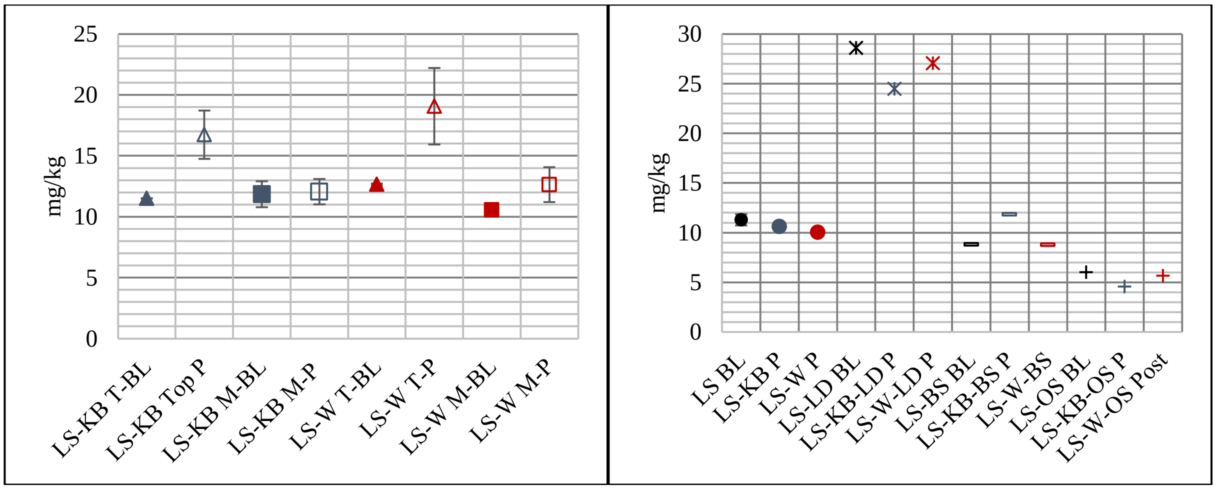

Figure 4.18 Cu Baseline (BL) & Post (P) in: Top (T) & Middle (M) Layers (left) & Base Layers (right)

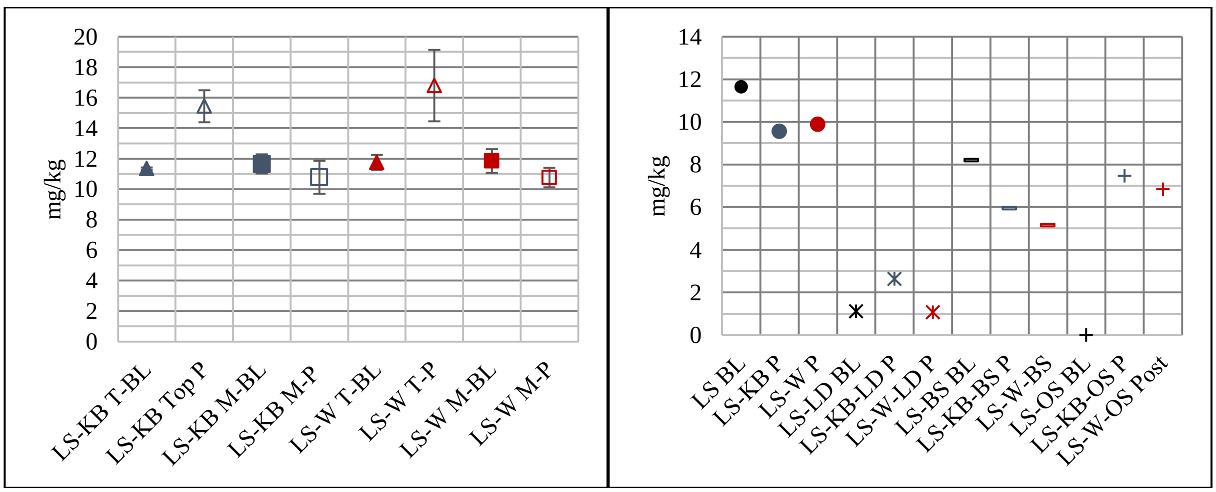

Figure 4.19 Pb Baseline (BL) & Post (P) in: Top (T) & Middle (M) Layers (left) & Base Layers (right)

Nitrogen

NH_3 Water Quality

The NH_3 removal efficiency ranged from 98% to 89% for the KB columns and 95% to 86% for the W columns (Table 4.18 and Figure 4.20). The difference between the influent and effluent concentration was statistically significant for all columns (p=0.001) whereas the differences in the effluent concentration were statistically insignificant (p>0.05) between the columns. These results suggest that neither type of biochar nor the composition of the base layer materials influenced the NH_3 treatment performance.

The pollutant reduction ratio (C_e/C_i) over time for both the W and KB columns generally declined over the first few rainfall simulations and then was consistently around C_e/C_i=0.02 (Figure 4.21). This trend in the graphs indicates that the treatment performance was consistent and there is no evidence that any of the columns were reaching capacity during the testing period.

These results are consistent with Chapter 3 in that both biochars reduced a significant amount of NH_3. The results are different than Chapter 3 in that the KB biochar reduced more (77%) compared to the W biochar (56%). In the Chapter 3 results, it was hypothesized that biochars with a lower pH and higher CEC may be better suited for applications that target NH_3 removal. Specifically, the quantity of NH_4^+ ions available for transformation (from NH_3) in a solution and subsequently sorption, increases as the pH decreases and the higher the CEC the higher the capacity for removing NH_4^+ ions from the solution. The differences in the Chapter 3 results compared to this study may be attributed to the addition of LS which appears to buffer the differences in the effluent pH.

Biochar's ability to reduce NH_3 is well documented (Spokas, Novak, & Venterea, 2012; Taghizadeh-Toosi et al., 2012; Tian et al., 2014; Yao et al., 2012). NH_3 reduction appears to occur first through the transformation of NH_3 to ammonium (NH_4^+) (Spokas et al., 2012; Taghizadeh-Toosi et al., 2012), after which the NH_4^+ cation is available for sorption to the negatively charged surface of the biochars (Spokas et al., 2012).

Table 4.18 NH_3 Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean	SD	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
SWI	14	0.411	0.107	-	-	-
LS-KB	14	0.012	0.012	95%	0.001	0.491
LS-W	14	0.012	0.017	98%	0.001	
LS-KB-BS	14	0.008	0.002	94%	0.001	0.730
LS-W-BS	14	0.014	0.023	96%	0.001	1.000
LS-KB-LD	14	0.013	0.012	91%	0.001	1.000
LS-W-LD	14	0.018	0.039	89%	0.001	0.713
LS-KB-OS	14	0.025	0.039	86%	0.001	0.491
LS-W-OS	14	0.032	0.058	95%	0.001	0.435

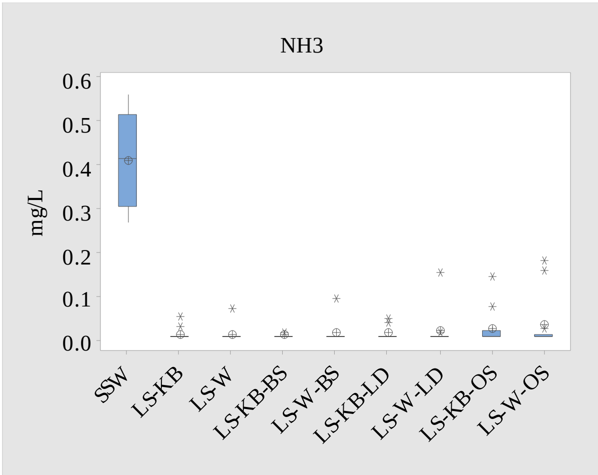

Figure 4.20 NH_3 Box Plots: Box Plots: Comparison of Mean Influent & Effluent

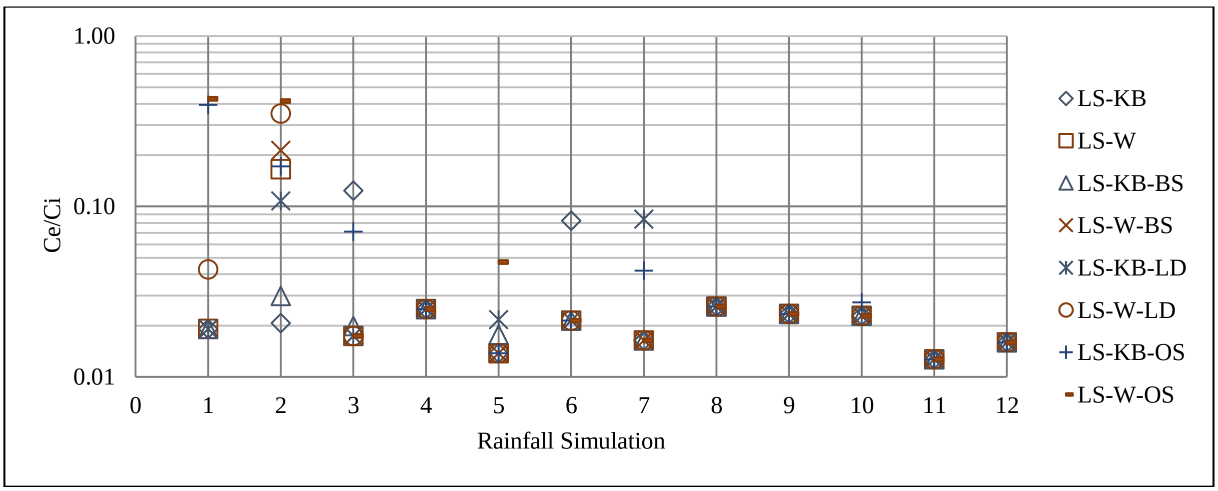

Figure 4.21 NH_3 Removal Efficiency (C_e/C_i logarithmic scale) vs Time

NO_3-NO_2 Water Quality

Concentrations of nitrate-nitrite leached from all eight columns ranging from -52% to -48% for KB columns and -48% to -33% for W columns (Table 4.19 and Figure 4.22). The effluent concentrations from all columns is significantly different ($p<0.05$) compared to the SSW concentration. While the W columns exhibited slightly less leaching than the KB columns the differences between the effluent concentrations from all columns was only statistically significant when comparing the LS-KB to the LS-W columns (Table 4.19). These results suggest that the type of biochar influences the treatment performance however; the differences in the base layer materials did not.

The NO_3-NO_2 pollutant reduction (C_e/C_i) for all columns varied over the testing period as shown in Figure 4.23 and there is no observable trend in the data.

These results are different from Chapter 3 in which there was an insignificant difference between the NO_3-NO_2 influent and effluent concentration (for the equivalent quantity of biochar). NO_3-NO_2 is highly soluble and researchers have reported that biochar has a limited ability to sorb NO_3-NO_2 (Lehmann & Joseph, 2015; Yao et al., 2012). The differences in the results between this study and Chapter 3 are likely attributed to the combination of sand and biochar in the 18-inch columns, which increased the retention time for stormwater within the columns allowing more time for nitrogen cycling to occur which increased the concentration of NO_3-NO_2 (Tian et al., 2014). Another possible theory is that NO_3-NO_2 leached from the biochar however; this was ruled out considering no leaching was observed from the Chapter 3 biochar only columns.

Table 4.19 NO_3-NO_2 Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean (mg/L)	SD (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
SWI	14	1.124	0.250	-	-	-
LS-KB	14	1.532	0.298	-50%	0.001	0.025
LS-W	14	1.406	0.260	-39%	0.001	
LS-KB-BS	14	1.496	0.245	-48%	0.001	0.727
LS-W-BS	14	1.348	0.321	-33%	0.009	0.605
LS-KB-LD	14	1.504	0.290	-46%	0.002	0.804
LS-W-LD	14	1.424	0.338	-37%	0.011	0.874
LS-KB-OS	14	1.558	0.328	-52%	0.001	0.830
LS-W-OS	14	1.454	0.297	-48%	0.001	0.649

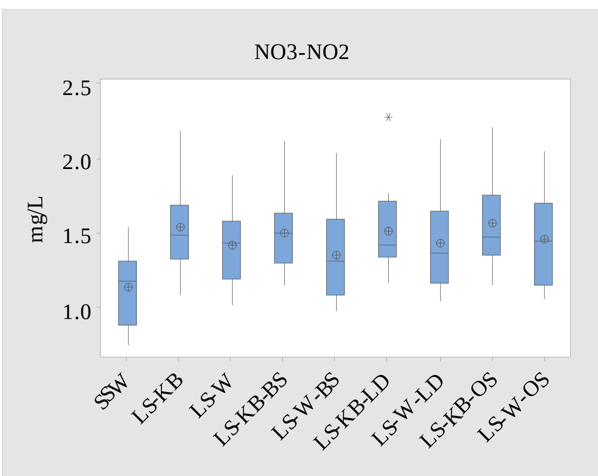

Figure 4.22 NO_3-NO_2 Box Plots: Influent Stormwater vs. Column Effluent

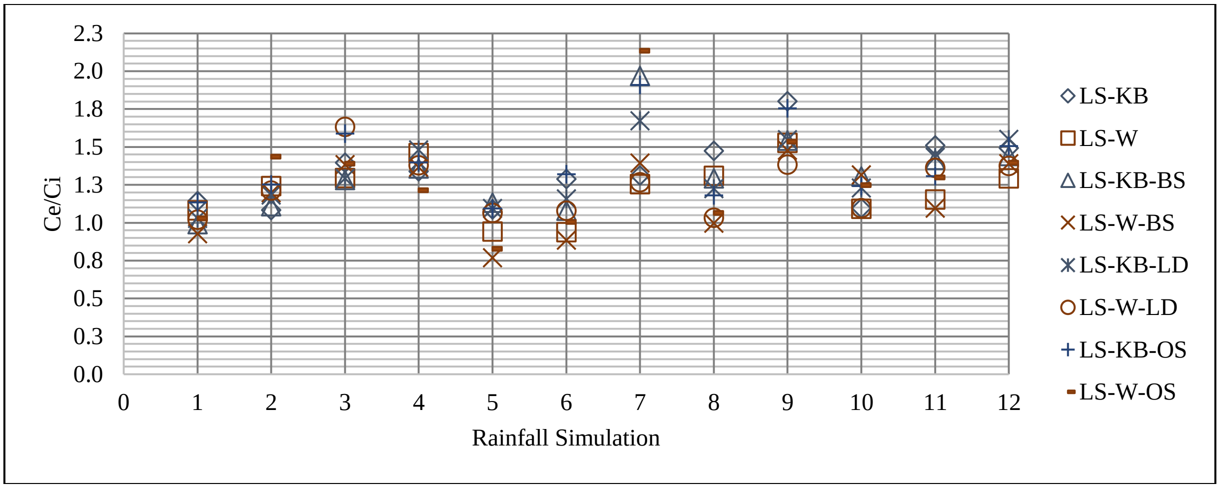

Figure 4.23 Part 3 NO_3-NO_2 Removal Efficiency (C_e/C_i) vs. Time

<u>TKN Water Quality</u>

All columns reduced the concentration of TKN and the difference between the influent and effluent concentrations are statistically significant. The reduction was slightly higher in the LS-W columns (43% to 56%) compared to LS-KB columns (20% to 43%) as shown in Table 4.20 and Figure 4.24. However, the differences in the effluent concentrations between all the columns are statistically insignificant (Table 4.20). These results suggest that neither the type of biochar nor the base layer materials significantly influenced the treatment performance of the columns.

The LS-BK-LD column leached TKN an average of -59% compared to the influent concentration. These results are due to one rainfall event when the TKN effluent concentration from this column was over 4 times higher than the influent concentration. However, the difference between the effluent concentrations for all the columns was statistically insignificant even with the LS-KB-LD effluent data from this one leaching event included in the data set. Furthermore, if the average removal efficiency for the LS-KB-LD column is determined without this one leaching event, the results fall within the range of the other three KB columns. Which suggests the result from this one rainfall maybe be an outlier.

Overall, the TKN reduction from all columns improved slightly over the testing period (same as Chapter 3) as shown in Figure 4.25. The only difference is the KB columns did not exhibit the same initial leaching over the first few rainfall events as occurred during Chapter 3. This difference between the results from Chapter 3 and this study may be attributed to rinsing the KB biochar prior to this study whereas the KB biochar was not rinsed for the Chapter 3 column study.

