Restoration of an Urban Creek Water Quality Using Sand and Biochar Filtration Galleries

by

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Abstract

Stormwater runoff from parking lots often contains a variety of elements and compounds in different forms and concentrations that may pose risks to biota in receiving aquatic systems. Heavy metals including copper (Cu) and zinc (Zn), and polycyclic aromatic hydrocarbons (PAHs) are of particular concern in such runoff due to their prevalence, toxicity to aquatic organisms and persistence in the environment. The ability of a commercially available biochar to remove pollutants of concern through column treatments was assessed in this research. Factors including the pollutant's concentration, total organic carbon (TOC), pH, and biochar particle size were considered. The biochar used in this study showed a significant heavy metals and PAH removal ability compared to sand, qualifying it as a potential substitute for sand in urban structural best management practices. Maximum percentage removal using biochar followed the order of naphthalene (NAP) > Zn > Cu. Regarding Cu and Zn removal, small biochar exhibited higher removal efficiency compared to medium biochar. In terms of NAP removal, both small and medium biochar exceeded sand with a five-fold percentage removal. However, biochar of different particle sizes had the same removal percentage.

Keywords: Biochar, Parking lot stormwater, Naphthalene, Stormwater management, Heavy metals, PAH, Infiltration swale

Dedication

“To my best friend who made this possible.”

هر کجا هستم، باشم
آسمان مال من است.
پنجره،
فکر،
هوا،
عشق،
زمین مال من است.
چه اهمیت دارد؟
گاه اگر می رویند
قارچ های غربت؟
چشمهارابایدشست، جوردیگربایددید
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سهراب سپهری

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List of Acronyms

A_C	Surface area of the column used in this project
A_t	Surface area of infiltration trench
BCIT	British Columbia Institute of Technology
BMPs	Structural best management practices
BOD	Biological oxygen demand
BTEX	Benzene, ethylbenzene, toluene and xylene
C Effluent	Concentration at the effluent
C Influent	Concentration at the influent
Cr	Chromium
Cu	Copper
DOC	Dissolved organic carbon
Dr	Depth (thickness) of rock reservoir
Ds	Soil layer depth (i.e., recommended depth of biochar to be used in the infiltration structure in mm)
H_B	Hydraulic loading rate of medium biochar
H_I	Hydraulic loading rate of the infiltration trench
HMWPAHs	High molecular weight PAHs
I/P	Ratio of impervious tributary area to swale base area
IDC	Information disrupting chemical
Ks	Saturated hydraulic conductivity of subsurface soil
L	Liter
LMWPAHs	Low molecular weight PAHs
MAHs	Monocyclic aromatic hydrocarbons
Ml	Milliliter
Mm	Millimeters
N	Porosity of drain rock in reservoir
NAP	Naphthalene
Ni	Nickel
PAHs	Polycyclic aromatic hydrocarbons
Pb	Lead
PCBs	Polychlorinated Biphenyls
Q_B	Flow rate of medium biochar used in this project

Q_P	Flow rate of rain water in BCIT parking lot
R	Rainfall capture depth
RE	Removal efficiency in percentage
SFU	Simon Fraser University
SUDs	Sustainable urban drainage systems
T	Allowable drain time (days)
TOC	Total organic carbon
TSS	Total suspended solid
Zn	Zinc
$\eta 2$	Partial eta-squared

Preface/Executive Summary/Image

Source: New Solutions for sustainable stormwater management in Canada, report September 2016.

Chapter 1.

Introduction

The phrase “urban stream syndrome” portrays the process of ecological degradation of streams and adjacent waters that drain urban landscapes (Walsh *et al*. 2005). Urban stormwater is believed to result in 15% percent of all impaired river miles (61,338.5 kms), 18% of all impaired lakes (3838.1 km^2) and 32% of all impaired estuaries (7101.7 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 quantity and quality of aquatic ecosystems (Goonetilleke *et al*. 2005). Surging impervious surfaces has resulted in increased volume of runoff and decreased rate of infiltration and evapotranspiration (Walsh *et al*. 2012). Klein (1979) studied twenty-seven watersheds and reported a relationship between the level of watershed urbanization and stream quality. He deduced that impairment of stream quality can only be prevented in watersheds with less than 15% (10% in sensitive ecosystems) impervious surfaces. Intensive stream quality impairment was observed in watersheds with 30% impervious surfaces. Arnold and Gibbons (1996) revealed a similar relationship between stream health and impermeable cover (Fig. 1.1).

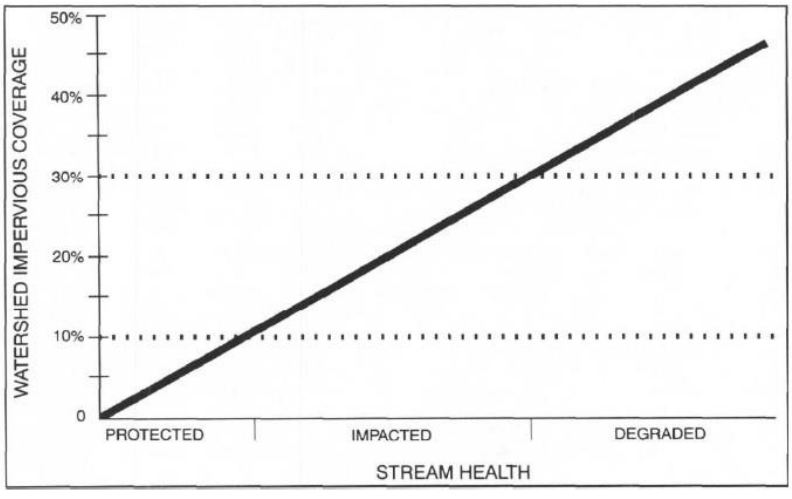

Figure 1.1. Relationship between stream health and impervious cover (Arnold and Gibbons 1996).

The deleterious effects of urbanization on aquatic ecosystems includes biological (e.g., decreased biotic richness, with increased dominance of tolerant species), chemical (e.g., elevated concentrations of contaminants and nutrients), and physical changes (e.g., a flashier hydrograph and altered channel morphology) (Klein 1979, Walsh *et al*. 2005, Walsh *et al*. 2012, Erickson *et al*. 2013). Stream hydrograph modification is one of the most consistent and noticeable features, as they experience more frequent and larger flow events due to diminished infiltration capacity and the engineered effective delivery of stormwater (Goonetilleke *et al*. 2004, Walsh *et al*. 2005). Such imbalanced fluctuation of erosive forces will lead to hydraulic disruption of in-stream biota, bank erosion, channel incision, and serious changes to water quality (Klein 1979, Walsh *et al*. 2005). The use of decentralised systems for treatment, utilisation, and detention of stormwater and snowmelt is increasing due to water shortages, flooding, and the costs associated with the combined treatment of storm and waste-water. Structural best management practices (BMPs) or sustainable urban drainage systems (SUDs) are widely used to reduce urban runoff peak flows as well as the amount of stormwater based pollutants entering the receiving water environment (Erikson *et al*. 2007).

1.1. Stormwater Pollutants

Toxic material such as heavy metals, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and nutrients (e.g., nitrogen and phosphorous) are common pollutants found in urban stormwater (Klein 1979, Walsh *et al*. 2005, Sivora 2015). Throughout a rain event, these contaminants are washed off of roofs, roads, and other surfaces into stormwater systems and are then released into surface water ways and estuaries (Brown and Peak 2006). Heavy metals and hydrocarbons are two main groups of pollutants found in parking lots, and they primarily originate from vehicles and road surface sealing (Laurenson *et al*., 2013). Heavy metals including zinc (Zn) and copper (Cu), and polycyclic aromatic hydrocarbons are priority pollutants because they are prevalent, toxic to aquatic organisms, and are durable in the environment (Borchardt and Sperling 1997, Brown and Peak 2006).

1.1.1. Heavy Metals

Chemistry

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 waterbodies worldwide (Davis *et al*. 2001, Buffleben *et al*. 2002). The most common heavy metals found in stormwater include: Cu, Zn, Lead and cadmium. In southern California, USA, several studies have documented heavy metals as main constituents of concern in stormwater runoff (Buffleben *et al*. 2002, Tiefenthaler *et al*. 2008). Heavy metals are problematic because they are toxic to aquatic organisms and can be bio-accumulated (Tiefenthaler *et al*. 2008).

Metals can be found 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). They can accumulate in the streambed, and be taken up by benthic organisms. Additionally, they can become soluble with decreasing pH, binding 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 (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 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, interaction between TOC and heavy metals can result in processes that concentrate the metals in the dissolved phase (Hernegen *et al*. 2005).

Effects on Biota

Being commonly affiliated with fine particles in stormwater, metals have the potential to accumulate in the sediments of downstream receiving waters (Liebens 2001, Tiefenthaler *et al*. 2008). Heavy metals pose a threat to an ecosystem at two different levels: 1) at the individual level, namely developmental abnormalities (Lavolpe *et al*.

2004) and DNA base alterations (Avery *et al*. 1996), avoidance behavior (Roper and Hickey 1994), depression in post exposure feeding (Moreira *et al*. 2006), and mortality (Gale *et al*. 2006), and 2) at the community level through effects such as modification in species diversity, richness, abundance, recruitment and community composition (Lande, 1977, Rygg 1985, Watzin and Roscigno 1997, Warwick 2001).

Cu and Zn are typical pollutants extensively distributed in aquatic ecosystems. Cu is a common olfactory toxicant, even at lower concentrations, and has been identified as an information disrupting chemical (IDC) for more than three decades (Kennedy *et al*. 2012). Physical impairment including reduced growth and swim speed, weakened immune response, disrupted reproduction performance and spawning behavior, as well as, sensory impairment such as reduced olfactory system response, and olfactory mediated behaviors (namely impairment in migration and predation) are some of the observed symptoms of Cu exposure in salmonids and other fish species (Price 2013). Cu is also shown to cause brain damage in mammals (DWAF 1996).

Zn has low toxicity to people while having high toxicity to fish. It can be easily bio accumulated in stream invertebrates which are a crucial food source for juvenile salmonids during rearing in freshwater systems. Reduced growth and survival, as well as increased rate of disease are some of the fish symptoms in Zn contaminated waters (Bowen *et al*. 2006). Physiological and behavioral effects of Zn and temperature on steel head trout (*Oncorhynchus mykiss*) and coho salmon (*Oncorhynchus kisutch*) was examined by Bowen *et al*. (2006) in the Navarro River in California, USA. Increased Zn concentrations in the liver and reduced growth rate were observed after Zn exposure. A study on Ballona Creek revealed deleterious effects of stormwater containing Zn and Cu to the endemic purple sea urchin residing in the above mentioned environment (Schiff *et al*. 2003).

Due to the ecological effects of heavy metals, a major affirmation on managing stormwater has concentrated on the elimination of these pollutants from urban watersheds (Tiefenthaler *et al*. 2008).

1.1.2. PAH

Chemistry

Aromatic compounds are cyclic hydrocarbons with alternating double and single bonds. Aromatic compounds can be monocyclic or polycyclic. Benzene, ethylbenzene, toluene and xylene are examples of monocyclic aromatic hydrocarbons (MAHs) that are collectively referred to as BTEX compounds. Polycyclic aromatic hydrocarbons (PAHs) with two rings are categorized as low molecular weight PAHs (LMWPAHs) and those with three or more rings are high molecular weight PAHs (HMWPAHs) (Fig 1.2).

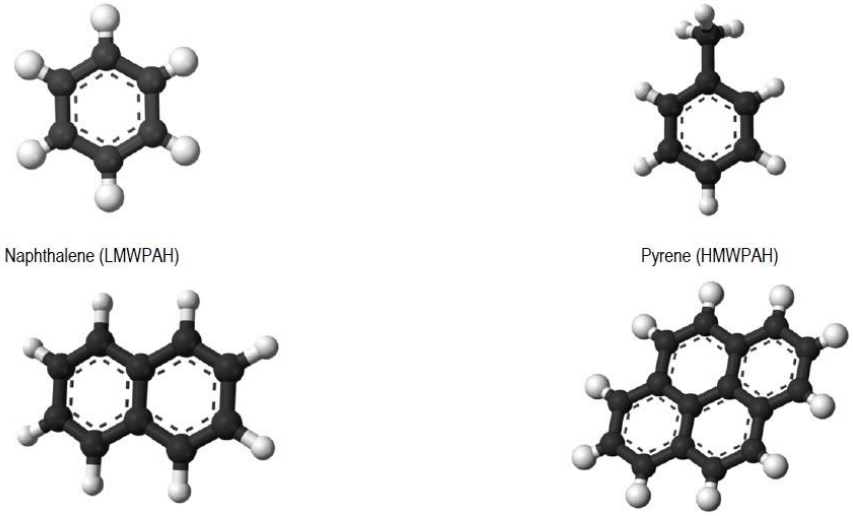

Figure 1.2 Monocyclic (top) and polycyclic (bottom) aromatic hydrocarbons (source: Kennedy et al. 2016).

PAHs are present in stormwater in both dissolved and particulate phase. However, in general they are found attached to particulate matter (Pitt *et al*. 1995, Hwang *et al*. 2006, Bathi *et al*. 2008). Among different PAHs, naphthalene (NAP), anthracene, and flourene are primarily concentrated in water phase (Bathi *et al*. 2008). PAHs have a relatively low solubility in water and are highly lipophilic. HMW hydrocarbons usually have less solubility in water than LMW hydrocarbons. Solubility is a determining factor in a hydrocarbon toxicity level. Soluble hydrocarbons are more acutely toxic in comparison to insoluble ones (Williamson 1993). Highly soluble

hydrocarbons are more biodegradable and can be readily moved through the hydrologic cycle and have low bio-concentration factors in aquatic environments and low adsorption coefficients in soil (Nyer *et al*. 1991, Williamson 1993). The solubility of a hydrocarbon is controlled by its structure. Having a low octanol/water coefficient makes hydrocarbons non-polar; meaning that they do not dissolve very well in polar solutions, such as water (Rodebush and Masterton 1954). Larger molecules are also less likely to dissolve in water. Environmentally relevant PAHs range from NAP ($C_{10}H_8$) to coronene ($C_{24}H_{12}$), with various chemical structures and characteristics (Manoli and Samara 1999). NAP is a LMW hydrocarbon and is one of the 16 PAHs that has been identified as primary pollutants by United States Environmental Protection Agency (USEPA 2013). It is one of the most detected PAHs in urban environments (Heintzman *et al*. 2015), and has been used as a representative PAH in many experiments (Correa and Coler 1983, Walters and Luthy 1984, Chen *et al*. 2007, Chen *et al*. 2008, Reddy *et al*. 2014, Xi and Chen 2014).

Effects on Biota

PAHs are potentially carcinogenic chemicals which are ubiquitous in the urban environment. Impervious surfaces in urbanized areas usually contain high amounts of PAH (Murakami *et al*. 2004, Lau and Stenstrom 2005, Zhao *et al*. 2009, 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). PAH are proved to be responsible for skin, lung, bladder, liver and stomach cancers, as well as, developmental toxicity in different group of species, including aquatic animals (Jha 2004, Hylland 2006), birds (Brunstrom *et al*.1990), and reptiles (Alam and Brim 2000). At high concentrations, interrupted egg yolk development, edemas, skull abnormalities, bleeding and death could occur in fish and aquatic invertebrates (McGrath and Di Toro 2009). Main effects of PAH exposure in fish includes impaired growth, reproduction, swimming performance and respiration (Kennedy *et al*. 2016).

1.2. Source of Different Contaminants in the Urban Stormwater Runoff

Urban stormwater runoff is being recognized as a substantial source of pollutants to receiving waters. These contaminants are typically generated from anthropogenic activities (Table 1.1). Many heavy metals, especially Cu and Zn, have been recognized as vehicular traffic-related pollutants (Wilber and Hunter 1979, Dong *et al*. 1984, Herngren *et al*. 2005). However, specific sources of heavy metals in an urban area also include corrosion of buildings and their fittings, atmospheric deposition, transport and various industrial activities and intentional and accidental spills (Christensen and Guinn 1979, Davis *et al*. 2001). PAHs are essentially produced by traffic emissions and incomplete combustion or spills of petroleum. Sources of heavy metals and PAH, and their contribution to urban stormwater runoff is significantly dependent on the land use (Herngren *et al*. 2005).

Table 1.1 Source of contaminants in the urban stormwater runoff (EPA 1999).

Pollutant	**Source**
Sediment and Floatable	Streets, lawns, driveways, construction activities, atmospheric deposition, drainage channel erosion
Pesticides and Herbicides	Residential lawn and gardens, roadsides, utility right-of-ways, commercial and industrial landscape area, soil wash-off
Organic Materials	Residential lawn and gardens, commercial landscaping, animal wastes
Heavy Metals	Automobiles, bridges, atmospheric deposition, industrial area, soil erosion, corroding metal surfaces, combustion processes
Oil and Grease/ Hydrocarbons	Roads, driveways, vehicular maintenance area, gas stations, parking lots, elicit dumping to the storm drain, direct wash off from vehicles
Bacteria and Viruses	Lawns, roads, leaky sanitary sewer lines, sanitary sewer cross connection, animal waste, septic system

1.3. Heavy Metals and PAHs in Relation to Land Use Activities

Characteristics of surfaces that stormwater passes over (i.e., roads, parking lots, roofing material, recreational areas), defines the quality of the stormwater and the physical, chemical or microbial properties of the present contaminants (Eriksson 2007). Ambient air quality and particular anthropogenic activities within each individual catchment are other factors affecting the combination of pollutants (Makepeace *et al*. 1995). Based on studies on stormwater, a large number of organic and inorganic pollutants, both in their dissolved and colloidal forms, may be present in stormwater (Makepeace *et al*. 1995, Eriksson 2002). Concentrations of these contaminants are site and event specific (Kayhanian *et al*. 2003, Eriksson 2007) (Table 1.2).

Heavy Metals and PAHs in Parking Lot Runoff

Parking lot stormwater usually carries a wide range of compounds in various forms and concentrations which are considered toxic to biota in receiving waters (Greenstein *et al*. 2004). During a rainfall event, rainwater or snowmelt reaches impervious or semi-impervious surfaces used for vehicle storage (i.e., parking lots), and mobilizes organic and inorganic components. Concentration, type, and therefore toxicity of parking lot stormwater runoff is highly influenced by rainfall characteristics (e.g., duration, intensity, and antecedent conditions), parking lot maintenance, and traffic intensity (Tiefenthaler *et al*. 2003, Greenstein *et al*. 2004). It is likely that stormwater runoff from campus parking lots is unique because of the variation and pattern of usage of the lots (McQueen 2010). Heavy metals including lead, Zn, Cu, aluminum, cadmium, iron and manganese are of interest in parking lot stormwater (Davis *et al*. 2001). Parking lot stormwater also usually has the highest concentration of organic constituents (e.g., oil and grease) in comparison to runoff from other urban and suburban land uses (e.g., street runoff, vehicle service areas, and landscaped areas) (Pitt *et al*. 1995). In general, there is limited data regarding chemical and physical characteristics of campus parking lots stormwater.

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Table 1.2 Representative average concentration of 10 pollutants in 11 types of surface runoff (source: Gobel et al. 2007).

	Pb (µg/l)	Cu (µg/l)	Zn (µg/l)	Ni (µg/l)	Cr (µg/l)	MAH (mg/l)	PAH (µg/l)	TSS (mg/l)	BOD (mg/l)	pH
Garden, grassed area, cultivated lands	9	11	80	2	3	0.38	0.39	12	2	5.0
Roof runoff, tiles, concrete, fiber cement, bitumen, glass, zinc gutters and downpipes	69	153	1851	4	4	0.70	0.44	43	12	5.7
Green roof	6	58	468	3	3	-	-	-	-	7.5
Copper roof	69	2600	370	4	4	0.70	0.44	43	12	5.7
Aluminum roof	69	153	370	4	4	0.70	0.44	43	12	5.7
Zinc roof	69	153	6000	4	4	0.70	0.44	43	12	5.7
Pedestrian and cycle way, yard	107	23	585	-	-	0.16	1.00	7.4	-	7.4
Car park	137	80	400	-	-	0.16	3.50	150	11	7.4
Service road	137	86	400	14	10	0.16	4.50	150	11	7.4
Main road	170	97	407	11	11	4.17	1.65	163	11	7.4
Motor way	224	65	345	27	13	4.76	2.61	153	32	7.4

1.4. Stormwater Pollution Control and Management

1.4.1. Structural Stormwater Best Management Practices

Structural stormwater best management practices (BMPs) are designed to compensate for the unfavorable impacts of development (i.e., 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: infiltration systems (i.e., soakaways, infiltration trenches and infiltration basins), storage facilities (i.e., lagoons, constructed wetlands, detention basins, retention ponds, storage tanks, roof storage), filter strips and swales, and alternative road structures including porous paving, porous asphalt surfaces (Scholes *et al*. 2005).

1.4.2. Identify Candidate Stormwater Source Controls

Every development has its own unique condition and requires a customized Stormwater Source Control solution. Best management practices suitable for a parking lot based on Metro Vancouver guideline (2012) includes absorbent landscapes, infiltration swales, rain gardens, pervious paving, and infiltration trenches (Table 1.3).

Table 1.3 Typical source control applications (adapted form Metro Vancouver Regional District 2012).

Development Type	Absorbent Landscape	Infiltration Swale	Rain Garden	Pervious Paving	Infiltration Trench or Shaft	Green Roof
Park / Open Space may include parking / buildings	*	*	*	*	*	*
Low Volume Road with roadside landscape or medians	*	*	*		*	
Surface Parking on-street or off-street w/ islands	*	*	*	*	*	
Single Family / Low Density 30 – 50% building coverage	*	*	*	*	*	*
High Density / Industrial/ Commercial/Institutional 50 – 90% building coverage	*	*	*	*	*	*
Ultra High Density >90% building coverage						*

Absorbent Landscape

An absorbent landscape is an absorbent layer of soil with vegetation. All parts of the landscape from shrubs, surface organic matter, and grasses to soil, play a role in the absorption process (Fig 1.3). Absorbent landscape could include native soils, compost soils, woods, planters, and other treatments to reduce runoff from landscape area. Adsorbent landscapes are an attempt to imitate the hydrologic function of undeveloped lands on a developed area. Absorption and infiltration of the direct rainfall is the primary reason for building this structure. However, it has limited capacity to accept and infiltrate runoff from impervious areas (the ratio of impervious area to absorbent landscape should not be more than 2:1). Adsorbent landscape is only suitable for limited parking areas such as driveways and is not practical for big parking spaces.

