Investigation of the Effects of Soil and Biochar in a Rain Garden on Stormwater Quality Improvement

by

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Ethics Statement

Abstract

Stormwater runoff from parking lots often contains a variety of elements and compounds in different forms and concentration that may pose risks to biota in receiving aquatic systems. Heavy metals including lead (Pb), cadmium (Cd) and polycyclic aromatic hydrocarbons (PAHs) are of particular concern in such runoff due to their prevalence, toxicity to aquatic organisms and persistence in environment. The ability of commercially available biochar to remove pollutants of concern through column treatments was assessed in this research. Different treatments of biochar were considered and their ability to remove pollutants was compared to soil. The biochar (Emergent and Cantimber) used in this study showed a significant higher molecular weight PAHs removal ability compared to soil and followed the order of Cantimber > Emergent > soil. The effects of heavy metals and PAHs on aquatic organisms and plants degradation can be mitigated by amending the soil media with biochar in the bioretention cells such as raingarden. This could be applied in real world where stormwater runoff can be treated before entering into river or stream therefore cutting the need of future restoration.

Keywords: Emergent Biochar; Cantimber Biochar; Parking lot stormwater; Low impact development; Heavy metals; PAHs; Constructed wetlands.

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1. Introduction

Water quality is altered by many non-point sources such as atmospheric deposition, sediment from improperly managed construction sites, runoff from parking lots and urban stormwater runoff. Of all land uses, urbanization arguably causes the largest changes in quality, volume and timing of flow running from catchments to streams and rivers, influencing the quality and quantity of lotic ecosystems. Urban stormwater is believed to result in 15% of all impaired rivers (61,338.5 km^2), 18% of all impaired lakes (3,838.1 km^2) and 32% of all estuaries (7,101.7 km^2) in the United States (Erickson *et al*. 2013; Sivora, 2015). Alteration in land use due to urbanization has drastically changed the local environment, influencing the quality and quantity of aquatic ecosystems (Goonetilleke et al. 2005). Creation of impervious surfaces has resulted in increased volume of runoff and decreased rate of infiltration and evapotranspiration (Walsh et al. 2012).

Petroleum hydrocarbons such as Polycyclic Aromatic Hydrocarbons (PAHs) are the most common form of stormwater contaminants (Davis & McCuen, 2005). These hydrocarbons are acutely toxic to aquatic life, as concentrations above 0.01-0.1 mg/L are known to impair fish health (Shepp, 1996). The most common source of PAHs are burning of trash and combustion of fuel. PAHs can be cytotoxic and carcinogenic and can cause reproductive complications (Bartelt Hunt et al., 2012; Thomos, 2002). In particular, aquatic organisms are vulnerable to the phototoxic effects of PAHs that accumulate in their tissues. The acceptable concentrations of the sum of priority PAHs in British Columbia are 0.3-6 μg/L (Ministry of Environment, 1993).

Toxic heavy metal pollutants such as cadmium, copper, lead and zinc can also be found in urban stormwater runoff. The most common source of toxic metals comes from the deterioration of motor vehicle parts. Metals such as copper, zinc, lead and cadmium can be carcinogenic to many life forms (Bakr et al., 2020). The acceptable standards for copper zinc and lead and in British Columbia are 3-7.5 μg/L to sustain aquatic life (Ministry of Environment, 2019). The recommended short-term maximum water quality guideline for dissolved cadmium to protect aquatic life at water hardness of mg/L $CaCO_3$ is 0.288 μg/L (Ministry of Environment, 2015).

Tire wear particles (TWP), generated from tire material during use on roads have gained increasing attention as a part of organic particulate contaminants such as, microplastics, in the aquatic environment. TWP emissions are traffic related and contribute 5-30% to non-exhaust emission from traffic (Wanger et al. 2018). A recent study conducted in the University of Washington showed that tire-related chemicals are largely responsible for half of the adult coho salmon death before the fish can spawn on return to Puget Sound's urban streams every fall (McIntyre et al. 2020). A recent study in Western North America has revealed an acute mortality syndrome in adult Coho salmon (*Oncorhynchus kisutch*), a species sensitive to poor water quality, when they return to spawn in urban freshwater creeks during the fall rainy season. Hierarchical cluster analysis indicated that tire wear particle (TWP) leachates were most chemically similar to water with observed toxicity, relative to other vehicle-derived sources. The results indicate TWPs are an under-appreciated contaminant source in urban watersheds and should be prioritized for fate and toxicity assessment, and removal (Tial et al., 2021).

An emerging method for reducing the impact of pollutants in stormwater runoff is the implementation of low impact development (LID) designs such as rain gardens and infiltration swales. LID components include topsoil and sand layers which are effective filtration media for capturing stormwater pollutants. To improve its effectiveness on capturing pollutants, a new design often incorporates biochar into the soil media. Biochar exhibits surface properties that show high rates of sorption to toxic contaminants and is cost effective and environmentally friendly media (Xiang et al., 2019; Ahmad et al., 2017).

1.1. Stormwater Pollutants.

Urban stormwater run-off from industrial activities and parking lots commonly carries heavy metals, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), pesticides and nutrients (nitrogen and phosphorus**;** Walsh *et al.* 2005; Sivora 2015). Throughout the rain event, these contaminants are washed off of roofs, roads and other surfaces into stormwater systems, before being discharged into estuaries and surface waterways. Heavy metals are problematic because they are toxic to aquatic organisms and can be bioaccumulated, resulting in increasingly large concentrations in living tissues. The most concerning toxicity of PAHs is their carcinogenicity (Collin et al. 1998; Kuo et al. 1998; Devi et al. 2016.) PAHs are transported into cells due to their hydrophobicity and then induce gene expression of the cytochrome P450 (CYP) enzyme group (Bekki et al. 2013; Ikenaka et al. 2013). Nitrogen and phosphorous are commonly used in lawn fertilizer. An excessive amount of nutrients leads to eutrophication of water bodies, which often causes a decrease in dissolved oxygen levels and results in low survivability for aquatic life (Schindler and Valentyne 2008). A major affirmation on managing stormwater has concentrated on the elimination of these pollutants from the urban watershed (Tiefenthaler *et al.* 2008).

1.1.1. Heavy Metals.

Heavy metals come from both natural and anthropogenic sources. Urban stormwater is believed to be the dominant contributor of trace metal pollution to many of the water bodies worldwide (Davis et al. 2001; Buffleben et al. 2002). The most common heavy metals found in stormwater include: copper, zinc, lead, and cadmium. In southern California, several studies have documented heavy metals as the main contaminants of concern in stormwater runoff (Buffleben *et al*. 2002; Tiefenthaler *et al*. 2008). Sources of heavy metals and their contribution to urban stormwater runoff are also significantly dependent on land use (Herngren et al., 2005).

Metals can be soluble in water or associated with solids. Most of the heavy metals in urban stormwater runoff are attached to suspended solids (Dong et al. 1984; Bodo 1989). These can accumulate in the streambed and be taken up by benthic organisms. Additionally, they can become soluble with decreasing pH, and bind to complexing agents (Liebens 2001). Soluble forms of metals can cause chronic and acute toxicity to aquatic organisms. Metal concentrations generally increase with decreasing particle size suspended solids (Ujevic et al. 2000; Liebens 2001). This is due to the relatively large surface area of fine particles and their higher cation exchange capacity (Dong et al. 1984). Furthermore, parameters such as dissolved organic carbon (TOC) and pH can significantly enhance the desorption of heavy metals from suspended solids. For example, Tai (1991) noted that the ratio of trace metals released into the dissolved phase at pH 6 vs. pH 8.1 is about 180, 45, and 25 for Zn, Pb and Fe respectively. Similarly, TOC plays a major role in the partitioning of metals between soluble and particulate fractions in stormwater (Hamilton et al. 1984). Consequently, with increasing TOC, the interaction between TOC and heavy metals can result in processes that concentrate the metals in the dissolved phase (Hernegen et al. 2005). A table of typically reported contaminants concentration is shown in table (Table 1.1)

Lead and cadmium, known to be the toxic metals (Kumar et al., 2008; Lim et al., 2008; Weng et al., 2008) with very little (Lane et al., 2005; Xu et al., 2008) or no nutrient value, are abundant almost everywhere in nature. Pollution of soils, sediments and water with lead and cadmium cause their incorporation into the food chain, which can result in a wide variety of adverse effects in animals and humans since it is a cumulative contaminant (Sanborn et al., 2002; International Agency for Research on Cancer, 2006). The effect of hardness on the combined outcome of metal mixtures was investigated using *Daphnia magna* and the bioassay test results showed that the degree of sensitivity to hardness on the toxicity change was in the order: Cd < Cu < Zn < Pb with 25, 66, 77 and 88% decrease in the LC_{50} (acute toxicity is expressed as median lethal concentration (LC_{50}) values, respectively (Yim et al. 2006)

1.1.2. PAH

PAHs are another toxic material found in urban stormwater. PAHs are potentially carcinogenic chemicals that are ubiquitous in the urban environment. Impervious surfaces in urbanized areas usually contain high amounts of PAH (Wang *et al*. 2010), which could be transported to adjacent water bodies by means of stormwater runoff, putting risk on human health and biota (Zheng *et al*. 2014). PAHs are essentially produced by traffic emissions and incomplete combustion or spills of petroleum. The U.S. Environmental Protection Agency (EPA) has defined 16 PAHs as a representative of all PAHs and is divided into two classes: low molecular weight PAHs (LPAHs) and high molecular weight PAHs (HPAs). The lower molecular weight PAHs (e.g., 2 to 3 ring group of PAHs such as naphthalenes, fluorenes, phenanthrenes, and anthracenes have significant acute toxicity to aquatic organisms, whereas the high molecular weight PAHs, 4 to 7 ring (from chrysenes to coronenes) do not. However, several members of the high molecular weight PAHs such as benzo[a]pyrene, indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene have been known to be carcinogenic (MELP, BC. 1993).

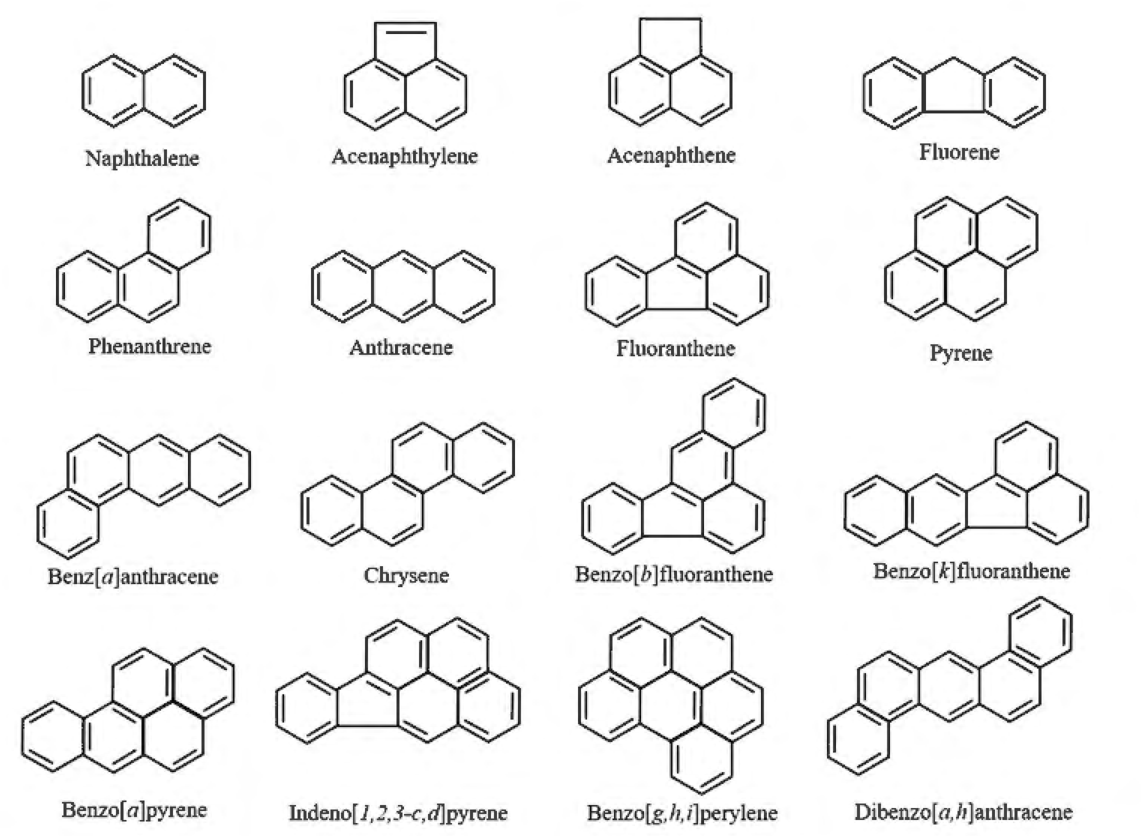

Figure 1.1: Chemical structure of the 16 representative polycyclic aromatic hydrocarbons (PAHs) as decided upon by the United States Environmental Protection Agency (US EPA).

The high molecular weight PAHs have characteristics of high hydrophobicity and can be strongly sorbed onto organic or fine particles. They may eventually sink down to the bottom sediments in aquatic systems. Increased PAHs concentrations in sediments are usually observed because they are resistant to microbial degradation (Feng et al., 2016, Qian et al., 2016). The transfer of PAHs from sediments to the benthic organism is a risk to ecosystems and human health due to the consumption of contaminated benthic organisms (Khairy et al., 2014). This results in a long term threat to the ecosystem via bioaccumulation and biomagnification effects after they enter a food chain (Li et al., 2015.; Xia et al., 2015).