Table 4.20 TKN Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean	SD	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns[a]
SWI	12	1.204	0.153	-	-	-
LS-KB	12	0.635	0.128	43%	0.001	0.006
LS-W	12	0.500	0.085	56%	0.001	
LS-KB-BS	12	0.710	0.265	28%	0.001	0.391
LS-W-BS	12	0.534	0.118	51%	0.001	0.427
LS-KB-LD	12 11[a]	1.098 0.685[a]	1.438 0.150[a]	-59% 36%[a]	0.001[a]	0.290[a]
LS-W-LD	12	0.510	0.035	56%	0.001	0.712
LS-KB-OS	12	0.718	0.321	20%	0.001	0.417
LS-W-OS	12	0.500	0.085	43%	0.001	1.000

a. *Percent difference reflects average with the outlier removed.*

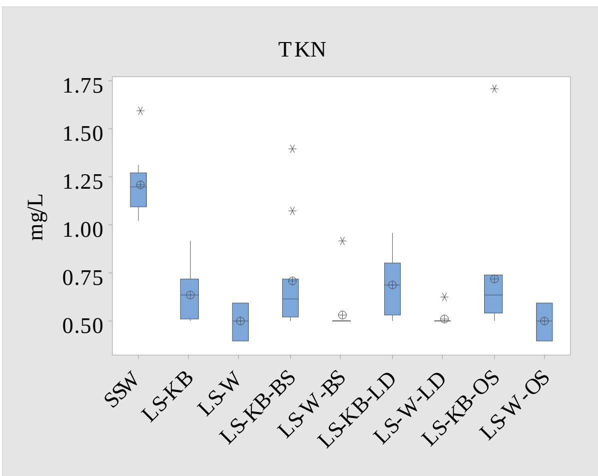

Figure 4.24 TKN Box Plots: Influent Stormwater vs. Each Column Effluent

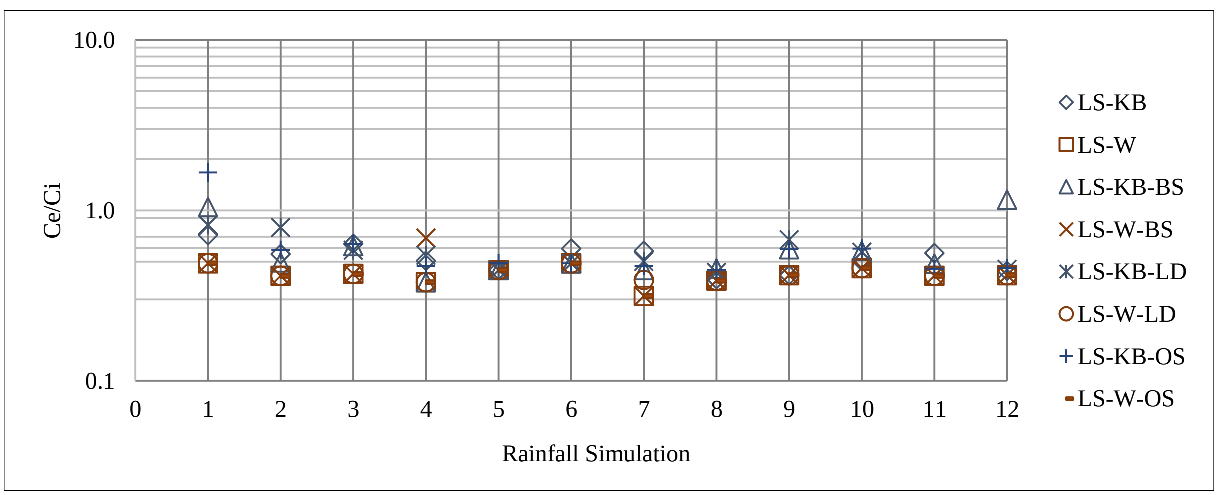

Figure 4.25 TKN Removal Efficiency (C_e/C_i logarithmic scale) vs Time (Rainfall Simulation Event)

Total Nitrogen Water Quality

Total nitrogen represents the sum of the different forms of nitrogen including nitrate-nitrite, ammonia, and organic/reduced nitrogen. The difference between the influent and effluent concentration was statistically significant for all columns except the LS-KB-BS, LS-KB-LD, and LS-KB-OS columns. The mean TN removal efficiency was higher for the LS-W columns (13% to 16%) compared to the LS-KB columns (-4% to 5%) as shown in Table 4.21 and Figure 4.26. The differences in the effluent concentrations were only statistically significant when comparing the LS-KB column to the LS-W column. These results suggest that the type of biochar influences the treatment performance (with the W biochar outperforming the KB biochar) however; the differences in the base layer materials did not. One justification for these results is that TN content in the KB biochars (1.5%) is twice that of the W biochars (0.6%) and 15 time higher than the 0.1% recommended in the Essential Properties section. As such, the KB biochar was expected to leach more nitrogen compared to the W biochar (Payne et al, 2015).

The pollutant reduction (C_e/C_i) ratio was consistently around 1.0 (Figure 4.27). This trend indicates that no change in the TN treatment performance was observed during the testing period.

Table 4.21 TN Influent and Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

	n	Mean Concentration (mg/L)	SD	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns[a]
SSW	12	2.320	0.192	-	-	-
LS-KB	12	2.104	0.26	5%	0.030	0.019
LS-W	12	1.854	0.232	16%	0.001	
LS-KB-BS	12	2.150	0.284	-1.0%	0.111	LS-KB: 0.680
LS-W-BS	12	1.830	0.338	15%	0.001	LS-W: 0.845
LS-KB-LD	12 11[a]	2.545 2.145[a]	1.389 0.218[a]	-51% 4.3%[a]	0.167 0.061[a]	LS-KB: 0.341 LS-KB: 0.584[a]
LS-W-LD	12	1.889	0.308	14%	0.002	LS-W: 0.757
LS-KB-OS	12	2.238	0.441	-4%	0.496	LS-KB: 0.376
LS-W-OS	12	1.907	0.264	13%	0.001	LS-W: 0.605

a. *The values reported reflect the results without the outlier.*

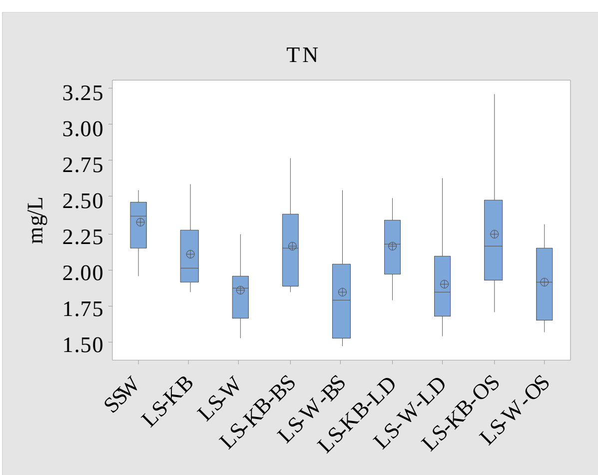

Figure 4.26 TN Box Plots: Influent Stormwater vs. Effluent

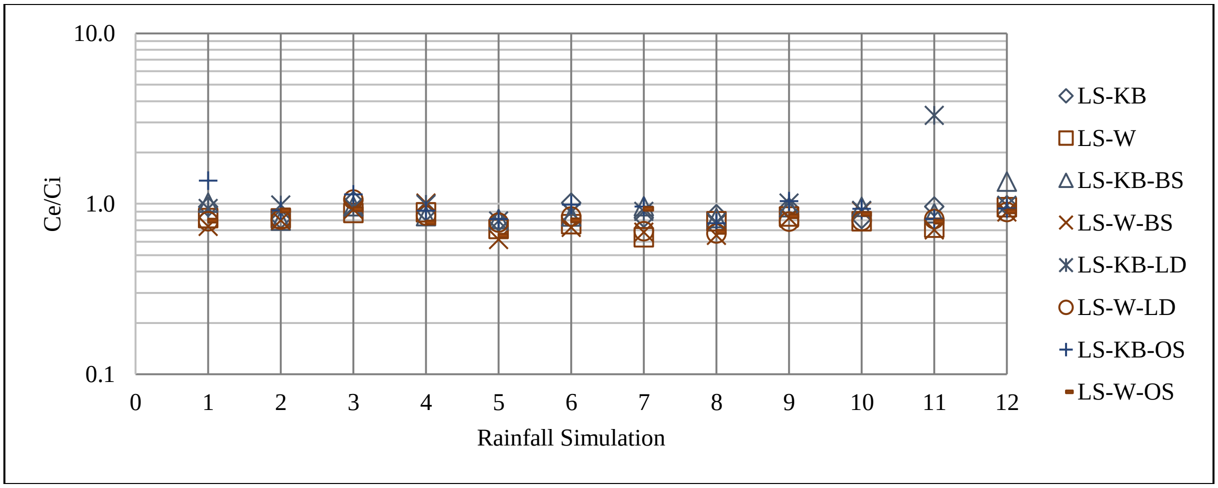

Figure 4.27 Total Nitrogen Pollutant Reduction Ratio (C_e/C_i) vs. Time

The Figure 4.28 bar graph illustrates the mean concentration of each nitrogen form present in the influent samples compared to the effluent samples. As shown the mean NH_3 and organic nitrogen consistently declined while the mean NO_3-NO_2 concentration consistently increased. This pattern suggests that nitrogen cycling is occurring. Specifically, organic nitrogen is converted to NH_4^+ through ammonification and ultimately NO_3-NO_2 through nitrification, which would increase the NO_3-NO_2 effluent concentration.

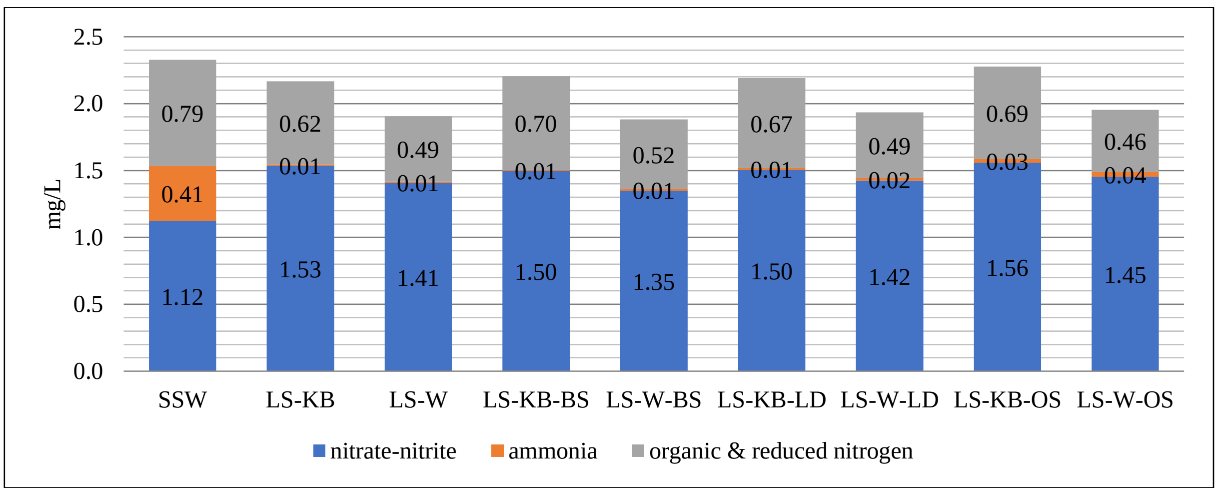

Figure 4.28 Mean TN Bar Graphs for Influent & Effluent

Nitrogen BSM-Biochar

The results from the BSM-Biochar testing are summarized in Tables 4.20-4.21 and Figures 4.29-4.30. The NH_4^+ concentration declined from the baseline to the post samples in the top and middle layers of the LS-KB columns (25% and 31%) and the LS-W columns (23.6% and 38.5%) however the differences are statistically insignificant ($p>0.05$ and $d<3$). The NO_3^- concentration increased from the baseline to the post samples in the top and middle layers of the LS-KB columns (-213% and -308%) and the LS-W columns (-367% and -92%) and these differences are statistically significant ($p<0.05$ and $d>3$). The change in TN concentration ranged from an increase of -6.5% to a decline of 30.5% however the differences are statistically insignificant ($p>0.05$ and $d<3$). The increase in the

NO_3^- concentration without a change in the TN concentration suggests that nitrogen cycling is occurring in the BSM-Biochar mix. These results are consistent with the water quality results.

Nitrogen cycling is typically the treatment mechanism for reducing stormwater NO_3-NO_2 concentrations in bioretention cells and biochar studies. Specifically, nitrification causes NH_3 or NH_4^+ to oxidize first to NO_2^- and then NO_3^- (Lehmann & Joseph, 2015, p. 353; Minton, 2012). Bioretention researchers have reported that larger media depths are associated with higher levels of NO_3-NO_2. Specifically, larger media depths typically have longer retention times of stormwater within the media providing more time for nitrogen cycling to occur (Hunt & Lord, 2006). This could explain the differences between the Chapter 3 NO_3-NO_2 results compared to the results from this study. Specifically, in Chapter 3 the difference between the influent and effluent ranged from -5% to 12%, compared to this study when an increase of -33% to -50% was observed from the influent to the effluent concentration. The differences in the results are likely attributed to the combination of sand and biochar in the 18-inch columns, compared to the equivalent quantity of biochar only in the column from Chapter 3. The addition of LS to the columns increased the retention time for stormwater within the columns, which allows more time for NH_3 to transform to NO_3-NO_2 (Tian et al., 2014). This theory would also suggest that some of the NH_3 reduction in the stormwater is attributed to nitrogen cycling.

As shown in Table 4.22 and Figures 4.29 to 4.31, the NH_4^+, NO_3^-, and TN concentration declined in all the base layers. The decline ranged from 25.9% to 77.3% for NH_3, 67% to 0% for NO_3^-, and 21.1% to 97.3% for TN (except for the LS-KB-BS base layer, which retained -150% of NO_3). While the sample size is insufficient to draw meaningful conclusions, all the base layers appear to leach nitrogen.

Table 4.22 BSM-Biochar Top and Middle Layer NO_3 Properties

	Parameter	Units	Baseline Mean (n=2)	Baseline Stdev	Post Mean (n=4)	Post Stdev	Mean %Diff.	Statistically Significant	t-test	d
	LS-KB									
Top	NH_4^+	mg/kg	3.65	0.21	2.73	0.60	25.1%	N	0.829	2.03
Mid			2.75	0.78	2.03	0.26	26.4%	N	0.739	1.25
	LS-W									
Top	NH_4^+	mg/kg	2.75	0.35	2.10	0.17	23.6%	N	0.250	2.33
Mid			2.60	0.57	1.60	0.17	38.5%	N	0.249	2.39
	LS-KB									
Top	NO_3^-	mg/kg	0.80	0.14	2.50	0.10	-213%	Y	0.043	13.88
Mid			0.40	0.28	1.63	0.21	-306%	Y	0.024	3.43
	LS-W									
Top	NO_3^-	mg/kg	0.75	0.07	3.07	0.15	-309%	Y	0.002	11.36
Mid			0.85	0.21	1.63	0.31	-92.2%	Y	0.077	2.98
	LS-KB									
Top	Total N	mg/kg	565	24	551	95	2.5%	N	0.829	0.20
Mid			435	6	461	142	-6.0%	N	0.739	0.26
	LS-W									
Top	Total N	mg/kg	347	95	343	118	1.0%	N	0.974	0.03
Mid			344	5	239	63	30.5%	N	0.103	2.34

Table 4.23 BSM-Biochar Base Layer Nitrogen Properties

Base Layer Material	Parameter	Units	Baseline Mean n=2	Baseline Stdev	LS-KB Post n=1	LS-W Post n=1	LS-KB %Diff.	LS-W %Diff.
LS	NO_3^-	mg/kg	1.55	0.49	1	0.5	35.5%	67.7%
LD			0.70	N/A	0.2	0.7	71.4%	0.0%
BS			0.20		0.5	0.2	-150%	0.0%
OS			30.9		5.5	4	82.2%	87.1%
LS	NH_4^+	mg/kg	2.70	0.85	1.8	2	33.3%	25.9%
LD			2.70	N/A	2	1.5	25.9%	44.4%
BS			3.70		3.1	1.4	16.2%	62.2%
OS			6.60		1.7	1.5	74.2%	77.3%
LS	Total N	mg/kg	224.5	30.41	174	104.8	22.5%	53.3%
LD			60.0	N/A	1.6	49.6	97.3%	17.3%
BS			91.0		6.2	8.4	93.2%	90.8%
OS			1060		836.8	623.5	21.1%	41.2%