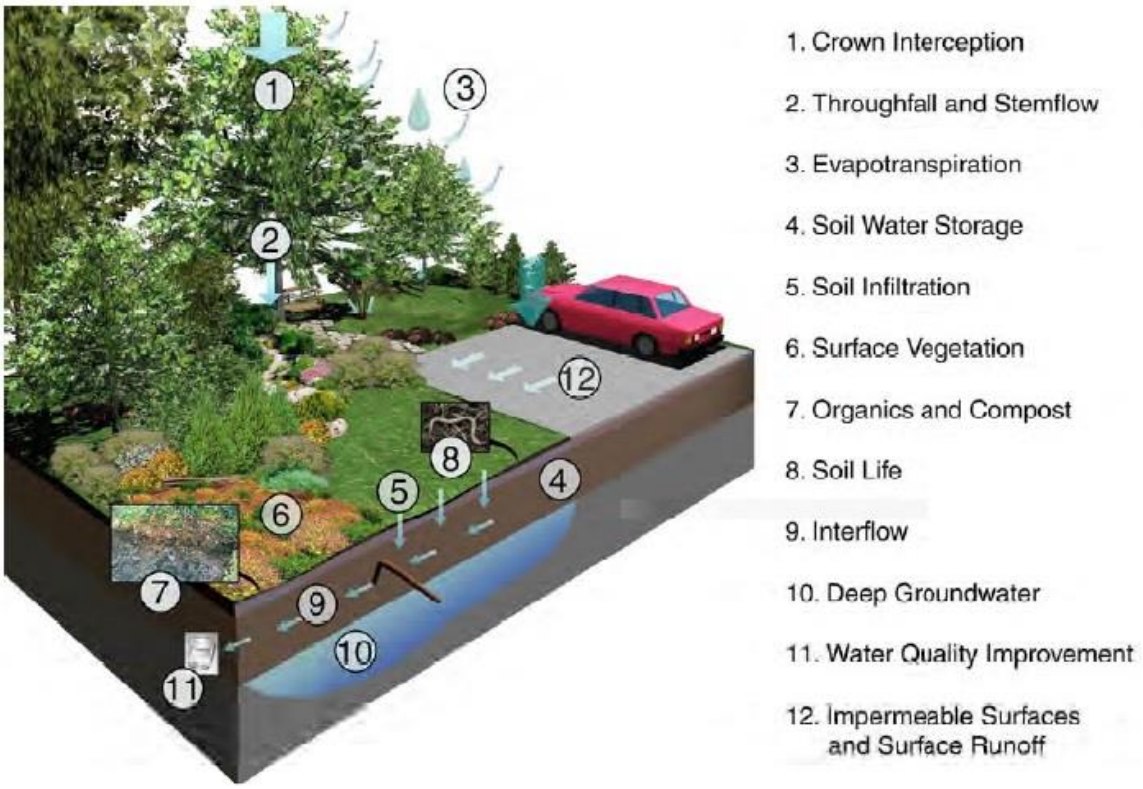


Figure 1.3. Stormwater variables of absorbent landscape (source: Metro Vancouver Regional District 2012).

Infiltration Trench

An infiltration trench is usually a subsurface linear trench shaped structure, designed to capture stormwater from rooftops, holding and soaking it into the ground. The fundamental segments of an infiltration trench are an inlet pipe or water source, catch basin sump, perforated delivery pipe, infiltration trench and an overflow to the storm drainage system (Fig 1.4) (City of Vancouver 2016, Metro Vancouver Regional District. 2012). An infiltration trench, mainly designed to volume and rate reduction, is suitable for places with unpolluted runoff including golf courses, parks and green spaces, residential areas or municipal office complexes. It is not advisable for heavy traffic roadways or parking lots unless a water quality pre-treatment structure is installed to remove heavy metals and hydrocarbon from storm runoff (Metro Vancouver Regional District. 2012).

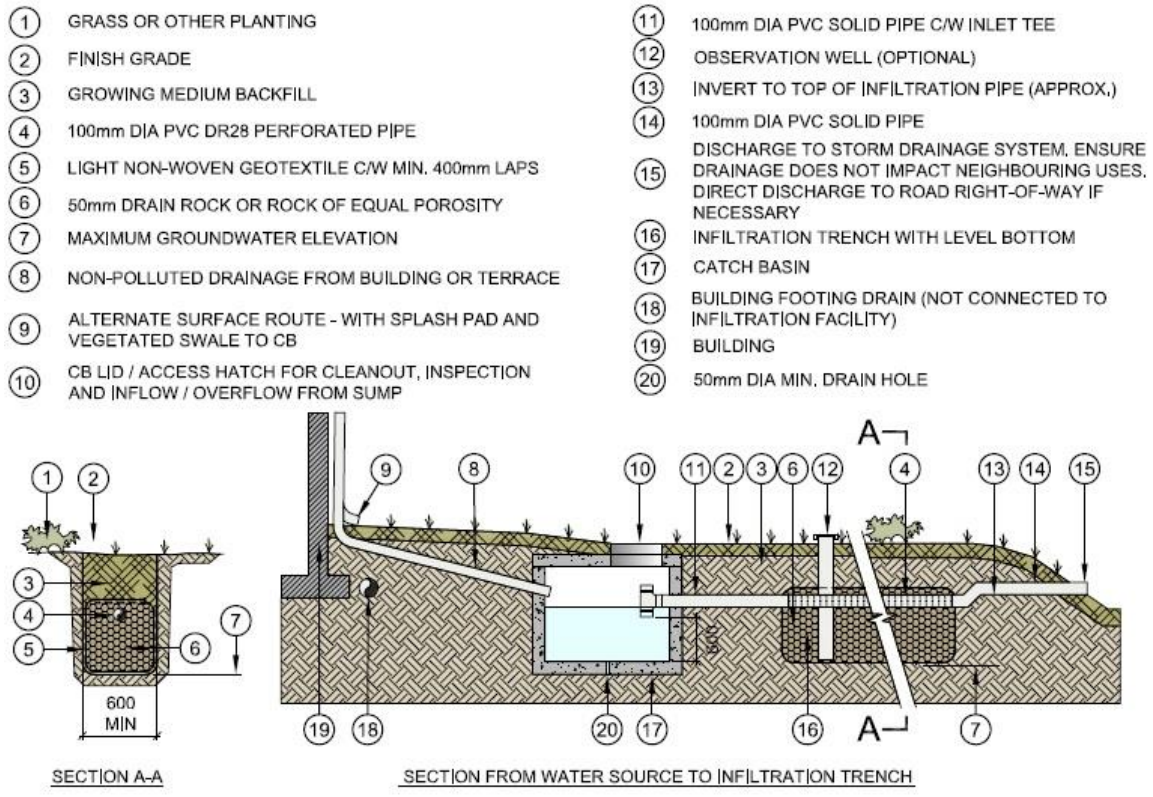


Figure 1.4. Infiltration trench structure (source: Metro Vancouver Regional District 2012).

Pervious Paving

Pervious paving consists of two main components: 1) a surface layer, and 2) a reservoir base. The surface layer captures stormwater, percolating it into the underlying base reservoir and can be made of porous asphalt or porous concrete, concrete modular pavers with gapped joints which let water infiltrate through, plastic grid or concrete filled with un-vegetated gravel or vegetated soil (Fig 1.5). The main purpose of designing a pervious paving is to infiltrate stormwater while having a hard surface (City of Vancouver 2016). The reservoir base stores stormwater, percolating it to underlying soils or directing that to subsurface drainage. Pervious paving is applicable for low traffic areas including service roads, driveways, bike paths, commuter parking areas, recreational vehicle pads, walkways, fire lanes and storage yard. However, it is not suitable for high traffic roads and parking lots with more than one vehicle per day per space since it doesn't acquire a soil layer to treat storm runoff, and hence, is prone to clogging from surface pollutants (Metro Vancouver Regional District. 2012). In a case where impervious area is two-fold greater than pervious pavement, alternative structures namely infiltration trench or rain garden should be considered.

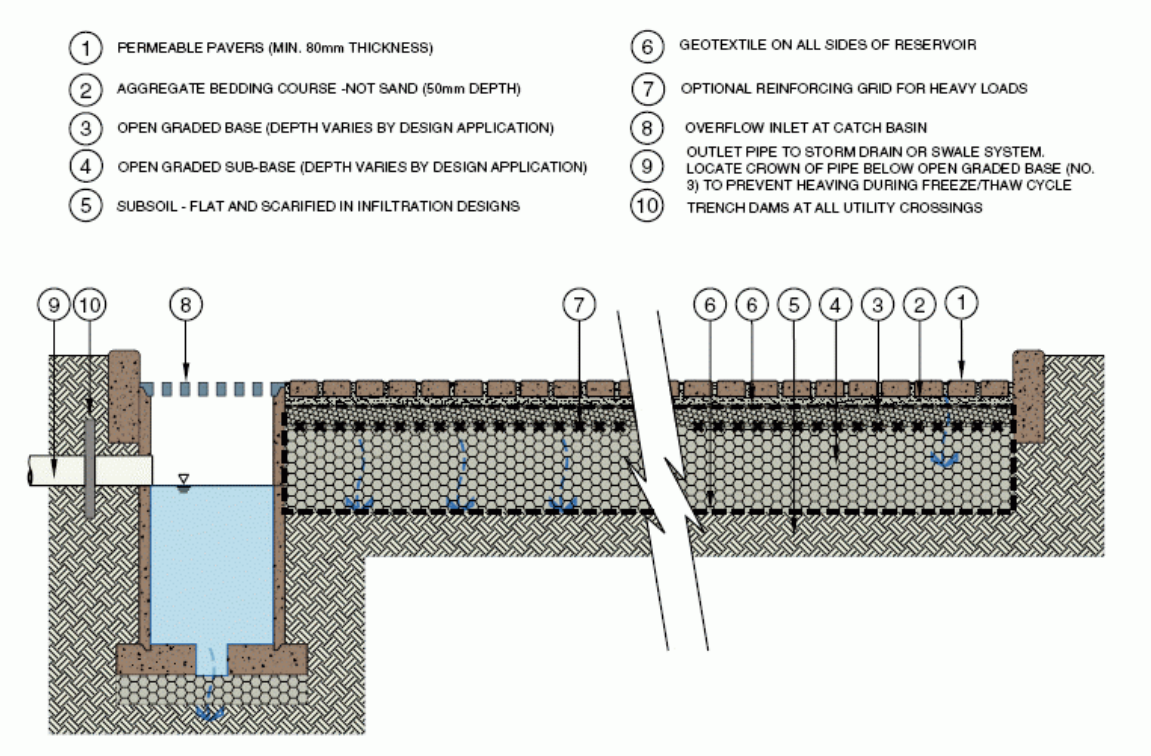
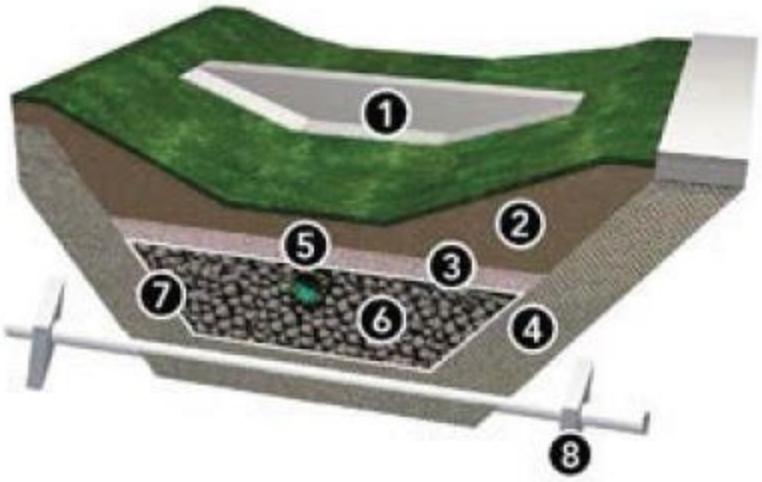


Figure 1.5 Pervious paving structure (source: Metro Vancouver Regional District 2012).

Infiltration Swale

An infiltration swale is a shallow channel with a cover of grass or other vegetation on the surface. It collects water from adjacent environments including roads or parking lots and holds it behind a weir to infiltrate into the soil and then to an underlying drain rock reservoir. The drain rock reservoir system and the surface soil act as storage for stormwater, allowing it to gradually infiltrate into the bottom soils. The underground overflow is collected using a perforated drain located near the top of the drain rock reservoir (Fig 1.6). Infiltration swales capture, hold, treat storm water, and convey large storm flows. An infiltration swale and a rain garden are almost identical in terms of function and design. The only difference is that an infiltration swale conveys non-captured flow, and collects less peak flow than a rain garden because of ponding. Although, a grassed swale is generally more economic to install compared to a rain garden (per unit area), it needs larger area to meet the same capture targets.



1. Weir Keyed into Swale Side Slope
2. Growing Medium (300 mm Min.)
3. Sand
4. Existing Scarified Subsoil
5. Perforated Underdrain (150 mm Dia. Min.)
6. Drain Rock Reservoir (300mm Min.)
7. Geotextile Along All Sides of Reservoir
8. Trench Dams at All Utility Crossing

Figure 1.6. Infiltration swale system structure (source: Metro Vancouver Regional District 2012).

Rain Garden

A rain garden is a bio-retention structure with both stormwater management and aesthetic function. They are usually designed in a concave shape to collects runoff from adjacent impervious area and roof tops, infiltrating it into underlying constructed soil and bed soil (Fig 1.7). A drain rock reservoir and a perforated drain system is often present to transfer away excess water (City of Vancouver 2016). Depending on the diverse soil moisture conditions in a garden, shrubs and ground covers are the main surface planting of a rain garden. In addition to sodded lawn areas for erosion control and multiple uses, trees, rushed, sedges, and other grass-like plants are used in designing rain gardens (Metro Vancouver Regional District. 2012). The main purpose of a rain garden includes stormwater treatment using soil layer and volume capture through infiltration from the

rock reservoir. Because of the surface ponding and plant uptake or moisture, a rain garden captures an increased volume rather than an infiltration trench.

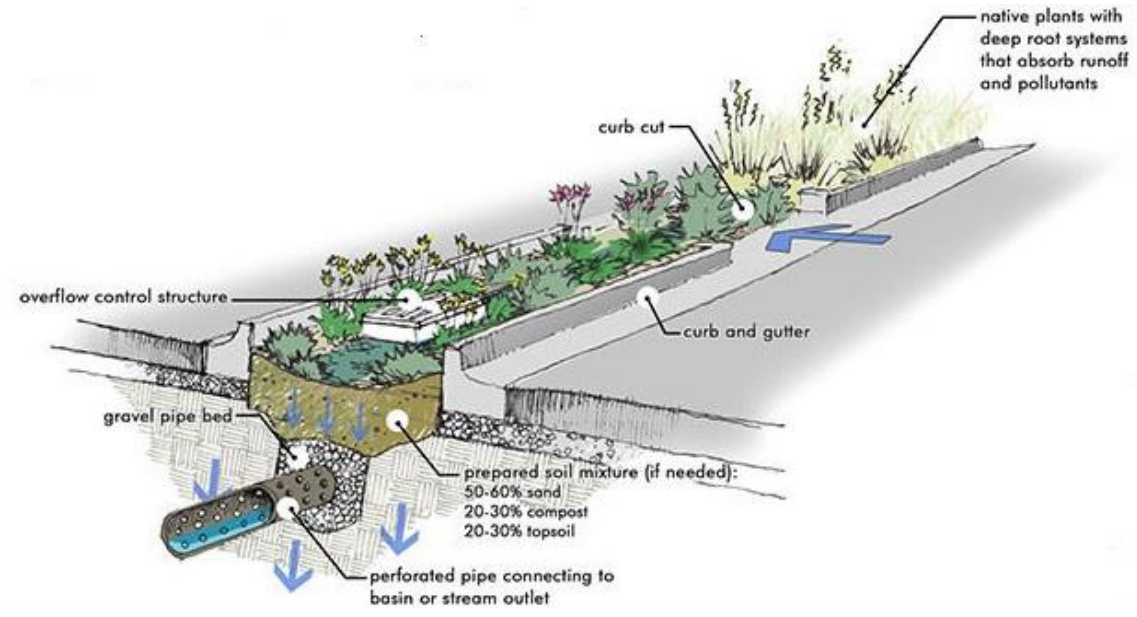


Figure 1.7. A curb side rain garden structure (source: Metro Vancouver Regional District 2012).

1.4.3. Design Targets for Stormwater Source Controls

Design targets provide a standard for Stormwater Source Control design to secure watercourses from development impacts such as reduced water quality, loss of fish habitat, and stream erosion. An integrated stormwater management plan (ISMP) sets design targets for a particular water course while department of fisheries and oceans (DFO) and local governments set general targets that could be applied over a wider area (Metro Vancouver Regional District. 2012) (Table 1.4).

Table 1.4. DFO Stormwater Source Control design guidelines (Metro Vancouver Regional District 2012).

Objective	Target
Volume Reduction	Retain the 6-month/24-hour post-development volume from impervious areas on-site and infiltrate to ground. If infiltration is not possible, the rate-of discharge from volume reduction Best Management Practices (BMPs) will be equal to the calculated release rate of an infiltration system
Water Quality	Collect and treat the volume of the 24-hour precipitation event equaling 90% of the total rainfall from impervious areas with suitable BMPs.
Detention or Rate Control	Reduce post-development flows (volume, shape and peak instantaneous rates) to pre-development levels for the 6-month/24-hour, 2-year/24-hour, and 5 year/24-hour precipitation events.

1.4.4. The Stormwater Source Control Design Process

The main steps and arrangements in designing a Stormwater Source Control practice is outlined in the following figure:

Table 1.5. Stormwater Source Control design process (source: Metro Vancouver Regional District 2012).

Design Stage	Objective
Design Targets for Stormwater Source Controls	Identify the watershed or local government requirements for Stormwater Source Control, and the related design targets or criteria.
Site analysis for Stormwater Source Control	Gather critical data: rainfall patterns, existing vegetation cover, infiltration constraints, soils mapping and infiltration tests.
Development Concepts that integrate Stormwater Source Controls	Integrate Stormwater Source Controls into the development concept: what mix and sizing of techniques fit with the site and the land use. Develop Stormwater Management Plan Concept
Detail Design of stormwater source controls	Design and size source controls. Create technical details in plan, cross section and profile. Incorporate Stormwater Source Controls in construction and maintenance specs.
Construction Staging of Stormwater Source Controls	Schedule the installation of Stormwater Source Controls to avoid problems with disturbance and sedimentation during construction.
Field Review and Monitoring of Stormwater Source Controls	Provide critical field inspections to ensure performance. Use post-construction monitoring and adaptive management to reduce costs.

1.4.5 Non-structural Stormwater Best Management Practices

Non-structural stormwater BMPs are used to avoid negative impacts of development from happening in development planning phase. It is more economical and effective to prevent stormwater management problems rather than designing a system to fit an existing development plan and solve the problem. Non-structural BMPs can be grouped into two extensive categories. First is planning, design, and construction of developments and redevelopments to minimize or terminate disturbing affects. The other includes education and training to promote awareness of the potential problems related to stormwater and of source control approaches that can help to solve those problems (Gibb *et al*. 1999).

1.5 Production and Properties of Biochar

Having a high amount of carbon, biochar is a black solid obtained by heating biomass, such as wood or manure, with little or lack of oxygen thorough a process called pyrolysis or charring (Sohi 2012). Biochar is applied to soil to enhance agricultural gains and carbon sequestration (Tan *et al*. 2015). Biochar stabilizes carbon into a form resembling charcoal, improving soil properties and fertility by improving moisture and nutrients retention and decelerating carbon release to the atmosphere from burning or degrading (i.e., is carbon negative) (Tang *et al*. 2013). Furthermore, the bioenergy generated from the pyrolysis process can be a potential replacement for fossil fuels (Lehmann 2007). Porous structure, mineral constituents, large specific surface area, and enriched surface functional groups are some of distinct characteristics of biochar, qualifying it as an excellent absorbent to remove pollutants from aqueous solutions. Activated carbon is another highly porous absorbent which has been successfully employed for removal of diverse pollutants from water worldwide (Chen *et al*. 2007). The production of activated carbon requires a higher temperature and additional activation process. However, production of biochar is cheaper with lower energy requirements. The feed stocks of biochar, including agricultural biomass and solid wastes, are abundant and inexpensive (Ahmad *et al*. 2012, Lu *et al*. 2012, Shen *et al*. 2012). Also, using invasive plant for biochar production can improve the invasive plant management and

protect the environment (Dong *et al*. 2013). 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). With the growing interest of scientific research and future engineering applications of biochar for the filtration of water and treatment of wastewater, an integrated understanding of biochar's function in aqueous solutions is necessary.

1.6 The Mechanism of Absorption of Pollutants on Biochar

Understanding the underlying mechanism of the adsorption process is essential for assessing the pollutants removal efficiency by biochar. Different contaminants are adsorbed by different processes on the biochar surface. The adsorption process is highly correlated with properties of contaminants and biochar, including porous structure, surface functional group, mineral components, and specific surface area.

1.6.1 Heavy Metals

In terms of heavy metals, the possible adsorption mechanism usually involves combining the effects of a number of interactions including ion exchange, precipitation, electrostatic attraction, surface complexation, and/or physical adsorption (Fig 1.8). The specific process of removal varies for different heavy metals and is highly influenced by the properties of the biochar.

There are plenty of surface functional groups (predominantly oxygen- containing groups, e.g. carboxylate (-COOH), and hydroxyl (-OH)) on biochar surface which can have strong interactions with heavy metals including ion exchange, electrostatic interaction, and surface complexation (Tan *et al*. 2015).