Table 1.1: **Typical Parking Lot Contaminants Ranges** (Jalizi, 2018; McQueen, 2010)

	pH	**TOC (mg/l)**	**TSS (mg/l)**	**BOD (mg/l)**	**Al (µg/l)**	**Cd (µg/l)**	**Cr (µg/l)**	**Cu (µg/l)**	**Fe (µg/l)**	**Pb (µg/l)**	**Zn (µg/l)**	**PAHs (µg/l)**
Min	3.6	0.001	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.5
Max	8.7	50	585	71	4756	5	42	770	4012	137	908	10

*ND is compound not detected.

1.2. Structural Stormwater Best Management Practices

According to previous knowledge and findings the earliest stormwater management designs were strictly water conveyance based and had a limited consideration for groundwater recharge or pollutant removal. Environmental degradation such as flooding, erosion, loss of recreational usage and damage to fish and aquatic life occurred as a result of negligence in controlling runoff. As society began to realize the negative impacts of neglecting the environment with previous designs, municipalities are opting to incorporate LIDs designs into future developments. Currently, there are very few performance data for bioretention and rain gardens, especially related to the removal of organic compounds (Davis et al. 2009; DiBlasi et al. 2008; Grebel et al. 2013). Existing studies indicate that these systems are effective in removing organic pollutants from stormwater; for hydrophobic compounds such as petroleum hydrocarbons and lower molecular weight PAHs, 80–90% reduction of the incoming load can be expected (DiBlasi et al. 2008; Hong et al. 2006; LeFevre et al. 2012a).

The low impact development (LID) as defined by the Environmental Protection Agency refers to systems and practices that use or mimic natural processes that result in the infiltration, evapotranspiration or use of stormwater in order to protect water quality and associated aquatic habitat. LID system such as rain gardens, green roofs and dry and wet ponds reduce the volume of overland flow during storm events, but they were not designed to remove most stormwater contaminants (US NRC, 2009).

Research investigations on stormwater runoff increasingly focus on evaluating stormwater runoff quality and the effectiveness of adopting stormwater best management practices (BMPs) to minimize pollutant input to receiving waters. Most pollutants in urban runoff, are in particulate form, or, are bound to particulates and tend to settle out of the water column and accumulate in sediments (Camleadell, 1994). Structural stormwater best management practices (BMPs) are designed to compensate for the unfavorable impacts of development (i.e., increased impervious surfaces, contamination of water resources, damage to fish and wildlife habitat, increased flooding and erosion/sedimentation, reduced groundwater recharge). Structural BMPs are classified into four primary categories: (1) infiltration systems (i.e., soak ways, infiltration trenches and infiltration basins); (2) storage facilities (i.e., lagoons, rain garden, constructed wetlands, detention basins, retention ponds, storage tanks, and roof storage); (3) filter strips and swales, and (4) alternative road structures including porous paving, porous asphalt surfaces (Scholes et al. 2005).

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A rain garden is a bio-retention structure with both stormwater management and aesthetic function. The main purpose of a rain garden includes stormwater treatment using a soil layer and volume capture through infiltration from the rock reservoir. They are usually designed in a concave shape to collect runoff from the adjacent impervious area and rooftops, allowing it to infiltrate into underlying constructed soil and bed soil. A drain rock reservoir and a perforated drain system are often present to remove excess water (City of Vancouver 2016). Depending on the soil moisture conditions in a garden, different shrubs and ground covers are planted on the surface of a rain garden. In addition to sodded lawn areas for erosion control and multiple uses, trees, rushes, sedges, and other grass-like plants are used in designing rain gardens (Metro Vancouver Regional District. 2012). Because of the surface ponding and plant uptake or moisture, a rain garden captures an increased volume as compared to the infiltration trench.

To increase removal of stormwater pollutants such as heavy metals and PAHs, filtration media in rain garden, native soil can be augmented with different materials (geomedia like biochar) of greater contaminant removal capacity (Figure 1.2). Biochar, a carbonaceous, porous, adsorbent media, meets all the criteria and has demonstrated to improve contaminant removal from contaminated waters (Ahmad et al., 2014; Rajapaksha et al., 2016). Biochar is produced as a co-product from waste biomass and expected to last for decades in the environment, as carbon in biochar is recalcitrant with an average half-life of over 100 years (Spokas, 2010).

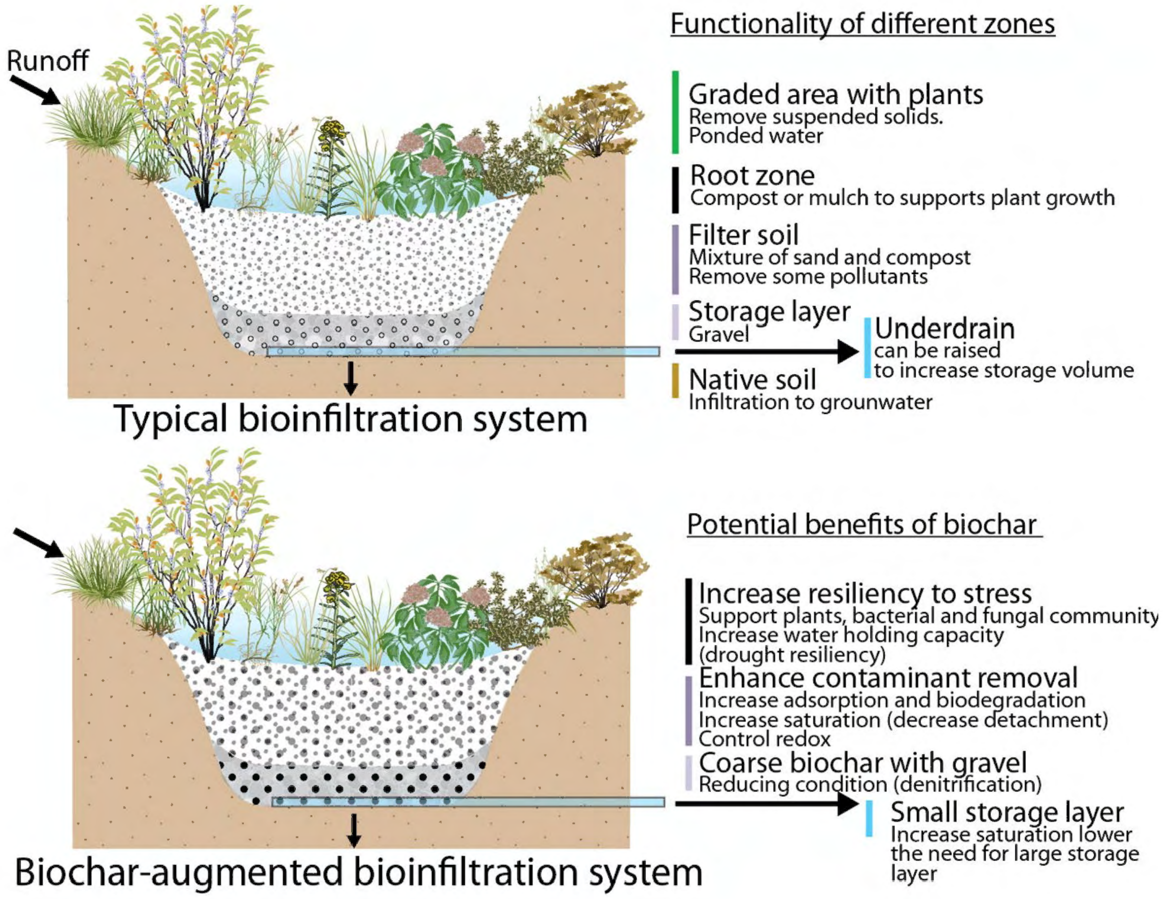

Figure 1.2: Advantages of amended bioinfiltration system using biochar From Mohanty et al, 2018.

1.2.1. Soil

Soil has a potential role to play in altering plant growth, water retention and removal of pathogens, nutrient, heavy metals and other contaminants such as PAHs, hence altering the function of rain gardens in a stormwater treatment system in urban areas. In the rain garden, soil media must be designed in coordination with vegetation to provide effective runoff treatment and flow control. Soil media should be selected based on its infiltration rate and hydraulic conductivity. Fine soil particles can reduce the conductivity required for drawdown (Hinman, 2009) and can reduce the infiltration rate. Coarse-grained (sand mixture) are optimal as they have hydraulic conductivity and infiltration rates suitable for soil media. Cation-Exchange-Capacity (CEC) is another measure that should be considered while preparing the soil media. This parameter is an indicator of a soil's ability to retain nutrients (e.g. Ca^{+2}, K^{+}, NH_4^{+}) and capture pollutant cations (e.g. Pb^{+2}). Clay and organic materials are the primary sources of providing receptor sites for cations, and that of determining the CEC.

1.2.2. Biochar

Biochar is a black solid obtained by heating biomass, such as wood or manure, with little or no oxygen through a process called pyrolysis or charring (Sohi 2012). Biochar is applied to soil to enhance agricultural gains and carbon sequestration (Tan et al. 2015). Porous structure, mineral constituents, large specific surface area, and enriched surface functional groups are some of the distinct characteristics of biochar, qualifying it as an excellent adsorbent to remove pollutants from aqueous solutions. Activated carbon is another highly porous adsorbent that has been successfully employed for the removal of diverse pollutants from water worldwide (Chen et al. 2007). Being a renewable resource, and because of its economic and environmental advantages, biochar is providing a promising resource for environmental technology used for water contaminant treatment (Tan et al. 2015).

The removal efficiency of different pollutants by biochar is determined by various factors including the properties of the biochar, pH, and co-existent ions (Figure 1.3). For heavy metals, the possible adsorption mechanism involved integrative effects of several kinds of interaction including electrostatic attraction, ion-exchange, and physical adsorption, surface complexion and/or precipitation. The specific mechanism of different heavy metals is different and the appropriate properties of biochar make a great contribution to the adsorption of heavy metals; the adsorption mechanism through which organic contaminants such as PAHs bind to biochar are also combined with different kinds of interaction for example, electrostatic interaction, hydrophobic effect, hydrogen bonds and pore-filling may be the main mechanism for the adsorption of organic contaminants onto biochar; adsorption efficiency of biochar is highly dependent on the properties of the biochar (i.e., surface area and porous amount), which is in turn a function of feedstock, pyrolysis time, pyrolysis temperature, and thermochemical conversion technology (Tan et al. 2015). Pyrolysis temperature is believed to be the most important factor. Chen et al. (2012) investigated the influence of different pyrolysis temperatures on the properties of cotton stalk driven biochar and indicated that the structural characteristics and isotherm shape of the biochar were more defined by pyrolytic temperature than the biomass feedstocks.

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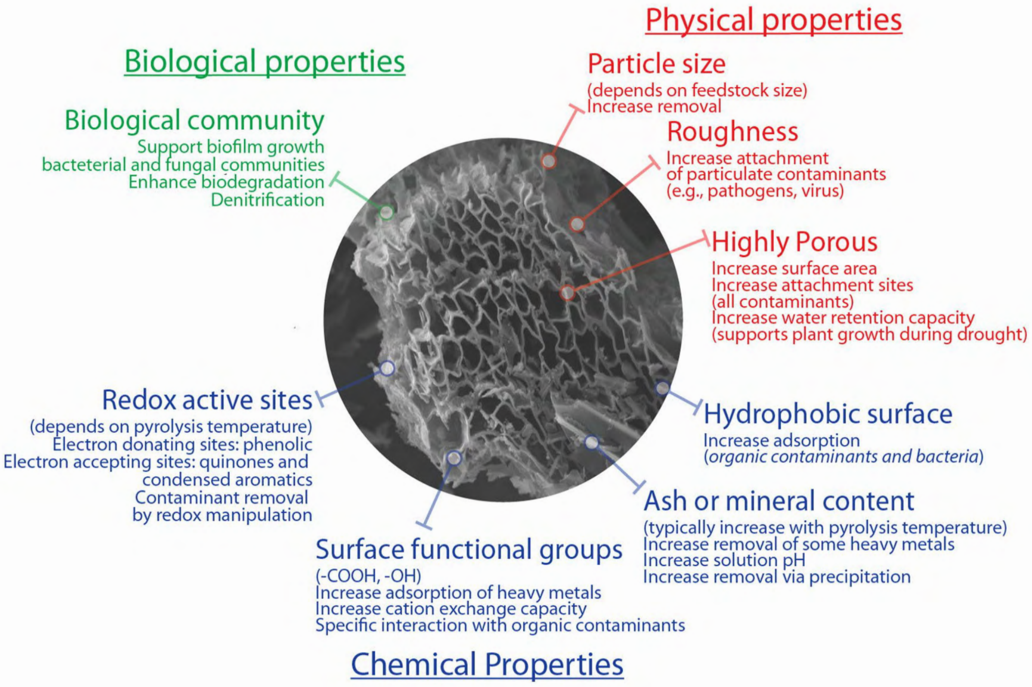


Figure 1.3 Variation of biochar properties according to their method of production and how they can help in removal of pollutants. From Mohanty et al, 2018

The effect of pH on biochar adsorption efficiency is a function of the type of biochar, surface properties, and the target contaminants. The solution pH has an impact on the adsorbent surface charge, degree of ionization, and speciation of the adsorbate (Li et al. 2013; Zhang et al. 2013). As pH changes, the behavior of the functional groups (e.g. – COOH, -OH) on the biochar's surface also changes. At low pH (<5), most of these functional groups are protonated, leading the biochar surface to be positively charged which will favor the adsorption of anions on the biochar surface (Oh et al. 2012). With increasing pH value, more cations was adsorbed by biochar surface because of the deprotonation of the functional groups, as well as a decrease in the competition of cations and protons for occupying binding sites on biochar surface (Lu et al. 2012). Studies have shown that biochar can effectively reduce organic pollutants, owing to its diverse range of mechanisms, such as pore filling, hydrophobic partitioning, hydrogen binding, and Ω-stacking interaction (Xiang et al., 2019).