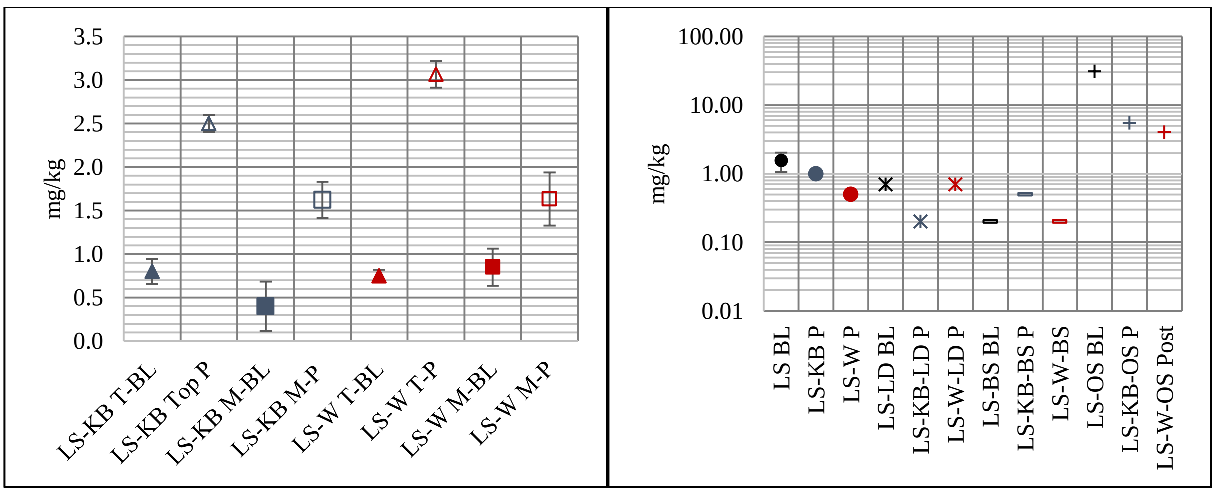

Figure 4.29 NO_3 Baseline (BL) & Post (P) in: Top (T) & Middle (M) Layers (left) & Base Layers (right)

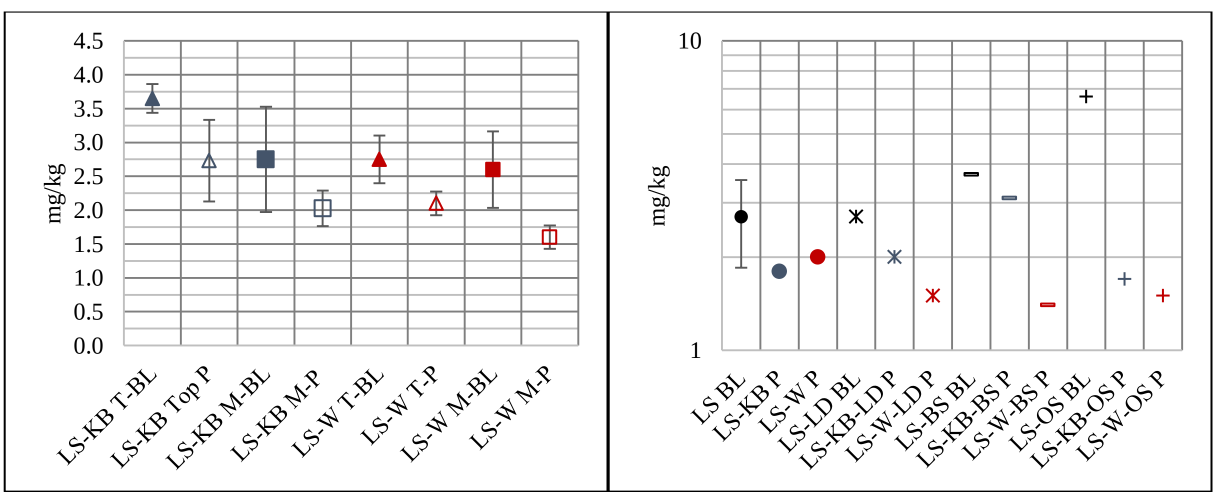

Figure 4.30 NH_4 Baseline (BL) & Post (P) in: Top (T) & Middle (M) Layers (left) & Base Layers (right)

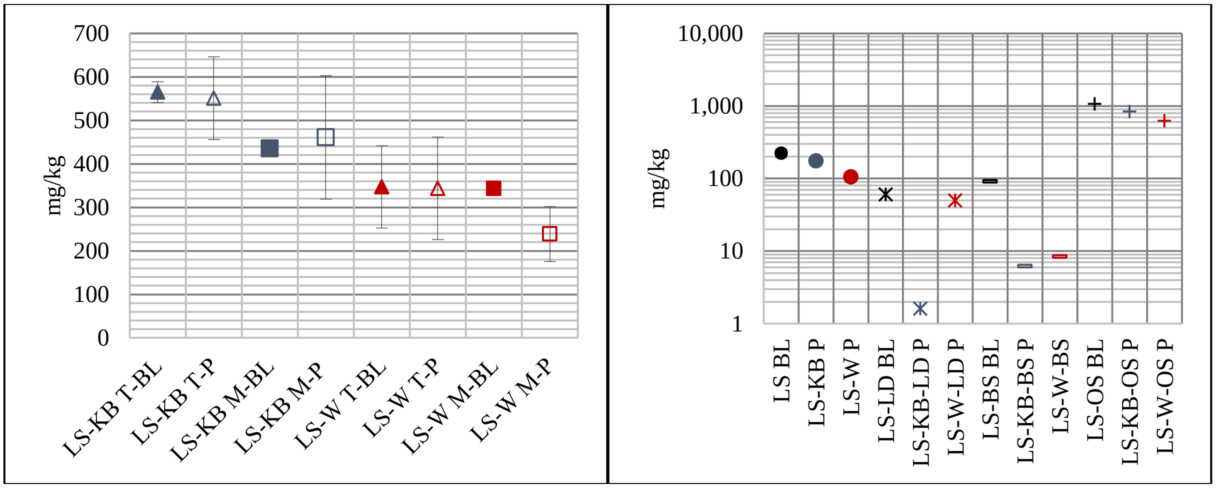

Figure 4.31 TN Baseline (BL) & Post (P) in: Top (T) & Middle (M) Layers (left) & Base Layers (right)

Phosphorus (P) Water Quality

None of the eight columns achieved the Ecology performance criteria of 50% TP reduction to a confidence interval of 95% (Table 4.24 and Figure 4.32). The W columns had the best treatment performance reducing total and dissolved phosphorus by 21% to 26% and 15% to 23% respectively compared to the KB columns which leached total and dissolved phosphorus by -77% to -101% and -52% to -110% respectively (Table 4.24).

These results are consistent with the Chapter 3 results, in that the treatment performance of the W columns was better than the KB columns. The pollutant reduction (C_e/C_i) over the testing period was also consistent with the Chapter 3 results: the phosphorus leaching from the KB columns decreased over the testing period while the phosphorus reduction from the W columns declined. The C_e/C_i for both biochars was approaching one (C_e/C_i=1.0) as shown on Figure 4.33. This trend indicates that the leaching from the KB columns declines over time while the efficacy of the W columns to reduce phosphorus appears to decline over time.

The results are statistically significant when comparing the mean influent to the mean effluent concentrations from all columns (p=0.001) however the differences between the mean effluent concentrations were only statistically significant (p=0.001) when comparing the LS-KB column to the LS-W column. These results suggest that the treatment performance is influenced by the type of biochar but not the base layer materials. These results suggest there is a relationship between the type of biochar selected and the phosphorus treatment performance. The P leaching from the KB biochar is likely attributed to the KB biochar P content (1.26%) which is 20-times the P content of the W biochar (0.06%). These results are consistent with the expected treatment behavior defined in the Essential Properties: biochar materials with a higher P content are expected to leach more P. Although the W biochar P content (0.06%) is slightly higher than the than the recommended biochar P content defined in the Essential Properties to prevent leaching (≤0.04%), these results suggest that a P content within this range (less than 0.06- to 0.04%) may be an acceptable targeted.

Table 4.24 P Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean (mg/L)	SD (mg/L)	95% CI Removal Efficiency	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total						
SWI	14	1.141	0.069			
LS-KB	14	1.934	0.615	-89%	0.001	0.001
LS-W	14	0.679	0.332	26%	0.001	
LS-KB-BS	14	1.998	0.731	-101%	0.001	LS-KB: 0.805
LS-W-BS	14	0.79	0.244	21%	0.001	LS-W: 0.325
LS-KB-LD	14	1.913	0.591	-89%	0.001	LS-KB: 0.926
LS-W-LD	14	0.73	0.315	23%	0.001	LS-W: 0.680
LS-KB-OS	14	1.832	0.495	-77%	0.001	LS-KB: 0.633
LS-W-OS	14	0.699	0.296	26%	0.001	LS-W: 0.868
Dissolved						
SWI	14	1.063	0.057	-	-	-
LS-KB	14	1.898	0.567	-97%	0.001	0.001
LS-W	14	0.667	0.316	23%	0.001	
LS-KB-BS	14	1.987	0.676	-110%	0.001	LS-KB: 0.708
LS-W-BS	14	0.793	0.244	15%	0.001	LS-W: 0.247
LS-KB-LD	14	1.899	0.534	-98%	0.001	LS-KB:0.997
LS-W-LD	14	0.735	0.315	17%	0.001	LS-W: 0.572
LS-KB-OS	14	1.846	0.559	-52%	0.001	LS-KB: 0.811
LS-W-OS	14	0.703	0.294	21%	0.001	LS-W: 0.753

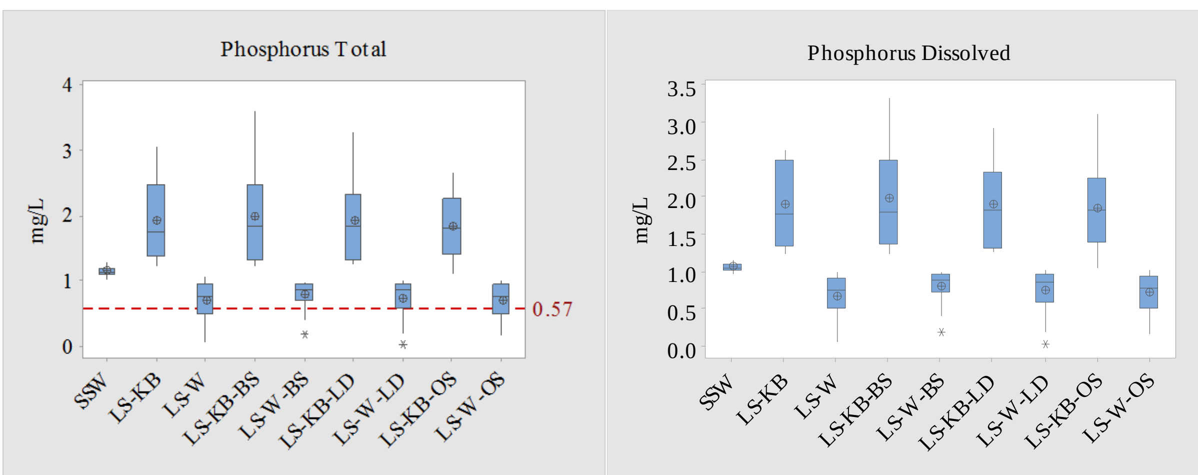

Figure 4.32 P Total (left) & Filtered (right) Box Plots: Comparison of Mean Influent & Effluent

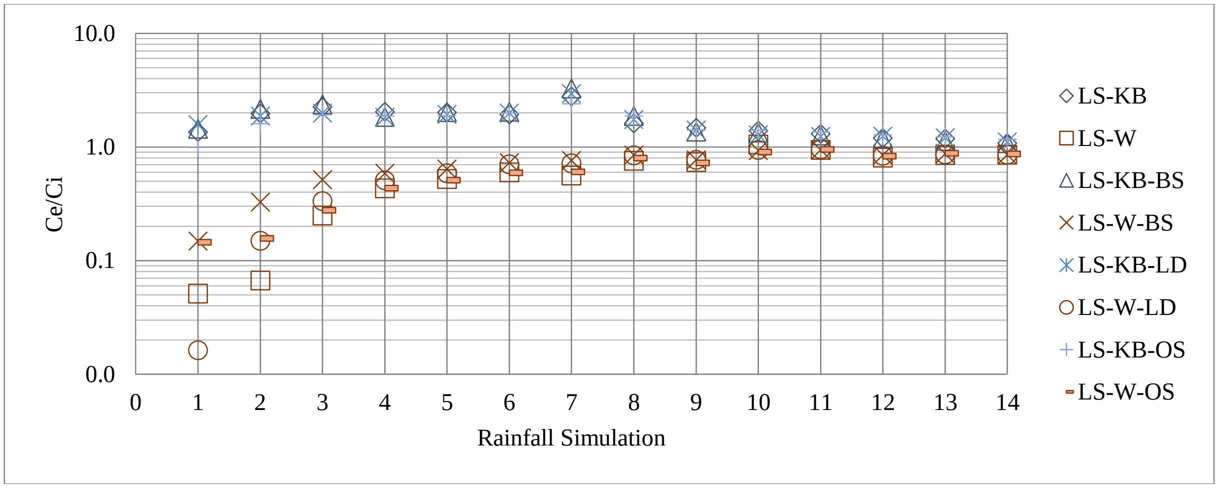

Figure 4.33 P (Dissolved) Pollutant Reduction Ratio (C_e/C_i) vs Time

Phosphorus BSM-Biochar

There was a statistically significant difference between the baseline and post sample P content in the top and middle layers. The P content in the LS-KB columns leached 40% and 30% from the top and middle layers respectively whereas the LS-W columns retained -367% and -329% from the top and middle layers respectively (Table 4.25 and Figure 4.34). The results are not surprising considering the top and middle layers of the KB biochar columns contains more than 30 times the P of the top and middle layers of the W biochar columns (Table 4.24). The P retention in the W biochar columns may be attributed to the higher quantity of Ca that leached from the W biochar compared to the KB biochar during the Chapter 3 desorption testing. Assuming the same desorption occurred during this study, more Ca ions were available in the SSW of the W biochar columns (compared to the KB biochar columns) to complex with dissolved P and form a precipitate (Hsieh et al., 2007). As a solid, P can become trapped in the pore spaces of the media as stormwater infiltrates through the BSM-Biochar media. The optimum pH range for complexation to occur is 7.0-9.0 with the peak precipitation occurring at around 8.0 (Brady & Weil, 1996). The stormwater solution pH increased from 7.67 in the influent to 7.81 to 8.03 in the effluent (Table 4.9).

Another justification for the higher P retention in the LS-W columns is that the W biochar appears to prefer Ca ions. Specifically, more Ca ions from the stormwater solution sorbed to the biochar and are available to complex to P. This theory is consistent with the higher Ca concentration measured in the top and middle layers of the post samples from the LS-W columns compared to the LS-KB columns (Table 4.27). Further the results indicate that the Ca increase in the LS-W top and middle layers (-130% to -76.2%) was statistically significant compared to the LS-KB top and middle layers in which the change in Ca concentration was statistically insignificant.

P was not detected in the baseline samples from the base layers that contained LS, BS, or LD and only 0.2 meq/100g was measured in the OS layer (Table 4.26 and Figure 4.34). The post sample P increased with the highest values measured in the KB columns (-2500% to -200%) compared to the W columns (-900% to -100%). The highest concentration of P was measured in the LS base layer for both biochars, which suggests that the LS layer immobilized more P compared to the other base layer materials.

Table 4.25 BSM-Biochar Top and Middle Layer Phosphorus Properties

	Parameter	Units	Baseline Mean (n=2)	Baseline Stdev	Post Mean (n=4)	Post Stdev	Mean %Diff.	Statistically Significant	t-test	d
	LS-KB									
Top	P	meq/100g	5.00	0.35	3.00	0.41	40.0%	Y	0.025	5.24
Mid			4.35	0.07	2.73	0.67	37.4%	Y	0.017	3.44
	LS-W									
Top	P	meq/100g	0.15	0.10	0.65	0.13	-333%	Y	0.034	4.35
Mid			0.14	0.09	0.60	0.01	-344%	Y	0.089	7.13

Table 4.26 BSM-Biochar Base Layer P Properties

Base Layer Material	Parameter	Units	Baseline Mean n=2	Baseline Stdev	LS-KB Post n=1	LS-W Post n=1	LS-KB %Diff.	LS-W %Diff.
LS	P	meq/100g	ND[a]	ND	1.3	0.5	-2500%	-900%
LD			ND[a]	Note 1	0.9	0.2	-1700%	-300%
BS			ND[a]		0.5	0.4	-900%	-700%
OS			0.20		0.6	0.4	-200%	-100%

a. The detection limit (0.05) was used to calculate the % difference between the base line and post samples.