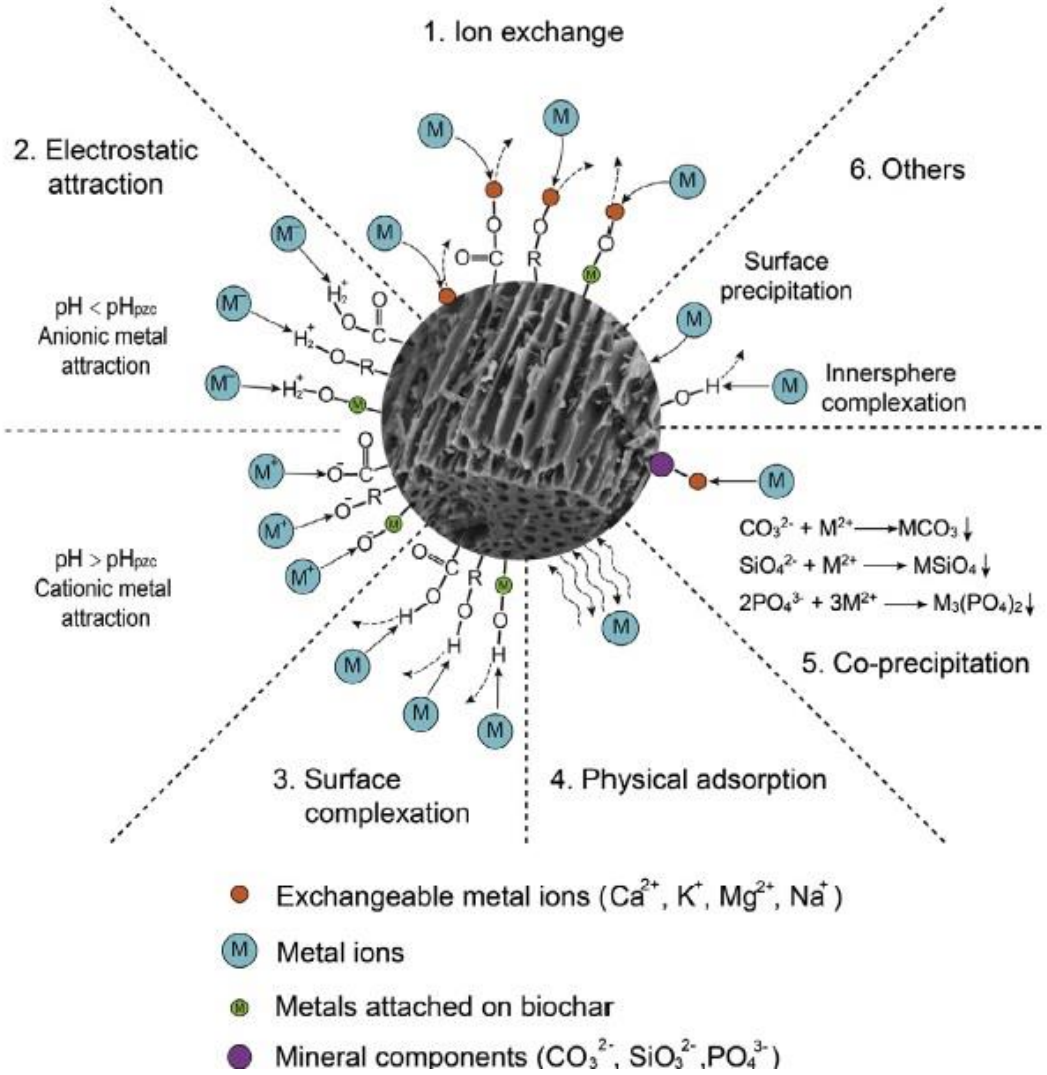


Figure 1.8. Various mechanisms for heavy metal absorption on biochar (source: Tan et al. 2015).

1.6.2 PAH

The main mechanisms for adsorption of organic pollutants onto biochar include: hydrogen bonds, electrostatic interaction, pore –filling, and hydrophobic effect (Fig. 1.9).

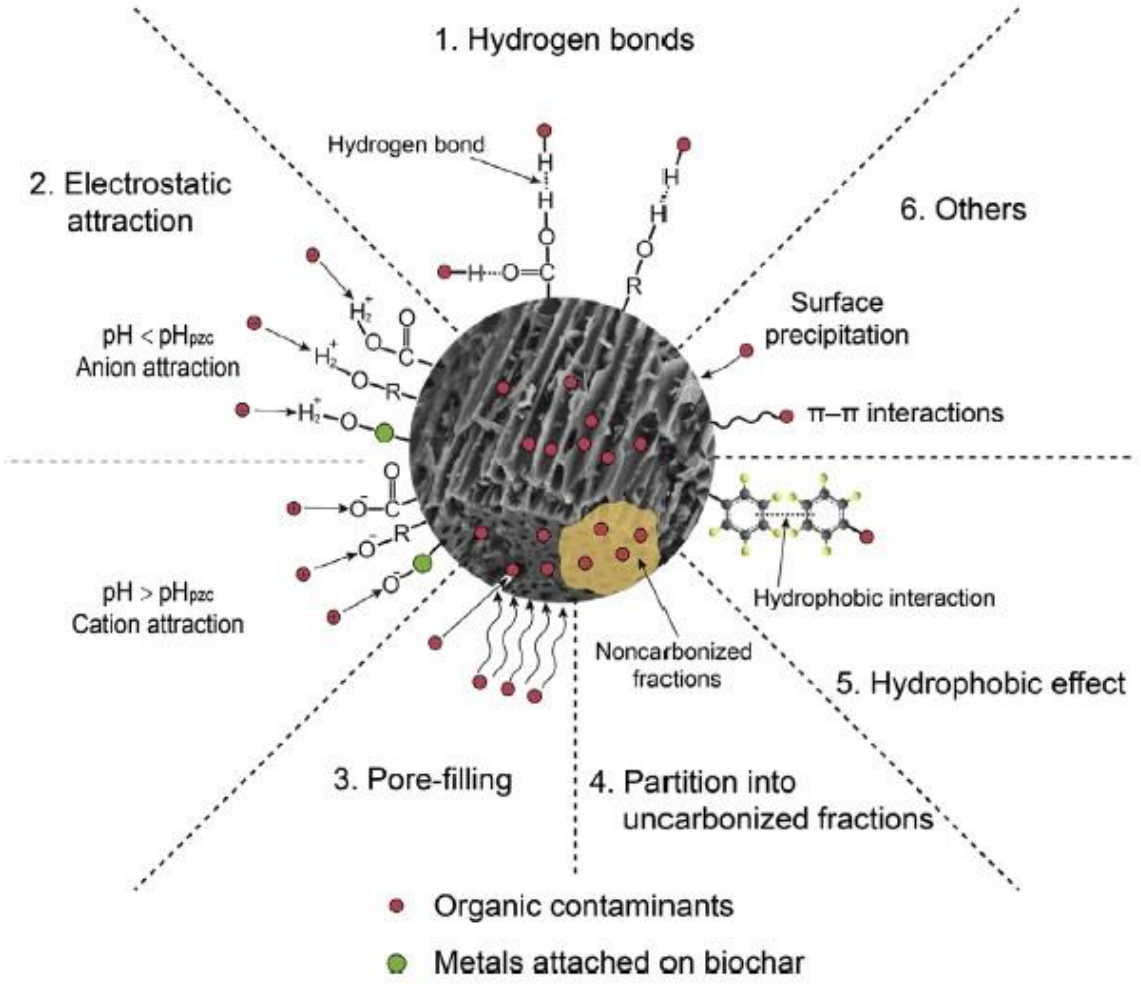


Figure 1.9. Various mechanisms for organic pollutants adsorption on biochar (source:. Tan et al. 2015).

Different organic contaminants have different adsorption mechanisms, which is also dependent on biochar properties. The surface properties of biochar is a determining factor in the adsorption process. The surface of biochar is heterogeneous because of the co-existent carbonized and non-carbonized portions which mainly exert different adsorption mechanisms. Both portions -carbonized (by adsorption) and non-carbonized (by partition)- contribute to organic pollutants uptake by biochar (Chen *et al*. 2008, Cao *et al*. 2009, Zheng *et al*. 2010). Some studies suggest that electrostatic attraction was the main mechanism for adsorption of organic contaminant, while others argued that as a contributing mechanism (Yang *et al*. 2014).

1.7 Factors Affecting Biochar Removal

The removal efficiency of different pollutants by biochar is determined by various factors including: the properties of the biochar, pH, and co-existent ions.

1.7.1 Properties of Biochar

Adsorption efficiency of biochar is highly affected by the properties of the biochar (i.e., surface area and porous amount), which, is in turn a function of feed stock, residence time (i.e., 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 temperature on 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 feed stocks. They also studied the combined adsorption and partition of aromatic contaminants by pine needle biochar with different pyrolytic temperatures and observed that with increasing temperature the adsorption of NAP significantly increased. In addition, sorption mechanisms of biochar changed from partitioning-dominant at low pyrolytic temperatures to adsorption-dominant at higher pyrolytic temperatures (Chen *et al*. 2008). At higher temperature more organic matter will be carbonized. As a result, more surface area and nano pores on biochar will be produced, leading to increased adsorption rate of pollutants by biochar (Zhou *et al*. 2010, Ahmad *et al*. 2013 a, Chen *et al* 2008). Natural composition of feedstock is another deciding factor in adsorption capacity of a biochar. The removal ability of biochar derived from different feed stocks vary for contaminants due to different mineral components (such as: CO_3^{2-}, PO_4^{3-}) originated from various raw biomass (Cao *et al* .2009, Xu *et al*. 2013b). The ability of dairy manure biochar and rice husk biochar in removing various heavy metals from aqueous solutions was investigated by Xu *et al*. 2011. The result showed that dairy manure biochar removed more Pb, Cu, Zn, and Cd from both mono and multi-metal solutions.

1.7.2 Solution pH

The effect of pH on biochar adsorption efficiency is a function of 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 behaviour of the functional groups (e.g. –COOH, -OH) on biochar surface change. At low pH, 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). Furthermore, an abundance of H^+ and H_3O^+ released into the solution will compete with cations for adsorption sites available on the biochar surface. As a result of the electrostatic repulsion happening between cations and biochar surface, less adsorption will occur on biochar surface. On the other hand, with increasing pH value, more cations will be absorbed by biochar surface because of the deprotonation of the functional groups, as well as decrease in the competition of cations and protons for occupying biding sites on biochar surface (Lu *et al*. 2012). Cu and Zn removal using hard wood and corn straw biochar was investigated by Chen *et al*. (2011). The result indicated that, at higher pH, the adsorption capacity of the biochar increased and maximum removal rate occurred at pH 5. In another study, with increasing pH from 3.5 to 6, Cu (II) adsorption on peanut straw, soybean straw, and canola straw biochar was increased significantly (Tong *et al*. 2011). A similar trend was observed for removing Pb using sludge derived biochar (Lu *et al*. 2012). In terms of organic pollutants, the adsorption of methyl violet by biochar derived from crop residues increased sharply with increasing pH from 7.7 to 8.7 (Xu *et al*. 2011).

1.7.3 Co-existent Ions

Different pollutants usually co-exist in the real water system, and interaction between these pollutants has a crucial impact on adsorption efficiency. Reports on the influence of these interactions are contradictory. In a study by Kong *et al*. (2011), co-existence of phenanthrene and Hg in aqueous solution resulted in direct competitive adsorption and following 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, in another study by Jia *et al*. (2013), by increasing Cu and Zn concentration, oxytetracycline removal by maize straw derived biochar improved.

1.8 Problems Concerning Biochar Use and Disposal

When using biochar as an absorbent media for toxic pollutants, such as heavy metals and organic pollutants, disposing the spent biochar is a key issue to consider. Biochar loaded with different nutrients or ammonium can be used as a slow-release fertilizer to improve soil fertility (Yao *et al*. 2011, 2013, Zhang *et al*. 2013). However, biochar that has been used as toxic absorbents should be handled with caution (Figure 1.10).

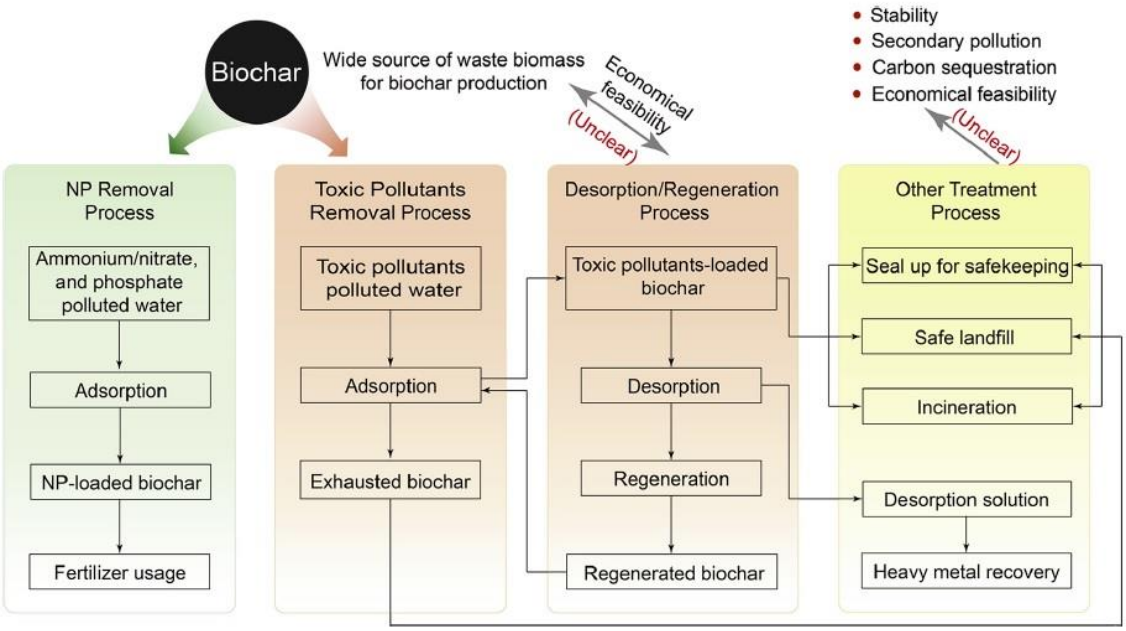


Figure 1.10. The schematic diagram of the system for pollutants removal from water, desorption/regeneration of biochar, and other treatment processes (Tan et al. 2015).

2 Experimental Plan

2.1 Goals and Objectives

The foremost goal of this study was to investigate the feasibility of using biochar as a new, environmental friendly, and inexpensive absorption media in infiltration galleries for removal of heavy metals including Cu, and Zn, and a representative PAH (i.e., NAP) from stormwater discharging into Guichon Creek at BCIT parking lots D and F. To reach this goal, the following objectives were pursued:

1) Determining environment relevant concentrations of target heavy metals and NAP in stormwater runoff from the above mentioned parking lots using current literature review and implementing water sampling.

2) Investigating the ability of a commercially available biochar in removing Cu, Zn, and NAP through implementing column treatments.

3) Proposing a suitable sizing of an infiltration system for the designated site based on results achieved from my experiment.

2.2 Research Questions

This research focused on the following questions:

1) Is biochar more efficient than sand in removing pollutants including Cu, Zn, and NAP form stormwater?

2) Which factor (i.e., concentration, pH, TOC, and particle size of the absorbent media) has the highest effect on Cu, Zn, and NAP removal by biochar and sand?

3) How the change in each factor's levels would influence the Cu, Zn, and NAP removal by biochar and sand?

2.3 Material and Method

2.3.1 Study Site

Stormwater samples were collected from two asphalt parking lots (Sites D and F) on the BCIT Burnaby campus that drain into Guichon Creek (Fig. 2.1). Study sites have similar attributes (i.e. size and usage). The area for each site is about 6830 m^2. Sample locations for these sites were stormwater drains located at the west end of the parking lots, that provide an appropriate indication of the quality of the stormwater discharging Guichon Creek. The parking lot designated Site D is a student/visitor asphalt parking lot with a total of 292 available spaces and average occupancy of 90% during regular semester hours. The parking lot designated Site F is a student/visitor asphalt parking lot with a total of 243 spaces and similar occupancy during semester hours (Personal observation 2017). The two sites are divided by an infiltration trench which is covered with vegetation. Also, both sites have filtration trenches covered with gravel in the east part of the parking lots. However, due to east–west grade of the area, most of the stormwater is directed to the storm drains located in the west part. Site D has a small area of permeable pavement in part of it, which is eroded and it is not functioning anymore.

2.3.2 Water Sampling

To achieve environmentally relevant concentrations, parking lot runoff samples were collected from five rain events at six storm drains at BCIT parking lots D and F (Fig 2.1.). To identify the potential change in physicochemical characteristics of storm runoff through the course of a rain event, the third and fourth series of sampling were performed at the beginning of the rain in the morning and the subsequent sampling was conducted at the end of that raining event in the afternoon (rain event duration for the first and second series of sampling were short, therefore only one set of samples were collected for these two rain events). Stormwater samples were collected in acid-washed 1-L polypropylene bottles. Water quality parameters including temperature and pH were measured using YSI Professional Plus multi-parameter meter on site. LaMotte 2020we Portable Turbidity Meter Kit was used to measure turbidity of water samples on site. Water samples were transferred to the BCIT Hydraulic Lab for Cu, Zn, and Pb concentrations and TOC analysis. In case of further analysis, water samples were

preserved using nitric acid (Hach) to a pH< 2 and stored at 4 C°. Since the organic pollutants were added to this research later, they were not measured in the stormwater water samples.

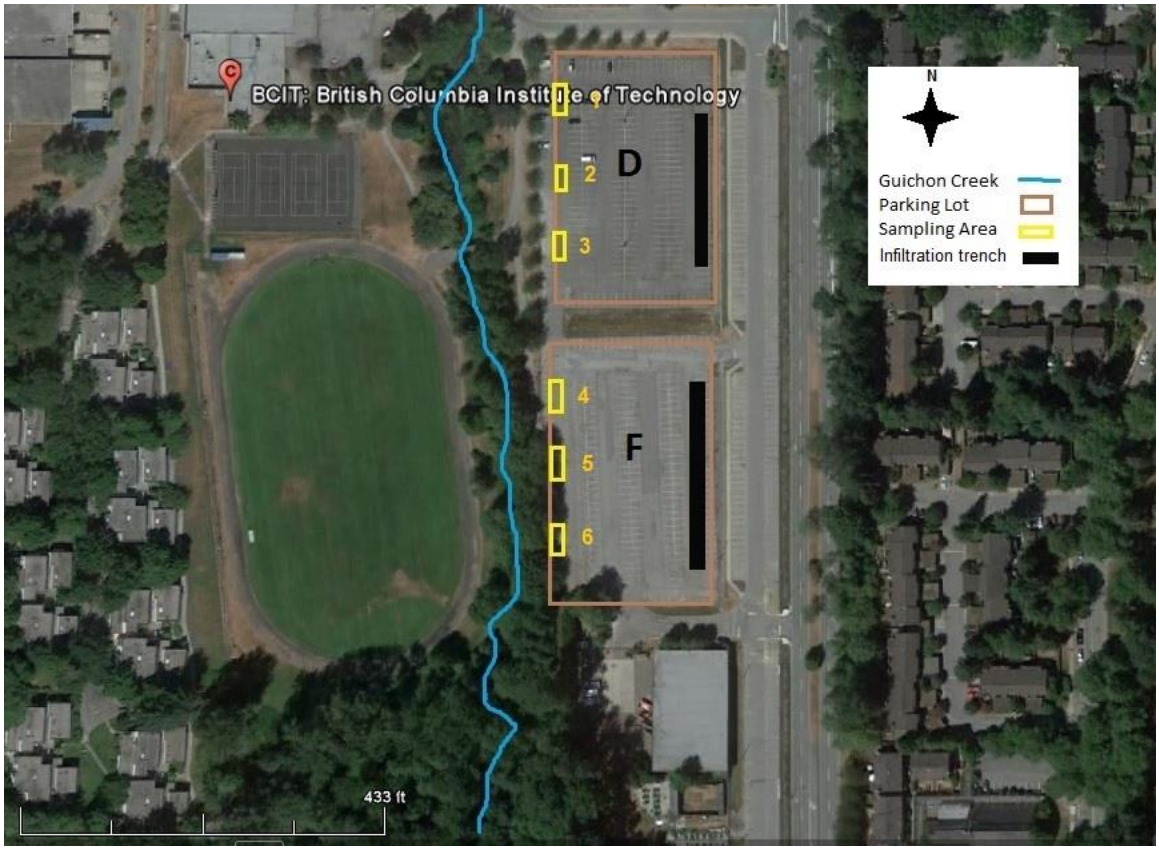


Figure 2.1. BCIT Parking Lot Stormwater Sampling Location, Burnaby, BC.

2.3.3 Biochar Characteristics and absorbent media preparation

A commercially available biochar from Biochar Now (LLC), Colorado, USA was used in this experiment. The biochar was produced by pyrolyzing pine wood at a temperature of 500-600 C° for 1-8 hours. Biochar had two different particle sizes: <0.3 mm and 0.3-0.7 mm. pH of biochar was 8. Prior to use the biochar, sand, and pea gravel were prepared by washing with distilled water and drying overnight in an oven at 120 °C. The biochar was then stored in an airtight container prior to use. River sand was used in the experiments.

2.3.4 Experimental Design

Two size of biochar (small and medium) and one size of sand were used as absorbent media in this experiment. Considering factors influencing biochar removal ability in an aquatic environment, four factors including pollutant concentration, TOC, pH, and particle size of biochar were selected. Based on literature review, the contaminants selected were Cu and Zn as they are two common and most problematic heavy metals in parking lot stormwater, and NAP as it is a representative PAH pollutant in parking lot stormwater. The relevant range of desired water quality parameters and pollutant concentration were determined through a comprehensive literature review and stormwater sampling (Table 2.1). Data is mainly derived from the following papers: Pit *et al*. 1995, Davis *et al*. 2003, Lee *et al*. 2003 and 2005, Tiefenthaler *et al*. 2003 and 2008, Grenstein *et al*. 2004, Herngren *et al*. 2005, Gobel *et al*. 2006, Kayhanian *et al*. 2008, Mc Queen *et al*. 2010, David *et al*. 2015. Two ranges of pollutant concentration (low and high range), two levels of TOC concentration (zero and 25 mg/l), two levels of pH (6.5 and 8.5) were chosen to added to 80 L of deionised water to prepare the synthetic stormwater for column experiments (Table 2.2). Three levels of particle size (i.e., small biochar, medium biochar, and sand) were used as absorbent media. Sand was used as a control absorbent media.

A full factorial design was used as the experimental design. Taking four factors including pollutant concentration, TOC, pH, and absorbent media type (Table 2.3.), and two replicates into account, 48 treatments were generated using Minitab software (Table A1in Appendix).