Different pollutants usually co-exist in urban stormwater runoff, and interactions between these pollutants have a crucial impact on adsorption efficiency of the biochar. Reports on the influence of these interactions are contradictory. Kong et al. (2011), found the co-existence of phenanthrene and mercury in aqueous solution resulted in direct competitive adsorption as a result there is decline in adsorption of both chemicals. The same result was observed by Zheng et al. (2010) when studying the concurrent removal of atrazine and simazine using green waste biochar. On the other hand, Jia et al. (2013) noted that by increasing Cu and Zn concentration, oxytetracycline removal by maize straw derived biochar improved.

1.2.3. Plant Growth

In stormwater treatment systems such as rain garden, plants serve multiple functions in addition to their aesthetic use. Plants reduce stormwater runoff volume by intercepting rainwater in their canopy, removing water via evapo-transpiration and increasing infiltration via root structure (Berland et al., 2017). Plants remove nutrients from soil by assimilation (Read et al., 2008), help retain metals/metalloids (Chen et al., 2014; Borecki et al., 2016). Thus it is important that the geomedia used in rain garden can support plant growth throughout dry and wet seasons. Biochar can mitigate abiotic stress to plants (Rizwan et al., 2016).Several studies showed that addition of biochar improved water retention (Abel et al., 2013.; Ibrahim et al., 2013), and helped survival against drought (Kammamm et al., 2011) and biotic stress (Elad et al., 2011).

One of my cohort has done her ARP to identify adequate rate of biochar (0.5, 1.5 and 5% w/w) that can enhance the properties of bioretention soil, survival and growth of native wetland plants such as slough sedge (*Carex obnupta*) and common rush (*Juncus effuses*) in bioretention cell.

My ARP was focused on how rain gardens can be used to minimize the deleterious effects of stormwater based pollutants such as heavy metals and PAHs entering the aquatic environment.

Specifically, I have investigated if biochar mixed with soil placed within the rain garden cell can increase the removal of specific stormwater pollutants and decrease the concentration of these contaminants prior to discharge into the receiving environment.

2. Experimental Plan

2.1 Goals and Objectives

The primary goal of this study was to investigate the feasibility of using biochar as an environmentally friendly and inexpensive absorption media in rain gardens for removal of heavy metals including lead, cadmium and 16 priority PAHs (as defined by EPA) to aid in the protection of urban streams and estuaries from non-point source pollution.

To achieve my goal, I followed 2 objectives:

1) Reviewed the concentrations of target heavy metals (lead and cadmium) and 16 priority PAHs in the influents and effluents passing through specific column treatments.

2) Investigated the heavy metals and PAHs removal ability at different biochar/soil ratios (0%, 0.5%, 1.5% and 5% w/w) for removal of lead, cadmium and 16 PAHs).

2.2 Research Question

This research was focused on how well the bioretention cell (rain garden) removes heavy metals and PAHs with soil media, with and without the biochar amendment.

2.3 Material and Methods

2.3.1 Study Site

The experimental setup was in the Environmental Lab SW3-1655 and the samples were analyzed in the Chemistry lab of Dr. Kevin Soulsbury on the BCIT campus.

2.3.2 Biochar Characteristics and Properties

A commercially available biochar, Emergent Biochar (Emergent Waste Solution) Canada, and a locally produced Cantimber Biochar (Cantimber Biotech Inc.) Richmond, BC, was used in this experiment. The Emergent Biochar (Table 2.1) was produced by pyrolyzing gray pine with bark at temperature ranging from 350˚ C to 1,000˚ C in a low oxygen thermal process. The pH of Emergent Biochar was 8.5.

The Cantimber Biochar (Table 2.1) was produced from a mixture of Douglas-fir, Hemlock and Western Red Cedar wood chips. The wood chips underwent four hours of increasing temperature in a low oxygen thermal process and incubation at 550˚ C. The pH of Cantimber Biochar was 8.0.

Table 2.1 Physical properties of Emergent and Cantimber Biochar

Properties	Emergent Biochar	Cantimber Biochar
Ash %	3.25	8.72
Sulfur %	0.06	0.15
Carbon %	81	77.15
Hydrogen %	2.99	1.26
Nitrogen %	0.19	0.24
Oxygen %	12.51	12.48

2.3.3 Soil Preparation

The final rain garden mixture was 1:1 ratio of 2 mm sieved sand (Island’s finest washed sand) and 2 mm sieved topsoil (Garden Work’s premium landscape and garden soil) by dry weight. The sand (9 bags of 20 kg per bag) and soil (15 bags of 30 L per bag) were air dried separately and sieved to 2 mm by using sieve 10 of U.S.A. Standard

Sieve Series. The soil preparation was done according to the guidelines of City of Vancouver to achieve infiltration rate under 15-350 mm/hr (MMCD, 2009; Kerr Wood Leidal, 2012), City of Eastern Washington (AHBL and HDR, 2013); Western Oregon (Green Girl Land Development, n.d.). The biochar/soil blend was created by using 0.5, 1.5 and 5% w/w biochar and it was thoroughly hand mixed in soil.

2.3.4 Influent Mixing Procedure

The mixing procedure was complex as PAHs are insoluble mainly the higher molecular weight PAHs and many strategies were tried but all of them resulted into inconsistent influent concentration. The influent was initially mixed by using two magnetic stirrers to achieve the theoretical concentration (Table 2.2), inconsistency was observed mainly in the PAHs concentration but it was better than the mixing procedure performed initially. The concentration of the influents was consistent when pipes of the peristaltic pumps with a flow rate of 180mL/min were used for mixing the influents in the 30 L tank for 20 minutes. (Table 3.1).

2.3.5 Experimental Design

A commercially available biochars (Emergent and Cantimber Biochar) were used to investigate the water quality of synthetic stormwater. PVC pipes of 90 cm long and 10.8 cm diameter were used for column treatments. The pipe column was filled with soil media amended with biochar (Emergent and Cantimber Biochar separately) up to 60 cm and pea gravel at 5 cm to the top and bottom of the column. These dimensions were representative of a typical rain garden (Figure 2.1). A typical rain garden does not have a layer of gravel above thick soil layer, this experimental design had 5 cm of pea gravel at the top of soil layer to prevent soil from flattening out. A 30 L water reservoir was used to prepare the synthetic stormwater and a peristaltic pump was used to pump the water into the column.

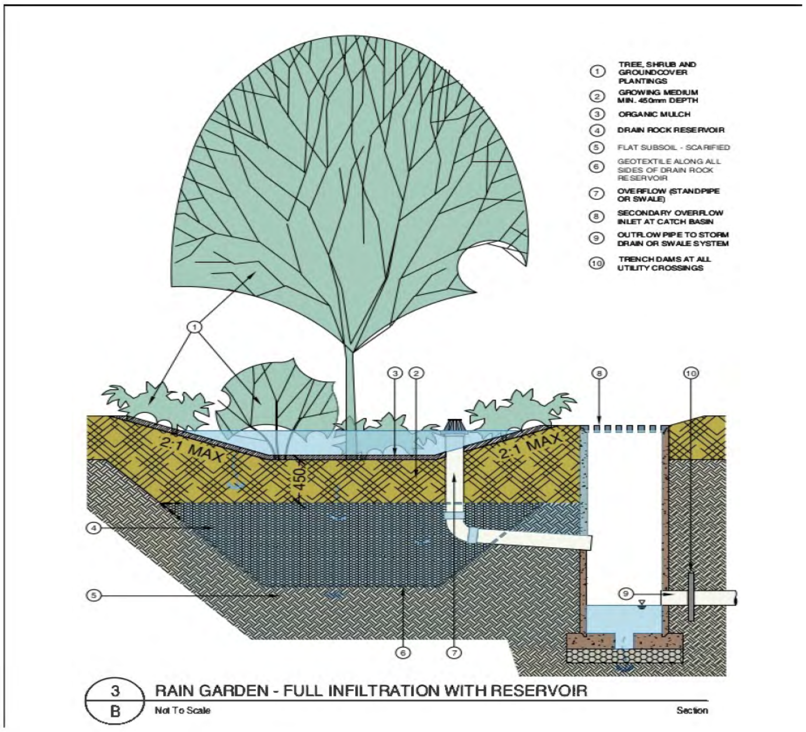


Figure 2.1: Rain Garden System with Under-drain (Metro Vancouver Regional District 2012)

This experiment had four treatments, 0, 0.5, 1.5 and 5% w/w, where 0% was a filtration column filled with 100% soil and 0.5, 1.5 and 5% were different biochar/soil ratio used as a filtration media in the column. The filtration experiments using Emenrgent and Cantimber Biochar had one replicate. The contaminants selected were lead (Pb), cadmium (Cd) and 16 priority PAHs, they are common contaminants in stormwater along with copper and zinc (US EPA, 1983).

The relevant range of pollutant concentrations was determined through a literature review as well as in terms of detection limits of instruments and dilution accuracy. A study preformed on the concentration of PAHs in urban stormwater from 2005-2008 in Madison, Wisconsin, showed that of 18 individual PAHs including 16 priority PAHs compounds for which samples were analyzed, 6 (acenaphthylene, dibenzo (A, H) (0.03 µg/L), anthracene (0.03 µg/L), fluorine (0.52 µg/L), 1-methylnaphthalene (0.06 µg/L), 2-methylnaphthalene (0.5 µg/L), and naphthalene (0.04 µg/L) were always below detection limits from all the source area (streets and strip mall) monitored. They were intermittently present in the samples from parking lots. On average, chrysene, fluoranthene, and pyrene were the dominant PAH compounds in all urban stormwater samples. Data was mainly derived from Tiefenthaler et al. 2001; Tiefenthaler et al.2003; Prestes et al. 2006 and Boni et al. 2020. The pollutant concentration was chosen to add to deionized water to prepare the synthetic stormwater for column treatment based on literature review, dilution accuracy and detection limit as most of the lower molecular weight PAHs is highly volatile (Table 2.2.).

Table 2.2: Composition of synthetic stormwater pollutants in a 30 L reservoir.

Stormwater Pollutants	Concentration (µg/L)
1 Acenapthene (ACE)	10
2 Acenaphthylene (ACY)	100
3 Anthracene (ANT)	10
4 Benz[a]anthracene (BaA)	10
5 Benzo[b]fluorathene (BbF)	10
6 Benzo[k]fluorathene (BkF)	10
7 Benzo[g,h]perylene (BghP)	10
8 Benzo[a]pyrene (BaP)	10
9 Chrysene (CHR)	10
10 Dibenz[a,h]anthracene (DahA)	10
11 Fluorathene (FLA)	10
12 Fluorene (FLU)	10
13 Indeno[1,2,3-cd]pryene (IcdP)	10
14 Napthalene (NAP)	50
15 Phenanthrene (PHE)	10

16 Pyrene	10
17 Lead (Pb)	30
18 Cadmium (Cd)	30

Comparison of pollutant removal efficiency by soil, 0.5, 1.5 and 5% w/w biochar was done by One-way ANOVA analysis in SPSS (IBM SPSS Statistics for Windows, version 24.0) software at 95% confidence interval (α=0.05).

2.3.6 List of Experiments

To test the error in case pollutants are adsorbed to the column, a blank experiment was performed where pollutants were mixed in 30 L of deionized water and passed through the empty column (Control 1) (Table 2.3) to see if plastic columns without media contribute to contaminant in the effluent. Another column packed with 100% soil and 5% biochar (Control 2) (Table 2.3) was fed with 30 L of tap water to see if the soil leaches any of the heavy metals and the PAHs. The control 2 experiment was done only for soil and 5% biochar because of limitation of pipes which was used to draw synthetic stormwater from the tank, water can be drawn only in the three columns used in an experiment running in parallel simultaneously i.e. columns with 0.5, 1.5 and 5% w/w biochar. The 5% w/w biochar showed minimum contaminant removal efficiency that is why decision was made to compare worst performing 5% w/w biochar with even worse soil. Water samples in all the three experiments were collected at every 20, 40 and 60 minutes (as shown by tracer analysis, section 2.3.9). The control 2 experiment for Cantimber Biochar could not complete because of time constrain. Each experiment from experiment 1 to experiment 4 had one replicate. The concentration of heavy metals was determined using Inductively Couple Plasma-Mass Spectrometry (ICP-MS) (EPA method 3111B). High Performance Liquid Chromatography (EPA 610) was used to define PAHs concentration

Table 2.3: List of Experiments

Experiments	Pollutants	Empty Columns	Control (Soil)	Emergent			Cantimber		
				0.5%	1.5%	5%	0.5%	1.5%	5%
Control 1	X	X							
Control 2			X			X			
Experiment 1	X			X	X	X			
Experiment 2	X		X			X			
Experiment3	X						X	X	X
Experiment4	X		X						X

* The concentration of influent in each of the experiment was different mainly for the PAHs because of inconsistencies in the mixing procedure.