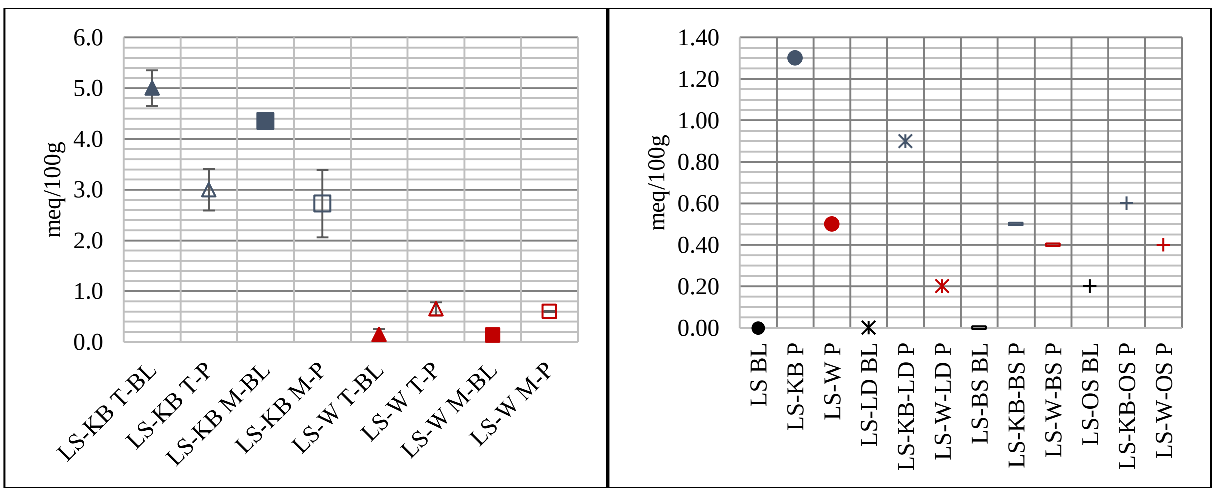

Figure 4.34 P Baseline (BL) & Post (P) in: Top (T) & Middle (M) Layers (left) & Base Layers (right)

BSM-Biochar Amendments for Enhancing P Removal

The BS, LD, and OS base layer materials were added to the columns to enhance P removal. For example, P can adsorb to materials that contain Fe or Al or complex and form a precipitate with Ca (Arias et al., 2001; Erickson et al., 2007; Randall & Bradford, 2013). The base layer materials were selected because of the anticipated Fe and Al content in the BS (37,110-mg/kg and 2,662-mg/kg) and LD (178-mg/kg and 6,363-mg/kg) and the Ca content in the OS (5.5-meq/100g). However, the LS base layer contained the highest concentration of Al (10,845-mg/kg) and the second highest concentration of Fe (37,110-mg/kg) compared to the other base layers. As previously noted, P was retained in all the base layers with the highest concentration (and percent retained) measured in the LS base layer. These results are consistent with the water quality results in which the differences between the column mean effluent concentrations did not significantly influence the phosphorus treatment performance of the columns.

The adsorption or complexation and precipitation of P to Fe, Al, and Ca is dependent upon the pH and hydraulic residence time (HRT). For example, Fe and Al adsorption rates are highest in acidic conditions compared to Ca, which is highest at a pH of 8.0. However, studies indicate that P adsorption and precipitation will occur outside the optimum pH just to a lesser degree (Arias et al., 2001; Erickson et al., 2007). Since the mean pH of the SSW and effluent ranged from 7.67 to 8.03, the highest removal rates were expected in the columns that contain the highest concentration of Ca however, the lowest P concentration was measured in the OS columns. These results may be due to the differences in the Fe, Al, and Ca concentrations: the Fe concentration was substantially higher (37,100 to 251-mg/kg) compared to Al (10,845- to 192-mg/kg) thus, more material was available for P adsorption to occur. In addition, the HRT may not have been sufficient for optimum P removal to occur. For example, a 2001 study conducted in Denmark found that the desirable HRT for optimum P removal was 24-hours (Arias et al., 2001). However, the permeability of the base layers in this research was measured at 29-inches/hour (BS), 18-inches/hour (LD), and 1.3-inches/hour (OS). Considering these base layers were 3-inches thick, the actual HRT was significantly less than the desirable HRT for optimum P removal. Considering the base layers all retained P, more research is recommended at a longer HRT using materials with a high Fe, Al, and Ca content.

The Fe and Al base line and post concentration were measured in all the column layers (Tables 4.27-4.28 and Figures 4.36-4.37). The Fe and Al content declined (leached) from both the LS-KB and LS-W top and middle layers (0.31% to 10.5% for Fe and 2.0% to 12.5% for Al). However, the leaching was only statistically significant from the LS-KB top layers. The LS base layers also leached Fe and Al (12.1% to 15.7% and 9.2% to 13.5% for the LS-KB and LS-W columns respectively) which is consistent with the heavy metal leaching (Zn, Cu, and Pb) previously described that was observed from the LS base layers. The LS-KB top layer contained 10,210 mg/kg of Al, which is consistent with the 10,450 mg/kg measured in the LS-W top layer. It is worth nothing that the top layer of the LS-W column leached slightly more Al (12.5%) however; these results were statistically insignificant. Since P can sorb to Fe and Al, if these minerals leach, P will not be immobilized in the soil as intended instead P could be transported along with Al through the BSM.

In the base layers, Fe and Al was retained in the BS, LD, and OS base layers. The OS columns retained the largest percent of both Fe and Al (-718% to -837% and -567% to -657% for the LS-KB and LS-W columns respectively). These results suggest that the OS material can sorb both Fe and Al. Overall the largest percent increase in the LS-KB of Fe and Al was in the base layers of the LS-KB columns which is likely attributed to the higher concentration of these minerals that leached from the top and middle layers of the LS-KB columns. Considering Fe and Al were retained in the base layers of the LS-W columns, the stormwater solution may have contained both Fe and Al ions (which was not tested).

Table 4.27 BSM-Biochar Top & Middle Layer Ca, Fe, & Al Properties

	Parameter	Units	Baseline Mean (n=2)	Baseline Stdev	Post Mean (n=4)	Post Stdev	Mean %Diff.	Statistically Significant	t-test	d
	LS-KB									
Top	Ca	meq/100g	1.60	0.14	1.63	0.22	-1.7%	N	0.878	0.15
Mid			1.69	0.16	1.45	0.21	14.2%	N	0.254	1.31
	LS-W									
Top	Ca	meq/100g	0.90	0.00	2.07	0.25	-130%	Y	0.015	6.56
Mid			1.05	0.07	1.85	0.30	-76.2%	Y	0.015	3.67
	LS-KB									
Top	Fe	mg/kg	17870	212	16571	357	7.3%	Y	0.036	4.42
Mid			17430	707	17367	311	0.4%	N	0.925	0.11
	LS-W									
Top	Fe	mg/kg	17785	544	16312	362	8.3%	N	0.184	3.19
Mid			16820	85	16768	161	0.3%	N	0.638	0.41
	LS-KB									
Top	Al	mg/kg	10210	170	9384	353	8.1%	Y	0.030	2.99
Mid			10019	285	9686	633	3.3%	N	0.441	0.68
	LS-W									
Top	Al	mg/kg	10450	424	9141	359	12.5%	N	0.166	3.33
Mid			9844	118	9641	553	2.1%	N	0.533	0.51

Table 4.28 BSM-Biochar Base Layer Ca, Fe, & Al Properties

Base Layer Material	Parameter	Units	Baseline Mean n=2	Baseline Stdev	LS-KB Post n=1	LS-W Post n=1	LS-KB %Diff.	LS-W %Diff.
LS	Ca	meq/100g	1.3	0.14	1.4	1.1	-7.7%	15.4%
LD			0.7	N/A	2.9	1.2	-314%	-71.4%
BS			1.1		1.6	1.4	-45.5%	-27.3%
OS			5.4		2.7	2.3	50.0%	57.4%
LS	Fe	mg/kg	18,870	240.42	16594	15915	12.1%	15.7%
LD			6363	N/A	8463	6634	-33.0%	-4.3%
BS			37,110		37,488	32,455	-1.0%	12.5%
OS			251		2054	2352	-718%	-837%
LS	Al	mg/kg	10,845	162.63	9849	9380	9.2%	13.5%
LD			178	N/A	1750	342	-883%	-92.1%
BS			2,662		3586	3029	-34.7%	-13.8%
OS			192		1281	1453	-567%	-657%

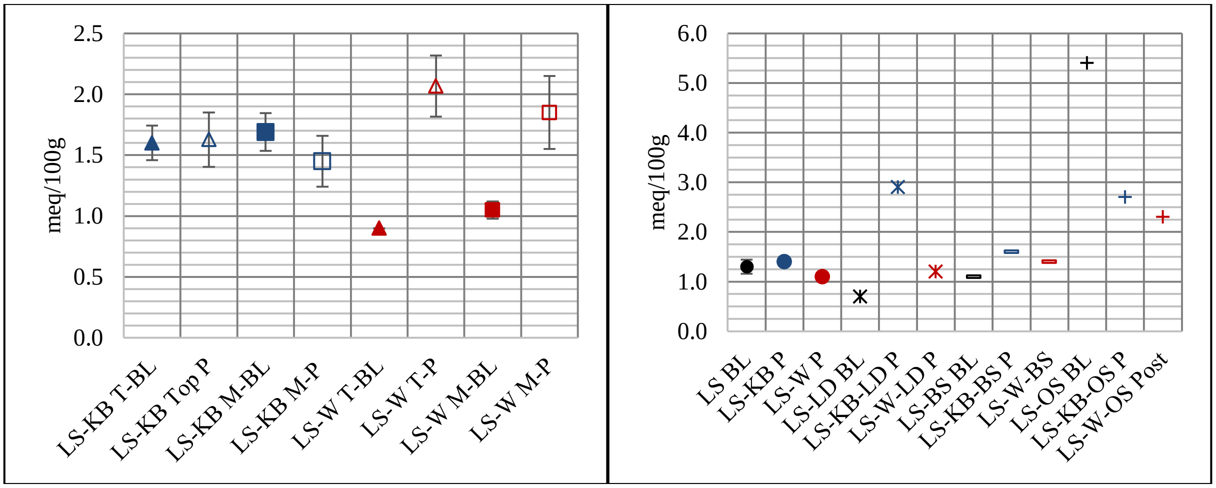

Figure 4.35 Ca Interval Plot Baseline & Post in: Top & Middle Layers (left) & Base Layers (right)

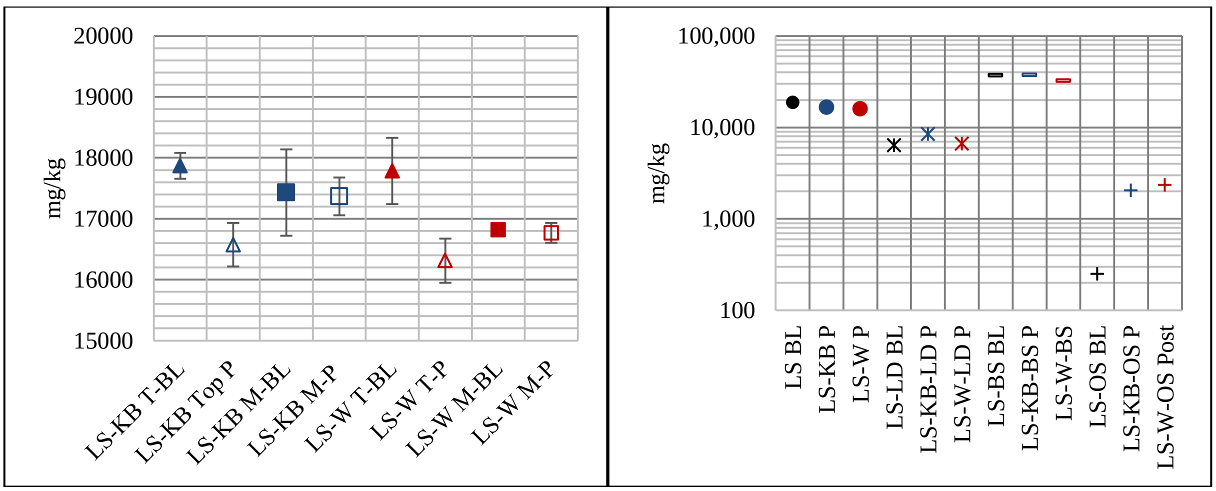

Figure 4.36 Fe Interval Plot Baseline & Post in: Top & Middle Layers (left) and Base Layers (right)

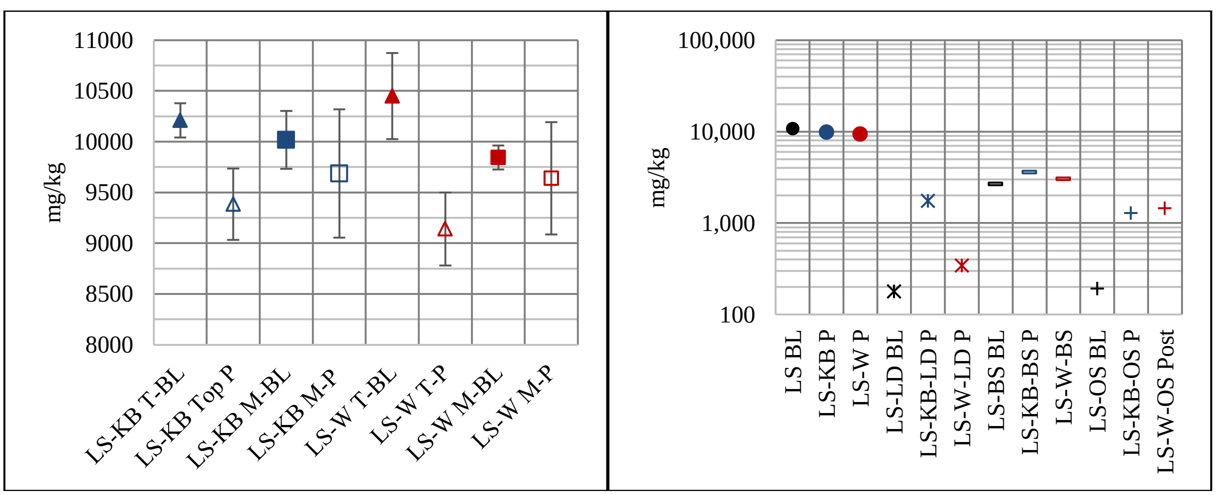

Figure 4.37 Al Interval Plot Baseline & Post in: Top & Middle Layers (left) and Base Layers (right)

Hardness Water Quality

The hardness, Ca, and Mg effluent concentration increased (leached from the columns) compared to the influent concentration for all columns (Tables 4.29 to 4.31 and Figures 4.38 to 4.40). However, the difference between the influent and effluent concentrations were only statistically significant for total and dissolved hardness from the LS-KB-OS column as well as total and dissolved Ca from the LS-KB-OS and LS-W-OS columns. The difference between the effluent concentration were only statistically significant when comparing the LS-KB column to the LS-KB-OS (total and dissolved hardness and Ca) and the LS-W column to the LS-W-OS column (total Ca). These results suggest that the OS base layer influenced the treatment performance of the columns: leaching of hardness and Ca from the columns. These results are not surprising considering the OS material was the only base layer to leach Ca by 50% and 57.4% from the LS-KB and LS-W columns respectively (Table 4.28 and Figure 4.35).

The trend in the pollutant reduction ratio (C_e/C_i) is similar for Ca and Mg (Figures 4.41 and 4.42). During the initial rainfall events C_e/C_i was more variable compared to the last four rainfall events (11-14) when C_e/C_i was consistently between 1.0 and 1.1. This trend in C_e/C_i suggests that the treatment performance of all the columns becomes more stable with time, which is consistent with the trend observed in Chapter 3.