Table 2.1. Composition of pollutants in urban and synthetic storm water

Stormwater components	Ranges in parking lot stormwater (Literature review)	Ranges in urban stormwater (Literature review)	Ranges in BCIT campus parking lot	Concentration in prepared synthetic stormwater
Heavy Metals(µg/l)				
Cu	<1- 770	0 - 355	4-117	50, 800
Zn	<1 - 908	5- 4880	14-450	200 ,1800
NAP (µg/l)	<1- 10	<1-600	-	10, 1000
TOC (mg/l)	<0.001- 8.9	<0.001- 9.4	13-50	0 , 25
PH	6.6- 8.7	6.5-7.3	6.3 – 7.7	6.5 , 8.5

Table 2.2. Composition of pollutants in synthetic stormwater

Synthetic storm water	Cu (µg/l)	Zn (µg/l)	NAP (µg/l)
Low	50	200	10
High	800	1800	1000

Table 2.3. Different factors and related levels for designing column treatments

Factor	Concentration	TOC (mg/l)	pH	Particle size(absorbent media)
Level 1	Low	0	6.5	Sand
Level 2	High	25	8.5	Small biochar (<0.3 mm)
Level 3	-	-	-	Medium biochar (0.3-0.7 mm)

2.3.5 Column Treatments

Ten PVC pipes (91.4 cm length and 10.2 cm diameter) were used for the column treatments. They were filled with the prepared small biochar, medium biochar or sand depending on the treatment. Five centimeters of pea gravel were used at each end of the columns to help with drainage (Fig 2.2.). The pea gravel consisted of gravel with size ranges between 1.2 mm and 6.4 mm. The filters were flushed several times with tap water prior to the start of treatments. A 90 L aquarium was used as synthetic stormwater reservoir. Synthetic stormwater was prepared using Cu reference standard solution (1,000 ppm ±1%/) from Fisher Scientific, Zn reference standard solution (1,000 ppm ±1%) from Fisher Scientific, and NAP crystals (99% purity) from Sigma-Aldrich. Humic acid sodium salt (70% purity) from Fisher Scientific was used as TOC representative in synthetic stormwater. To achieve 25 mg/l TOC concentration in 80 L of synthetic storm water, 1 L of humic acid solution with 5.6 g/l concentration was used (5.6 g of humic acid crystals in 1 L of deionized water). Sodium hydroxide solution (N=2) from Fisher Scientific and nitric acid (64 to 66% purity) from Fisher Scientific were used to adjust pH of the synthetic storm water. pH of the solution was measured by HQ11D Portable pH meter from Hach. Synthetic stormwater was directed using small tubes to each column. During each treatment application, 80 L of synthetic stormwater was continuously discharged to the column and water sampling was performed after each 10 liters until all water was out of the column (eight samples). 300 ml air tight glass amber bottles were used for collecting samples. All sample were filled to top to avoid NAP volatilization and were instantly preserved using nitric acid to a pH < 2 after collection and stored at 4 C° in a refrigerator. Samples were usually analyzed within five to seven days after

collection. All treatments were conducted at room temperature. Each treatment had two replicates.

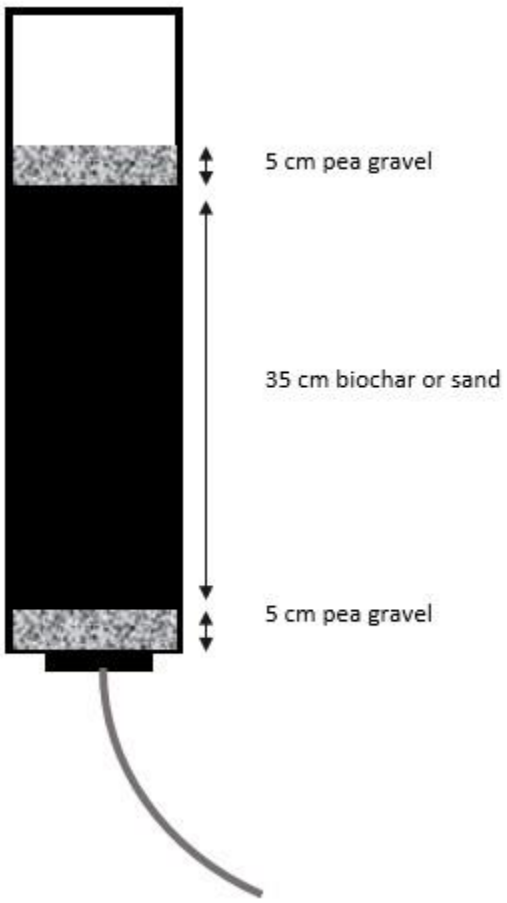


Figure 2.2 Filter column cross section

2.3.6 Sample Analysis

Stormwater samples from the parking lots were 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 from the parking lot and

also from column treatments were determined using graphite furnace (EPA method 7010) and Atomic Absorption spectroscopy (AA) (EPA method 7000B). To define NAP concentration in water samples, Gas Chromatography Mass Spectrometry (GC-MS) was used (EPA method 5021). For TOC analysis, TOC TNT plus vial test kit (1.5 - 30.0 mg/L C) (UEPA method 10267) from Hach, and DR6000 Laboratory Spectrophotometer from Hach were used. External standards were used in the analysis, as well as blanks and duplicate samples as a quality control measure.

2.3.7 Tracer Analysis

The pore volume of the biochar and sand used in these treatments were measured through a tracer test. The columns which were packed with 100% of small biochar, 100% of medium biochar, and 100% of sand, were filled with tap water. Then, 7 L of NaCl solution with 1,285 µs/cm conductivity were discharged through each column (slug technique) and conductivity of the effluent samples were measured using a Hach HQ 14d conductivity meter for each 0.5 L.

2.3.8 Statistical Analysis

Concentration difference of pollutants in influent and effluent water samples was used as the indicator of the removal capability of the absorbent media. The removal efficiency for each treatment was determined by means of the following equation (Komkiene and Baltrenaite 2015):

$$RE = \frac{\text{C Influent} - \text{C Effluent}}{\text{C Influent}} * 100 \qquad (1)$$

where,
RE = the removal efficiency in percentage,
$C_{Influent}$ = concentration at the influent,
$C_{Effluent}$ = concentration at the effluent.

Factorial ANOVA was performed for statistical analysis of the results using SPSS 20 software at 95 % confidence (α= 0.05). Tukey post hoc tests were used for comparing means. Partial eta-squared (η^2) is an estimate of effect size. It represents how much variance is explained by each independent variable. η^2 was also calculated for each factor.

2.3.9 Flow Rate

Flow rate of the biochar filter and sand were calculated based on the time needed to fill a 100 ml graduated cylinder at the beginning of the treatment when there was a maximum pressure head in the filter (i.e. when the filter was full and the height of water was about 91.4 cm). Hydraulic loading rates for sand, small size biochar, and medium size biochar based on three measurements were 0.45 (SD=0.10), 0.43 (SD=0.02), and 0.48 (SD=0.12) L/min respectively.

2.3.10 Breakthrough Curve

The efficiency of a column can be discussed using breakthrough curves, which is achieved by plotting column effluent concentration versus volume treated or time of treatment. Breakthrough curves provide valuable information to help design a fixed-bed adsorption process in field application. The main elements of a breakthrough curve include: breakthrough capacity, exhaustion capacity and degree of column utilization. When synthetic storm water is introduced through the inlet of the column, pollutants are absorbed most rapidly and effectively by the upper few layers of the sorbent. As the feed water continues to flow into the column, the top layers of the absorbent media become saturated with the pollutants. As a result, sorption zone moves downwards to the regions of fresher sorbent in the column. As sorption zone moves downwards, more pollutants manage to escape from the column until the whole absorbent media become saturated and it reaches it's zero removal efficiency ($C_{Influent} = C_{Effluent}$). The plots of C/C_0 (C: pollutant concentration in effluent and C_0: pollutant concentration in influent) versus time or volume of effluent, for a constant flow rate portrays the rise in the ratio of C/C_0 as absorption zone moves through the column. Breakthrough curves usually display a characteristic S shape with changing degree of steepness (Fig 2.3).

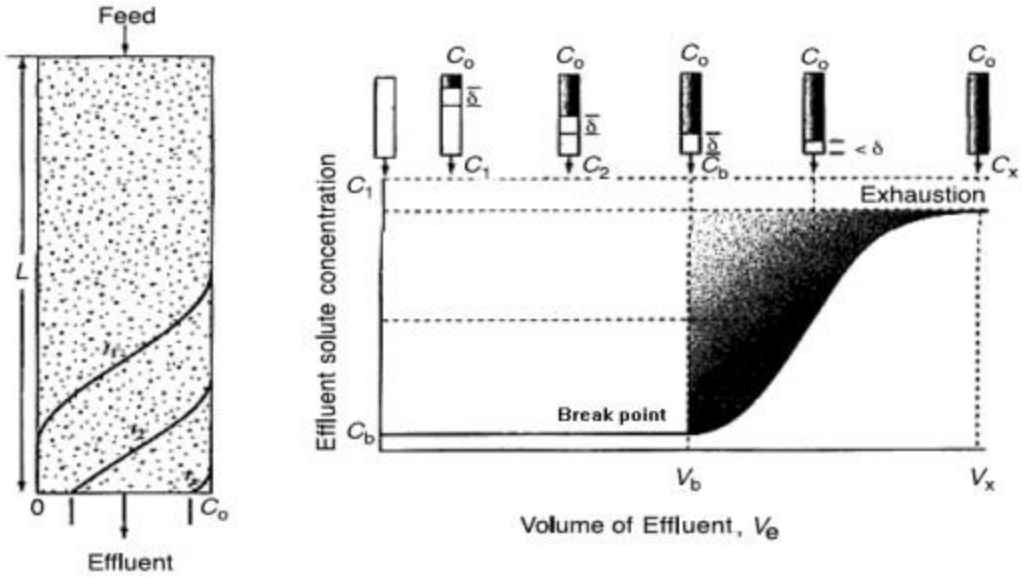


Figure 2.3. Representation of the movement of primary sorption zone and formation of breakthrough curve source: http://shodhganga.inflibnet.ac.in/bitstream/10603/3037/12/12_chapter%206.pdf

2.3.11 Blank Experiment:

To test the heavy metal and NAP contribution of biochar and sand, a blank experiment was implemented as follows: two columns, one packed with 100% biochar and the other one packed with 100% sand (35 cm of the length of column), plus 5 cm of pea gravel at each end, were fed with 80 L of deionized water. Water samples were collected for each 10 liters discharged. The process was repeated seven times for each absorbent media. The concentration of heavy metals in water samples were determined using graphite furnace (EPA method 7010) and Atomic Absorption spectroscopy (AA) (EPA method 7000B). To define NAP concentration in water samples, Gas Chromatography Mass Spectrometry (GC-MS) was used (EPA method 5021).

3 Results

3.1 Physicochemical Characterization of Campus Parking Lot Stormwater

Stormwater samples of BCIT parking lot were collected from September 2017 through March 2018. General water chemistry was analyzed from a total of 20 samples for parking lot D and 22 samples for parking lot F collected during five storm events (Table 3.1). 24 h rainfall for each event were source: www.theweathernetwork.com.

Table 3.1 Characteristics of stormwater sampling events from BCIT parking lot F and D, 2017-2018. Antecedent days represent number of days between two subsequent rainfalls.

Event	Sample Dates	Sample Duration (Hours)	Start-End time	24 h Rainfall (mm)	Antecedent days
1	08/09/2017	1.00	9:00 am- 10:00 am	3.4 mm	25
2	09/09/2017	0.50	10:40 am- 11:30 am	5.4 mm	0
3	12/10/2017	3. 15	10:30 am- 1:45 pm	31.4 mm	0
4	08/03/2018	6.05	8:10 am – 2:15 pm	16.8 mm	3
5	13/03/2018	3.25	11:50 am – 3:15 pm	9.1 mm	4

Analysis of general water chemistry for parking lot F and D included pH from 6.3 to 7.7, turbidity from 3 to 37 NTUs and water temperature from 8.3 to 20.5 °C. Stormwater samples from these storm events had heavy metals concentration of 4 to 117 µg/l for Cu and 14 to 450 µg/l for Zn. The maximum concentration of heavy metals followed the range of Zn> Cu> Pb. TOC showed a range of 1 to 122 mg/l (Table 3.2).

Table 3.2. Overall range of different water parameters from all rain events from BCIT parking lot F and D, 2017-2018.

Parameter	Temperature (°C)	pH	Turbidity (NTU)	Pb (µg/l)	Zn (µg/l)	Cu (µg/l)	TOC (µg/l)
Range	8.3-20.5	6.3 - 7.7	3 -37	1-15	14-450	4-117	13-50

Mean water quality parameters of different rain events is exhibited in Figure 3.1. As shown, temperature and turbidity have a declining trend, however, pH has increased through different rain events which was expected because of the change in the season of sampling.

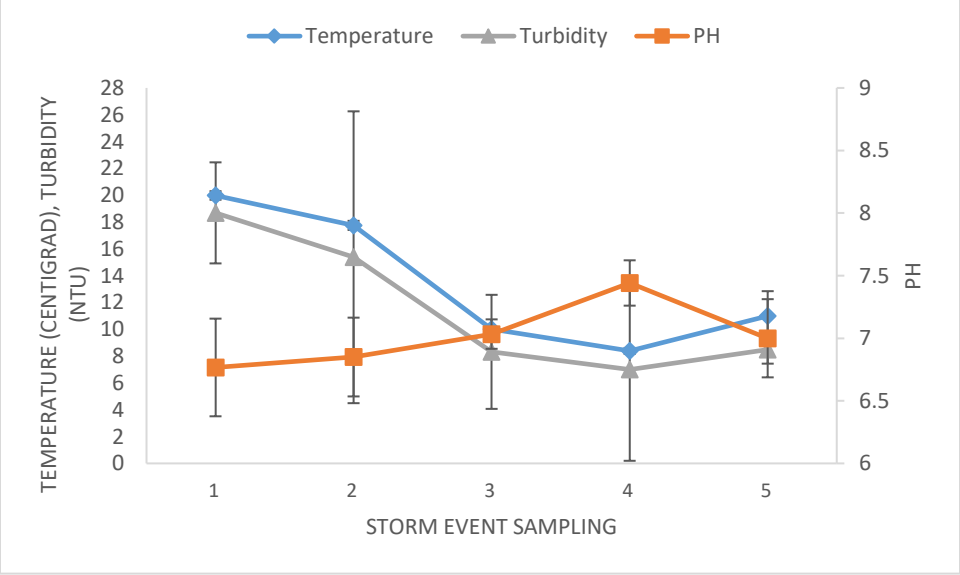


Figure 3.1 Mean temperature, turbidity, and pH of different rain events from BCIT campus parking lot F and D, Burnaby, BC. From September 2017 to March 2018. Bars represent standard deviation based on data from six drain storm.

Result showed that samples from the first rain event were more toxic than samples collected in later events, indicating the first flush phenomenon (Table 3.2). In addition, Zn had the highest mean concentration among other heavy metals tested

(M=156). However, Cu had the highest decline (89%) in concentration compared to Zn (87%) and lead (83%).

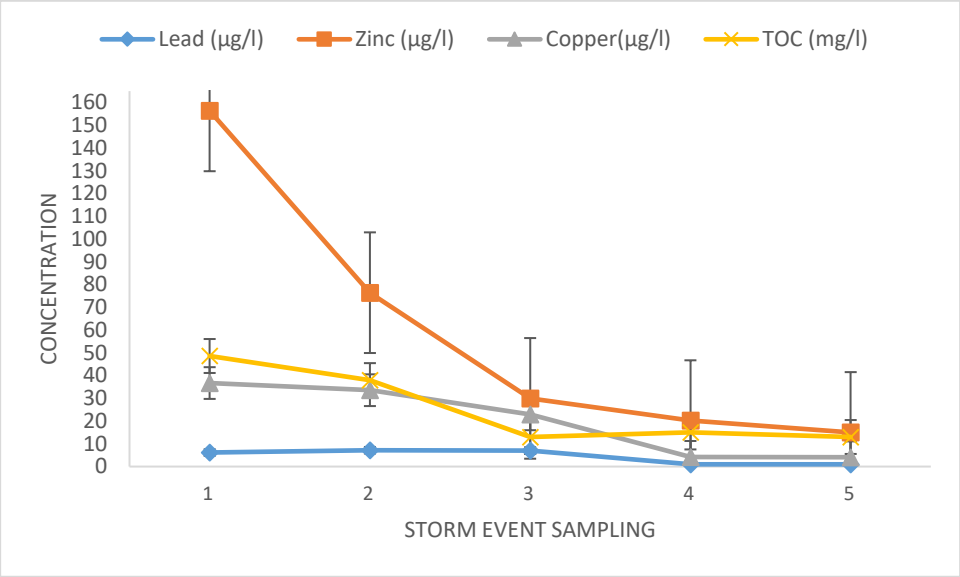


Figure 3.2 Different heavy metal and TOC concentrations of sampling rain events from BCIT campus parking lot F and D, Burnaby, BC. From September 2017 to March 2018. Bars represent standard deviation based on data from six drain storm.

Temperature and pH of the storm water samples was almost constant during the course of three rain events (Figure 3.3). However, there was a big decline in turbidity through the course of the rain events. In terms of heavy metals, the lead concentration did not show the similar trend for two rain events and concentrations were below detectable range in the second sampling event. Same as TOC, although Cu concentration had a steep increase through the course of one rain event, the concentrations increased in other rain event. Zn concentration increased through all three of the rain events.

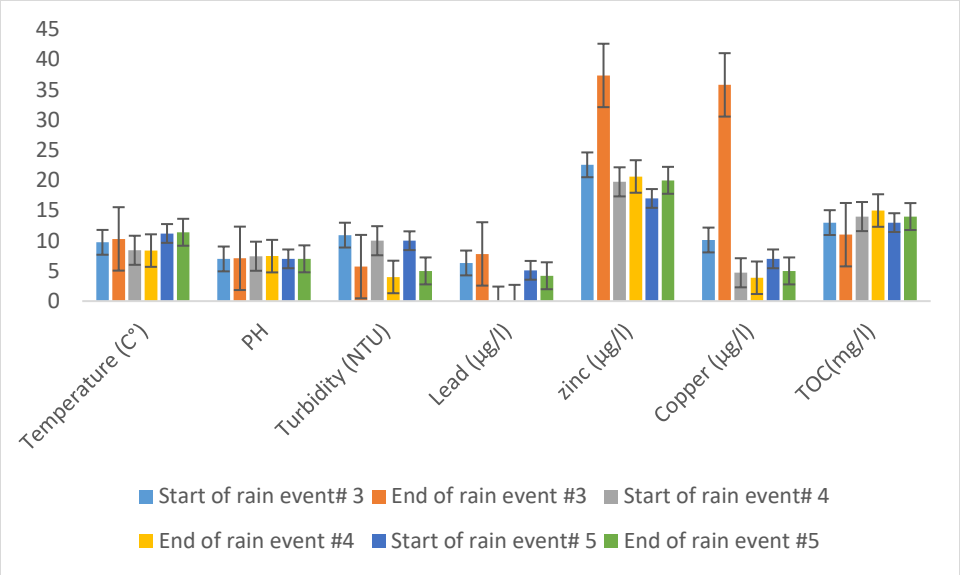


Figure 3.3. Changes in water quality characteristics and heavy metal concentration through the course of three rain events from BCIT campus parking lot F and D, Burnaby, BC. From September 2017 to March 2018.

3.2 Tracer Analysis

As shown in the following graphs, conductivity recovery (i.e., the steady part in the graph) for all absorbent media (medium biochar, small biochar, and sand) occurred around 10 L showing approximate pore volume of 10 L for these filters (Figures 3.4 to 3.6).