2.3.7 Column Filtration Experiments

PVC pipes were used (90 cm length and 10.8 cm diameter) for the column treatment and only three of them were run in parallel for three different treatments of biochar at a time, different PVC were used for different experiments. They were filled with soil, sand and biochar depending on the treatments. Five centimeters of pea gravel was used at each end to improve drainage (Fig 2.2). The columns were flushed with tap water prior to start of filtration experiments. A 30 L tank was used as a synthetic stormwater reservoir. Stormwater was prepared by using 30 L of deionized water; 1.5 ml of Sigma-Aldrich PAHs diluted in 100 ml of methanol and 900 µg/L of lead and cadmium to achieve the required concentration mentioned in Table 2.1. The peristaltic pump was turned on for 20 minutes before experiment to mix the pollutants thoroughly in the water. Synthetic stormwater was directed using small tubes to each column (Fig 2.3).

During each filtration experiments, 30 L of synthetic stormwater was continuously discharged at a flow rate of 160 mL/min to the column and water sampling of influent and effluent was performed at every 20, 40 and 60 minutes. Influent and effluent sample for PAHs were collected in HPLC vials of 2 ml; whereas lead and cadmium was collected in a 50 ml centrifuge tubes at every 20, 40 and 60 minutes. The samples for PAHs were filled to the top to avoid volatilization and the samples for lead and cadmium were preserved by using nitric acid to a pH<2 (100 µg/L) after collection and stored in a refrigerator at 4˚ C. Samples were usually analyzed within five to seven days after collection. All treatments were conducted at room temperature and each treatment had one replicate.

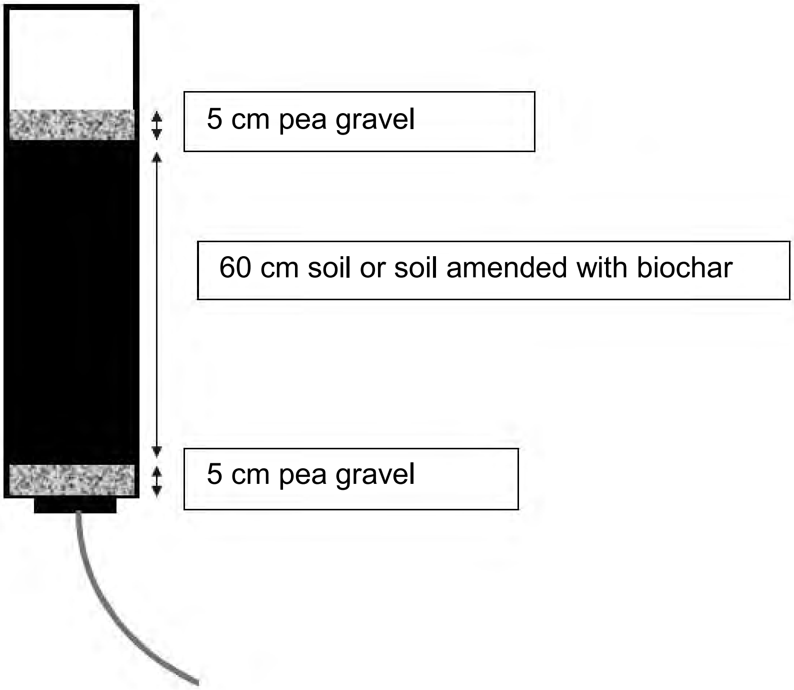


Figure 2.2: Filter Column

Figure 2.3: BCIT Civil Engineering lab filtration experiment set up.

2.3.8 Sample Analysis

The stormwater sample was digested for heavy metal analysis using a nitric acid digestion procedure as described by USEPA, Method 1640. In case of further analysis, water samples were preserved using nitric acid to a pH < 2 and stored at 4 C°. The concentration of heavy metals in water samples was determined by using Inductively Couple Plasma-Mass Spectrometry (ICP-MS) (EPA method 3111B) and to define the 16 priority PAHs concentration in water samples High Performance Liquid Chromatography was used (EPA method 610).

The concentration difference of pollutants in influent and effluent water samples was used to determine the removal capability of the adsorbent media.

2.3.9 Tracer Analysis

The tracer analysis of the experiment involved periodic sampling of the effluent and measuring the conductivity of solute. A tracer test on the soil and biochar media filter using NaCl solution was performed at room temperature of 20˚C to determine the the pore volume of soil and biochar filter. The solute was prepared by mixing NaCl with water. The columns were packed with 100% soil, 0.5% and 5% w/w biochar and before passing the solute through the columns, water was used first to wet the soil mixture and water was flowed through continuously to establish a steady flow rate. Once the steady flow rate was determined, water level was restored to 30 L and NaCl was mixed into the water tank and the conductivity of water was measured using YSI meter as 9,870 µS/cm. Samples were collected every five minutes and data was recorded for 75 minutes. Results were plotted in real- time to ensure conductivities tapered off, which indicates that most of the tracer concentration has passed through the column. The result showed that the conductivity of the water changed after 20 minutes and the conductivity was recovered around 60 minutes, which indicated a pore volume of 9.6 L for these filters.

2.3.10 Sample Collection

Tracer analysis showed that the conductivity of water changed after 20 minutes, which means that the solute takes 20 minutes to come out from the column. Based on this, the influents were sampled at 20 minutes i.e. the time when peristaltic pump starts feeding the synthetic stormwater to the columns and the influents were sampled at the time interval of 20, 40 and 60 minutes. The effluents were samples after 20 minutes, i.e. 20 minutes after the peristaltic pump started feeding the water to the column as the influent which was sampled at the time peristaltic pumps started feeding the water to the columns takes 20 minutes to come out from the column and the effluent was sampled at 20, 40 and 60 minutes time interval.

2.3.11 Flow Rate

Flow rate of the soil and biochar filter were calculated based on graduated cylinder filled in one minute at the beginning of the treatment when there was maximum pressure head in the filter (7.5 cm) and it was constant throughout the experiment. For this experiment the total flow rate was 160 ml/min to all the three columns operating simultaneously. The peristaltic pump with flow rate of 160 mL/min resulted in maintaining a constant level of water on the columns (inflow=outflow). The tracer analysis showed that the experiment could last for one hour with a total flow rate of 160 mL/min during which a 30 L tank can deliver water to three filters simultaneously (53 mL/min per filter) with infiltration rate of 349 mm/hr in each column which is under the guidelines of City of Vancouver.

2.3.12 Statistical Analysis

Concentration difference of pollutants in influent and effluent water samples was used as the indicator of the removal capacity of the adsorbent media. The removal efficiency for each treatment was determined by means of the following equation:

$$RE = \frac{MLR_{influent} - MLR_{effluent}}{ML_{influent}} * 100 \qquad \text{Equation (1)}$$

Mass Loading Rate (MLR) of influent and effluent by calculated by following equation:

$$MLR\ (mg/min) = V_{flow}\ (L/min) * \text{Concentration}\ (mg/L)$$

Where,

RE = the removal efficiency in Percent,

MLR = Mass Loading Rate

$MLR_{\mathbf{\underline{influent}}}$ = Mass Loading Rate of influent,

$MLR_{\mathbf{\underline{effluent}}}$ = Mass Loading Rate of effluent.

V_{flow} = Volumetric Flow

The tracer analysis showed that the conductivity of the water changed after 20 minutes and it was recovered around 60 minutes. Based on this the influent concentration in the tank was sampled at the intervals of 20, 40 and 60 minutes. The effluent was also sampled at the time interval of 20, 40 and 60 minutes. In the removal efficiency calculation the influent and effluent concentration at every 20, 40 and 60 minutes were used.

One-way ANOVA was performed in SPSS (IBM SPSS Statistics for Windows, version 24.0) software at 95% confidence ($\alpha=0.05$).

3. Results

3.1 Tracer Analysis

As shown in the graphs of tracer analysis, conductivity recovery (i.e. steady part of the graphs) for all the adsorbent media (soil, 0.5% and 5% w/w biochar) occurred around 60 minutes for all these filters (Fig. 3.1 to 3.3). Based on this, the influent and effluents were collected at every 20 (marked as change in conductivity), 40 minutes (sampling time after change in conductivity and before conductivity recovery and 60 minutes (marked as conductivity recovered). Influents were also collected at these time interval to observe any change in concentration as each of them has different molecular weight and solubility in water.

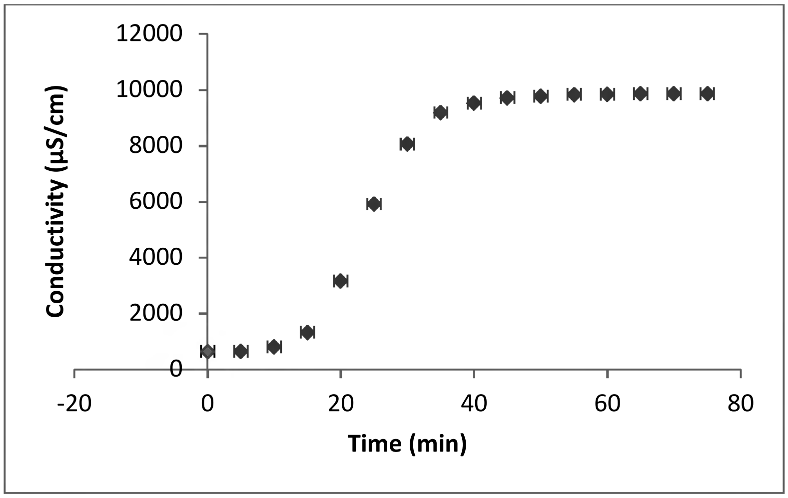


Figure 3.1: Tracer analysis result for soil.

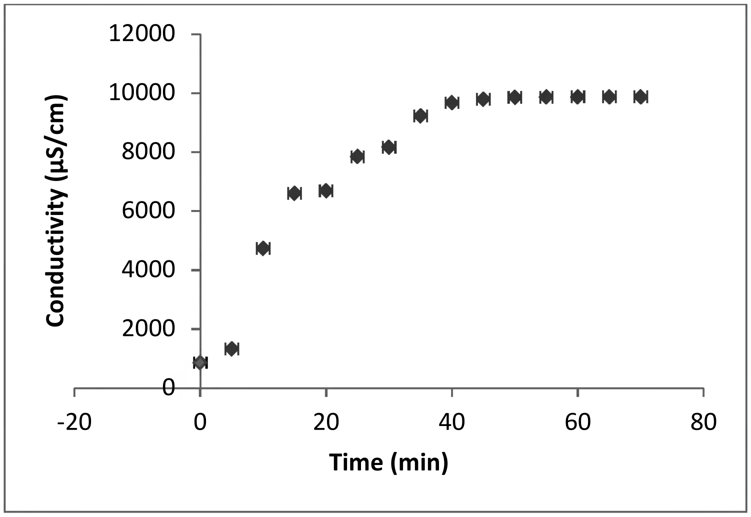


Figure 3.2: Tracer Analysis results for 0.5% Biochar

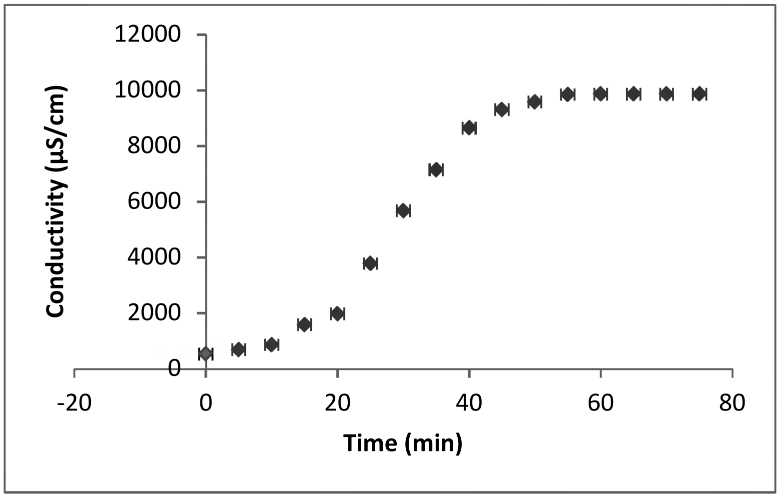


Figure 3.3: Tracer Analysis for 5% biochar.

3.2 Control Experiments

Based on the results from control 1 experiment conducted from the list of experiments (Table 2.3), it can be concluded that change in the influent concentration at time 40 and 60 minutes (for PAHs) and 20, 40 and 60 minutes (for Cd and Pb) did not vary a lot over time (Table 3.1 to Table 3.3). The samples of influent and effluent concentration were collected at time interval of 20, 40 and 60 minutes. The samples collected at 20 minutes could not be analyzed for the PAHs because there was large shift in retention time. The retention time is the primary means of chromatographic peak identification and the shifts indicates leaks, pump malfunction and changes in column temperature. In this case there was change in the column temperature because of which the samples collected at 20 minutes could not be analyzed.

The effluent concentration (Table 3.4 and 3.5) from the blank column (Control 1) is variable for all the PAHs (more for the lower molecular weight PAHs) at time 40 minutes in comparison to the influent. The reason for this could be their water solubility and volatile nature and error caused by the PVC pipe (pollutants might get adsorbed onto the pipes). The high molecular weight PAHs are more stable in comparison to the lower molecular weight PAHs as they are hydrophobic in nature because of the presence of 4-6 benzene rings. The percent difference between influent and effluent concentration of the PAHs from blank columns at 40 and 60 minutes are presented in Table 3.4 and 3.5.

Over time change in the influent concentration for Pb and Cd was not very high (Table 3.3) and the effluent concentration of Pb and Cd from blank column at 20, 40 and 60 minute interval did not vary over the time (Figure 3.4).

In the other control experiment (Control experiment 2) with 100% soil and 5% biochar, none of the samples and none of the analytes gave a measurable concentration in the analysis. Lead was found in the soil but the concentration was too low (0.01-0.03 μg/L) to say that there was Pb present in the samples.