Table 4.29 Hardness Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean Concentration (mg/L)	SD (mg/L)	95% Confidence Interval	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total						
SSW	14	215.250	16.53	-	-	-
LS-KB	14	221.843	20.21	-4.5%	0.346	0.629
LS-W	14	217.029	12.91	-2.7%	0.818	
LS-KB-BS	14	226.886	29.26	-7.9%	0.301	LS-KB: 0.748
LS-W-BS	14	202.821	54.4	-2.6%	0.945	LS-W: 0.800
LS-KB-LD	14	225.407	17.85	-6.3%	0.118	LS-KB: 0.625
LS-W-LD	14	217.914	15.25	-2.4%	0.679	LS-W: 0.870
LS-KB-OS	14	233.707	15.22	-10.8%	0.008	LS-KB: 0.042
LS-W-OS	14	224.436	14.2	-6.5%	0.108	LS-W: 0.161
Dissolved						
SSW	14	209.660	15.031	-	-	-
LS-KB	14	216.271	16.566	-5%	0.395	0.565
LS-W	14	212.221	15.568	-3%	0.448	
LS-KB-BS	14	215.707	28.751	-8%	0.696	LS-KB: 0.492
LS-W-BS	14	211.771	15.957	-3%	0.713	LS-W: 0.800
LS-KB-LD	14	216.886	19.340	-6%	0.300	LS-KB: 0.927
LS-W-LD	14	211.121	17.013	-3%	0.679	LS-W: 0.870
LS-KB-OS	14	230.021	18.400	-12%	0.008	LS-KB: 0.048
LS-W-OS	14	215.862	18.483	-6%	0.369	LS-W: 0.161

Table 4.30 Ca Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean Concentration (mg/L)	SD (mg/L)	95% Confidence Interval	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total						
SSW	14	48.870	3.930	-	-	-
LS-KB	14	50.229	4.420	-5%	0.358	0.854
LS-W	14	50.063	3.072	-4%	0.462	
LS-KB-BS	14	52.959	9.716	-15%	0.215	LS-KB: 0.357
LS-W-BS	14	50.551	4.084	-5%	0.232	LS-W: 0.724
LS-KB-LD	14	50.962	3.774	-6%	0.198	LS-KB: 0.641
LS-W-LD	14	49.936	3.567	-4%	0.408	LS-W: 0.921
LS-KB-OS	14	54.809	3.200	-15%	0.002	LS-KB: 0.005
LS-W-OS	14	52.652	3.206	-10%	0.009	LS-W: 0.039
Dissolved						
SSW	14	47.600	3.558	-	-	-
LS-KB	14	49.036	3.822	-5%	0.358	0.800
LS-W	14	49.093	3.952	-5%	0.334	
LS-KB-BS	14	50.501	9.999	-14%	0.448	LS-KB: 0.713
LS-W-BS	14	49.233	4.369	-5%	0.280	LS-W: 0.930
LS-KB-LD	14	49.136	4.127	-5%	0.301	LS-KB: 0.947
LS-W-LD	14	48.517	4.157	-5%	0.408	LS-W: 0.710
LS-KB-OS	14	53.739	4.096	-16%	0.001	LS-KB: 0.004
LS-W-OS	14	50.464	4.666	-9%	0.049	LS-W: 0.420

Table 4.31 Mg Influent & Effluent: Mean, SD, 95% CI Removal Efficiency, p-values

ID	n	Mean Concentration (mg/L)	SD (mg/L)	95% Confidence Interval	Effluent p-value Compared to SSW	Effluent p-value Comparison to Other Columns
Total						
SSW	14	22.630	1.676	-	-	-
LS-KB	14	23.378	2.515	-6%	0.491	0.358
LS-W	14	22.347	1.593	-1%	0.747	
LS-KB-BS	14	22.969	2.224	-4%	0.854	LS-KB: 0.653
LS-W-BS	14	22.198	2.413	-2%	0.613	LS-W: 0.849
LS-KB-LD	14	25.258	6.498	-22%	0.183	LS-KB: 0.505
LS-W-LD	14	22.620	1.721	-2%	1.000	LS-W: 0.667
LS-KB-OS	14	23.516	2.176	-6%	0.346	LS-KB: 0.878
LS-W-OS	13	22.548	2.065	-2%	0.945	LS-W: 0.776
Dissolved						
SSW	14	22.030	1.521	-	-	-
LS-KB	14	22.759	1.912	-6%	0.334	0.260
LS-W	14	21.790	1.608	-1%	0.748	
LS-KB-BS	14	21.754	1.395	-1%	0.597	LS-KB: 0.730
LS-W-BS	14	21.554	1.976	-1%	0.535	LS-W: 0.732
LS-KB-LD	14	22.906	2.337	-7%	0.334	LS-KB: 0.857
LS-W-LD	14	21.904	1.685	-2%	0.927	LS-W: 0.857
LS-KB-OS	14	23.279	2.286	-9%	0.141	LS-KB: 0.519
LS-W-OS	13	21.830	2.194	-3%	0.610	LS-W: 0.958

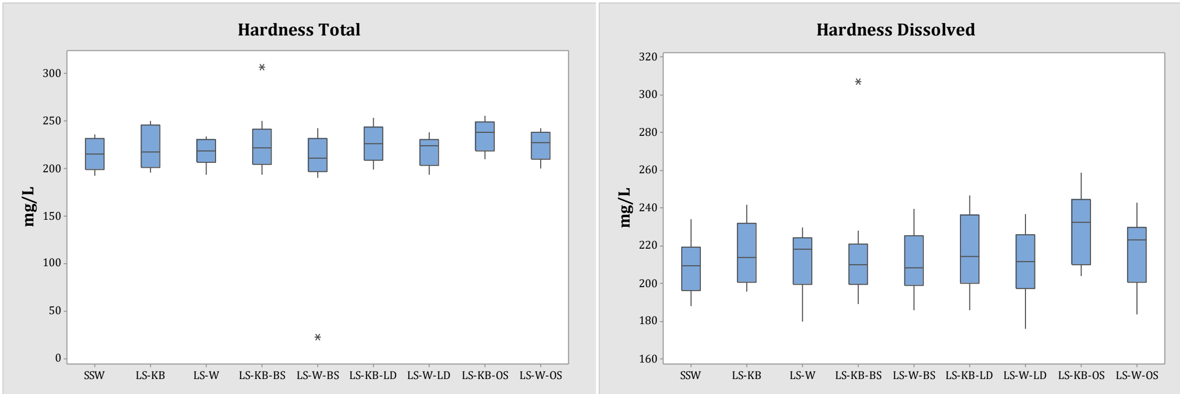

Figure 4.38 Hardness Box Plots: Comparison of Mean Influent & Effluent Total (a) & Dissolved (b)

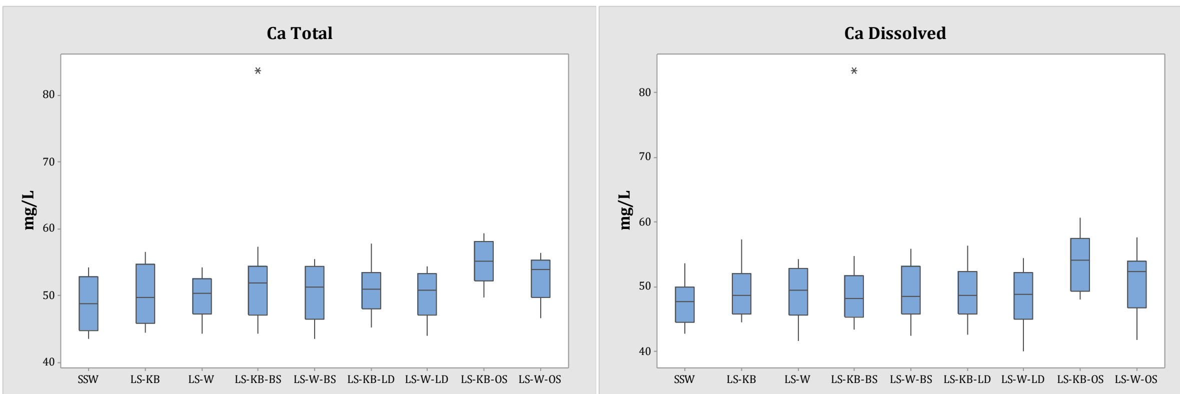

Figure 4.39 Ca Box Plots: Comparison of Mean Influent & Effluent Total (a) & Dissolved (b)

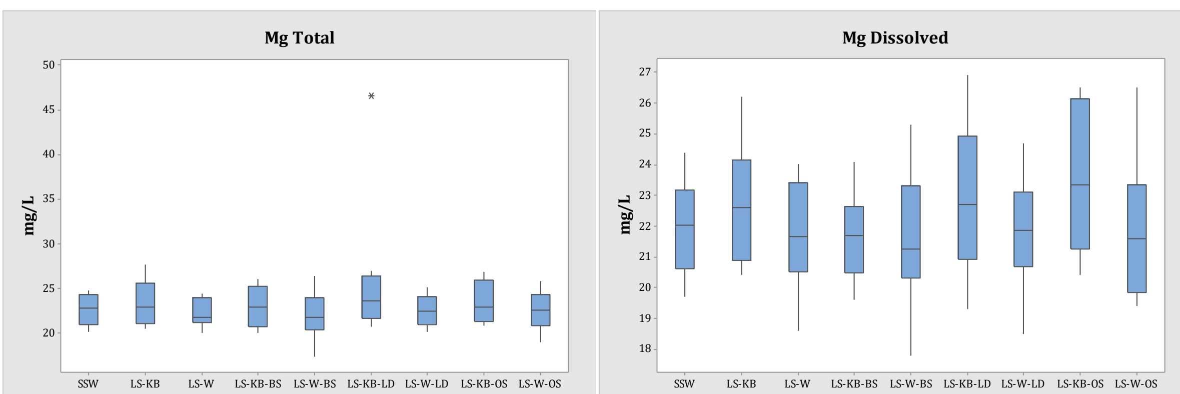

Figure 4.40 Mg Box Plots: Comparison of Mean Influent & Effluent Total (a) & Dissolved (b)

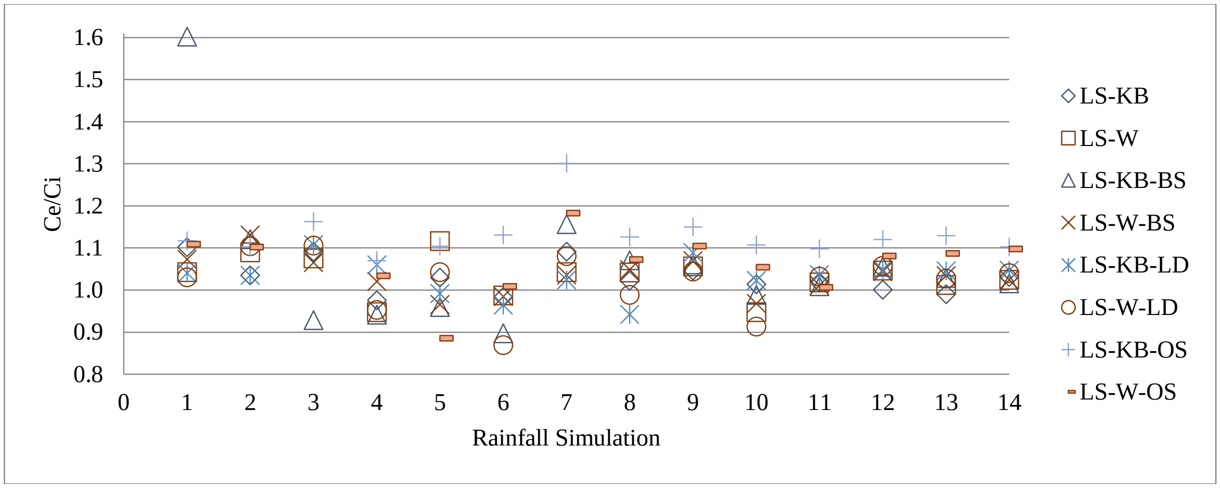

Figure 4.41 Ca Pollutant Reduction Ratio (Ce/Ci) vs Time

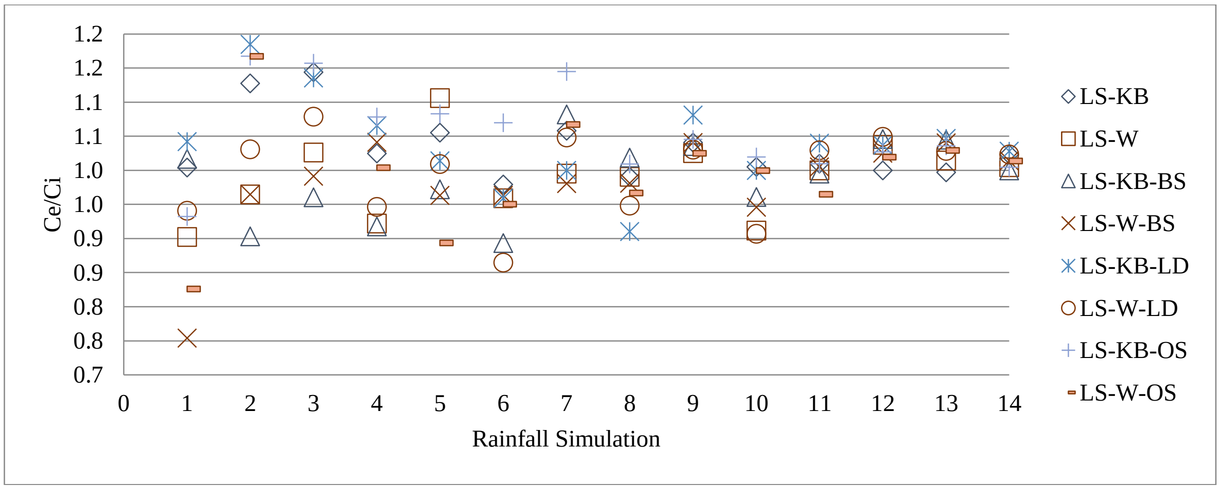

Figure 4.42 Mg Pollutant Reduction Ratio (Ce/Ci) vs Time

Ca and Mg BSM-Biochar

The difference in the Ca and Mg concentration between the baseline and post samples is statistically significant for the LS-W top and middle layers whereas the difference is insignificant for the LS-KB top and middle layers. (Tables 4.27 and 4.32 and Figures 4.35 and 4.43). The LS-W columns retained Ca (-130% and -76.2%) and Mg (-187% and -117%) in the top and middle layers respectively. These results support the Chapter 3 results in that the W biochar appears to have a preference for both Ca and Mg cations. However the KB biochar does not appear to have the same cation preference.

The differences in the Ca and Mg content in the base layers varied between columns (Tables 4.28 and 4.33 and Figures 4.35 and 4.43). The LS-KB columns retained Ca and Mg in all the base materials (-7.7% to -314% and -37.5% to -140% respectively) except the OS base layer which leached Ca and Mg (50% and 46.2% respectively). Whereas the LS-W columns only retained Ca in the LS and BS base layer (-71.4% and -27.3%) and Mg in the BS base layer (-120%). Leaching of Ca from the LS-W was observed in the columns that contained LS (15.4%) and

OS (57.4%) in the base layers. The leaching of Ca and Mg from the OS columns is likely attributed to the higher Ca (5.4 meq/100g) and Mg (2.6 meq/100g) content of the OS material which is greater than 4 and 2 times the Ca and Mg content of the other base layers respectively.

Table 4.32 BSM-Biochar Top & Middle Layer Mg Properties

	Parameter	Units	Baseline Mean (n=2)	Baseline Stdev	Post Mean (n=4)	Post Stdev	Mean %Diff.	Statistically Significant	t-test	d
	LS-KB									
Top	Mg	meq/100g	1.40	0.00	1.29	0.18	7.7%	N	0.356	0.86
Mid			1.40	0.14	1.13	0.17	19.6%	N	0.172	1.75
	LS-W									
Top	Mg	meq/100g	0.50	0.01	1.43	0.21	-187%	Y	0.016	6.33
Mid			0.60	0.01	1.30	0.18	-117%	Y	0.005	5.41

Table 4.33 BSM-Biochar Base Layer Mg Properties

Base Layer Material	Parameter	Units	Baseline Mean n=2	Baseline Stdev	LS-KB Post n=1	LS-W Post n=1	LS-KB %Diff.	LS-W %Diff.
LS	Mg	meq/100g	0.8	0	1.1	0.8	-37.5%	0.0%
LD			1	N/A	2.4	1	-140%	0.0%
BS			0.5		1.2	1.1	-140%	-120%
OS			2.6		1.4	1.3	46.2%	50.0%

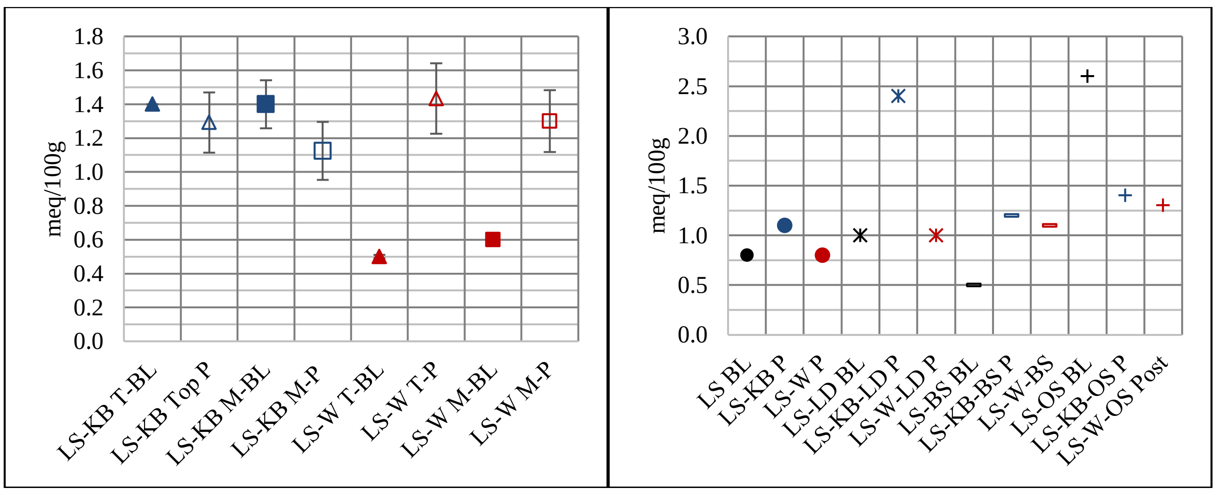

Figure 4.43 Mg Interval Plot Baseline & Post in: Top & Middle Layers (left) & Base Layers (right)

Additional Soil Chemistry

CEC

The average baseline CEC for the top and middle layers ranged from 3.33-3.23-meq/100g in the LS-KB columns to 3.08-2.88-meq/100g in the LS-W columns. The difference between the baseline and post CEC values is statistically insignificant for both the top and middle layers of the LS-KB and LS-W columns. The base layer CEC ranged from 4.9-meq/100g (BS), 3.58-meq/100g (LS), 2.7-meq/100g (OS), to 0.6-meq/100g (LD). These results are summarized in Tables 4.34-4.35 and Figure 4.44.