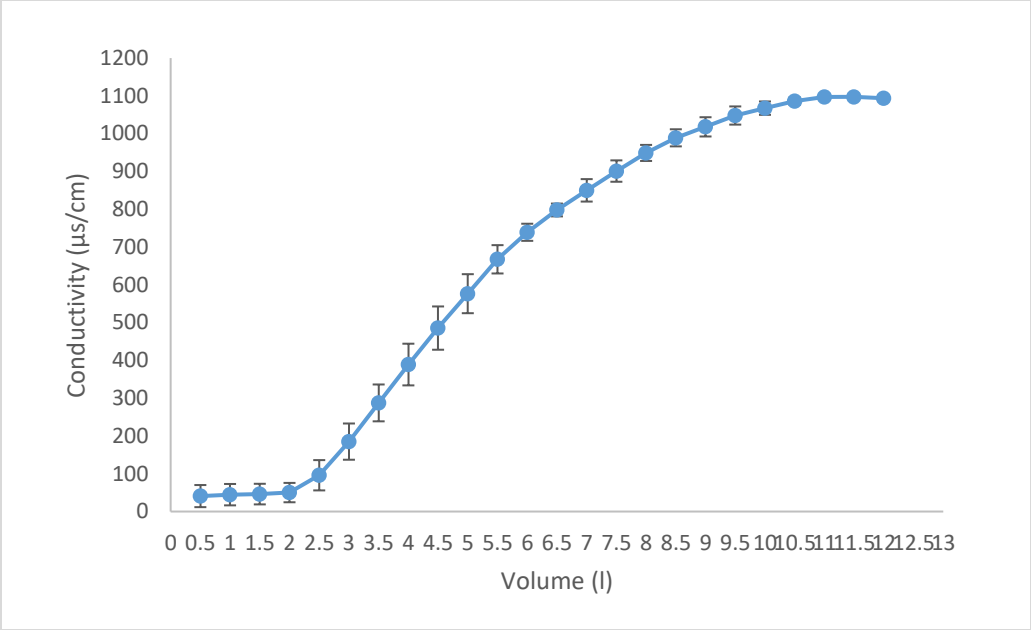


Figure 3.4. Tracer analysis result for medium sized biochar, bars based on standard deviations of two replicate. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

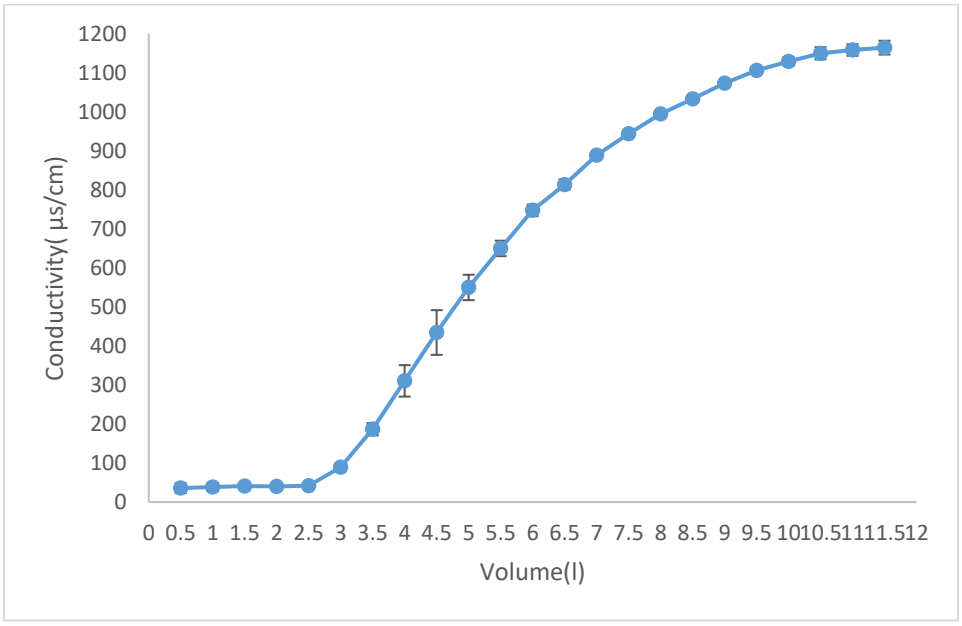


Figure 3.5. Tracer analysis result for small biochar. Bars based on standard deviations of two replicate. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

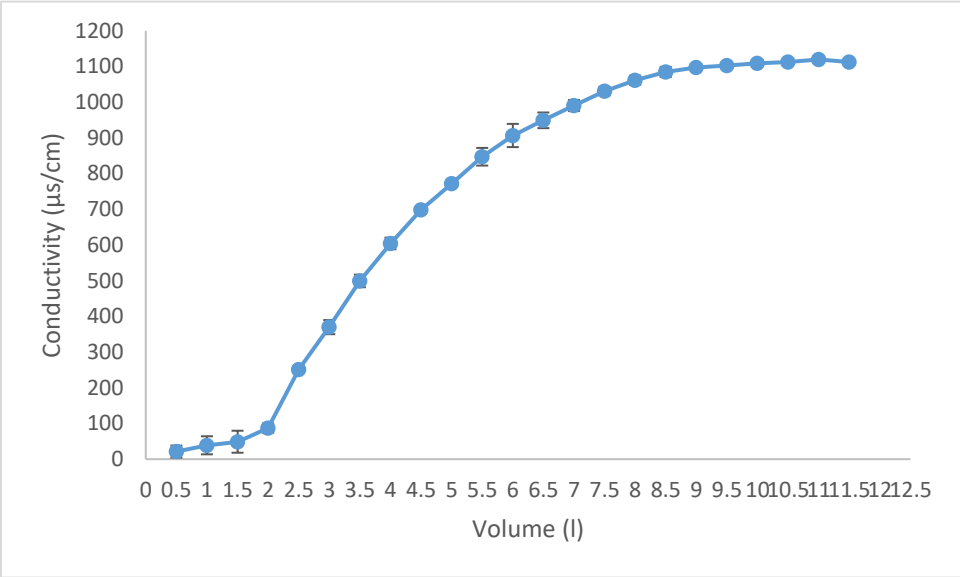


Figure 3.6. Tracer analysis results for sand. Bars based on standard deviations of two replicate. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

3.3 Breakthrough Curve

None of the breakthrough point and complete exhaustion point occurred for any of three pollutants. Breakthrough curves for all treatments are included in the Appendix (Figures B1 to B15). Treatments 31 and 32 (small biochar, high concentration of pollutants, pH=8.5, and TOC=25), showed the fastest decline in Cu concentration (28%) (Table B1). Treatments 25 and 26 (small biochar, high concentration of pollutants, pH=6.5, and TOC=25) had the fastest decline in Zn concentration (42%). The fastest decline in NAP concentration was observed in 25, 26 (20%) and 31, 32 treatments (20%). Several treatments exhibited zero decline in Cu, Zn, and NAP concentrations (Table B1).

3.4 Blank Experiments

Based on results from blank experiments I conducted biochar and sand did not contribute to Zn, and NAP concentrations. However, because of an error in Cu data, the

same conclusion can not be deduced. A summary of blank experiments result is included in Table C7 and C8 in the Appendix C.

3.5 Contaminant Removal Efficiency

A factorial ANOVA was conducted to compare the main effect of concentration, pH, TOC, and particle size and the interaction effect between them on Cu, Zn, and NAP removal by biochar and sand.

3.5.1 Cu Removal

The result revealed that all the main effects were statistically significant at the 0.05 significance level except for the pH factor. The main effect for concentration of different pollutants yielded an F ratio of F (2, 24) = 8.9, p= 0.006, suggesting that Cu removal was significantly higher in high concentration (M=57.6%, SD= 39.5) compared to low concentration of synthetic storm water elements (M= 50.7%, SD= 47.7) (Table 3.3). Small biochar and sand absorbed more Cu in high concentration of pollutants. Cu % removal for medium biochar in low and high concentration were almost the same (Figure 3.8).

Table 3.3 Selected ANOVA details for Cu removal of column treatments at 95% confidence interval using SPSS software version 16.0.

Source	df	F	Mean Square	Sig.	Partial Eta squared (η^2)	Levels	Mean	Standard Deviation
						High	57.6	39.5
Concentration	1	8.9	567.6	0.006	0.270	Low	50.7	47.7
						6.5	52.7	44.46
PH	1	1.5	95.7	0.233	0.059	8.5	55.6	43.44
						TOC=0	95.9	6.1
TOC	1	1308.6	83545.8	0.000	0.98	TOC=25	12.4	13.9
						Sand	54.7	46.3
Absorbent Media	2	7.2	461.7	0.003	0.37	Medium biochar	48.5	44.5
						Small biochar	59.2	41.6
						Concentration Low, TOC=0	96.7	2.7
Concentration*TOC	1	13.7	876.2	0.001	0.36	Concentration Low, TOC=25	4.7	12.0
						Concentration High, TOC=0	95.1	8.4
						Concentration High, TOC=25	20.2	11.5

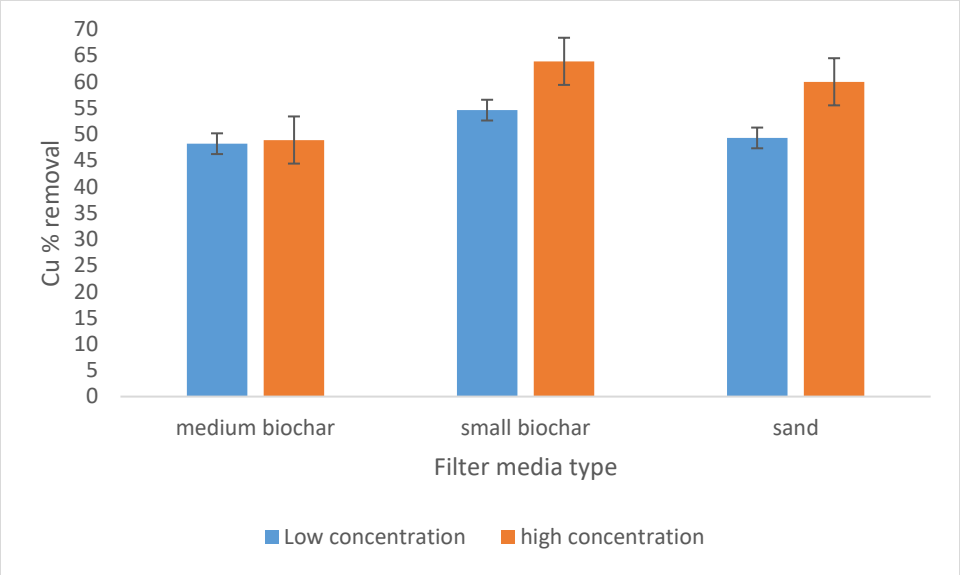


Figure 3.8. Cu removal percentage by different absorbent media at different concentration. Bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

Also, there was significant main effect of TOC on Cu removal ($F(1, 24) = 1308.6$), $p<0.05$, meaning that three different absorbent media absorbed more Cu in the absence of TOC (M= 95.9%, SD=6.1) in comparison to TOC=25 mg/l (M= 12.4%, SD= 13.9) (Fig 3.9). It is worth mentioning that with increasing TOC concentration from zero to 25mg/l, in some treatments (including treatments with biochar or sand), resulted in higher Cu concentration in the effluents compared to influent (Table A1 where Cu %removal equals zero and Figures B5, B6, B14).

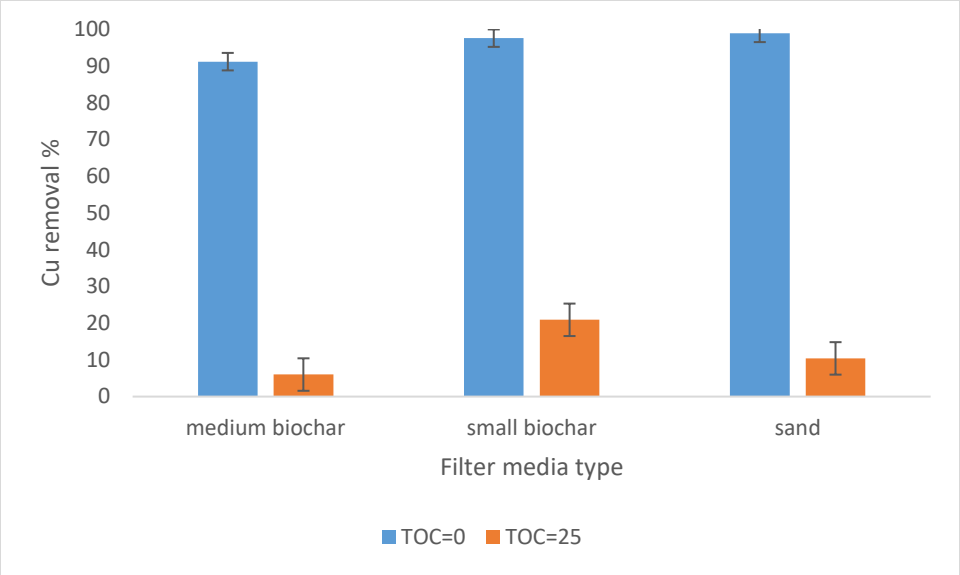


Figure 3.9. Cu removal percentage by different absorbent media at different TOC concentration. Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

The main effect for absorbent media (i.e., sand, medium biochar, small biochar) resulted in an F ratio of F (2, 24) = 7.2 and p= 0.003, indicating statistically significant difference in Cu removal among medium size biochar (M= 48.5%, SD= 44.5), small biochar (M=59.2%, SD= 41.6), and sand (M=54.7%, SD= 46.3) (Fig 3.10). However, there was no main effect of pH on Cu removal (F (1, 24) = 1.5, p > .05). A significant interaction between Influent Cu concentration and TOC was observed (F (1,24) = 13.7 and p= 0.001) (Table 3.3). The nature of this interaction suggested that, in the absence of TOC (TOC=0), Cu removal by different absorbent media at low TOC concentration (M= 96.7%, SD= 2.7) were almost the same as high concentration (M= 95%, SD= 8.4). On the other hand, where TOC = 25 mg/l, high concentration (M=20.1%, SD=11.5) favored Cu removal compared to low concentration (M= 4.7%, SD= 11.5). All the other interactions were not significant (Table C1). Post hoc comparisons using the Tukey HSD test indicated that the mean Cu removal for medium biochar (M = 48.5%, SD = 44.5) was significantly different than small biochar (M = 59.2%, SD = 41.6) (Fig 3.10). However, the sand's ability to remove Cu (M = 54.7%, SD = 46.3) did not significantly differ from the medium biochar and small biochar (Table C2). The effect of TOC (η^2 = .98) was stronger than absorbent media type (η^2 = 0.37) and concentration levels (η^2 =

0.27). Refer to Table C1 in the Appendix C for the complete ANOVA details for Cu removal.

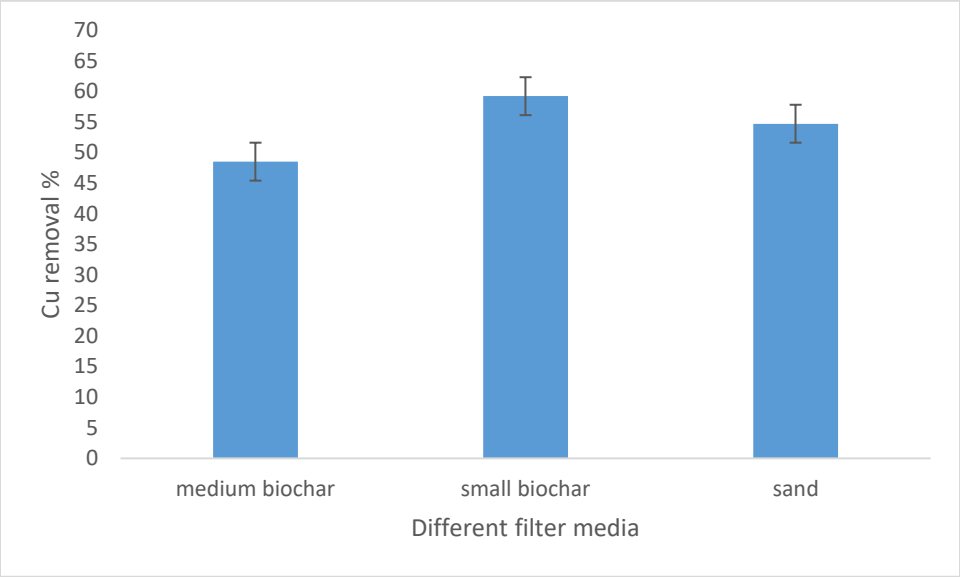


Figure 3.10. Overall Cu removal percentage by three different absorbent media. Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC

3.5.2 Zn Removal

Based on the result, the main effects including concentration ((F (1,24) = 1.64), p> 0.05) and pH (F (1,24) = 0.44, p> 0.05) were not statistically significant at the 0.05 significance level (Table 3.4). However, the main effect for TOC yielded an F ratio of F (2, 24) = 90.9, p< 0.05) suggesting that Zn removal was significantly higher in absence of TOC (M=90.9%, SD= 15.8) compared to TOC=25 mg/l (M= 55.2%, SD= 27.4) (Fig 3.11).

Table 3.4 Selected ANOVA detail for Zn removal of column treatments at 95% confidence interval using SPSS software version 16.0.

Source	df	F	Mean Square	Sig.	Partial Eta squared (η^2)	Levels	Mean	Standard Deviation
Concentration	1	1.64	248.7	0.212	0.064	Low	70.8	31.2
						High	75.3	26.2
pH	1	0.4	6.7	0.835	0.002	6.5	73.5	28.6
						8.5	72.7	29.2
TOC	1	101.4	15371.1	0.000	0.809	TOC=0	90.9	15.8
						TOC=25	55.2	27.4
Absorbent Media	2	35.6	5397.9	0.000	0.748	Sand	88.4	18.5
						Medium biochar	52.7	30.8
						Small biochar	78.0	23.4
Concentration*TOC	1	16.0	2429.7	0.001	0.400	Low Concentration, TOC=0	95.8	4.8
						High Concentration, TOC=0	86.1	21.1
						Low Concentration, TOC=25	45.8	25.5
						High Concentration, TOC=0	64.5	27.0
TOC*Absorbent Media	2	4.8	737.5	0.017	0.289	TOC=0, Medium Biochar	75.5	20.2

	TOC=0, Small Biochar	98.8	1.5
	TOC=0, Sand	98.6	1.5
	TOC=25, Medium Biochar	29.9	21.0
	TOC=25, Small Biochar	57.3	14.0
	TOC=25, Sand	78.3	22.3

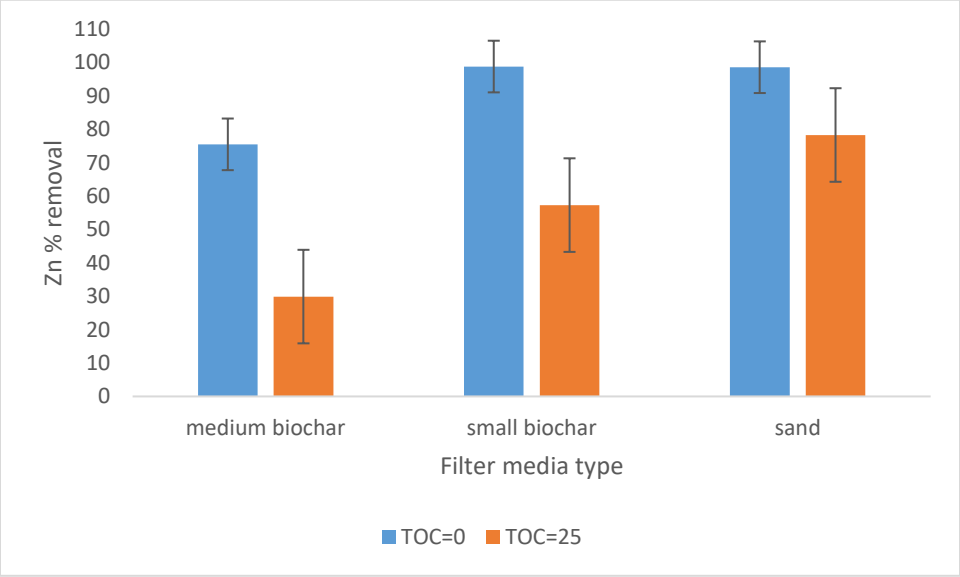


Figure 3.11. Zn removal percentage by different absorbent media at two different TOC concentrations. Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

Also, there was a significant main effect of absorbent media type on Zn removal ($F(1, 24) = 35.6$), $p < 0.05$, meaning that three different absorbent media (medium biochar (M= 52.7, SD= 30.8), small biochar (M= 78.0%, SD= 23.4), and sand (M=

88.4%, SD= 18.5) absorbed different amounts of Zn from synthetic storm water (Fig 3.12.). A significant interaction between concentration and TOC was observed ($F(1,24) = 16.0$), $p = 0.001$. The nature of this interaction suggested that, in the absence of TOC (TOC=0), Zn removal by different absorbent media were higher at low concentration (M= 95.8%, SD= 4.8) compared to high concentration (M= 86.1%, SD= 21.1). In contrary, where TOC = 25 mg/l, high concentration (M=64.1%, SD=27.0) favored Zn removal compared to low concentration (M= 45.8%, SD= 25.5). In addition, there was a significant interaction between TOC and absorbent media type ($F(2,24) = 4.8$), $p = 0.017$. The nature of this interaction suggested that, with increasing TOC concentration from zero to 25 mg/l, Zn removal ability by all three absorbent media decreased significantly (Table 3.4). All the other interactions were not statistically significant at the 0.05 significance level (Table C3). Post hoc comparisons using the Tukey HSD test indicated that the mean Zn removal for medium biochar (M = 52.7%, SD = 30.8) was significantly different than small biochar (M = 78.0%, SD = 23.4) and sand (M= 88.4%, SD= 18.5) (Fig 3.12). However, the small biochar ability to remove Zn did not significantly differ from sand (Table C4). The effect of TOC ($\eta^2 = 0.80$) was approximately as strong as absorbent media type ($\eta^2 = 0.74$). Refer to Table C3 in the Appendix C for the complete ANOVA details for Zn removal.

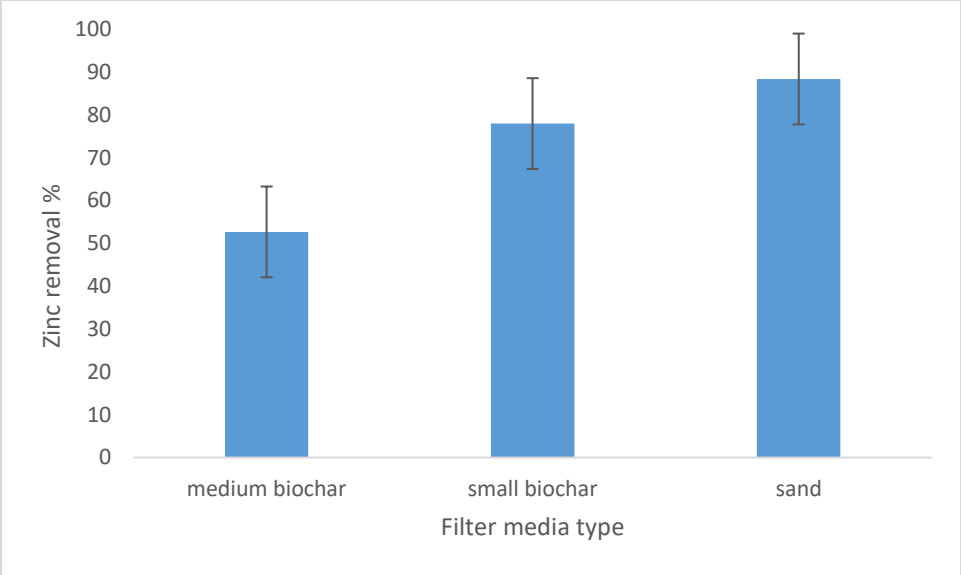


Figure 3.12. Overall Zn removal by different absorbent media. Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

3.5.3 NAP Removal

In terms of NAP removal, the main effect concentration of pollutants was statistically significant at the 0.05 significance ($F(2, 24) = 4.7$), $p = 0.039$, suggesting that NAP removal was significantly higher in high concentration (M=63.9%, SD= 35.3) compared to low concentration of synthetic storm water elements (M= 51.6%, SD= 36.4) (Table 3.5). All three different absorbent media absorbed more NAP in high concentration of pollutants compared to low concentration (Figure 3.13).

Table 3.5 Selected ANOVA detail for NAP removal of column treatments at 95% confidence interval using SPSS software version 16.0.