Table 3.1: **Comparison between theoretical and actual value of lower molecular weight PAHs in the influent at 40 and 60 minutes**

Lower Molecular Weight PAHs	Theoretical Conc. (µg/L) in 30 L	Actual Conc (µg/L)	
		40	60
1. Naphthalene (NAP)	50	29.70	28.81
2. Acenaphthylene (ACY)	100	60.80	59.60
3. Acenaphthene (ACE)	10	6.06	5.84
4. Fluorene (FLU)	10	6.28	5.76
5. Phenanthrene (PHE)	10	3.13	3.03
6. Anthracene (ANT)	10	2.91	2.95

*Influent concentration at 20 minutes could not be analyzed for lower molecular weight PAHs

Table 3.2: **Comparison between theoretical and actual value of higher molecular weight PAHs in the influent.**

Higher/ Molecular Weight PAHs	Theoretical Conc. (µg/L) in 30 L	Actual Conc (µg/L)	
		40	60
1. Fluorathene (FLA)	10	6.52	6.55
2. Pyrene (PYR)	10	3.35	3.47
3. Benz[a]Anthracene (BaA)	10	5.12	5.04
4. Chrysene (CHR)	10	5.33	5.44
5. Benzo[b]Fluorathene (BbF)	10	11.15	11.55
6. Benzo[k] fluorathene (BkF)	10	5.82	6.06
7. Benzo[a]Pyrene (BaP)	10	5.65	5.50
8. Dibenz[a,h]Anthracene (DahA)	10	5.50	5.44
		10.20	9.72

9. Benzo[g,h,i]Perylene	10	NA	7.41
10. Indeno[1,2,3-cd]Pyrene (IcdP)	10		

*Influent concentration at 20 minutes could not be analyzed for higherr molecular weight PAHs

Table 3.3: Comparison between theoretical and actual value of Cd and Pb in the influent at 20, 40 and 60 minutes

Heavy Metals		**Theoretical Conc. (µg/L) in 30 L**	**Actual Conc (µg/L)**		
			20	**40**	**60**
1.	Cadmium (Cd)	30.0	30.78	30.81	30.54
2.	Lead (Pb)	30.0	30.01	30.13	30.65

Table 3.4: Percent (%) Difference between Influent and Effluent Concentration for Lower Molecular Weight PAHs (at time 40 and 60 minutes (Control 1- empty column with no filtration media)

Lower Molecular Weight PAHs	Influent Conc.(µg/L)		Effluent Conc.(µg/L)		% Difference Between Influent and Effluent	
	40	60	40	60	40	60
1. Naphthalene (NAP)	29.70	28.81	25.41	26.55	14.44	7.84
2. Acenaphthylene (ACY)	60.80	59.60	48.10	42.51	20.88	28.67
3. Acenaphthene (ACE)	6.06	5.84	5.39	4.92	11.0 5	15.75
4. Fluorene (FLU)	6.28	5.76	5.28	4.82	15.92	16.31
5. Phenanthrene (PHE)	3.13	3.03	2.59	2.40	17.25	20.79
6. Anthracene (ANT)	2.91	2.95	2.45	2.33	15.80	21 .01

Table 3.5 Percent (%) Difference between Influent and Effluent Concentration for Higher Molecular Weight PAHs at time 40 and 60 minutes (Control 1- empty column with no filtration media)

Higher Molecular Weight PAHs	Influent Conc.(µg/L)		Effluent Conc.(µg/L)		% Difference	
	40	60	40	60	40	60
1. Fluorathene (FLA)	6.52	6.55	5.22	5.19	19.99	20.76
2. Pyrene (PYR)	3.35	3.47	2.82	3.15	15.82	9.22
3. Benz[a]Anthracene (BaA)	5.12	5.04	4.88	4.43	4.68	14.08
4. Chrysene (CHR)	5.33	5.44	4.91	4.41	7.87	18.93
5. Benzo[b]Fluorathene (BbF)	11.15	11.55	8.91	9.2 2	20.08	20.17
6. Benzo[k] fluorathene (BkF)	5.82	6.06	5.51	5.33	5.32	12.04
7. Benzo[a]Pyrene (BaP)	5.65	5.50	5.50	4.91	2.65	10.72
8. Dibenz[a,h]Anthracene (DahA)	5.50	5.44	5.28	5.12	4.00	5.88
9. Benzo[g,h,i]Perylene (BghiP)	10.20	9.72	8.93	8.49	12.45	12.65
10. Indeno[1,2,3-cd]Pyrene (IcdP)	NA	7.41	NA	6.92	NA	6.66

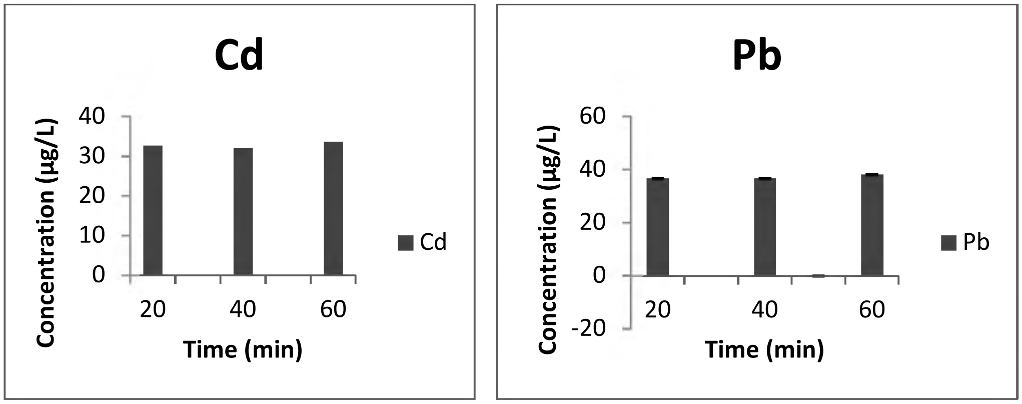


Figure 3.4: Effluent Concentration of lead and cadmium at 20, 40 and 60 minutes from blank column (Control 1- empty column with no filtration media).

3.3 Contaminant Removal Efficiency of Emergent Biochar

One-way ANOVA was conducted to compare the removal efficiency of soil (0%) and 0.5, 1.5 and 5% w/w Emergent Biochar for the sample collected at 60 minutes as all the contaminants had chance to pass through the column as showed by the tracer test and the standard deviation was calculated based on normal distribution. The result revealed that the peak was not detected in the analysis using HPLC for lower molecular weight PAHs in soil and 0.5, 1.5 and 5% w/w biochar except for acenaphthylene (ACY). The peak was detected for all the higher molecular weight PAHs except for fluoranthene (FLA) and that means the concentration of FLA was <0.001 µg/L.

The samples from 0.5, 1.5 and 5% w/w were collected at 20, 40 and 60 minutes and change in removal efficiencies were observed, however the change in removal efficiencies were not significant (Table 3.6 to Table 3.8)

3.3.1 Lower Molecular Weight Removal Efficiency Of Emergent Biochar

The result revealed that the peak was not detected in the analysis using HPLC for lower molecular weight PAHs in soil and 0.5, 1.5 and 5% w/w biochar except for ACY. In the case of other lower molecular weight PAHs such as NAP, ACN, FLU, PHN and ATN the peak was not detected in the analysis. They were present in the effluent samples but the concentration was less than 0.001µg/ L. For PAHs it is very impossible to come up with a hard and fast detection limit as all the 16 PAHs are treated differently and it would vary from day to day as is normal.

3.3.2 Acenaphthylene (ACY) Removal

The result revealed that there was no significant difference between the removal efficiency of soil and 0.5, 1.5 and 5 w/w Emergent Biochar ($F_3 = 4.03$, p = 0.051) (Table A1 in appendix A.) The result suggested that ACY removal was high for soil (Mean= 100%, SD= 0), as compared to 0.5 (Mean = 96.7, SD= 0.84), 1.5 (Mean= 96.8%, SD= 0.98) and 5% w/w (Mean= 96.4%, SD= 0.14) (Figure 3.5)

3.3.3 Benzo[a]Anthrecene (BaA) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 386.85, p = <0.001) among the treatments (Table A2, Appendix A). The result suggested that BaA removal was significantly high for 0.5 (Mean= 89.5%, SD= 4), 1.5 (Mean= 89.9 %, SD= 4.5) and 5% w/w (Mean= 89.9%, SD= 8.3) Emergent Biochar compared to soil (Mean= 79.5%, SD= 3.0) (Figure 3.8)

3.3.4 Chrysene (CHR)Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 40.48, p = <0.001) among the treatments (Table A3, Appendix A). The result suggested that CHR removal was significantly high for 0.5 (Mean= 88.3%, SD= 2.3), 1.5 (Mean= 88.3%, SD= 2.3) and 5% w/w (Mean= 88.3%, SD= 7.4) Emergent Biochar compared to soil (Mean= 68.16%, SD= 3.5) (Figure 3.7)

3.3.5 Benzo[b]Fluoranthene (BbF) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 1947, p = <0.001) among the treatments (Table A4, Appendix A)). The result suggested that BbF removal was significantly high for 0.5 (Mean= 91.4%, SD= 1.9), 1.5 (Mean= 91.8%, SD= 5.5) and 5% w/w (Mean= 91.5%, SD= 7.4) Emergent Biochar compared to soil (Mean= 62.6%, SD= 1.1) (Figure 3.9)

3.3.6 Benzo[k]Fluoranthene (BkF) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 110.77, p = <0.001) among the treatments (Table A5, Appendix A). The result suggested that BkF removal was significantly high for 0.5 (Mean= 87.3%, SD= 4), 1.5 (Mean= 84.4%, SD= 2.4) and 5% w/w (Mean= 82.7%, SD= 4.8) Emergent Biochar compared to soil (Mean= 64.86%, SD= 0.28) (Figure 3.10)

3.3.7 Benzo[a]Pyrene (BaP) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 210.49, p = <0.001) among the treatments (Table A6, Appendix A). The result suggested that BaP removal was significantly high for 0.5 (Mean87.1%, SD= 4.17), 1.5 (Mean= 90.2%, SD= 1.4) and 5% w/w (Mean= 83.5%, SD= 4.17) Emergent Biochar as compared to soil (Mean= 55%, SD= 2.8) (Figure 3.11)

3.3.8 Dibenzo[a,h]Anthracene (DahA) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 9.59, p = 0.005) among the treatments (Table A7, Appendix A). The result suggested that DahA removal was significantly high for 0.5 (Mean= 73.9%, SD= 2.1), 1.5 (Mean= 71.1%, SD= 0.7) and 5% w/w (Mean= 72%, SD= 2) Emergent Biochar as compared to soil (Mean = 60, SD=3) (Figure 3.12)

3.3.9 Benzo[g,h,i]Perylene (Bghip) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 221.20, p = <0.001) among the treatments (Table A8, Appendix A). The result suggested that BghiP removal was significantly high for 0.5 (Mean= 84.4%, SD= 6), 1.5 (Mean= 87.2%, SD= 0.4) and 5% w/w (Mean= 87%, SD= 2.8) Emergent Biochar compared to soil (Mean= 45% SD= 2.1) (Figure 3.13)

3.3.10 Indeno[1,2,3-cd]Pyrene (IcdP) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 58.29, p = <0.001) among the treatments (A9, Appendix A). The result suggested that IcdP removal was significantly high for 0.5 (Mean= 90.3, SD= 5.1), 1.5 (Mean= 88.4%, SD= 4) and 5% w/w (Mean= 87.4%, SD= 3.6) Emergent Biochar compared to soil (Mean= 46% SD= 1.41) (Figure 3.14)

3.3.11 Cadmium Removal

Cadmium removal was 100% from soil and 0.5, 1.5 and 5% w/w Biochar (Figure 3.15).

3.3.12 Lead Removal

There was no significant difference between removal efficiency among the treatments, soil removed 99.7% (SD= 0.35), 0.5 removed 99% (SD=0.35), 1.5 removed 99% (SD=0.07) and 5% w/e removed 99% (SD=0.21) (Figure 3.16)

3.4 Contaminant Removal Efficiency of Cantimber biochar

One-way ANOVA was conducted to compare the removal efficiency of soil and 0.5, 1.5 and 5% w/w Cantimber Biochar for the sample collected at 60 minutes as all the contaminants had chance to pass through the column as showed by the tracer test and the standard deviation was calculated based on normal distribution. The result revealed that the peak was not detected in the analysis using HPLC for lower molecular weight PAHs in soil and 0.5, 1.5 and 5% biochar except for naphthalene (NAP) acenaphthylene (ACY). The peak was detected for all the higher molecular weight PAHs except fluoranthene (FLA). The data was not available for Benzo[a]Anthracene (BaA).