The accuracy of the CEC results is questionable. Specifically, the LS base layer CEC (3.58-meq/100g) was higher compared to the top LS-KB (3.33-meq/100g) and LS-W (3.08-meq/100g) layers and the middle LS-KB (3.23-meq/100g) and LS-W (2.88-meq/100g). However, the top and middle layers contained 30% biochar (by volume) and the baseline CEC of the KB and W biochar was measured at 29-meq/100g and 19-meq/100g respectively (Table 4.2). As such, the CEC results for the top and middle layers was expected to be higher compared to LS. Further, the CEC declined from the baseline to the post samples by ≤1% for the W columns and ≤6.3% for the KB columns. These differences are insignificant which is different from the Chapter 3 results in which the CEC declined by 51% (KB biochar) and 69% (W biochar) when exposed to an equivalent quantity of stormwater as the Chapter 3 columns. As such, the CEC measured in the BSM-Biochar does not appear representative of the actual CEC in the top and middle layers.

CEC is typically measured by converting all of the cations to one form, displacing them with another cation, and then measuring the displaced cations to quantify CEC (McLaughlin et al., 2009). The analytical testing method used to measure CEC during the initial biochar material characterization (SM 2320B) is different from the method used on the BSM-Biochar samples during Chapter 3 (S-10.10). One possible justification for the differences in the CEC results is differences in the testing method; specifically S-10.10 was developed to measure CEC in soils and may not adequately quantify CEC for biochar. As such, it is not possible to draw meaningful conclusion from these results.

Table 4.34 BSM-Biochar Top and Middle Layer CEC Properties

	Parameter	Units	Baseline Mean (n=2)	Baseline Stdev	Post Mean (n=4)	Post Stdev	Mean %Diff.	Statistically Significant	t-test	d
	LS-KB									
Top	CEC	meq/100g	3.33	0.10	3.12	0.33	6.1%	N	0.409	0.84
Mid			3.23	0.15	3.09	0.14	4.5%	N	0.312	0.99
	LS-W									
Top	CEC	meq/100g	3.08	0.36	3.05	0.15	0.72%	N	0.915	0.08
Mid			2.88	0.15	2.86	0.12	0.66%	N	0.851	0.14

Table 4.35 BSM-Biochar Base Layer CEC Properties

Base Layer Material	Parameter	Units	Baseline Mean n=2	Baseline Stdev	LS-KB Post n=1	LS-W Post n=1	LS-KB %Diff.	LS-W %Diff.
LS	CEC	meq/100g	3.58		3.3	2.84	7.8%	20.7%
LD			0.6	Note 1	1.34	1	-123%	-67%
BS			4.9		4.84	5.29	1.2%	-8.0%
OS			2.7		2.25	1.93	16.7%	28.5%

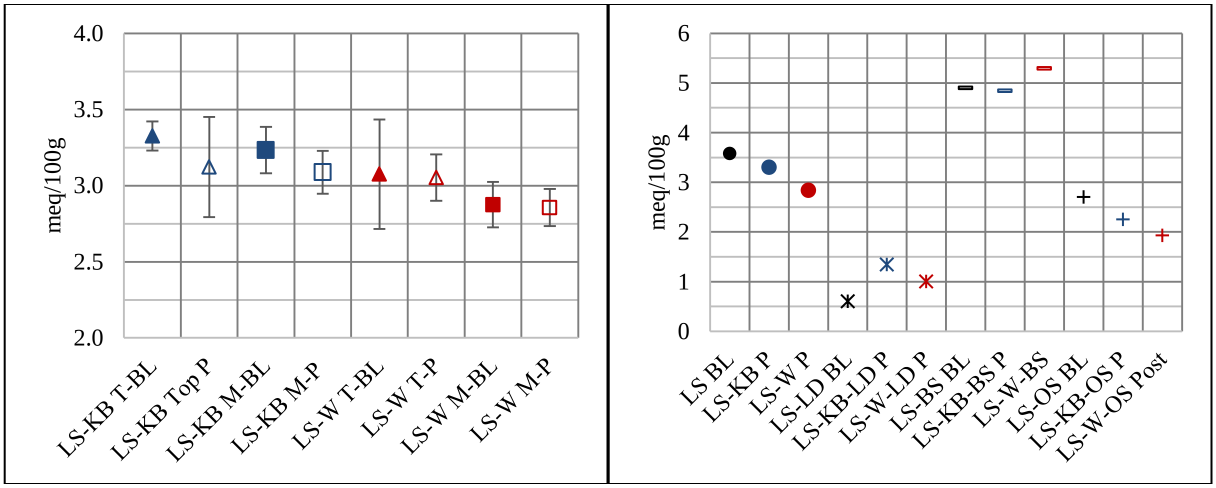

Figure 4.44 CEC Interval Plot Baseline & Post in: Top & Middle Layers (left) & Base Layers (right)

Na

The difference between the baseline and post Na concentration was statistically significant for the LS-KB top and middle layers which retained -920% and -558% whereas a statistically insignificant Na concentration leached from the LS-W top and middle layers, 20.4% and 7.6% respectively (Table 4.36). These results suggest that SSW may have contained Na (which was not tested). The stormwater was harvested from a roof top catchment, which included a portion that had passed through a green roof. All water contains dissolved salt, which can accumulate in the soil when water evaporates or is extracted by the plant roots. Both processes separate Na from water leaving the Na in the soils, which was likely flushed through the green roof into the effluent during irrigation (Reeve & Fireman, 1967). These results suggest that Na cations are preferred by the KB biochar compared to the W biochar, which does not appear to have the same cation preference.

The increase in the Na concentration of the LS-KB top and middle layers and the increase of the Ca and Mg concentration of the LS-W layers could explain the CEC results from Chapter 3. Specifically, the Chapter 3 CEC decreased by 51% (KB biochar) and 69% (W biochar) which was significantly higher compared to the known heavy metal cation content of the SSW. Based on the Na, Ca, and Mg retention observed in the top and middle layers, it possible that some of the CEC was reduced because the W biochar sorbed Ca and Mg cations while the KB biochar sorbed Na cations.

The Na content of the base layers (Table 4.37) increased for columns ranging from -179% (LS-W-BS) to -5900% (LS-KB-LD). The OS columns were the exception, this base layer leached 93% (LS-KB-OS) and 93.4% (LS-W-OS). These results are maybe attributed to the higher Na content of the OS base layer, 15 meq/100g, compared to 0.1 to 0.34 meq/100g in the other base layers.

Table 4.36 BSM-Biochar Top & Middle Layer Na Properties

	Parameter	Units	Baseline Mean (n=2)	Baseline Stdev	Post Mean (n=4)	Post Stdev	Mean %Diff.	Statistically Significant	t-test	d
	LS-KB									
Top	Na	meq/100g	0.09	0.01	0.87	0.13	-921%	Y	0.001	8.44
Mid			0.12	0.04	0.79	0.08	-554%	Y	0.001	10.86
	LS-W									
Top	Na	meq/100g	0.96	0.21	0.76	0.03	20.4%	N	0.409	1.33
Mid			0.85	0.48	0.79	0.05	7.6%	N	0.464	0.19

Table 4.37 BSM-Biochar Base Layer Na Properties

Base Layer Material	Parameter	Units	Baseline Mean n=2	Baseline Stdev	LS-KB Post n=1	LS-W Post n=1	LS-KB %Diff.	LS-W %Diff.
LS	Na	meq/100g	0.18	0.01	0.87	0.69	-383%	-283%
LD			0.10	N/A	6	0.56	-5900%	-460%
BS			0.34		1	0.95	-194%	-179%
OS			15.04		1.06	1	93.0%	93.4%

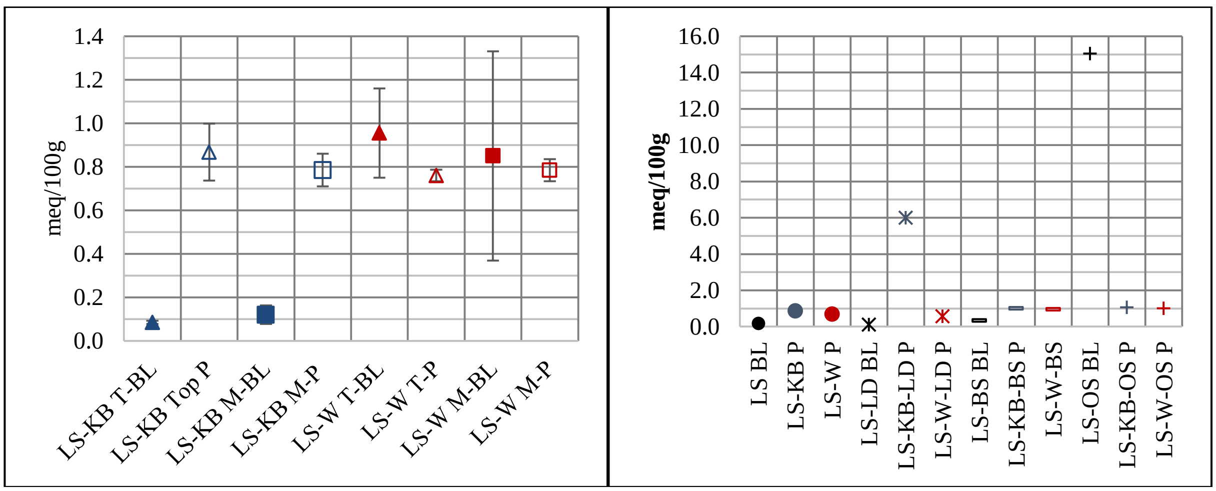

Figure 4.45 Na Interval Plot Baseline & Post in: Top & Middle Layers (left) & Base Layers (right)

Sodium Adsorption Ratio (SAR)

The SAR characterizes the soil sodicity: the concentration of salt forming ions specifically Na. Salts can accumulate in the soils and adversely affecting plant growth (Brady & Weil, 1996) and restricting infiltration (Ecology, 2014). SAR represents the portion of Na to exchangeable cations, specifically Ca and Mg in the soil (Equation 5).

$$SAR = \frac{[Na^+]}{(0.5[Ca^{2+}]+0.5[Mg^{2+}])^{0.5}} \quad \text{Equation 5}$$

The SAR in the LS-KB columns significantly increased in the top (-929%) and middle (-590%) layers. Conversely, in the SAR in the LS-W columns declined in the top (49.1%) and middle (33.0%) layers however these results were statistically insignificant (Table 4.38 and Figure 4.46). SAR limits vary depending on soil type, but generally, a baseline of less than 5 is recommended for stormwater infiltration BMPs to prevent the Na content from forming an impermeable layer (Ecology, 2014). Considering the Na content of the LS-KB layer was only 0.72 (top layer) and 0.69 (middle layer) if the BSM-KB Biochar is subjected to the same Na loading in the field, it would take 7 years to the reach an SAR of 5. However, these results also indicate that more Na will be retained in a BSM-KB biochar mix so it is expected that the permeability will decline at a faster rate compared to BSM with W biochar.

The SAR results in the base layers show an increase in all columns except the OS columns (Table 4.39 and Figure 4.46). The SAR increase ranged from -3255% (LS-KB-LD) to -124% (LS-KB-BS and LS-W-BS). Whereas the SAR in the OS base layer declined by 90% in both the LS-KB-OS and LS-W-OS columns.

Table 4.38 BSM-Biochar Top & Middle Layer SAR Properties

	Parameter	Units	Baseline Mean (n=2)	Baseline Stdev	Post Mean (n=4)	Post Stdev	Mean %Diff.	Statistically Significant	t-test	d
	LS-KB									
Top	SAR		0.07	0.01	0.72	0.06	-933%	Y	0.001	14.42
Mid			0.10	0.04	0.69	0.04	-611%	Y	0.003	14.22
	LS-W									
Top	SAR		1.15	0.26	0.58	0.02	49.8%	N	0.280	3.15
Mid			0.95	0.56	0.63	0.01	34.1%	N	0.572	0.81

Table 4.39 BSM-Biochar Base Layer SAR Properties

Base Layer Material	Parameter	Units	Baseline Mean n=2	Baseline Stdev	LS-KB Post n=1	LS-W Post n=1	LS-KB %Diff.	LS-W %Diff.
LS	SAR		0.17	0.01	0.78	0.71	-359%	-318%
LD			0.11	Note 1	3.69	0.53	-3255%	-382%
BS			0.38		0.85	0.85	-124%	-124%
OS			7.52		0.74	0.75	90.2%	90.0%

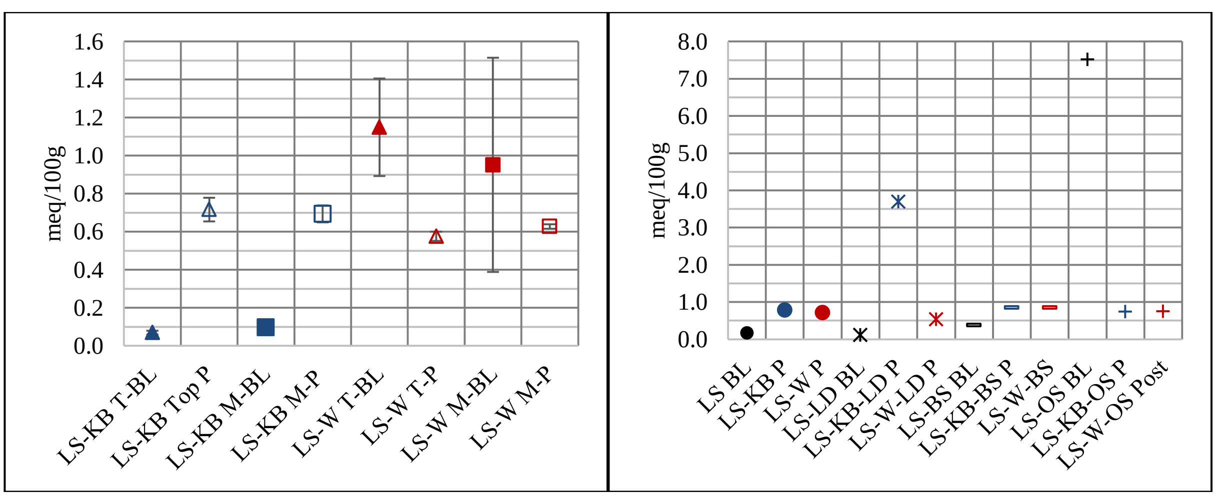

Figure 4.46 SAR Interval Plot Baseline & Post in: Top & Middle Layers (left) & Base Layers (right)

Organic Matter (OM)

The differences in the OM content between the baseline and post samples were insignificant for all layers varying between –12.3% and 1.8% (Table 4.40 and Figure 4.47). The standard method used to measure the OM in BSM is ASTM D2974, which is the same method that was used to in this research. This method measures OM based on the ash content remaining after igniting an oven dried sample. Since a significant portion of the biomass was converted to ash during the processing of biochar, a low ash content (and subsequently a low OM) is expected using this method.