Source	df	F	Mean Square	Sig.	Partial Eta squared (η^2)	Levels	Mean	Standard Deviation
Concentration	1	4.7	1816.8	0.039	0.166	High	63.9	35.3
						Low	51.6	36.4
pH	1	1.3	491.4	0.267	0.051	6.5	61.0	35.6
						8.5	59.6	38.6
TOC	1	1.5	580.2	0.220	0.600	TOC=0	54.3	35.6
						TOC=25	61.2	37.0
						Sand	15.1	21.1
Absorbent Media	2	579	22045.9	0.000	0.828	Medium biochar	81.8	15.1
						Small biochar	78.5	21.5

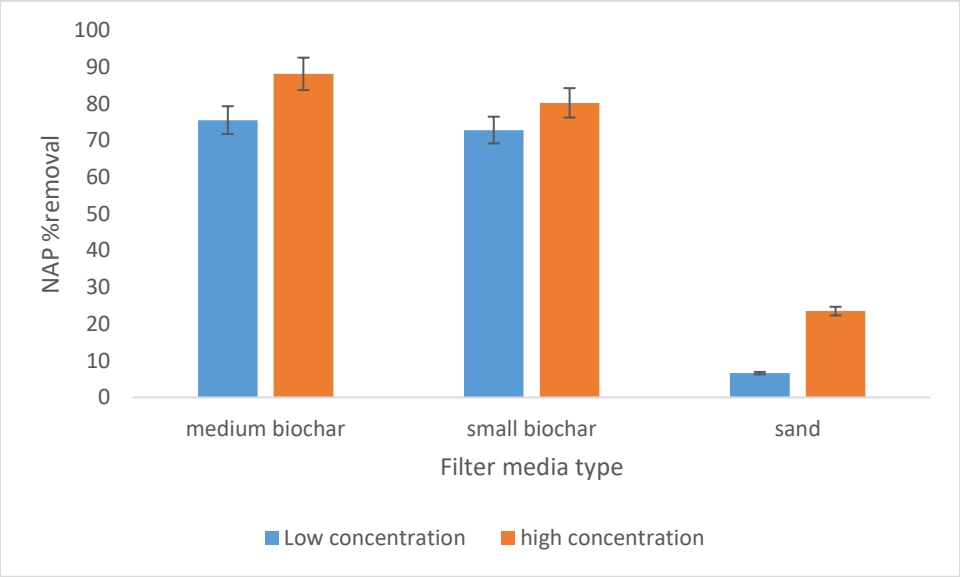


Figure 3.13. NAP removal percentage by different absorbent media at different concentration of pollutants. Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

There was no main effect of pH ($F(1, 24) = 1.3$, $p > 0.05$) and TOC ($F(1, 24) = 1.5$, $p > 0.05$) on NAP removal. However, the main effect for absorbent media resulted in a F ratio of $F(2, 24) = 57.8$, $p < 0.05$, indicating statistically significant difference in NAP removal among medium size biochar (M= 81.8%, SD= 15.1), small biochar (M=76.5%, SD= 21.5), and sand (M=15.1%, SD= 21.1. All the interactions between factors were not statistically significant at 0.05 significance level (Table C5). Post hoc comparisons using the Tukey HSD test indicated that the mean NAP removal for medium biochar (M= 81.8%, SD= 15.1), was significantly different from sand (M=15.1, SD= 21.1) (Table C6). However, the medium biochar ability to remove NAP did not significantly differ from the small biochar (M=76.5%, SD= 21.5), (Fig 3.14). The effect of absorbent media type (η^2 = .82) was approximately five times as strong as concentration ($\eta^2 = 0.16$). Refer to Table C5 in the Appendix C for the complete ANOVA details for NAP removal.

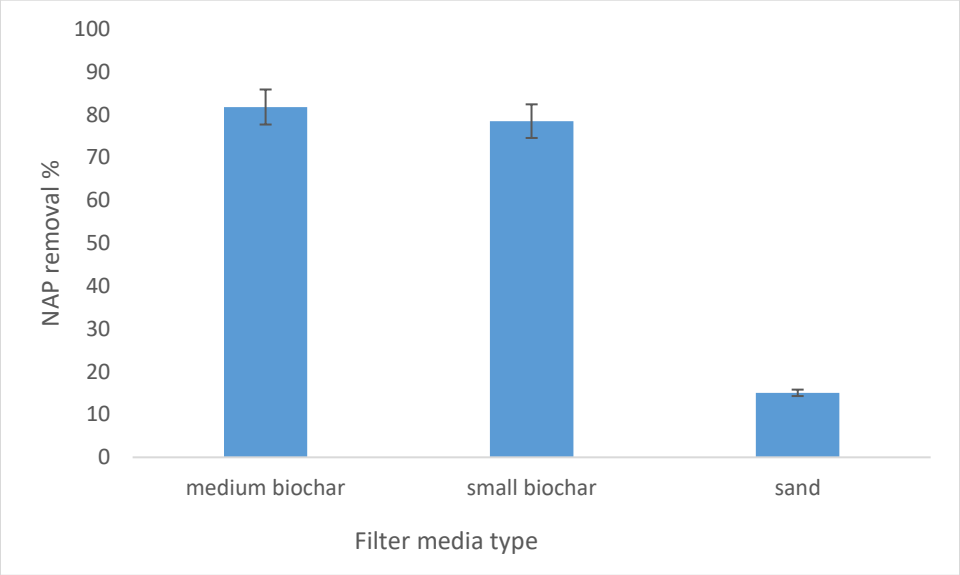


Figure 3.14. The overall NAP removal percentage by different absorbent media. Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

Figure 3.15 compares the overall removal abilities of Cu, Zn, and NAP by all three different absorbent media. As shown, maximum percentage removal using biochar followed the order of NAP > Zn > Cu. In the case of sand, maximum percentage removal was highest for Zn among the all tested pollutants, whereas that was lowest for NAP.

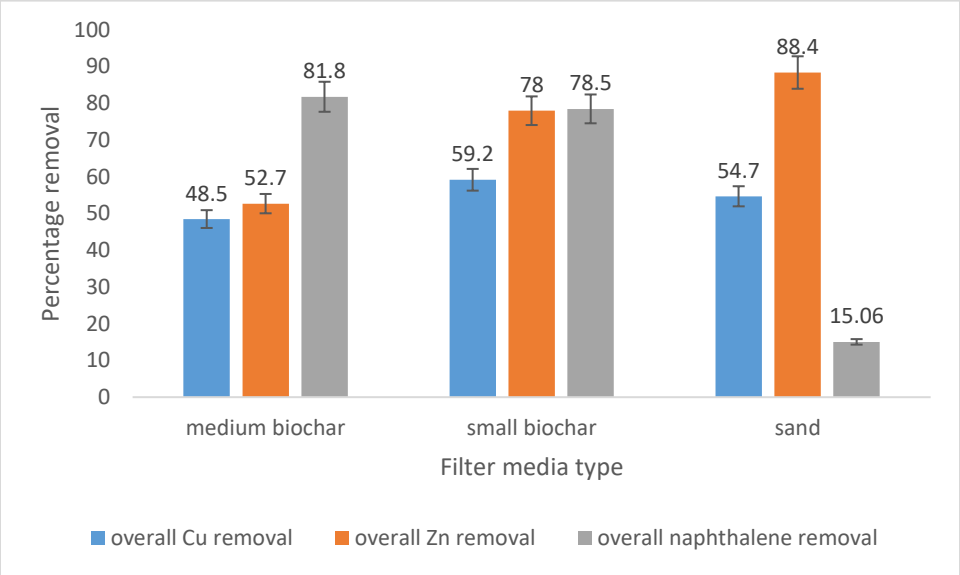


Figure 3.15. Comparison of the overall removal abilities of Cu, Zn, and NAP using medium biochar, small biochar, and sand. Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

4 Discussion

4.1 Constituents of Concern

A constituent of concern is defined as a physical or chemical component in water at adequate concentration to pose potential risks to receiving water biota. To identify the constituents of concern in campus parking lot stormwater, British Columbia Approved Water Quality Guidelines for Aquatic Life, Wildlife and Agriculture (Ministry of Environment and Climate Change Strategy 2018) were used (Table 4.1). Based on the guidelines, both Cu concentration(4-117µg/l) and Zn concentration (14-450µg/l) in storm samples exceeded the permitted concentration (for ranges of concentrations refer to Table 3.2).

Table 4.1 Water quality guidelines for total Cu and Zn (source: Ministry of Environment and Climate Change Strategy 2018).

	Water use	**Long-term Average (µg/l)**	**Short term maximum (µg/l)**
Cu	Freshwater Aquatic Life (When Water Hardness ≤ 50 mg/L $CaCO_3$)	≤ 2	WQG = 0.094 hardness** + 2 E.g. When hardness = 25 mg/L $CaCO_3$ WQG = 0.094 × 25 + 2 = 4.350
	Freshwater Aquatic Life (When Water Hardness > 50 mg/L $CaCO_3$)	WQG ≤ 0.04 (mean hardness*) E.g. Mean hardness = 75 mg/L $CaCO_3$ WQG ≤ 0.04 (75) ≤ 3	WQG = 0.094 hardness** + 2 E.g. Mean hardness = 75 mg/L $CaCO_3$ WQG = 0.094 × 75 + 2 = 9.050
	Marine and Estuarine Aquatic Life	≤ 2	3
Zn	Freshwater aquatic life-water hardness ≤ 90 mg/l	7.5	33

	Freshwater aquatic life-water hardness > 90 mg/l	WQG = 7.5 + 0.75 (hardness - 90) E.g. When hardness = 100 mg/L $CaCO_3$ WQG = 7.5 + 0.75(100 – 90) = 7.5 + 7.5 = 15.0	WQG = 33 + 0.75 (hardness - 90) E.g. When hardness = 100 mg/L $CaCO_3$ WQG = 33 + 0.75(100 – 90) = 33 + 7.5 = 40.5
	Marin life	10	55
Pb	Freshwater Aquatic Life (Water Hardness ≤ 8 mg/L CaCO3)	-	3
	Freshwater Aquatic Life (Water Hardness > 8 mg/L CaCO3)	WQG ≤ 3.31 + e[1.273 ln (hardness*) - 4.704] E.g. Hardness = 50 mg/L CaCO3 WQG ≤ 3.31 + 2.718[1.273 ln(50) – 4.704] ≤ 3.31 + 2.718[1.273(3.912) – 4.704] ≤ 3.31 + 2.718[0.276] ≤ 3.31 + 1.318 ≤ 4.628	WQG = e[1.273 ln (hardness*) -1.460] E.g. Hardness = 50 mg/L CaCO3 WQG = 2.718[1.273 ln(50) – 1.460] = 2.718[1.273(3.912) – 1.460] = 2.718[3.520] = 33.785
	Marine & Estuarine Aquatic Life	≤ 2 total lead (80% of values ≤ 2 total lead)	140

4.2 Column Treatments

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 solution and soils (Beesley and Marmiroli 2011, Karami *et al*. 2011, Mendez *et al*. 2012, 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 biochar used in this study, showed a good

heavy metals and PAH removal ability compared to sand, qualifying it as a potential substitute for sand or to be used in combination with sand in urban structural best management practices. Maximum percentage removal by biochar used in this study followed the order of NAP > Zn > Cu. The same results were observed by Park *et al*. (2015) when using chicken bone derived biochar and also by Xue *et al*. (2012) using peanut hull hydrochar to remove heavy metal. In the case of sand, maximum percentage removal was highest for Zn among the all tested pollutants, whereas that was lowest for NAP. The higher Zn adsorption compared to Cu is probably because of its high concentration in the synthetic storm water (Cu concertation of 50-800 µg/l compared to Zn concertation of 200-1,800 µg/l). Regarding Cu and Zn removal, small biochar exhibited higher removal efficiency compared to medium biochar potentially due to larger surface area of the small biochar. Komkiene and Baltrenaite (2015) concluded that due to smaller porosity and smaller pore surface area of silver birch, it showed higher adsorption of Pb and Zn compared to Scoth pine biochar. In terms of NAP removal, both small and medium biochar exceeded sand with a five-fold percentage removal. However, biochar with different particle size had the same removal percentage.

It was expected that by increasing the pollutants concentration, available adsorption sites on absorbent media surface would be occupied, resulting in declining removal efficiency of them (Komkiene and Baltrenaite 2015). However, Cu and NAP percentage removal by different absorbent media increased significantly by increasing the concentration of synthetic storm water pollutants from low to high concentration. As shown in breakthrough curves, exhaustion point and breakthrough point did not occur for biochar even with high concertation of pollutants meaning that biochar had higher adsorption capacity than expected for the volume of water filtered in this project. In high concentration of pollutants more sites will be occupied by Cu, Zn, and NAP while these sites were not occupied in low concertation of pollutants.

TOC had the highest effect on heavy metal removal ability by different absorbent media (η^2 = .98 for Cu and η^2 = .80 for Zn). TOC plays a major role in partitioning of metals between soluble and particulate fractions in stormwater (Hamilton *et al*. 1984). Consequently, competition for adsorption between TOC and heavy metals can result in processes that concentrate the metals in the dissolved phase (Hernegen *et al*. 2005). This could be the possible explanation for increased concentration of Cu and Zn in effluent samples and reduced percentage of both heavy metal removal following TOC

addition to synthetic storm water (Table A1 where Cu% removal equals zero and Fig B5, B6, and B14).

pH has shown to have a contradictory effect on pollutant removal capabilities using biochar. In some studies, increasing pH (pH< 7 to pH= 9) favored heavy metal and organic pollutants adsorption using different biochar (Tai 1991, Kim *et al*. 2013, Taha *et al*. 2014, Liu *et al*. 2015). On the other hand, removal capacities of biochar declined following increasing solution pH to more than 8 (Balati *et al*. 2015). In this study, effect of pH on heavy metal and NAP removal was not statistically significant which was in accordance with result found by Lamichhane *et al*. (2016). Also, Zhang et al. (2014) indicated that maximum sorption capacity of green waste derived biochar occurred at pH < 6, and pH did not have impact on sorption capacity for the pH between 7 to 10.

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5 Stormwater Source Control Design

5.1 Sizing for Stormwater Source Controls

The area of an infiltration swale, is usually sized based on the upstream impervious area that it serves. This relationship can be characterized by I/P ratio which is the ration of upstream impervious area (or catchment area) to pervious area (or base area of the swale). Infiltration rate varies with soil type. Considering soil condition of the area, different designs of full or partial infiltration source controls are suitable for the area. To identify soil type of the BCIT parking lot, a geological map of the Vancouver Metropolitan Area (1998) was used. According to the map, till up to 25 m thick is the dominant surface and near-surface material over much of the Vancouver upland, where it is overlain by patchy marine silt and sand. Till is a heterogeneous glacial deposit consisting of clay, silt, sand, and stones ranging from pebble to boulder size. Based on the soil type saturated hydraulic conductivity of 0.6 mm/hr was used (Metro Vancouver Regional District. 2012). In soils with very low infiltration rates (around and less than 1 mm/hr), partial infiltration with reservoir and sub drain and partial infiltration with flow restrictor are two appropriate source control designs (Metro Vancouver Regional District. 2012). It is worth mentioning that for sizing of the base area of the storm source control, the depth capture criteria of X mm of stormwater in 24 hours are used here. According this criterion, maximum rock depth is calculated using the following equation (Metro Vancouver Regional District. 2012):

$$Dr = \frac{Ks * T * 24}{n} \qquad (2)$$

Where,
Dr = Depth (thickness) of rock reservoir (mm)
Ks = Saturated hydraulic conductivity of subsurface soil (mm/hr)
T = allowable drain time (days)
n = porosity of drain rock in reservoir (unitless).

Considering till saturated hydraulic conductivity of 0.6 mm/hr (Metro Vancouver Regional District. 2012) and maximum allowable drain days (i.e., 4 days) (Metro Vancouver Regional District. 2012), and standard porosity of drain rock in reservoir (i.e., 0.35) (Metro Vancouver Regional District. 2012), maximum depth rock was calculated:

$$Dr = \frac{0.6\,mm/hr * 4\,days * 24hrs/day}{0.35} = 164.6\,mm$$

To find swale base area, I/P ration needs to be determined:

$$Base\ Area = \frac{Impervious\ Tributary\ Area}{I/P} \qquad (3)$$

The following equation is used to calculate I/P ratio:

$$\frac{I}{P} = \frac{24 * Ks + Dr * n + 0.2 * Ds}{R} - 1$$

Where:
I/P = Ratio of impervious tributary area to swale base area (unitless)
Ks = Saturated hydraulic conductivity of subsurface soil (mm/hr)
Dr = Depth (thickness) of rock reservoir (mm)
n = porosity of drain rock in reservoir (unitless)
D_S = Soil layer depth (i.e., recommended depth of biochar to be used in the infiltration structure in mm)
R = Rainfall capture depth (mm)

Considering total pavement area of BCIT parking lots D and F, which equals 6,830 m^2 for each lot (google map) and 6 month- 24 hr rainfall capture target of 39 mm (Metro Vancouver Regional District. 2012), following parameters were calculated (for porosity of the drain rock, the standard value of 0.35 were used):

$$\frac{I}{P} = \frac{24hr * 0.6\,mm/hr + 164.6\,mm * 0.35 + 0.2 * 2600mm}{39mm} - 1 = 14.1$$

$$Base\ Area = \frac{6830m^2 + 6830\ m^2}{2.6} = 969\ m^2$$

The maximum allowable I/P ratio for a parking lot with more than one car per day per parking space equals 20:1. Since the calculated I/P ratio meets the criteria of the maximum allowable I/P ratio (14.1 < 20), a partial infiltration swale with flow restrictor design is not necessary. Area of 969 m^2 was calculated by this sizing method is the base area (i.e. the flat area at the bottom with uniform layers of topsoil and drain rock) and any infiltration that may be provided by the sloped sides of the system is not accounted here. The above mentioned sizing is the typical sizing procedure based on Metro Vancouver Guideline. To incorporate result from this project to sizing procedure the hydraulic loading rate for biochar (H_B) that will be potentially used in an infiltration trench in BCIT parking lot was compared to the hydraulic loading rate of the infiltration trench (H_I):

$$H_B = \frac{Q_B}{A_C} = \frac{0.43\ L/min}{3.14 * (\frac{10.2}{2})^2 cm^2} = 52.6\ \ L/m^2 min \qquad (4)$$

where,

H_B = hydraulic loading rate of medium biochar,

A_C =surface area of the column used in this project,

Q_B= Flow rate of medium biochar used in this project

and,

$$H_I = \frac{Q_P}{A_t} = \frac{39\ mm * (6830m^2 + 6830\ m^2)/24\ hr}{969m^2} = 0.38\ L/m^2 min \qquad (5)$$

where,

H_I = hydraulic loading rate of the infiltration trench,

A_t =surface area of infiltration trench

Q_P= Flow rate of rain water in BCIT parking lot which equals depth of rain fall (6 month-24 hr rainfall capture target of 39 mm) * surface area of BCIT parking lot

As indicated biochar used in this study had higher hydraulic loading rate compared to the infiltration trench (52.6>0.38 L/m^2 min). In addition, my experiments revealed that even in high pollutant concentration (which was higher than observed concentration of pollutants in BCIT parking lot runoff), none of the breakthrough point and complete exhaustion point occurred for any of Cu, Zn, and NAP for the volume of water used in this experiment, demonstrating biochar high absorption capacity for different pollutants. Considering the fact that high concentration of pollutant only occurs for a short period of time (first flush at the start of a raining season) and the most raining events are associated with low concentration of pollutants, and taking into account the smaller hydraulic loading rate of the infiltration trench compared to biochar hydraulic loading rate and 39 mm/hr rain capture target for BCIT parking lot, it is estimated that the biochar used in this experiment will have an extended service life when used in an infiltration structure.

5.2 Post-Construction Environmental Monitoring

The objective of post construction monitoring is to evaluate the function of the source controls. The acquired data are used to verify if the stormwater capture targets were achieved. Also, they provide an important source of information to developers, municipalities, and practitioners for the adaptive management process. In large, multi-phase developments, monitoring can supply data for adaptive management for later phases. Post- construction monitoring may include rainfall characteristics measurements, flow and water quality measurements downstream of the constructed source control and groundwater levels.

6 Conclusions and Recommendations

The ability of a commercially available biochar to remove Zn, Cu, and NAP from a synthetic stormsynthetic storm water was demonstrated through a series of column treatments. The effect of different concentration of pollutants, pH, TOC, and biochar particle size were also examined and the comparison with sand was conducted at the same time. Biochar indicated high Cu and Zn removal similar to sand (M=59% for Cu and M=78% for Zn). However, biochar showed a five-fold NAP removal ability compared to sand (M= 82%), making it an effective sorption media in filters and reactive barriers to remove pollutants from water flow. Even in high pollutant concentration (which was higher than observed concentration of pollutants in BCIT parking lot runoff), none of the breakthrough point and complete exhaustion point occurred for any of Cu, Zn, and NAP for the volume of water used in this experiment, demonstrating biochar high absorption capacity for different pollutants. Considering the fact that high concentration of pollutant only occurs for a short period of time (first flush at the start of a raining season) and the most raining events are associated with low concentration of pollutants, it is estimated that the biochar used in this experiment will have an extended service life when used in an infiltration structure. The result indicated that TOC had a large impact on removal efficiency of pollutants by biochar. Sand filters have been shown to have some ability in removing TOC from water (Kazemi 2016). It is recommended that placing an additional sand layer on top of the biochar layer in the filtration structure or placing a grass strip on the side slope of the infiltration trench may minimize TOC concertation before entering to the biochar layer. Also addition of sand layer may capture particulates which may prevent clogging of the biochar layer. This will help to increase the life time of the biochar used in the system and will impact the replacement time and cost eventually.

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). Recent studies have shown that the olfactory toxicity of copper is similar in coho and steelhead, and also among fish raised in hatchery and natural environments (Baldwin *et al*. 2011, Mcintyre *et al*. 2012). Using innovative and environment friendly approaches for improving quality of water (i.e.

reducing pollutant of concern concentrations including PAHs and heavy metal like Cu) entering urban creeks like Guichon creek could potentially improve juvenile salmonids survival and abundance, thereby assisting ongoing efforts to recover depressed stocks (Mcintyre *et al*. 2012). Todays, classic solutions of bigger pipes and pumps are not the answer for the stormwater problems and they are not able to even keep up with peak flows from climate change. However, small solutions including distributed infiltration, roof gardens, and all manner of green infrastructure are an efficient, environment friendly, and cost-conscious approach to non-point pollution (Stephens and Dumont 2011). Nowadays, it is accepted that an effective green infrastructure is the essential component of the responsible rainwater management. Which has resulted in a transition from pipe and convey solution to the solutions that incorporate “designing with nature “to protect our streams and fishery resource before degradation takes place. Science based approaches for designing with nature and implementing green infrastructure in early stages of development, provide an effective solution in protecting watershed and urban stream health, cutting the needs for subsequent expensive and intrusive restoration treatments and making land development and stream health compatible.