The samples from 0.5, 1.5 and 5% w/w were collected at 20, 40 and 60 minutes and change in removal efficiencies were observed, however the change in removal efficiencies were not significant (Table 3.6 – Table 3.8)

3.4.1 Naphthalene (NAP) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 25.89, p = <0.001) among the treatments (Table B1, Appendix B). The result suggested that NAP removal was significantly high for soil (Mean= 100, SD= 0) as compared to 0.5% (Mean= 96.9, SD= 1.3), 1.5 (Mean= 97%, SD= 1.5) and 5% w/w (Mean= 97.1%, SD= 1.7) Cantimber Biochar (Figure 3.5)

3.4.2 Acenaphthylene (ACY) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level .There was a significant difference between removal efficiency (F_3 = 400.93, p = <0.001) among the treatments (Table B2, Appendix B). The result suggested that ACY removal was significantly high for soil (Mean= 100%, SD= 0) as compared to 0.5% (Mean= 89, SD= 0.8), 1.5 (Mean= 88.1%, SD= 4) and 5% w/w (Mean= 87.9% SD= 4) Cantimber Biochar (Figure 3.6)

3.4.3 Chrysene (CHR) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 192.53, p = <0.001) among the treatments (Table B4, Appendix B). The result suggested that CHR removal was significantly high for 0.5, 1.5 and 5% w/w (Mean= 100%, SD= 0) Cantimber Biochar as compared to soil (Mean= 78.9%, SD= 2.1) (Figure 3.7)

3.4.4 Benzo[b]Fluorathene (BbF) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 1261.07, p = <0.001) among the treatments (Table B5, Appendix B). The result suggested that BbF removal was significantly high for 0.5 (Mean= 97.5%, SD = 0.56), 1.5 (Mean= 98%, SD= 0.77) and 5% w/w (Mean= 98%, SD= 0.77) Cantimber Biochar as compared to soil (Mean= 71.5%, SD= 2.1) (Figure 3.8)

3.4.5 Benzo[k]Fluorathene (BkF) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 1600, p = <0.001) among the treatments (Table B6, Appendix B). The result suggested that BkF removal was significantly high for 0.5, 1.5 and 5% w/w (Mean = 100, SD = 0) Cantimber Biochar as compared to soil (Mean= 62.8%, SD= 1.4) (Figure 3.10)

3.4.6 Benzo[a]Pyrene (BaP) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 2209, p = <0.001) among the treatments (Table B7, Appendix B). The result suggested that BaP removal was significantly high for 0.5, 1.5 and 5% w/w (Mean = 100, SD = 0) Cantimber Biochar as compared to soil (Mean= 65%, SD= 1.4) (Figure 3.11)

3.4.7 Dibenz[a,h]Anthracene (DahA) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 5929, p = <0.001) among the treatments (Table B8, Appendix B).. The result suggested that DahA removal was significantly high for 0.5, 1.5 and 5% w/w (Mean = 100, SD = 0) Cantimber Biochar as compared to soil (Mean= 64.5%, SD= 0.7) (Figure 3.12)

3.4.8 Benzo[g,h]Perylene (BghiP) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 605.49, p = <0.001) among the treatments (Table B9, Appendix B). The result suggested that BghiP removal was significantly high for 0.5 (Mean= 91%, SD=1.5), 1.5 (Mean= 91.3%, SD= 2.4) and 5% w/w (Mean= 89.9%, SD= 3.4) Cantimber Biochar as compared to soil (Mean= 41.5%, SD= 2.1) (Figure 3.13)

3.4.9 Indeno[1,2,3-cd]Pyrene (IcdP) Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 81.95, p = <0.001) among the treatments (Table B10, Appendix B). The result suggested that IcdP removal was significantly high for 0.5 (Mean= 81.6 %, SD= 1.2, 1.5 (Mean= 79%, SD= 4.5) and 5% w/w (Mean= 76.9%, SD= 2.7) Cantimber Biochar as compared to soil (Mean= 44%, SD= 2.8) (Figure 3.14)

3.4.10 Cadmium Removal

Cadmium removal was 100% from soil and 0.5, 1.5 and 5% w/w Biochar (Figure 3.15)

3.4.11 Lead Removal

The result revealed that the effects were statistically significant at the 0.05 significance level. There was a significant difference between removal efficiency (F_3 = 5.57, p = 0.015) among the treatments (Table B11, Appendix B). The result suggested that Pb removal was significantly high for soil (Mean= 99.5%, SD= 0.77) as compared to 0.5% (Mean= 94.5%, SD= 0.4), 1.5% (Mean= 92 %, SD= 0.7) and 5% w/w (Mean= 90%, SD = 2.82) Cantimber Biochar (Figure 3.16)

3.5 Removal Efficiencies of Lower Molecular Weight PAHs

The removal efficiencies of both Emergent and Cantimber Biochar for lower molecular weight PAHs for which peaks were detected in the analysis are presented in the following graphs. The following graphs are for the sample collected at 60 minutes as all the contaminants had chance to pass through the column as showed by the tracer test and the standard deviations were calculated based on normal distribution.

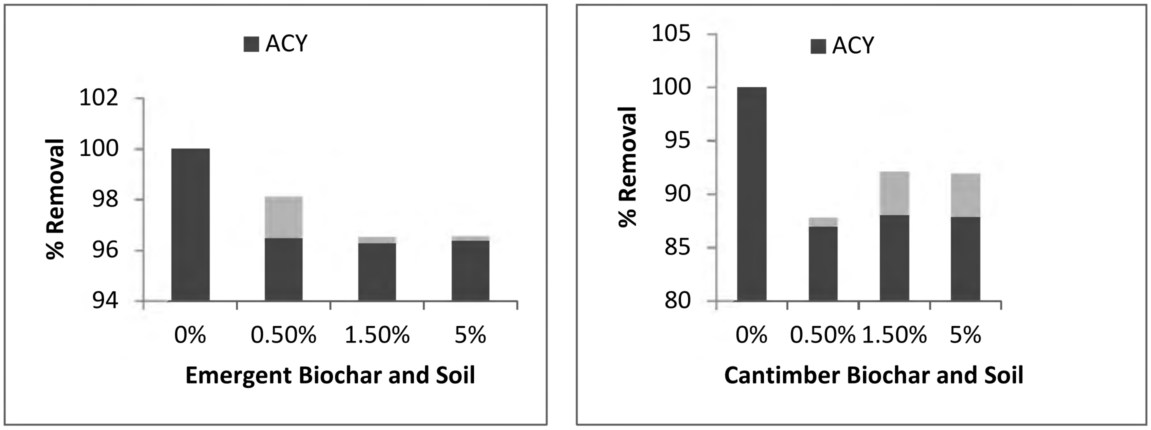
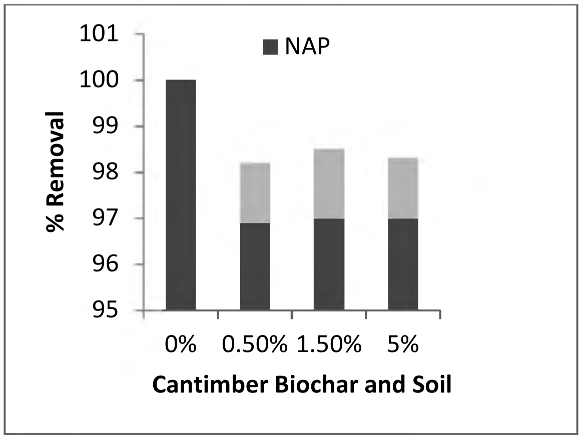


Figure 3.5: Percent removal of ACY using Emenrgent and Cantimber Biochar at 60 minutes. The stacked bar represents deviation based on replicate.



. Figure 3.6: Percent removal of NAP using Cantimber Biochar at 60 minutes. The stacked bar represents deviation based on replicate.

3.6 Removal Efficiencies of Higher Molecular Weight PAHs

During the analysis of higher molecular weight PAHs, peaks were detected for every PAHs except for fluoranthene. The removal efficiencies of both Emergent and Cantimber Biochar for higher molecular weight PAHs for which peaks were detected in the analysis are presented in the following graphs. The following graphs are for the sample collected at 60 minutes as all the contaminants had chance to pass through the column as showed by the tracer test and the standard deviations were calculated based on normal distribution. Benzo[a]Anthracene (BaA) could not be analyzed in the analysis of Cantimber Biochar.

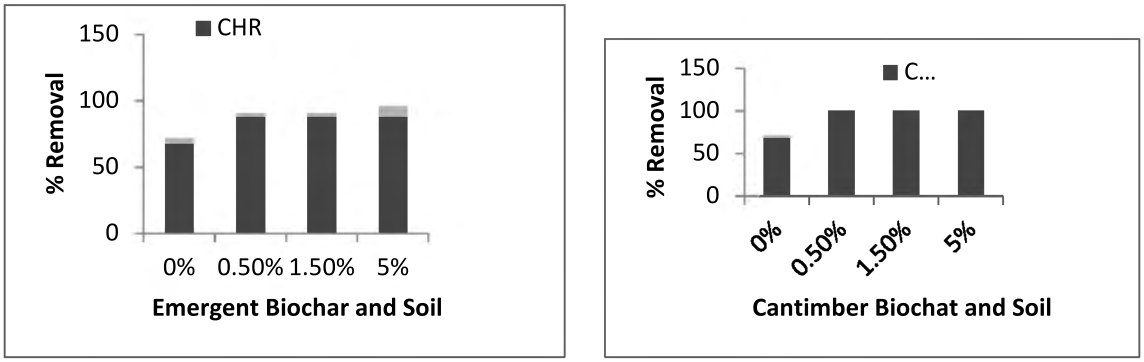


Figure 3.7: Percent removal of CHR using Emergent and Cantimber Biochar at 60 minutes. The stacked bar is representative of deviation based on replicate.

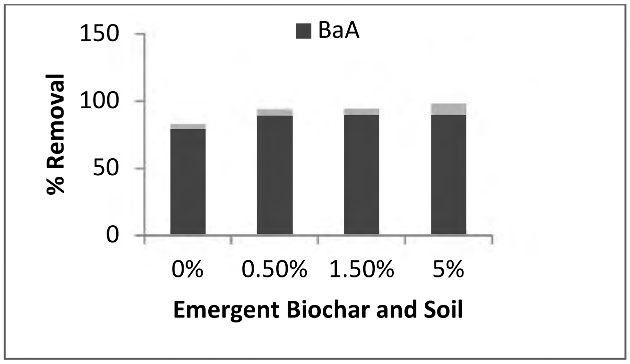


Figure 3.8: Percent removal of BaA using Emergent Biochar at 60 minutes. The stacked bar is representative of deviation based on replicate.

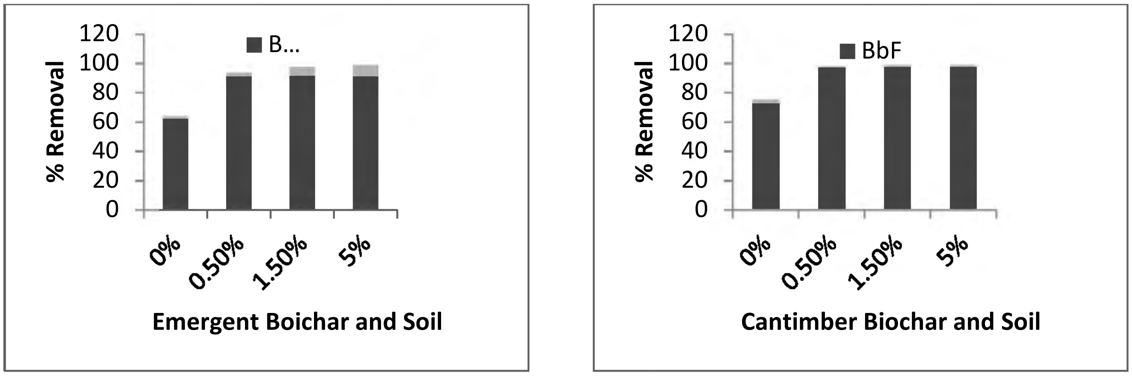


Figure 3.9: Percent removal of BbF using Emergent and Cantimber Biochar at 60 minutes. The stacked bar is representative of deviation based on replicate.

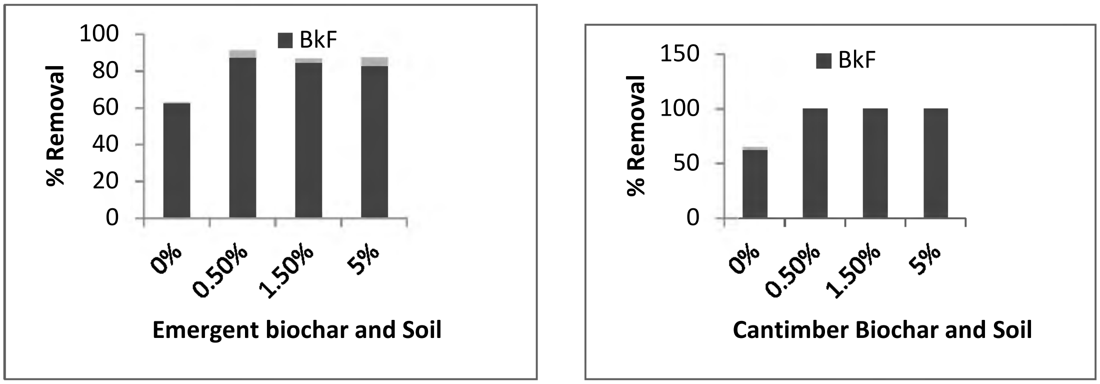


Figure 3.10: Percent removal of BkF using Emergent and Cantimber Biochar at 60 minutes. The stacked bar is representative of deviation based on replicate.