The OM content in the base layers was less than 0.25% for all layers which was expected since none of these materials are known to provide a significant contribution of OM to soils (Table 4.41 and Figure 4.47).

Table 4.40 BSM-Biochar Top & Middle Layer OM Properties

	Parameter	Units	Baseline Mean (n=2)	Baseline Stdev	Post Mean (n=4)	Post Stdev	Mean %Diff.	Statistically Significant	t-test	d
	LS-KB									
Top	OM	%	1.13	0.15	1.00	0.23	11.3%	N	0.477	0.65
Mid			0.80	0.06	0.85	0.11	-6.6%	N	0.514	0.58
	LS-W									
Top	OM	%	0.65	0.02	0.62	0.05	4.4%	N	0.483	0.72
Mid			0.56	0.21	0.49	0.06	12.6%	N	0.719	0.46

Table 4.41 BSM-Biochar Base Layer OM Properties

Base Layer Material	Parameter	Units	Baseline Mean n=2	Baseline Stdev	LS-KB Post n=1	LS-W Post n=1	LS-KB %Diff.	LS-W %Diff.
LS	OM	%	0.23	0.03	0.32	0.21	-39.1%	8.7%
LD			0.20	Note 1	0.2	0.1	-42.9%	28.6%
BS			0.08		0.07	0.03	12.5%	62.5%
OS			0.44		0.25	0.2	43.2%	54.5%

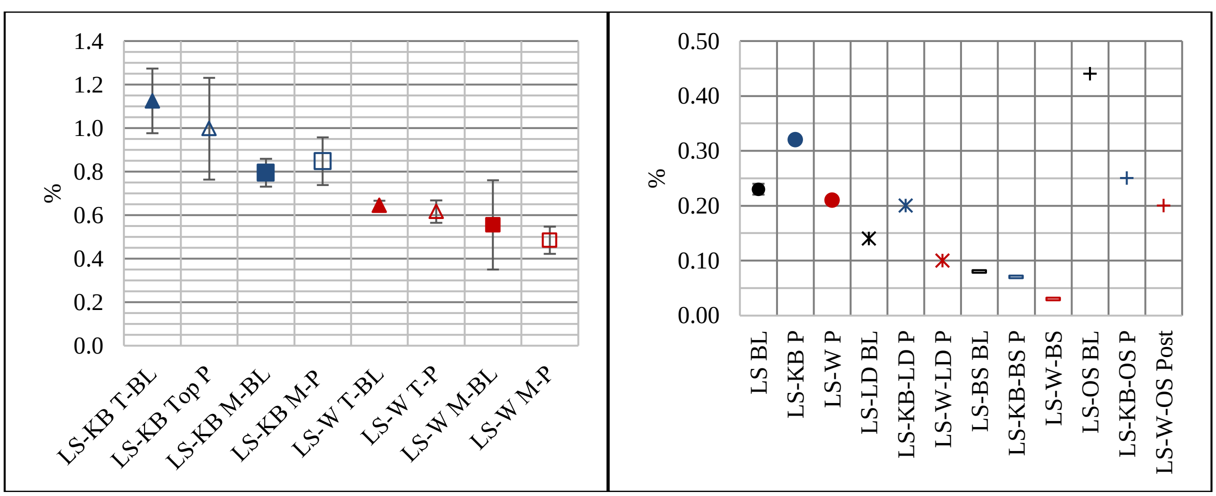

Figure 4.47 OM Interval Plot Baseline & Post in: Top & Middle Layers (left) & Base Layers (right)

EMPIRICAL OBSERVATIONS

As noted in Chapter 3, biochar has hydrophobic tendencies. This behavior was also noted during this research only to a lesser degree. The biochar from the top of the columns floated on the water surface during the falling head testing and some of the biochar remained on the walls of the columns after the testing was complete as shown in Figure 4.48. There was less biochar observed floating (compared to Chapter 3) which is likely attributed to the rock mulch that was placed on the top of the BSM-biochar mix to hold the biochar down. These results suggest that the hydrophobic tendencies may have less of an influence on the biochar in the field. However, it is anticipated that under ponding conditions, some biochar will float on the top of the ponded water in a bioretention cell.

Figure 4.48 Empirical Observations

BSM-BIOCHAR SPECIFICATION RECOMMENDATIONS

This section provides a summary of the recommendations for the field application of biochar as an amendment in BSM for bioretention cells based on the finding from this research and the Chapter 3 research. In addition, requirements defined by Ecology for custom BSM mixes (Ecology, 2015) were also included to develop a more comprehensive specification. A copy of the proposed specification is in located in the Appendix.

- Phosphorus – Based on the findings, the KB BSM-Biochar is leaches TP compared to a reduction of TP with the W BSM-Biochar. However, the trend in the data suggests that the TP leaching from the KB columns declined over time compared to the W columns in which the efficacy for removing TP declined over time. These results suggest that neither the leaching nor the reduction of TP are expected to be sustained over the long-term. Amendments were added to the base layers to enhance TP removal; however, the results indicate that the differences in the TP treatment performance are only significant when comparing the control columns: LS-KB to LS-W. These results suggest that the treatment performance is influenced by the type of biochar but not the base layer materials. These results support the predicted treatment performance defined in the Essential Properties in that biochar with a higher TP content (>0.04%) are more likely to leach. Since the W biochar contained 0.06% TP and did not leach, it is recommended that the limit be increased to 0.06% for the BSM-Biochar specification. The HRT between the SSW and the base layers that contained BS, LD, and OS may not have been sufficient for TP removal to occur. More research is recommended with a longer HRT to determine whether the desired TP removal can occur in BSM-Biochar mix. Based on these findings, no amendments will be added to the proposed BSM-Biochar specification.

- Nitrogen – Both the LS-KB and LS-W columns reduced TN. The LS-W column reduced significantly more TN compared to the LS-KB column, 16% compared to 5% respectively. These results may be attributed to the nitrogen content of the biochars, which was higher for the KB biochar (1.5%) compared to the W biochar (0.6%). However, both biochars have a higher nitrogen content than recommended in the Essential Properties (<0.1%) as such both biochars were expected to leach TN. This difference between the predicted results (defined in the Essential Properties) compared to the results of this study, particularly for the W biochar, may be attributed to nitrogen cycling which appeared to be responsible for changes in the different forms of nitrogen. Since W biochar reduced TN by 48% during the Chapter 3 research and 16% for this research, it is recommended that the limit increase to 0.6% for the BSM-Biochar specification).
- Heavy Metals – The heavy metal (Zn, Cu, Pb) results were consistent with the predicted treatment performance defined in the Essential Properties in that both biochars have an excellent sorption capacity for immobilizing dissolved metals. This is because the biochars have a balance of sorptive capabilities (W biochar has a high surface area and low CEC whereas the KB biochar which has a low surface area and high CEC) and since neither biochar is fully carbonized (C_{org}=100%), both adsorption and cation exchange processes are expected to occur simultaneously. The biochar CEC and surface area limits are recommended to be consistent with the lowest measured values of the biochar: CEC ≥ 19-meq/100g and surface area ≥ 209-m^2/g dry.
- Biochar has hydrophobic tendencies, which causes some of the biochar to float on the water surface during ponding conditions, which is expected to occur following a high intensity rainfall event in the field. To reduce the likelihood of this occurrence, it is recommended that river rock be used as a mulch layer on top of the BSM-biochar to hold the biochar down.
- Ca, Mg, and Na: for applications where Ca and Mg removal are targeted, the W biochar is recommended as it appears to have preference for these ions. Conversely, if Ca and Mg removal is not desired, the KB biochar is recommended since this biochar does appear to have the same ion preference. For applications where NA removal is targeted, the KB biochar is recommended as it appears to have preference for this ions. Conversely, if Na removal is not desired, the W biochar is recommended since this biochar does appear to have the same ion preference.
- CEC and pH – The Chapter 3 results hypothesized that biochars with a lower pH and higher CEC were better suited for applications where NH_3 removal is targeted. For this study, both biochars reduced NH_3

by 95-98% as such the difference in the biochars does not appear to have the influence on NH_3 removal when biochar is amended with LS. As such the pH limits for the specification are the same as recommended by Ecology in the stormwater manuals (Ecology, 2015; AHBL &HDR, 2013), 5.5 to 7.0, however the limit has been extend to 8.5 to include the biochars from this study.

- Aggregate – Only LS was evaluated as part of this study as such this the aggregate that is recommended for the specification. Other aggregate materials such as Sandy Loam and C-33 sand may also be acceptable.
- Maintenance – This study focused on the short-term effectiveness of the BSM-Biochar mixes and an investigation of maintenance requirements was not part of the scope. As such, recommendations for maintenance are based on the literature. Specifically, recommendations for extending the lifespan of a bioretention pond and maintaining the treatment performance include placing a layer of mulch over the top of the BSM mix, which will prevent the media from clogging (Minton, 2012). The mulch layer should then be replaced every 2 to 3-years Hunt & Lord, 2006).
- BSM Configuration – The Zn, Cu, and Pb content in the top BSM-Biochar layers significantly increased for both the LS-KB and LS-W columns whereas the difference in middle layers was insignificant for all columns. These results are consistent with other bioretention research, which suggest that heavy metals removal primarily occurs in the top 4-inches to 8-inches of the BSM. As such, the layered BSM-Biochar configuration appears to be sufficient to for metals reduction.
- BSM Placement, Permeability, and Physical Contaminants – Recommendations for soil placement, permeability, and physical contaminants have been included in the recommended BSM-Biochar specification (Appendix). These recommendations are based on the design requirements for custom bioretention soil media as defined in the Ecology stormwater manuals (Ecology, 2015; AHBL &HDR, 2013).

CONCLUSION

The goal of this research was to develop a specification for a BSM amended with biochar (BSM-Biochar) that provides treatment of regional pollutants of concern (POC) and can be used by practitioners to design and construction bioretention BMPs in the field. This goal was achieved by conducting a literature search to identifying the composition and configuration of a BSM-Biochar mix that appears to optimize the treatment performance. The results from Chapter 3 were also used to develop the specification, specifically the recommended quantity of biochar for a BSM and the Essential Properties of biochar were used to develop a BSM-Biochar specification. The two biochars selected for this study were selected because they provide a range of Essential Properties to evaluate and compare. The treatment performance of the proposed specification was evaluated using flow through column and different BSM-Biochar mixes. The results from the column testing were used to refine the proposed specification and develop recommendations for field applications. The following is a summary of the specific research questions that were answered during this study:

Do the selected BSM-Biochar mixes leach nutrients (N and P) or metals (Cu, Zn, Pb, Ca, and Mg)?

- No leaching of heavy metals was observed
- The phosphorus concentrations from the KB columns (-77% to -101%) were significantly higher compared to the influent concentrations. The trend in the P leaching appears to decline over time (rainfall simulations) which suggests that leaching may only be a short-term concern.
- The only form of nitrogen that leached from the columns was NO_3-NO_2. Specifically, the LS-KB columns leached (-52% to -46%) significantly more compared to the LS-W columns (-39% to -48%). The increase in the mean NO_3-NO_2 concentration was likely attributed to nitrogen cycling.
- The hardness, Ca, and Mg effluent concentrations are only significantly higher than the influent concentration for total and dissolved hardness from the LS-KB-OS column (-10.8% and -12%) and total and dissolved Ca from the LS-KB-OS (-15% and -16%) and LS-W-OS (-10% and -9%) columns. These results suggest that the OS base layer influenced the hardness and Ca leaching.

What is the short-term effectiveness of the BSM-Biochar mixes for reducing the POC?

- TSS - The TSS removal efficiency ranged between 96% to 98% for all columns. The TSS treatment performance was not influenced by the type of biochar or the differences in the base layer materials. These results are consistent with Chapter 3 except the flushing of the finer particles during the initial rainfall event was not observed. The difference is likely attributed to rinsing the KB biochar prior to testing for this study as such there was less fines in the BSM-Biochar mix to "flush" from the columns.
- Zn - The total and dissolved Zn removal efficiency for all columns was 97% and 96%. The Zn removal efficiency does not appear to be influenced by the type of biochar or the materials in the base layer.
- Pb - The total Pb removal efficiency for all columns ranged from 96% to 99%. The Pb removal efficiency does not appear to be influenced by the type of biochar or the materials in the base layer.
- Cu – The total and dissolved Cu removal efficiency ranged from 86% to 96% for the LS-W columns and 49% to 77% for the LS-KB columns. The Cu removal efficiency does not appear to be influenced by the type of biochar or the materials in the base layer.
- Total Phosphorus - The W columns had the best treatment performance reducing total and dissolved phosphorus by 21% to 26% and 15% to 23% respectively compared to the KB columns which leached total and dissolved phosphorus by -77% to -101% and -52% to -110% respectively. The P treatment performance appears to be influenced by the type of biochar but not the base layer materials. The pollutant reduction (C_e/C_i) over the testing period was also consistent with the Chapter 3 results: the phosphorus leaching from the KB columns decreased over the testing period while the phosphorus reduction from the W columns declined. The C_e/C_i for both biochars was approaching one (C_e/C_i=1.0). This trend indicates that the leaching from the KB columns declines over time while the efficacy of the W columns to reduce phosphorus declines over time.

- Ammonia - The mean NH_3 removal efficiency for all columns ranged from 86% to 98% for the KB columns compared to the 95% to 86% for the W columns respectively. Neither type the of biochar nor the composition of the base layer materials appears to influence the NH_3 treatment performance.
- Nitrate-Nitrite - The NO_3-NO_2 removal efficiency ranged from -52% to -48% for KB columns and -48% to -33% for W columns. The type of biochar appears to influence the NO_3-NO_2 treatment performance (less leaching from the W columns) however; the composition of the base layer materials did not.
- TKN – The TKN deduction was slightly higher in the W columns (43% to 56%) compared to KB columns (20% to 43%). Neither the type of biochar nor the base layer materials appeared to influence the treatment performance.
- Total Nitrogen - The mean TN removal efficiency was higher for the LS-W columns (13% to 16%) compared to the LS-KB columns (-4% to 5%). The type of biochar appears to influence the TN treatment performance however the differences in the base layer materials did not.

How does the hydraulic performance of the BSM-Biochar mixes change over the duration of testing?

- The saturated hydraulic conductivity (K_{sat}) generally declined over the testing period for all columns. This was expected since TSS accumulates in the top of the media, which reduces K_{sat} over time.
- The final BSM-Biochar K_{sat} (falling head) is estimated at less than 2.93 in/hr for all columns except the W columns that contained BS, LD, and OS in the base 6" layer which were estimated at greater than 2.93-inches/hour. The baseline K_{sat} in the top and middle layers was higher for the W columns (6.2- and 3.2-inches/hour) compared to the KB columns (1.8- and 1.7-inches/hour) by a factor of 3 and 2 respectively. The K_{sat} of the LS base layer was 4.7-inches/hour. These results were not expected since biochar amended with soils reportedly increases the permeability above that of the soil alone. However, research published since this study was conducted indicates that while biochar will increase porosity above that of soil alone this increase does not always result in an increase in K_{sat}. The influence of biochar on the soils K_{sat} appears to be dependent upon the biochar particle size (larger particles sizes are associated with larger pore spaces) and the connectively of the biochars pores (to provide a flow pathway for stormwater).

How does the physiochemical properties of the BSM-biochar change of the testing period?

Ca, Mg, Na SAR

- The top and middle layers of the W columns retained a significant quantity of Ca and Mg cations compared to the KB biochar, which leached in insignificant amount. These results suggest that the W biochar has a preference for Ca and Mg cations whereas the KB biochar do not.
- The top and middle layers of the LS-KB columns retained a significant quantity of Na cations (-920% and -558%) compared to the LS-W top and middle layers which leached Na (33.9% and 7.1%). These results suggest that Na cations are preferred by the KB biochar compared to the W biochar, which does not appear to have the same cation preference.

- The SAR significantly increased in the top (-929%) and middle (-590%) layers of the KB biochar columns however the SAR declined in the top layer (49.1%) and middle layers (33.0%) of the W biochar. Salts can accumulate in the soil decreasing the infiltration rate over time. The results suggest that if the BSM-KB Biochar was subjected to the same Na loading in the field, it would take 7 years to the reach an SAR that could impact infiltration.

Heavy Metals

- The Zn, Cu, and Pb content of these metals in the top layers significantly increased for both the LS-KB and LS-W columns whereas the difference in middle layers was insignificant for all columns. These results are consistent with other bioretention research, which suggest that heavy metals removal primarily occurs in the top 4-inches to 8-inches of the BSM.
- The LS base layer leached Cu, Zn, and Pb
- The OS base layer retained more Zn and Pb from compared to any other base layer. These results suggest that OS as a BSM amendment has potential for enhancing both Zn and Pb removal.