In conclusion, since biochar can be derived from diverse biomass residues such as wood by- products, manure, and agricultural residues, and it is economically efficient, it can provide a potential alternative for many remediation applications, such as wastewater treatment and groundwater remediation. To expand the use of biochar in practice, further experiments should be focused on investigating the potential of the other commercially available biochar to remove different pollutants which are specific for different land uses and optimization the removal condition for these pollutants. Using locally produced biochar will help with waste management and will provide more free energy from pyrolysis process. However, when using biochar as an absorbent media for toxic pollutants such as heavy metals and organic pollutants, disposing the spent biochar is a key issue to consider. Composition of different elements associated with biochar is highly influenced by feedstock material and pyrolytic temperature. To prevent further pollution, using safe and toxicant free feedstock should be considered when producing biochar. In addition, for a sustainable biochar development and its safe application in soil and water, International Biochar Initiative (IBI) guidelines should be followed (Initiative 2012)

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Appendix A Column Treatments

Column treatment detail and mean percentage removal of different pollutants are summarized in the following table:

Table A1 Column treatments detail and mean %removal of different pollutants

Run order	Synthetic storm water	pH	TOC	Absorbent media	Cu% Removal	Zn% Removal	NAP% Removal
1	Low	6.5	0	Medium biochar	99	94	50
2	Low	6.5	0	Medium biochar	96	83	87
3	Low	8.5	0	Medium biochar	97	98	54
4	Low	8.5	0	Medium biochar	94	90	60
5	High	6.5	0	Medium biochar	92	65	89
6	High	6.5	0	Medium biochar	73	38	85
7	High	8.5	0	Medium biochar	84	59	80
8	High	8.5	0	Medium biochar	94	77	97
9	Low	6.5	25	Medium biochar	0	29	98
10	Low	6.5	25	Medium biochar	0	9	79
11	Low	8.5	25	Medium biochar	0	22	100
12	Low	8.5	25	Medium biochar	0	18	76
13	High	6.5	25	Medium biochar	16	26	92
14	High	6.5	25	Medium biochar	13	30	82
15	High	8.5	25	Medium biochar	11	26	90
16	High	8.5	25	Medium biochar	8	79	90

17	Low	6.5	0	small biochar	90	98	50
18	Low	6.5	0	small biochar	98	99	53
19	Low	8.5	0	small biochar	95	100	46
20	Low	8.5	0	small biochar	100	99	87
21	High	6.5	0	small biochar	100	100	96
22	High	6.5	0	small biochar	100	100	92
23	High	8.5	0	small biochar	99	95	46
24	High	8.5	0	small biochar	99	100	98
25	High	6.5	25	small biochar	14	52	55
26	High	6.5	25	small biochar	36	61	97
27	Low	6.5	25	small biochar	0	66	92
28	Low	6.5	25	small biochar	0	73	95
29	Low	8.5	25	small biochar	41	33	66
30	Low	8.5	25	small biochar	13	46	93
31	High	8.5	25	small biochar	15	53	58
32	High	8.5	25	small biochar	48	74	98
33	Low	6.5	0	sand	97	97	4
34	Low	6.5	0	sand	98	97	5
35	Low	8.5	0	sand	98	98	7
36	Low	8.5	0	sand	99	97	7
37	High	6.5	0	sand	100	100	10
38	High	6.5	0	sand	100	100	88
39	High	8.5	0	sand	100	100	5

40	High	8.5	0	sand	100	100	8
41	Low	6.5	25	sand	3	73	0
42	Low	6.5	25	sand	0	79	25
43	Low	8.5	25	sand	0	73	1
44	Low	8.5	25	sand	0	28	3
45	High	6.5	25	sand	15	95	14
46	High	6.5	25	sand	27	98	25
47	High	8.5	25	sand	18	92	14
48	High	8.5	25	sand	21	88	24

Appendix B Breakthrough Curves

Breakthrough curves for all treatments are presented below:

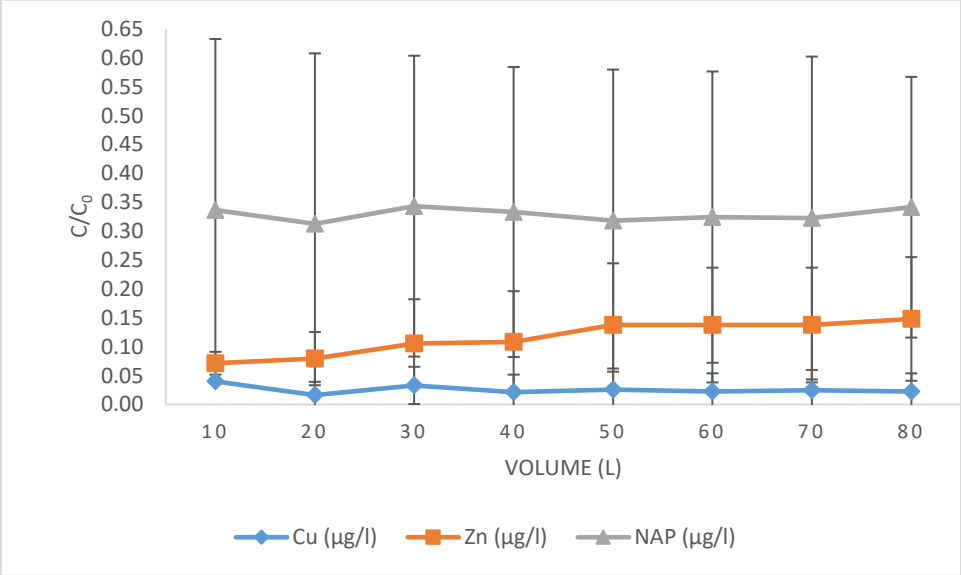

Figure B1 Breakthrough curve for column treatments 1and 2 (Medium biochar, low concentration of pollutants, PH=6.5, and TOC=0), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

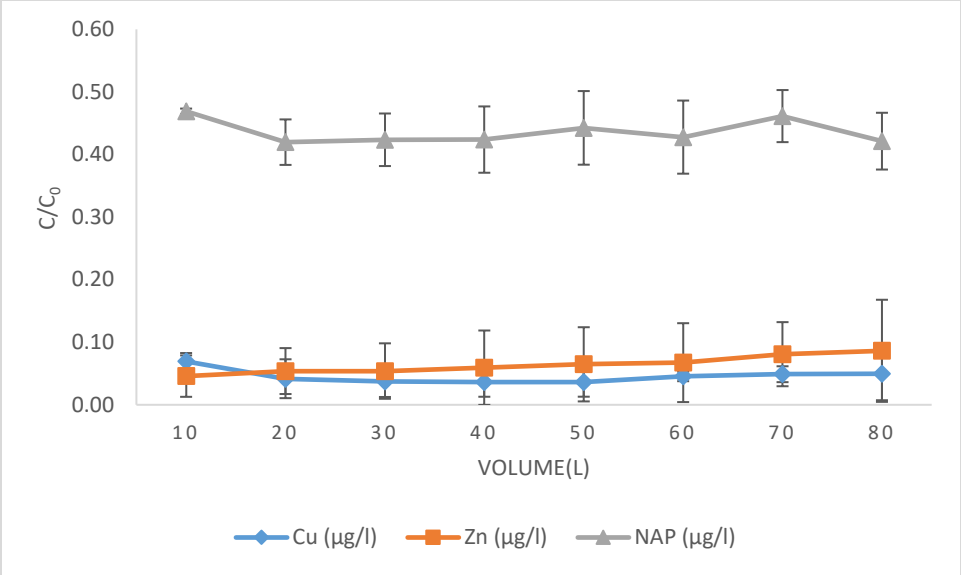

Figure B2 Breakthrough curve for column treatments 3 and 4 (Medium biochar, low concentration of pollutants, PH=8.5, and TOC=0), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

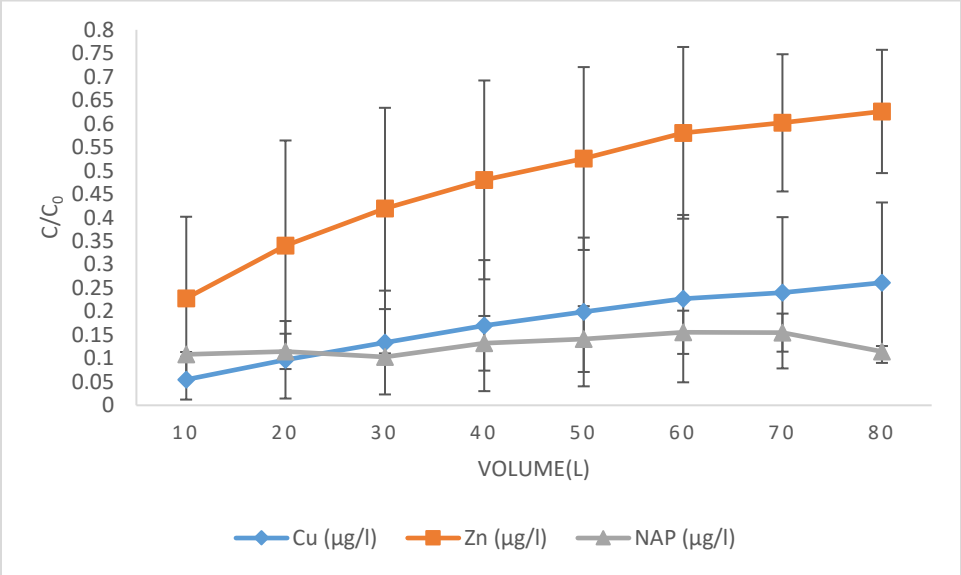

Figure B3 Breakthrough curve for column treatments 5 and 6 (Medium biochar, high concentration of pollutants, PH=6.5, and TOC=0), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

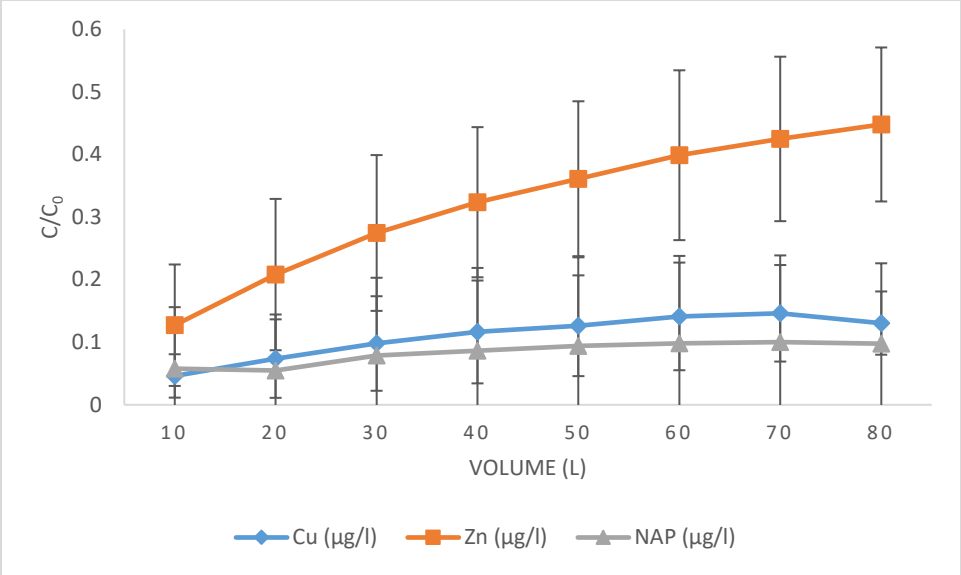

Figure B4 Breakthrough curve for column treatments 7 and 8 (Medium biochar, high concentration of pollutants, PH=8.5, and TOC=0), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

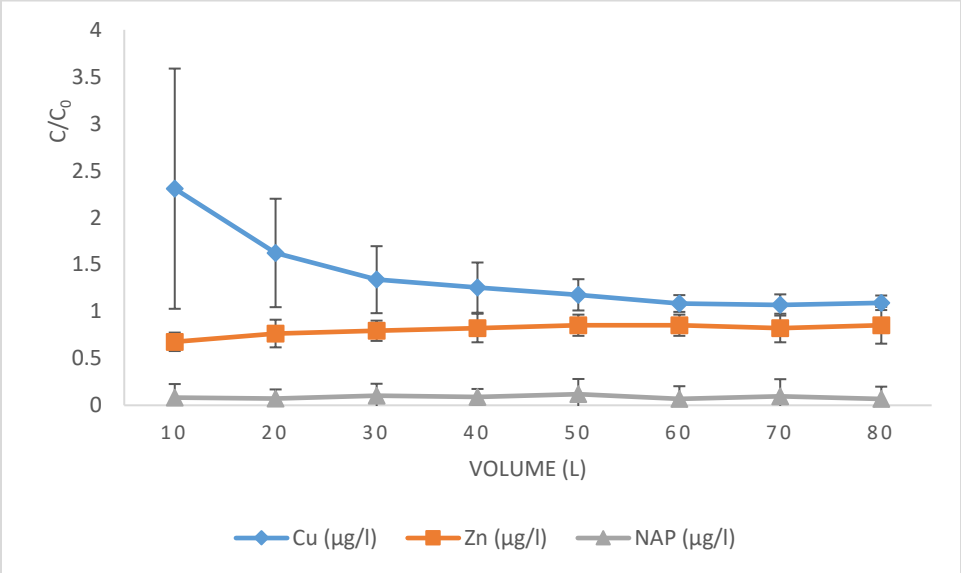

Figure B5 Breakthrough curve for column treatments 9 and 10 (Medium biochar, low concentration of pollutants, PH=6.5, and TOC=25), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

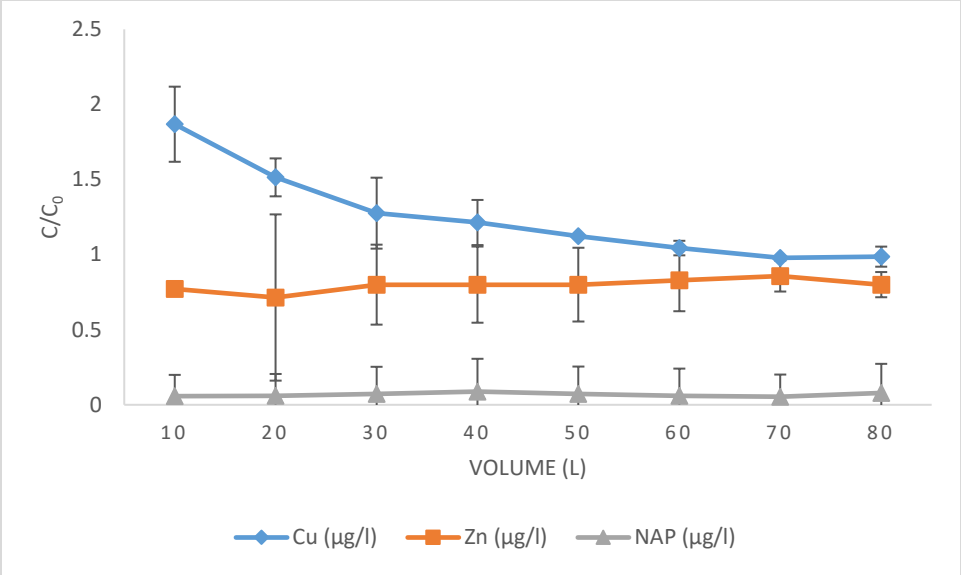

Figure B6 Breakthrough curve for column treatments 11 and 12 (Medium biochar, low concentration of pollutants, PH=8.5, and TOC=25), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

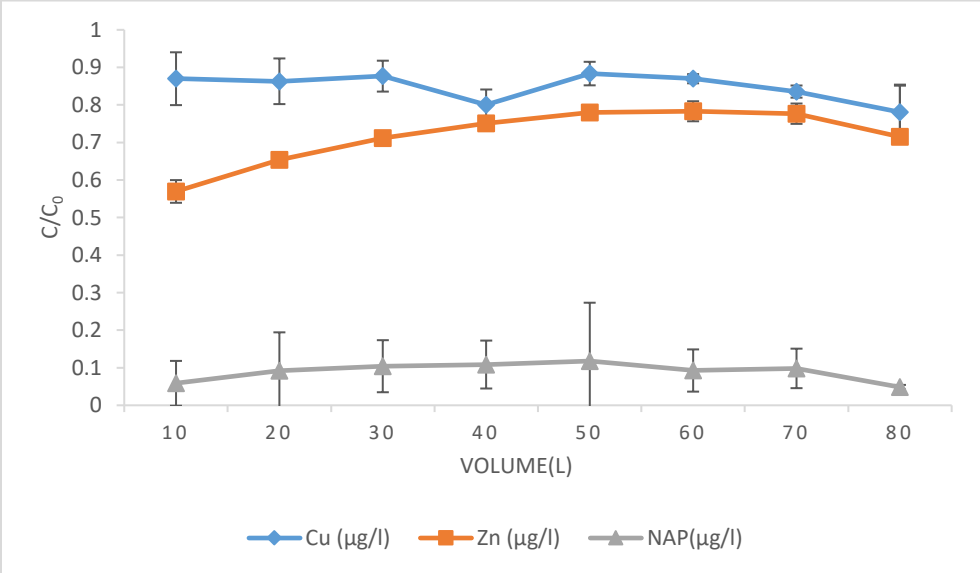

Figure B7 Breakthrough curve for column treatments 13 and 14 (Medium biochar, high concentration of pollutants, PH=6.5, and TOC=25), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

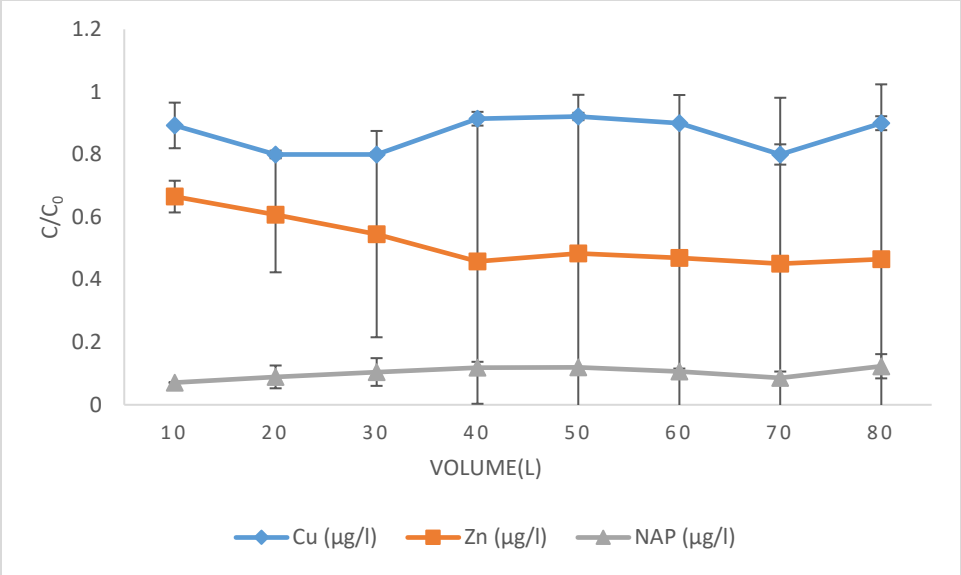

Figure B8 Breakthrough curve for column treatments 15 and 16 (Medium biochar, high concentration of pollutants, PH=8.5, and TOC=25), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

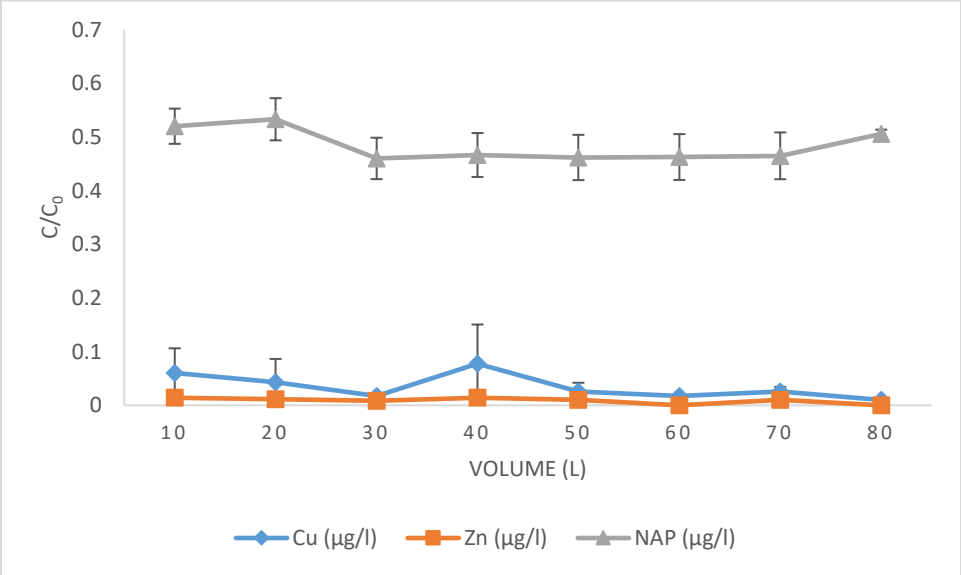

Figure B9 Breakthrough curve for column treatments 17 and 18 (small biochar, low concentration of pollutants, PH=6.5, and TOC=0), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

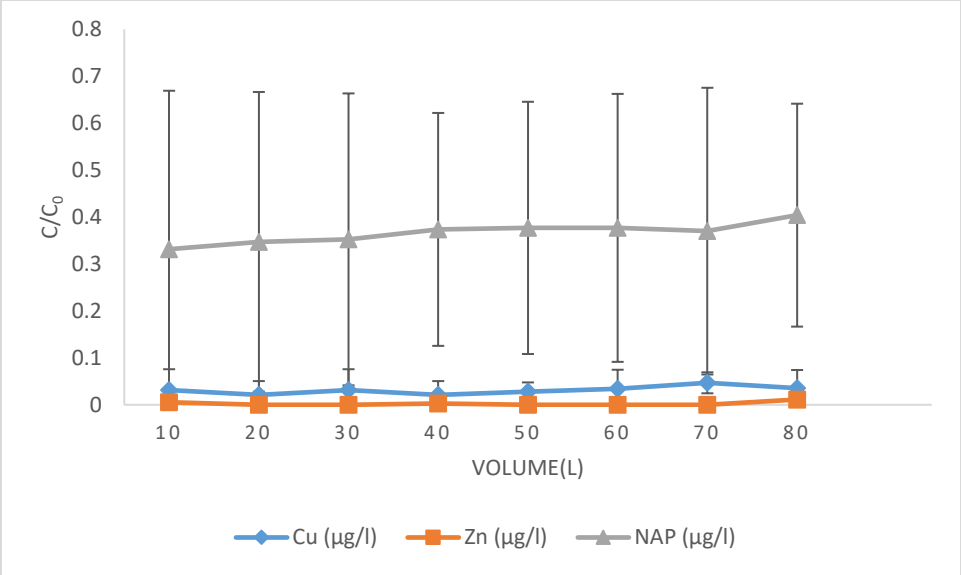

Figure B10 Breakthrough curve for column treatments 19 and 20 (small biochar, low concentration of pollutants, PH=8.5, and TOC=0), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