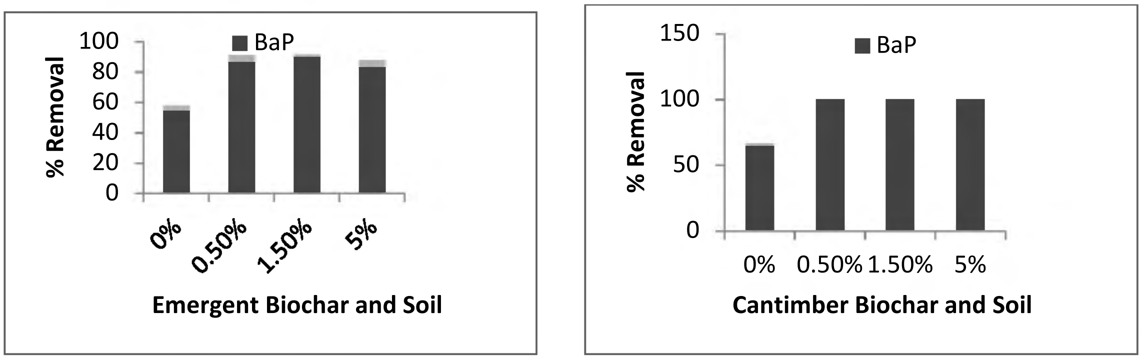


Figure 3.11: Percent removal of BaP using Emergent and Cantimber Biochar at 60 minutes. The stacked bar is representative of deviation based on replicate

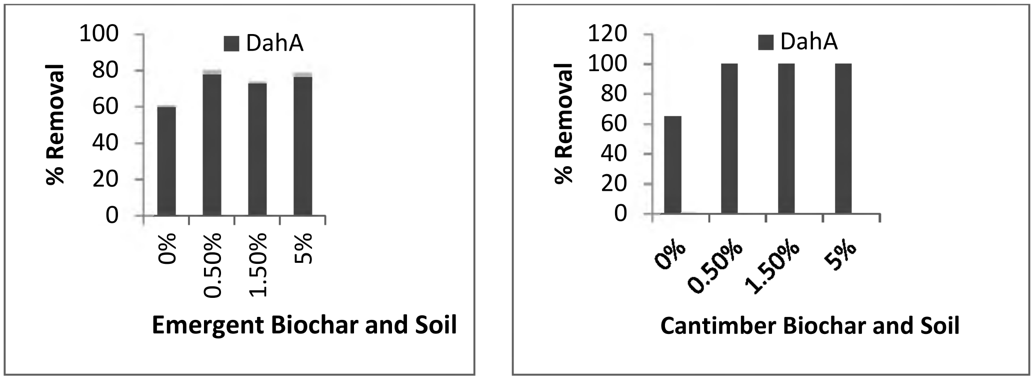


Figure 3.12: Percent removal of DahA using Emergent and Cantimber Biochar at 60 minutes. The stacked bar is representative of deviation based on replicate

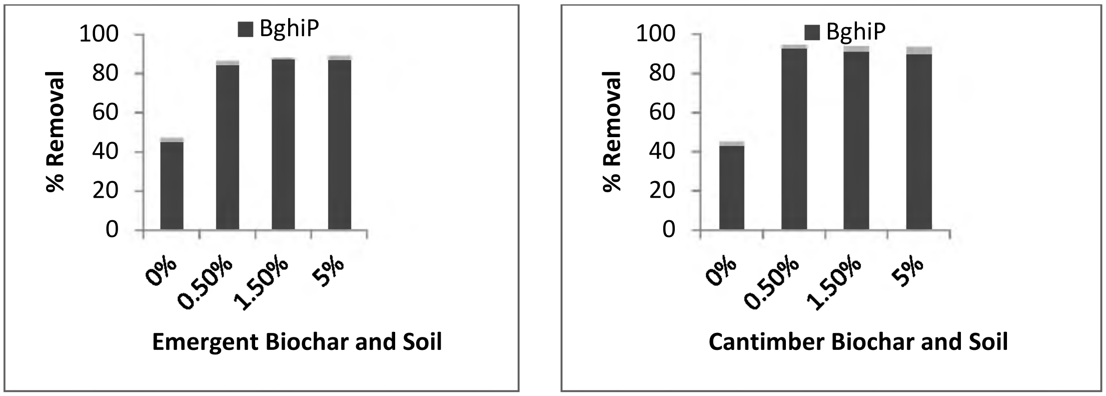


Figure 3.13: Percent removal of BghiP using Emergent and Cantimber Biochar at 60 minutes. The stacked bar is representative of deviation based on replicate

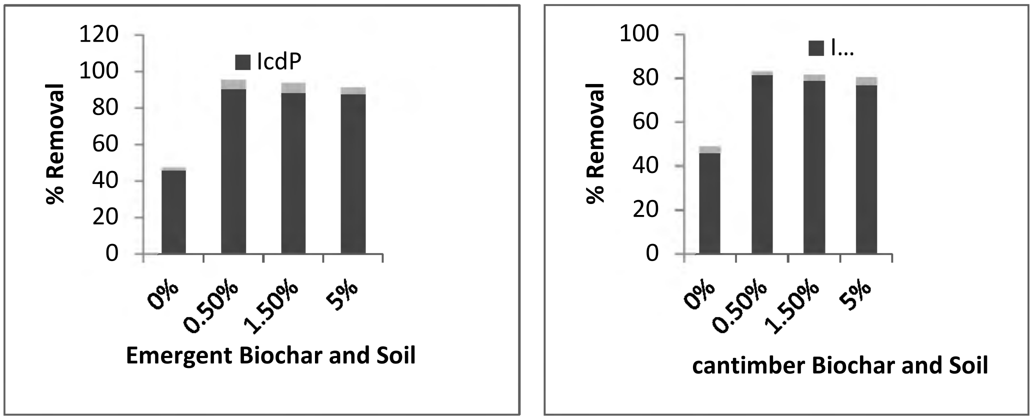


Figure 3.14: Percent removal of IcdP using Emergent and Cantimber Biochar at 60 minutes. The stacked bar is representative of deviation based on replicate.

3.7 Removal Efficiencies of Cd and Pb

The removal efficiencies of both Emergent and Cantimber Biochar for Cd and Pb are presented in the following graphs. Cadmium removal was 100% for all the filtration media (Figure 3.17). The following graphs are for the sample collected at 60 minutes as all the contaminants had chance to pass through the column as showed by the tracer test and the standard deviations were calculated based on normal distribution.

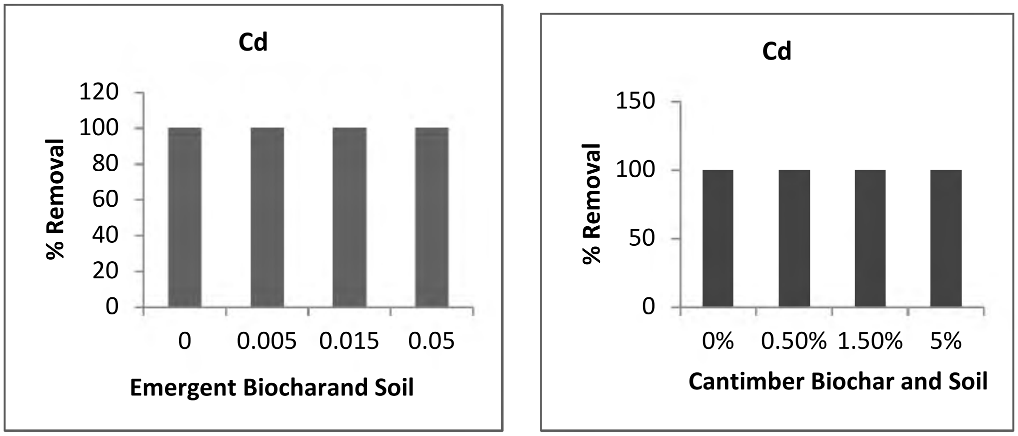


Figure 3.15: Percent removal of Cd using Emergent and Cantimber Biochar at 60 minutes

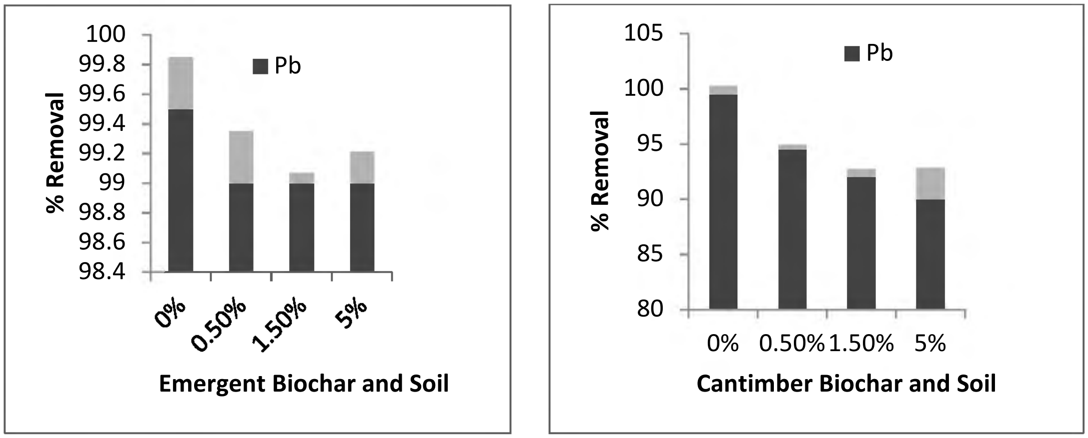


Figure 3.16 Percent removal of Pb using Emergent and Cantimber Biochar at 60 minutes. The stacked bar is representative of deviation based on replicate.

Table 3.6: **Removal efficiency (%) of filtration media for lower molecular weight PAHs at time 20, 40 and 60 minutes**

PAHs	Soil	Time (min)	Emergent Biochar			Cantimber Biochar		
			0.5%	1.5%	5%	0.5%	1.5%	5%
NAP	100	20	100	100	100	97.4	97.6	97.6
		40	100	100	100	97.8	97.5	97.5
		60	100	100	100	96.9	97	97.1
ACY	100	20	97.2	96.7	96.5	90.7	90.3	89.7
		40	97.1	96.6	95.8	89.1	90	89.8
		60	96	96.3	96.4	89	88.1	87.9

Table 3.7: Removal efficiency (%) of filtration media for highermolecular weight PAHs at time 20, 40 and 60 minutes

PAHs	Soil	Time (min)	Emergent Biochar			Cantimber Biochar		
			0.5%	1.5%	5%	0.5%	1.5%	5%
CHR	69-71	20	96.2	94.5	88.3	100	100	100
		40	92.9	92.2	89.15	100	100	100
		60	88.3	88.3	88.3	100	100	100
BaA	79- 88	20	96.5	96.2	92.9	NA	NA	NA
		40	94.8	95.3	93.	NA	NA	NA
		60	89.5	89.9	89.9	NA	NA	NA
BbF	68-72	20.	93.1	92.7	89.4	98	98	98
		40	92	92	88.8	98	98	98
		60	91.4	91.8	91.1	97.5	98	98

BkF	65-70	20	96.5	94	87.4	97	93	94
		40	92.4	88.9	87.8	100	100	100
		60	87.3	84.4	827	100	100	100
BaP	58-69	20	96.5	93.9	87.2	100	100	100
		40	92.1	90.6	90.5	100	100	100
		60	87.1	90.2	83.5	100	100	100
DahA	60-63	20.	93.6	83	75.3	100	100	100
		40	88.4	79.7	74.1	100	100	100
		60	73.9	71.1	72	100	100	100
BghiP	45-50	20	89.9	86.2	81.5	98.1	98.9	98.7
		40	94	87.2	86.5	97.9	98.7	99.1
		60	84.4	87.2	87	92.9	91.3	89.9

IcdP	45-50	20	93	91.7	87.5	94.9	87.1	85.5
		40	91.3	87.8	90.7	85.5	83.1	83.5
		60	90.3	88.45	87.45	81.6	79	79

* For Acenaphthene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Pyrene (PYR) and Fluoranthene (FLR) peak was not detection in the analysis.

Table 3.8: Removal efficiency (%) of filtration media for Pb and Cd at time 20, 40 and 60 minutes

PAHs	**Soil**	**Time (min)**	**Emergent Biochar**			**Cantimber Biochar**		
			0.5%	**1.5%**	**5%**	**0.5%**	**1.5%**	**5%**
Cd	100	20	100	100	100	100	100	100
		40	100	100	100	100	100	100
		60	100	100	100	100	100	100
Pb	99.5	20	99	98.7	98.4	92.7	92.6	82
		40	98.7	99	98.3	94.6	92.6	88.3
		60	99	99	99	94.5	92	90

4. Discussion

4.1. Column Treatment

The result showed that the lower molecular (mainly NAP), Pb and Cd removal ability of soil was 99-100% (Table 3.6 and Table 3.8). Literature showed that laboratory column studies conducted on heavy metals using soil as a filtration media, including Pd and Cd, Cd removal rates was up to 95% or higher (Sun and Davis, 2007). The Pb removal rates was 62% to more than 99% (Hsieh and Davis, 2005), greater than 98% (Davis et al., 2001) and 95% to 97% (Sun and Davis, 2007). Two different laboratory studies reported more than 90% NAP removal (Hong et al., 2006; LeFevre et al., 2015).