Nutrients

- The LS-KB columns leached 40% and 30% phosphorus from the top and middle layers respectively compared to the LS-W columns, which retained -367% and -329% from the top and middle layers respectively. The results are not surprising for the KB biochar, which contains four times more total P compared to the W biochar. These results also indicate that the W biochar retained P which is not surprising considering the quantity of Ca that was retained in the top and middle layers
- The base layer materials (BS, LD, OS) were included in the columns to enhance P reduction. While P was retained in the base layers of all columns, the base layer materials did not significantly influence the P treatment performance. These results are likely attributed to an insufficient hydraulic residence time (HRT) between the base layer material and the stormwater solution.
- The change in the NH_3 and TN concentration was statistically insignificant for the top and middle layers whereas the NO_3 concentration increased from the baseline to the post samples in the top and middle layers of the LS-KB columns (-213% and -308%) and the LS-W columns (-367% and -91.8%). These results suggest that nitrogen cycling is occurring in the columns.

What is the estimated lifespan of the biochar for reducing pollutants when amended in a BSM mix?

- It is not possible to use the water quality data to estimate the lifespan of the biochars for reducing pollutants. However, the pollutant reduction ratio (C_e/C_i) vs the rainfall simulations event graphs can be used to assess changes in the treatment performance including whether the biochars appears to be reaching capacity (lifespan) for pollutant removal (as indicated by a consistent increase in C_e/C_i over time). This trend was only observed for dissolved phosphorus in the columns that contained W biochar: there was a gradual increase in the C_e/C_i over all the rainfall simulations, which was approaching zero by the last simulation.

- The baseline and post CEC values were measured for the BSM-biochar mix in each column layer (top, middle, and base). The differences ranged from 0.66% to 6.1%, which would suggest that the lifespan is greater than 16-years. However, the CEC baseline values for the BSM-Biochar mix are less than the base layer which only contained LS. Considering the column top and middle layers contained 40% biochar with a CEC of 29- to 19-meq/100g, the baseline CEC was expected to be higher in the top and middle layers. As such, the CEC values do not appear to be representative of the true CEC value which is likely attributed to differences in the CEC testing methods.

Which biochar physiochemical properties (or range of properties) appear to indicate treatment performance for stormwater applications?

- P leaching appears to be influenced by the type of biochar. Specifically, the KB biochar leached P whereas some reduction of P was observed from the W biochar. These differences are attributed to the lower TP content in the W biochar (0.06%) compared to the KB biochar (1.26%). Based on these results (as well as recommendations in the Essential Properties section) a limit of 0.04% to 0.06% TP content in biochar is recommended.
- The NO_3-NO_2 leaching appears to be influenced by the type of biochar. The higher NO_3-NO_2 leaching from the LS-KB columns is likely attributed to the higher TN content in the KB biochars (1.5%) which is twice that of the W biochars (0.6%). Considering the W biochar reduced TN by 48% during the Chapter 3 research and 16% for this research, it is recommended that the limit increase to 0.6% for the BSM-Biochar specification).
- The heavy metal (Zn, Cu, Pb) results were consistent with the Essential Properties in that both biochars have an excellent sorption capacity for immobilizing dissolved metals. This is because the biochars have a balance of sorptive capabilities (W biochar has a high surface area and low CEC whereas the KB biochar which has a low surface area and high CEC) and since neither biochar is fully carbonized (Corg=100%), both adsorption and cation exchange processes are expected to occur simultaneously. The biochar CEC and surface area limits are recommended to be consistent with the lowest measured values of the biochar: CEC ≥ 19-meq/100g and surface area ≥ 209- m2/g dry.
- A copy of the recommended BSM-Biochar specification is located in the Appendix

Future Research Recommendations

The purpose of this section is to identify areas where more research is needed to further develop and refine the BM-Biochar Specification.

- Investigate whether the BSM-Biochar mix will support plant growth including the optimum portion (quantity) of biochar for the mix and whether additional organic matter is needed for plant establishment

- Investigate other methods for enhancing phosphorus reduction such as mixing oyster shells into the BSM-Biochar mix (instead of the bottom of the base layer) and using less biochar by only amending biochar into the top 12- to 6-inch layers
- Investigate why the biochar broke apart and the impact on a BSM performance including permeability rates and particulate biochar sorbed with metals becoming mobile in the stormwater solution
- Methods for evaluating acceptable toxin levels in biochar need to be developed with respect to physical contaminants and understanding the impacts on receiving water bodies
- Investigate methods for reducing nitrogen content when using a BSM-Biochar mix
- Investigate the role of plants in nutrient removal when using the BSM-Biochar mix
- OS appears to have a preference for sorbing heavy metals, specifically Zn, Pb, Al, and Fe. As such, additional research is recommended on OS amendments in BSM media for heavy metals removal

APPENDIX

BSM-Biochar Mix SPECIFICATION RECOMMENDATIONS

The proposed bioretention soil mix includes a loamy sand (classified per USDA texture triangle) amended with biochar that meets the specification shown. The subsequent sections describe the mix installation guidelines.

Biochar

The biochar should be prewash prior to installation to reduce nutrient leaching and the quantity of fines. This should include using a soil fabric (<150 mesh) to retain the material and rinsing the biochar with a volume of water equivalent to three times the volume of biochar.

Soil Media Mix Placement

The BSM should be installed in 6-inch lifts. The base 6" shall include only loamy sand. Well mix 2/3 of the biochar into the top 12" of the BSM. The remaining 1/3 should be tilled into the top 3" of the soil column. Compact each lift to a relative compaction of 80% by boot packing (Ecology, 2015). To avoid over compacting, which can reduce permeability, do not use heavy equipment in the bioretention cell.

Maintenance

Recommendations for extending the lifespan of the BMP and maintaining the treatment performance include placing a layer of mulch over the top of the BSM mix which will prevent the media from clogging [35]. The mulch layer should then be replaced every 2 to 3-years [5].

NOTE: This document is not intended to fully replace current bioretention soils guidelines; additional information needed to complete the installation of the soil mix specified should follow the requirements specified in the applicable stormwater manuals (AHBL & HDR, 2013).

BSM-BIOCHAR SPECIFICATION

TOP SOIL GRADATION

3/8" - 100%
#4 - 98%
#10 - 95%
#40 - 67%
#100 - 4-10%
#200 - 2-5%

PH

5.5-8.5

BIOCHAR CEC

>19 MEQ/100GRAMS

BIOCHAR SURFACE AREA

>200 M^2/G DRY

BSM PERMEABILITY RATE

>1.0 IN/HR

MAX COMPACTION

80%

TOTAL BSM MIX DEPTH

18-INCHES

BIOCHAR:SAND PORTIONS

TOP 12"
30%:70% ($V_{BIOCHAR}$:V_{LS})
2.6%:97.4% ($W_{BIOCHAR}$:W_{LS})[1]

ORGANIC MATTER (OM)[2]

2%-4.5% BIOCHAR ONLY
0.2% TOP SOIL ONLY

MULCH

1-1½ INCH RIVER ROCK

BIOCHAR NUTRIENT LIMITS

≤0.06% TOTAL PHOSPHORUS
≤0.60% TOTAL NITROGEN

PHYSICAL CONTAMINANTS

MAX. TEQ=9.0 NG/KG-DRY

1. *Based on the dry weight*
2. *The biochar OM content was estimated using a standard conversion factor and the portion of C_{org} in the biochar.*

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CHAPTER FIVE – DISSERTATION CONCLUSION

This dissertation followed a three-paper format which included multidisciplinary research in the fields of engineering education (Chapter 2) and bioretention best management practice (BMP) design research (Chapters 3 and 4). This chapter provides an overview of each study followed by the major findings, lessons learned, research limitations, and recommendations for future research.

CHAPTER 2

Study Overview

A goal of the work described in Chapter 2 was to develop culturally relevant engineering education (CR-EE) activities and explore their impact on Native American students' engagement in the activity. It was imperative to create a CR-EE framework that attended to K-12 engineering content standards while implementing a culturally relevant context into a single educational experience. A unique CR-EE framework was created and guided the development of lesson plans for the activities and resulted in the implementation of two engineering activities (fish weir and fish smoker). The community involved in this study comprised researchers, teachers and Tribal members.

Major Findings

- Most students were engaged in the CR-EE activity. This finding is significant because it supports the conceptual framework assumption that CR-EE activities motivate Native American students to engage in learning. Three primary factors were observed that supports to engagement students in the engineering activities: 1) building and testing their model fish weir or fish smoker, 2) opportunities for collaborative learning, and 3) learning about their culture from the Tribal community. One reason why students' may have been more engaged by these parts of the CR-EE activity is because they align with traditional Tribal learning styles.
- The Tribal community's involvement appeared to have a significant influence on students' responses. Students applied information they learned from presentations given by the Tribal community to their engineering designs, and the more involved the Tribal community was during the activity, the higher the occurrences of cultural representations in the students' responses.
- Students provided limited but promising responses regarding their perceptions of engineering. Specifically, participating in the CR-EE activity appears to demonstrate the relevance of engineering to their Tribe. This finding supports the conceptual pathway theory that engineering education can demonstrate the relevance of engineering to the Tribal community, which may increase Native American students' interest in engineering.

Lessons Learned

- While the University Team defined the design constraints for each engineering activities (i.e., fish weir and fish smoker), students had a tendency to develop engineering designs that included additional design constraints based on the cultural content presented by the Tribe (e.g., release holes in the fish weirs). This unplanned deviation from the lesson plan provided a glimpse of how Native American students could combine western and Indigenous perspectives to develop engineering solutions. Researchers and teachers should be prepared for students to incorporate cultural content from the Tribe's contribution into the engineering activity, and adapt their lesson plans as needed.

- The application of knowledge is an integral part of the engineering design process; as such, it makes sense for Native American students to apply Indigenous Knowledge to develop their engineering solutions. Therefore, include Indigenous Knowledge with math, science, and technology as students develop their engineering solutions.
- The students were more likely to describe the materials they used during the activity (i.e., popsicle sticks, pipe cleaners, etc.) rather than traditional materials the Tribe described during the cultural content presentations. Culturally relevant engineering activities may be enhanced by using traditional native materials, such as branches, twigs, and twine, to build the models.

Research Limitations and Future Research Recommendations

- This study was conducted with one Tribal community. There are over 500 Tribes located in the United States and each Tribe has unique ways of knowing. As such, results may vary between tribal communities. Additional studies are needed to investigate whether CR-EE will have a similar impact on students from other Tribal communities.
- This study explored the influence of the CR-EE activity on student from two 3-hour events. Additional research is needed to understand the influence of the CR-EE activity on students when the activities are incorporated into a teacher's lesson plans.
- This study focused on the initial steps of the proposed conceptual pathway, specifically whether the students are engaged and what engages them in the CR-EE activities. Additional research is needed to evaluate how other aspects of the conceptual pathway impact Native American students' including whether the conceptual pathway will ultimately result in a higher representation of Native Americans in the engineering work force.

CHAPTER 3 AND 4

Chapters 3 and 4 describe a study which explored the use of biochar and bioretention soil media (BSM) amended with biochar for stormwater treatment. The intent of the work described in Chapter 3 was to identify the Essential Properties of biochar (the physiochemical properties), i.e., those that enhance or inhibit the effectiveness of the treatment mechanisms and are thus important to the design process. These properties were first identified through a literature search and then evaluated for efficacy and efficiency by laboratory experimentation (jar testing and flow through column testing). The results from this study include recommendations for biochar properties used in bioretention BMPs. The intent of the work described in Chapter 4 was to develop a BSM-biochar specification that can be applied by stormwater practitioners to design and construct bioretention BMPs. This study builds upon the findings from Chapter 3, specifically the recommendations for Essential Properties and common citations in bioretention BMP literature were used to develop a draft BSM-Biochar specification. This specification was then evaluated in the flow through columns using a natural stormwater solution. Results from the Chapter 4 column testing were used to refine the BSM-Biochar draft specification.

Chapter 3 Major Findings

The major findings from the study are summarized below. These findings were used to develop recommendations for a BSM-Biochar specification for Chapter 4.

- Phosphorus Treatment Performance. Neither the W nor the KB biochar was effective for reducing total phosphorus concentrations. Leaching of phosphorus was observed from the KB biochar and leaching appears to be a function of the quantity of biochar (large quantities leached more phosphorus) and the content of phosphorus in the biochar (biochars with a large phosphorus content are more likely to leach phosphorus).
- TSS and Metals Treatment Performance. The treatment performance of the two biochars was similar for TSS (>89%) and Zn and Pb (>91%). The treatment performance for Cu was slightly higher for the W biochar (>88%) compared to the KB biochar (>47%).
- Hydrophobicity of Biochar. Biochar has hydrophobic tendencies, which causes some of the biochar to float on the water surface during ponding conditions, which are expected to occur following a high intensity rainfall event in the field. This phenomenon may influence the treatment performance by reducing the area of the biochar that is available for sorption.

Chapter 4 Major Findings

- BSM-Biochar Phosphorus Treatment Performance. Neither the W nor the KB biochar was effective in reducing stormwater phosphorus concentrations. While columns that contained the BSM-W biochar slightly reduced phosphorus concentrations, the columns that contained the BSM-KB biochar leached phosphorus. The trend over the testing period indicate that both reduction and leaching declined over time and was approaching zero by the end of the testing.
- Cation Preference. The W biochar preferentially sorbed Ca and Mg cations, and as such, this biochar is recommended for applications where Ca and Mg removal is targeted. The KB biochar preferentially sorbed Na cations, and as such, this biochar is recommended for applications where Na removal is targeted.
- BSM-Biochar Configuration. The BSM-Biochar mix was packed into the columns in layers, such that the base 6-inch layer did not contain biochar while the upper 12-inches layer contained a homogenous mix of two-thirds of the biochar with the remaining one-third tilled into the top 3-inches of the upper 12-inch layer. This configuration is recommended for future applications because:
    - The results from the physiochemical BSM-Biochar testing indicate that most of heavy metal (Zn, Cu, and Pb) treatment occurs in the top 6-inches of the mix. This is consistent with other

bioretention research, which indicates that heavy metal removal occurs in the top 4 to 8 inches of the BSM.

  - The phosphorus treatment performance improved (less leaching) compared to Chapter 3. This is partly attributed to the layered column, i.e., removing biochar from the base 6 inches and reducing the overall quantity of biochar (compared to the 4-inch diameter columns).

Lessons Learned

The two-primary lesson learned during these studies are:

- Throughout the work described in Chapters 3 and 4, I attempted to create conditions in the laboratory that are representative of field conditions. During the jar testing this approach presented some challenges. Specifically, I ran the jar test experiments for the same duration as stormwater is expected to be in contact with an 18-inch thick column of BSM-biochar. However, this time was not sufficient to determine the sorption capacity for the biochars, so it was not possible to use this data to answer my research questions. While the results still provided valuable information, which I used to develop recommendations for a BSM-Biochar mix, for future research to determine the sorption capacity the jar testing run time should be extended beyond the anticipated 18-hour contact time.
- During the work described in Chapter 4, I evaluated eight different BSM-biochar mixes. This resulted in a significant amount of data and time required to analyze and interpret the data. In retrospect, I was trying to answer too many questions with one study. If I could run this study again, I would limit the number of BSM-biochar mixes to two (one for each biochar) and setup triplicate columns of each mix for a total of six columns.

Chapter 3 and 4 Research Limitations

- Only two types of biochars were assessed. While the two biochars were selected because they provide a range of Essential Properties to evaluate and compare, the finding from these studies are limited accordingly.
- Neither studies included replicate samples of influent or effluent. However, replicate samples are typically preferred to demonstrate the quality of the data collected. As such, it is anticipated that the lack of replicate samples will limit the number of journals that will publish these studies.

Recommendations for Future Research

- The Chapter 3 recommendations for future research were used to develop the Chapter 4 BSM-biochar specification. These recommendations describe: limits for the phosphorus and nitrogen content in biochars (to reduce leaching), the quantity of biochar to include in the BSM-Biochar mix, using a rock mulch to prevent biochar from floating, and a list of Essential Properties for biochar.
- More research is needed to further develop and refine the BSM-Biochar Specification. These recommendations include:

- Investigate whether the BSM-biochar mix will support plant growth; determine the optimum portion (quantity) of biochar for the mix, and whether additional organic matter is needed for plant establishment.
- Investigate other methods for enhancing phosphorus reduction such as including mixing oyster shells in the BSM-biochar mix (instead of the bottom of the base layer) and using less biochar by only amending biochar into the top 6-inch thick layer.
- Investigate the role of plants in nutrient removal when using the BSM-Biochar mix.