Biochar has been indicated to perform as an efficient sorbent for a broad range of contaminants including heavy metals and organic chemicals due to its enormous surface area and special structure. In terms of heavy metal remediation, many reports provided data on the removal ability of different biochar up to 100 % removal of various heavy metals from aqueous solutions and soils (Beesley and Marmiroli 2011; Karami et al., 2011; Mendez et al., 2011; Jiang et al., 2012). Also large number of studies indicated biochar's significant ability in organic pollutants remediation (Zheng et al., 2010; Xu et al., 2011; Kong et al., 2011). The commercial biochars (Emergent and Cantimber) used in this study varied in heavy metal removal ability (Table 3.6). The results showed that the soil itself can remove Pb and Cd effectively. The Pb removal ability of soil and Emergent Biochar was almost same and it was better than the Cantimber Biochar (Table 3.8); the removal ability of 0.5 % w/w Emergent and Cantimber Biochar amended in soil was more than the 1.5 and 5% w/w; however there was no significant difference between the removal efficiency of 0.5, 1.5 and 5% w/w Emergent and Cantimber Biochar (Table 3.8). Cd removal was 100 % for all the filtration media (Table 3.8)

The 16 PAHs used in the study were the lower molecular weight PAHs and higher molecular PAHs. The removal efficiency of all filtration was different for the lower molecular weight PAHs (Table 3.6). The NAP removal efficiency followed the order of soil = Emergent Biochar > Cantimber Biochar. The NAP removal was 100% for soil and 100% from 0.5, 1.5 and 5% w/w Emergent Biochar. The removal of NAP using

Cantimber Biochar was 96.9, 97 and 97.1% for 0.5, 1.5 and 5% w/w respectively. This result is for 60 min as this was the time when all the pollutants had chance to pass through the column as shown by tracer analysis.

The ACY removal efficiency followed the order of soil > Emergent Biochar > Cantimber Biochar. The different treatments removal ability followed the order of 0.5 > 1.5 > 5 % w/w for both Emergent and Cantimber Biochar and there was no significant difference between the removal ability of 0.5, 1.5 and 5% w/w Emergent and Cantimber Biochar (Table 3.6). In the case of other lower molecular weight PAHs (ACN, FLU, PHN and ANT) the peak was not detected in the analysis, they were present in the effluent samples but the concentration was less than 0.001µg/ L. For PAHs it is very impossible to come up with a hard and fast detection limit as all the 16 PAHs are treated differently and it would vary from day to day as is normal.

The removal efficiency for higher molecular weight PAHs vary for all the filtration media (Table 3.7). The maximum removal efficiency for higher molecular weight followed the order of Cantimber Biochar > Emergent Biochar > soil. The removal ability of Emergent Biochar followed 0.5 > 1.5 > 5% w/w and the removal ability of Cantimber Biochar for all the treatments were same for CHR, BaP and DahA (100%) and BbF, BkF, BghiP and IcdP were removed with different rate using 0.5, 1.5 and 5% w/w Cantimber Biochar (Table 3.7). Emergent Biochar removed IcdP more efficiently than Cantimber Biochar (Table 3.7). There was a difference in the removal efficiency of Emergent and Cantimber Biochar because the physical properties of both the biochars are different (Table 2.2). The main difference is the source of origin and the pyrolysis temperature as discussed in the section 2.3.2. This factors along with the physical and chemical properties of the Emergent and Cantimber Biochar changes the functional groups (-COOH, -OH) present on the surface of Biochar, as a result there is a change in interaction with organic compounds, PAHs in this case. All these factors affect the removal efficiencies of Emergent and Cantimber Biochar.

The filtration experiment result showed that the biochar removes higher molecular weight PAHs more efficiently than the soil. Soil works more efficiently for the lower molecular weight PAHs and addition of biochar (Cantimber) is rather decreasing its capacity to remove the pollutants like NAP and ACY. The higher molecular weight

PAHs are of more concern because they are hydrophobic and carcinogenic in nature and they can be strongly sorbed onto organic or fine particles. Cantimber Biochar with application rate of 0.5% w/w exhibited higher removal efficiency compared to 1.5 and 5% w/w biochar. The result was same for the Emergent Biochar, 0.5% w/w removed higher molecular weight PAHs more efficiently than soil, however the difference between removal efficiencies between the treatments were not significant for Emergent and Cantimber Biochar (Table 3.7 for 60 minutes only, because 60 minute was the time when all the pollutants had chance to pass through the column).

There are few sources of uncertainties that should be taken into account with these results such as; there was a time lag in the analysis of the samples of each experiment and it might change the concentration of PAHs in the samples; there was inherent error in the sampling for example, the change in influent concentration overtime mainly for lower molecular weight PAHs discussed in (TABLE 3.1 and Table 3.2) that is why some reservations is needed when analyzing the data and looking into conclusion how 0.5% biochar is better that 5% w/w; error caused by HPLC instrument, as for PAHs it is very impossible to come with a hard and fast detection limit as all the PAHs are treated differently.

4.2. Protection *versus* Restoration of Aquatic ecosystem

Biochar has a high potential to remove stormwater contaminants, and this study showed that the biochar can efficiently remove pollutants, mainly the higher molecular weight PAHs when small amount (0.5% w/w) of it is mixed with soil as the combination with the soil lead to heterogeneities in the soil profile and improve the stormwater quality. Scientific studies have documented detrimental impacts from PAHs on aquatic organism. For example, In Austin, Texas biological studies revealed loss of species and decreased number of organisms in streams with PAHs (Van Metre 2005); In Puget Sound, Washington’s Ambient Monitoring Program (WA DFW) found PAHs associated with liver lesions and tumour in fish, liver problems leading to reproductive impairment, reduction in aquatic plant (eel-grass) that provide fish habitat; Brown bullhead catfish and English sole have been documented as among most sensitive bottom-dwelling fish to carcinogenic effects of PAHs (Garrett 2004). Urban stormwater is a primary source of contamination to aquatic environment, posing a serious threat to the ecological integrity of receiving waters. As an example, acute mortality syndrome of coho salmon (*Oncorhynchus kisutch*) takes place when they return to their spawning habitat in urban freshwater creeks in western North America during the rainy season of fall (Peter et al. 2018).

This research showed how effectively biochar removes the higher molecular weight PAHs (insoluble, stable and hydrophobic). The effects of PAHs on aquatic organisms and plants degradation can be mitigated by amending the soil media with biochar in bioretention cells such as raingardens. A number of published reports have suggested using biochar in constructed wetlands (CWs) to improve water quality.This could be applied in real world where stormwater runoff can be treated before entering into river or stream, therefore reducing the need of future restoration.

4.3. Biochar Aging and Replacement

According to Minnesota Stormwater manual, biochar undergoes transformation in soil after application, primarily through oxidation process, typically mediated by microbes. Several researchers have studied the effects of aging on biochar properties. Although, they observed similar changes in the chemical and physical properties of biochar with aging. It is therefore difficult to draw conclusions about likely changes in the effects of biochar aging on fate of pollutants and soil hydraulic properties. More research needs to be done to investigate the effect of biochar on contaminants removal with time.

One of the key issues is disposing the used biochar. Landfill storage is one of the options to dispose biochar which has been used to remove stormwater pollutants, however this area needs further investigation because removal of contaminated soil and biochar from a bioretention cell is costly, as the bioretention cell such as raingarden is heavily vegetated hence removal and rebuilding could be costly. For a sustainable biochar development and its safe application in soil and water, International Biochar Initiative (IBI) guidelines should be followed (Initiative 2012).

4.4. Cost of Rain Garden

The cost of rain garden mainly depends on complexities of design, the amount and variety of landscape and how water is directed into a rain garden. The material (soil, sand, biochar, drain rock/gravels) cost of building a 2 m x 3 m x 0.5 m (0.5 m is recommended by Cougar Creek Streamkeepers.ca, North Delta) on a commercial and industrial site would be \$10 - \$40 square feet that is \$645 - \$2,580, this rate is according to the Watershed Activities to Encourage Conservation. According to Deborah Jones, a Rain Garden Coordinator, Cougar Creek Streamkeepers.ca, a total of 54 plants in a small 10 cm pots would be enough for a six square meter rain garden and that would cost \$200 - \$250. The excavation and labour costs to dig a 2 m x 3 m x 0.5 m rain garden would be approximately \$1,000.

5. Conclusions and Recommendations

The ability of commercially available biochar to remove PAHs, Cd and Pb from a synthetic stormwater was demonstrated through a series of column experiments. The effects of different concentration of pollutants were examined and comparison with soil was conducted at the same time at different time interval (20, 40 and 60 minutes). Biochar indicated maximum higher molecular weight removal (Cantimber > Emergent) ability as compared to soil for higher molecular weight PAHs. The lower molecular weight PAHs removal ability of soil was more than Emergent and Cantimer Biochar (soil > Emergent > Cantimber Biochar). The Cd removal efficiency was same for soil and Emergent and can timer Biochar. However, Pb removal was in the range of 99.5 - 99 % for 0.5 and 5% w/w respectively, for both soil and Emergent Biochar. Pb removal using Cantimber was less than the soil and Emergent Biochar (94.5 – 90%), these results are for 60 minutes only, because 60 minute was the time when all the pollutants had chance to pass through the column . There was an interesting trend observed in this study that most of time the removal efficiency was maximum in the samples collected at 20 minutes (Table 3.6 to Table 3.8), this needs further investigation.

My cohort Alyssa Johnston has used Emergent Biochar to identify the adequate rate of biochar (0.5, 1.5 and 5% (w/w)) that can enhance the properties of bioretention soil, survival and growth of native wetland plants such as slough sedge (*Carex obnupta*) and common rush (*Juncus effuses*) in bioretention cell. The result showed that for *J. effuses,* 0.5% had the greatest growth rate and least was in the 5% Emergent Biochar. *J. effuses showed* significant difference between the soil and 5% as well as between 0.5 and 5% treatments for total biomass.

Based on both the results it can be concluded that the biochar has high potential to remove stormwater contaminants (mainly the higher molecular weight PAHs) and maintain plant health in stormwater treatment system. Soil can be amended by biochar for plant growth, which can substitute the use of organic amendments such as compost that have negative impact on contaminant leaching. Biochar can be used as filter media for contaminant attachment/removal, particularly useful to remove organic contaminants from stormwater, whereas removal of metals/metalloids, nutrients and pathogens varies by a wide range based on surface properties, contaminants properties and water chemistry. The current state of research on using biochar for stormwater treatment and management are laboratory or bench-scale based, mostly using synthetic stormwater containing few of the target contaminants. However, storm events are highly complex and intermittent with variable characteristics of intensity and duration that in turn impact their pollutant load. Due to this, the impact of complexities of stormwater like flow changes, changing weather, pollutant concentrations etc cannot be fully understood on such a smaller scale and results from the lab tests cannot be expected to be the same on the field.

Additionally, most lab scale studies investigate removal of only a few pollutants in a less complicated matrix compared to stormwater. Several pollutants may interact with each other and competition may occur, but it is not yet known how the media may remove contaminants under such a mixture of compounds. Moreover, as there is currently a disconnect between our understanding of the contaminant removal processes at the laboratory scale versus the field scale, future work should seek to bridge this gap by incorporating current knowledge into design considerations and monitoring system performance over multiple years. This will require interdisciplinary efforts among researchers in chemistry, biology, and hydrology, as well as collaborations between researchers and practitioners to ensure effective diffusion of this technology into broader practice.

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Appendix A

ANOVA Table for Emergent Biochar

Table A1: Selected ANOVA detail of ACY removal using emergent biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	7.95	4.03	**0.051**

Table A2: *Selected ANOVA detail of BaA removal using emergent biochar for column treatment at 95% confidence interval using SPSS software version* 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	120.24	386.85	**<0.001**

Table A3: Selected ANOVA detail of CHR removal using emergent biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	224.85	40.48	**<0.001**

Table A4: Selected ANOVA detail of BbF removal using emergent biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	734.99	1947	**<0.001**

Table A5: Selected ANOVA detail of BkF removal using emergent biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	611.28	110.77	**<0.001**

Table A6: Selected ANOVA detail of BaP removal using emergent biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	478	210.49	**<0.001**

Table A7: Selected ANOVA detail of DahA removal using emergent biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	1033.41	9.59	0.005

Table A8: Selected ANOVA detail of BghiP removal using emergent biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	976.97	221.20	**<0.001**

Table A9: Selected ANOVA detail of IcdP removal using emergent biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	994.57	58.29	**<0.001**

Appendix B

ANOVA Table of Cantimber Biochar

Table B1: Selected ANOVA detail of NAP removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	41	25.89	**<0.001**

Table B2: Selected ANOVA detail of ACY removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	156.36	400.93	**<0.001**

Table B3: Selected ANOVA detail of PYR removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	2.08	25.0	**<0.001**

Table B4: Selected ANOVA detail of BaA removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	332.85	1542.17	**<0.001**

Table B5: Selected ANOVA detail of CHR removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	670.50	192.53	**<0.001**

Table B6: Selected ANOVA detail of BbF removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	446.63	1261.07	**<0.001**

Table B7: Selected ANOVA detail of BkF removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	1200	1600	**<0.001**

Table B8: Selected ANOVA detail of BaP removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	df	Mean Square	F	p
Between Groups (Soil, 0.5, 1.5 and 5%)	3	1150.52	2209	**<0.001**

Table B8: Selected ANOVA detail of DahA removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	df	Mean Square	F	p
Between Groups (Soil, 0.5, 1.5 and 5%)	3	4446.75	5929	**<0.001**

Table B9: Selected ANOVA detail of BghiP removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	df	Mean Square	F	p
Between Groups (Soil, 0.5, 1.5 and 5%)	3	2721.17	605.49	**<0.001**

Table B10: Selected ANOVA detail of IcdP removal using Cantimber biochar for column treatment at 95% confidence interval using SPSS software version 24.0

Source	df	Mean Square	F	p
Between Groups (Soil, 0.5, 1.5 and 5%)	3	1542.60	81.959	**<0.001**

Table B11: Selected ANOVA detail of Pb removal using cantimber biochar for columntreatment at 95% confidence interval using SPSS software version 27.0

Source	**df**	**Mean Square**	**F**	**p**
Between Groups (Soil, 0.5, 1.5 and 5%)	3	40.20	7.29	**0.015**