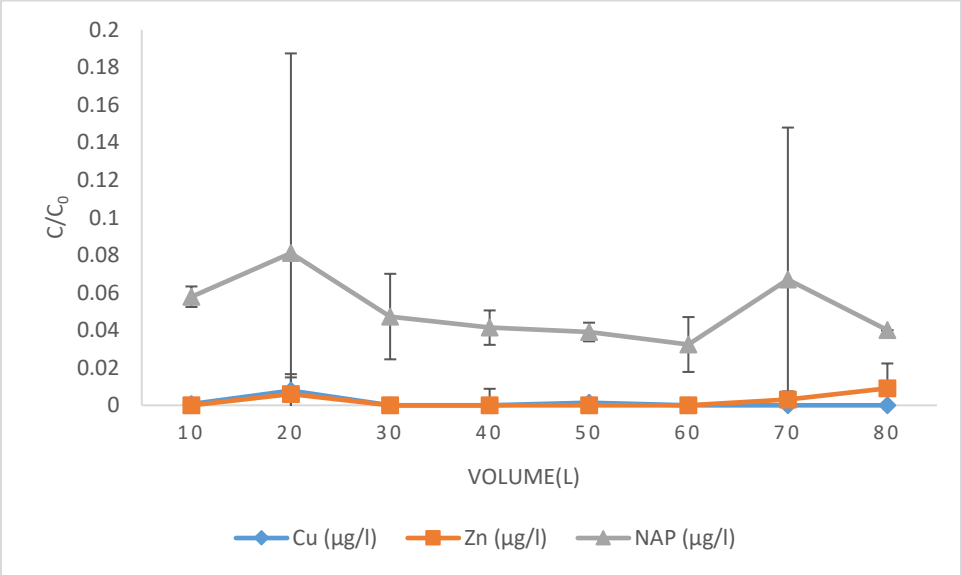

Figure B11 Breakthrough curve for column treatments 21 and 22 (small biochar, high concentration of pollutants, PH=6.5, and TOC=0), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents standard deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

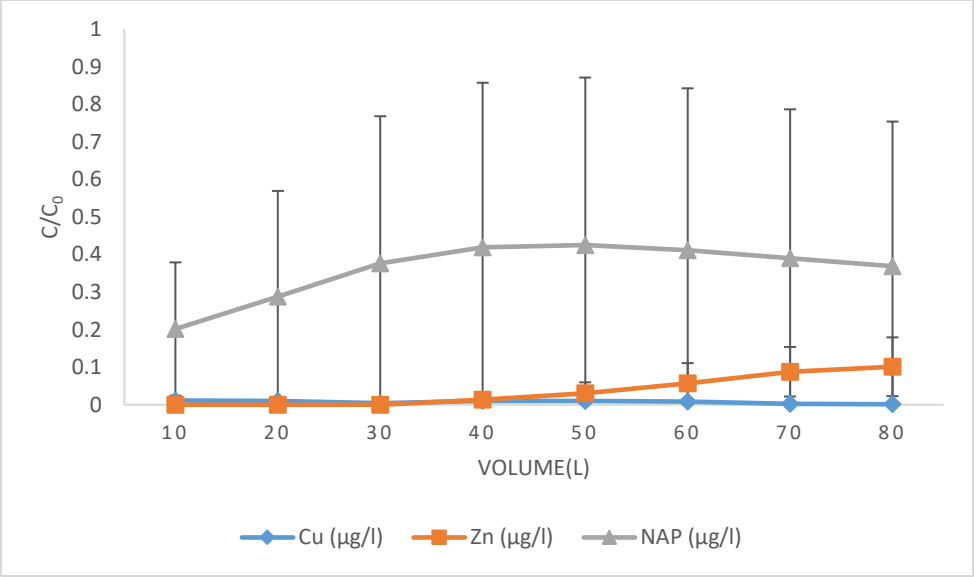

Figure B12 Breakthrough curve for column treatments 23 and 24 (small biochar, high concentration of pollutants, PH=8.5, and TOC=0), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

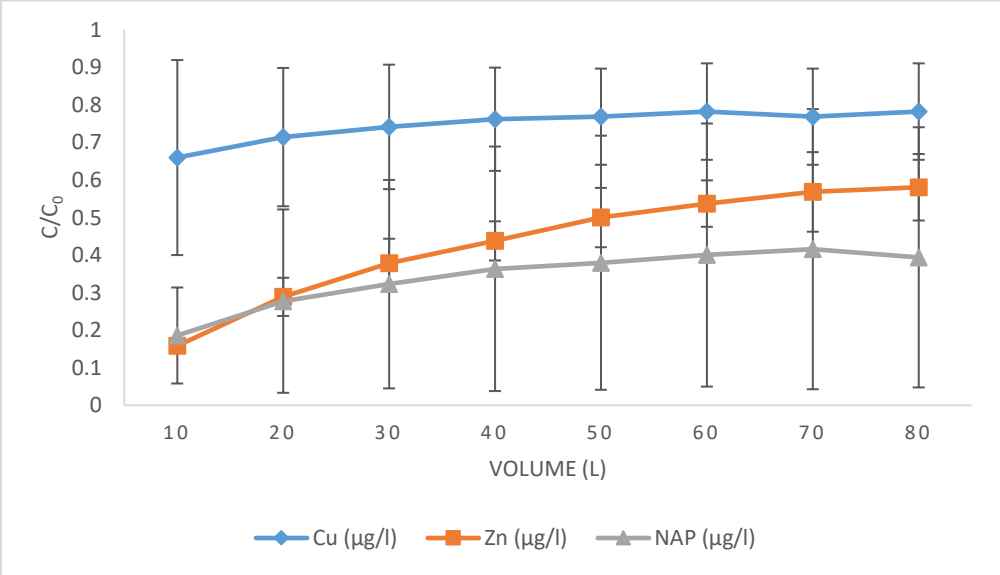

Figure B13 Breakthrough curve for column treatments 25and 26 (small biochar, high concentration of pollutants, PH=6.5, and TOC=25), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

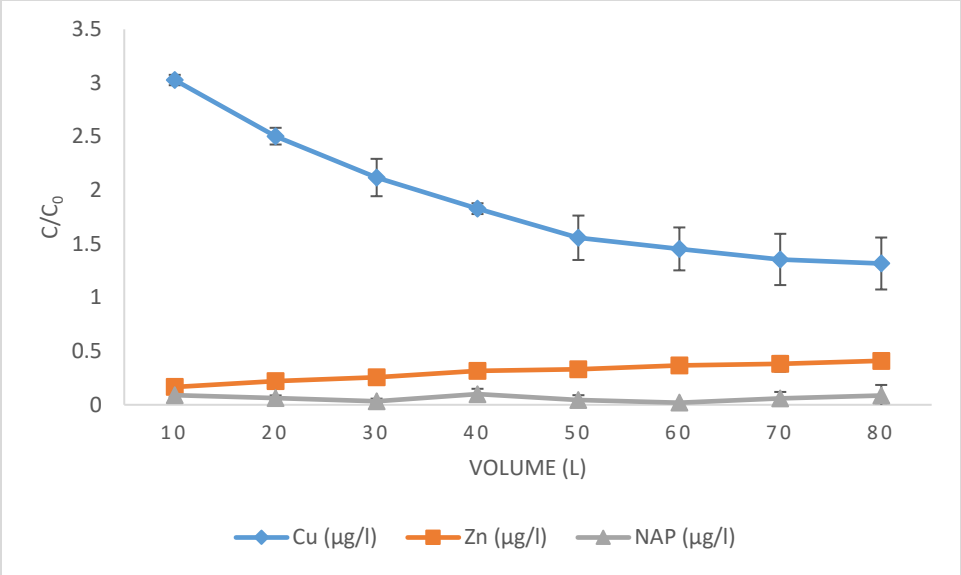

Figure B14 Breakthrough curve for column treatments 27 and 28 (small biochar, low concentration of pollutants, PH=6.5, and TOC=25), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

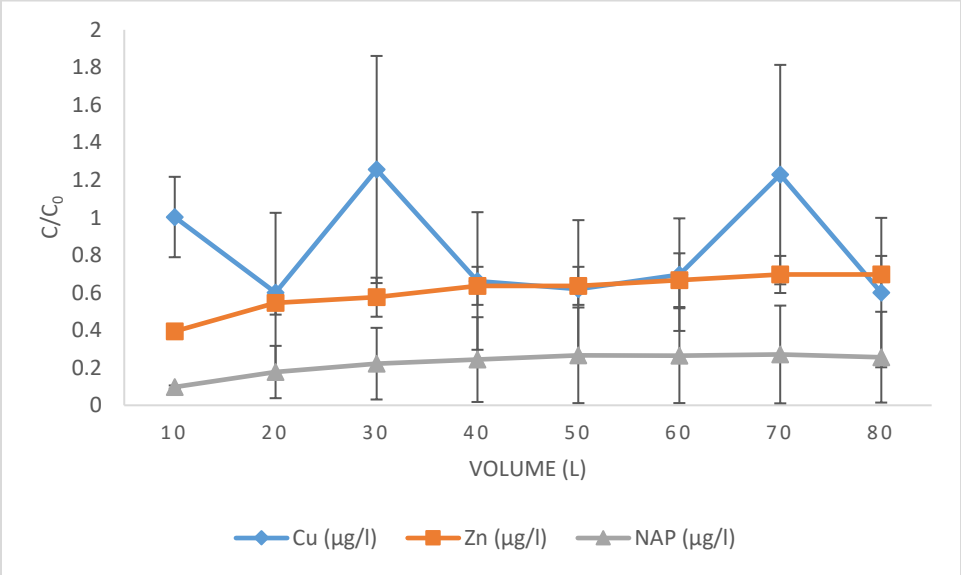

Figure B15 Breakthrough curve for column treatments 29 and 30 (small biochar, low concentration of pollutants, PH=8.5, and TOC=25), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

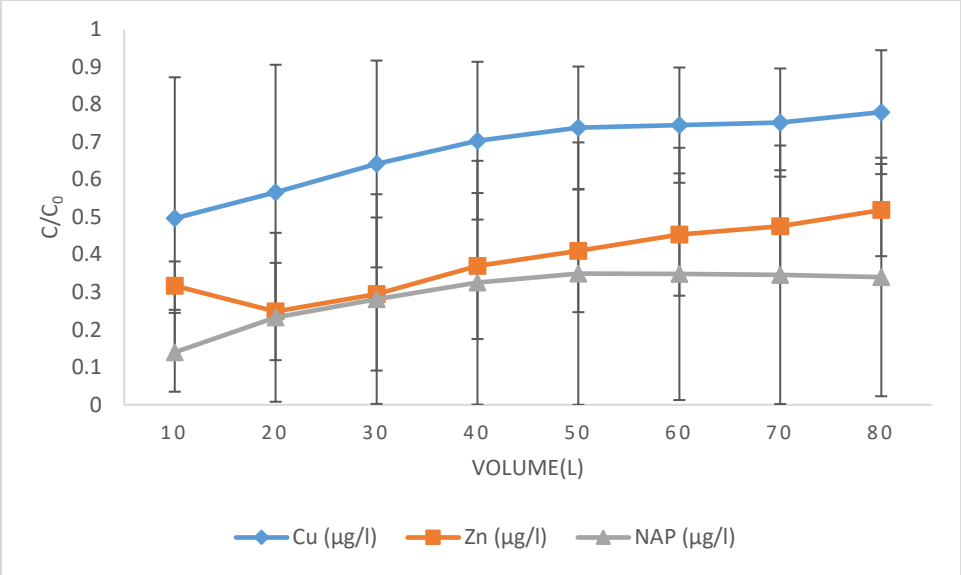

Figure B16 Breakthrough curve for column treatments 31 and 32 (small biochar, high concentration of pollutants, PH=8.5, and TOC=25), C: Pollutant concentration in effluent and C_0: Pollutant concentration in Influent, Error bars represents deviation based on two replicates. The study was conducted in 2017-2018 at BCIT Hydraulic lab, Burnaby, BC.

Summary of the breakthrough curves for all treatments are presented in the following table:

Table B1 Summary of the breakthrough curves for all column treatments, C: Mean pollutant concentration in effluent and C_0: Mean pollutant concentration in Influent

Treatment	Initial Cu C/C_0	After 80 L Cu C/C_0	% Difference Cu C/C_0	Initial Zn C/C_0	After 80 L Zn C/C_0	% Difference Zn C/C_0	Initial NAP C/C_0	After 80 L NAP C/C_0	% Difference NAP C/C_0
1, 2	0.04	0.02	0	0.07	0.15	8	0.34	0.34	0
3, 4	0.07	0.05	0	0.05	0.09	4	0.47	0.42	0
5, 6	0.05	0.26	21	0.23	0.63	40	0.11	0.11	0
7, 8	0.05	0.13	8	0.13	0.45	32	0.06	0.10	4
9, 10	2.31	1.09	0	0.68	0.85	17	0.08	0.07	0
11, 12	1.87	0.99	0	0.77	0.80	3	0.06	0.08	2

13, 14	0.87	0.78	0	0.57	0.72	15	0.05	0.05	0
15, 16	0.89	0.90	1	0.67	0.47	0	0.07	0.12	5
17, 18	0.06	0.01	0	0.01	0.00	0	0.52	0.51	0
19, 20	0.03	0.04	1	0.01	0.01	0	0.33	0.40	7
21, 22	0.00	0.00	0	0.00	0.01	1	0.06	0.04	0
23, 24	0.01	0.00	0	0.00	0.01	1	0.20	0.37	17
25, 26	0.66	0.78	12	0.16	0.58	42	0.19	0.39	20
27, 28	3.03	1.32	0	0.17	0.41	24	0.09	0.09	0
29, 30	1.00	0.60	0	0.39	0.70	31	0.10	0.26	16
31, 32	0.50	0.78	28	0.32	0.52	20	0.14	0.34	20

Appendix C ANOVA Tables

Table C1 ANOVA details for Cu removal

Source	Type III Sum of Squares	df	Mean Square	F	Sig.	Partial Eta Squared
Corrected Model	87377.075[a]	23	3799.003	59.507	.000	.983
Intercept	140990.066	1	140990.066	2208.460	.000	.989
Concentration	567.684	1	567.684	8.892	.006	.270
PH	95.735	1	95.735	1.500	.233	.059
TOC	83545.895	1	83545.895	1308.658	.000	.982
ABSORBENTMEDIA	923.472	2	461.736	7.233	.003	.376
Concentration * PH	41.414	1	41.414	.649	.428	.026
Concentration * TOC	876.176	1	876.176	13.724	.001	.364
Concentration * ABSORBENTMEDIA	235.501	2	117.750	1.844	.180	.133
PH * TOC	24.946	1	24.946	.391	.538	.016
PH * ABSORBENTMEDIA	240.450	2	120.225	1.883	.174	.136
TOC * ABSORBENTMEDIA	294.898	2	147.449	2.310	.121	.161
Concentration * PH * TOC	69.531	1	69.531	1.089	.307	.043
Concentration * PH * ABSORBENTMEDIA	113.462	2	56.731	.889	.424	.069
Concentration * TOC * ABSORBENTMEDIA	68.955	2	34.477	.540	.590	.043
PH * TOC * ABSORBENTMEDIA	237.771	2	118.886	1.862	.177	.134
Concentration * PH * TOC * ABSORBENTMEDIA	41.187	2	20.594	.323	.727	.026
Error	1532.182	24	63.841			
Total	229899.322	48				
Corrected Total	88909.256	47				

Table C2 Tukey HSD test for Cu % removal. Absorbent media 1= medium biochar, 2=small biochar, and 3=sand

(I) ABSORBENTMEDIA	(J) ABSORBENTMEDIA	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1.00	2.00	-10.7059*	2.82491	.002	-17.7605	-3.6513
	3.00	-6.1357	2.82491	.097	-13.1903	.9189
2.00	1.00	10.7059*	2.82491	.002	3.6513	17.7605
	3.00	4.5702	2.82491	.258	-2.4844	11.6249
3.00	1.00	6.1357	2.82491	.097	-.9189	13.1903
	2.00	-4.5702	2.82491	.258	-11.6249	2.4844

Table C3 ANOVA details for Zn removal

Source	Type III Sum of Squares	df	Mean Square	F	Sig.	Partial Eta Squared
Corrected Model	34860.595[a]	23	1515.678	10.000	.000	.906
Intercept	256495.207	1	256495.207	1692.206	.000	.986
Concentration	248.797	1	248.797	1.641	.212	.064
PH	6.717	1	6.717	.044	.835	.002
TOC	15371.108	1	15371.108	101.410	.000	.809
ABSORBENTMEDIA	10795.973	2	5397.987	35.613	.000	.748
Concentration * PH	621.200	1	621.200	4.098	.054	.146
Concentration * TOC	2429.729	1	2429.729	16.030	.001	.400
Concentration * ABSORBENTMEDIA	949.877	2	474.939	3.133	.062	.207
PH * TOC	215.407	1	215.407	1.421	.245	.056
PH * ABSORBENTMEDIA	932.833	2	466.416	3.077	.065	.204
TOC * ABSORBENTMEDIA	1475.131	2	737.566	4.866	.017	.289
Concentration * PH * TOC	437.722	1	437.722	2.888	.102	.107
Concentration * PH * ABSORBENTMEDIA	38.349	2	19.174	.127	.882	.010
Concentration * TOC * ABSORBENTMEDIA	1075.150	2	537.575	3.547	.045	.228
PH * TOC * ABSORBENTMEDIA	164.961	2	82.480	.544	.587	.043
Concentration * PH * TOC * ABSORBENTMEDIA	97.641	2	48.821	.322	.728	.026
Error	3637.787	24	151.574			
Total	294993.589	48				
Corrected Total	38498.382	47				

Table C4 Tukey HSD test for Zn% removal. Absorbent media 1= medium biochar, 2=small biochar, and 3=sand

(I) ABSORBENTMEDIA	(J) ABSORBENTMEDIA	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1.00	2.00	-25.2970*	4.35279	.000	-36.1672	-14.4268
	3.00	-35.7173*	4.35279	.000	-46.5875	-24.8471
2.00	1.00	25.2970*	4.35279	.000	14.4268	36.1672
	3.00	-10.4203	4.35279	.062	-21.2905	.4499
3.00	1.00	35.7173*	4.35279	.000	24.8471	46.5875
	2.00	10.4203	4.35279	.062	-.4499	21.2905

Table C5 ANOVA details for NAP removal

Source	Type III Sum of Squares	df	Mean Square	F	Sig.	Partial Eta Squared
Corrected Model	52102.452[a]	23	2265.324	5.949	.000	.851
Intercept	160466.707	1	160466.707	421.402	.000	.946
Concentration	1816.875	1	1816.875	4.771	.039	.166
PH	491.486	1	491.486	1.291	.267	.051
TOC	580.222	1	580.222	1.524	.229	.060
ABSORBENTMEDIA	44091.971	2	22045.985	57.895	.000	.828
Concentration * PH	128.033	1	128.033	.336	.567	.014
Concentration * TOC	1554.071	1	1554.071	4.081	.055	.145
Concentration * ABSORBENTMEDIA	181.072	2	90.536	.238	.790	.019
PH * TOC	108.195	1	108.195	.284	.599	.012
PH * ABSORBENTMEDIA	255.076	2	127.538	.335	.719	.027
TOC * ABSORBENTMEDIA	647.195	2	323.598	.850	.440	.066
Concentration * PH * TOC	794.349	1	794.349	2.086	.162	.080
Concentration * PH * ABSORBENTMEDIA	358.620	2	179.310	.471	.630	.038
Concentration * TOC * ABSORBENTMEDIA	279.186	2	139.593	.367	.697	.030
PH * TOC * ABSORBENTMEDIA	150.434	2	75.217	.198	.822	.016
Concentration * PH * TOC * ABSORBENTMEDIA	665.667	2	332.833	.874	.430	.068
Error	9139.019	24	380.792			
Total	221708.178	48				
Corrected Total	61241.471	47				

Table C6 Tukey HSD test for NAP% removal. Absorbent media 1= medium biochar, 2=small biochar, and 3=sand

(I) ABSORBENTMEDIA	(J) ABSORBENTMEDIA	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1.00	2.00	5.3684	6.89921	.720	-11.8609	22.5977
	3.00	66.8091*	6.89921	.000	49.5798	84.0384
2.00	1.00	-5.3684	6.89921	.720	-22.5977	11.8609
	3.00	61.4408*	6.89921	.000	44.2115	78.6701
3.00	1.00	-66.8091*	6.89921	.000	-84.0384	-49.5798
	2.00	-61.4408*	6.89921	.000	-78.6701	-44.2115

Table C7 Summery of blank experiment result for medium biochar. Influent and all effluent concentration for Zn and NAP concentration were zero for all seven replicates.

Replicate	Cu Influent (µg/l)	Cu effluent 10L(µg/l)	Cu effluent 20L(µg/l)	Cu effluent 30L(µg/l)	Cu effluent 40L(µg/l)	Cu effluent 50L(µg/l)	Cu effluent 60L(µg/l)	Cu effluent 70L(µg/l)	Cu effluent 80L(µg/l)
1	11.37	0.85	1.7	1.74	1.68	1.55	1.73	1.47	1.2
2	13.41	2.05	0.86	1.01	0.29	1.69	2.98	2.59	8.58
3	11.34	0.7	0.55	0.13	0.15	0.36	0.5	0.43	1.1
4	5.04	0.1	0.6	0.49	0.12	0.3	0.32	0.7	0.46
5	4.17	0.42	0.48	0.25	0.63	0.8	0.5	0.73	0.95
6	10.06	1.5	0.68	0.25	1.4	0.4	0.76	0.04	1.35
7	5.2	0.6	1.4	0.69	0.05	0.3	0.87	0.09	1.06

Table C8 Summery of blank experiment result for sand. Influent and all effluent concentration for Zn and NAP concentration were zero for all seven replicates

Replicate	Cu Influent (µg/l)	Cu effluent 10L(µg/l)	Cu effluent 20L(µg/l)	Cu effluent 30L(µg/l)	Cu effluent 40L(µg/l)	Cu effluent 50L(µg/l)	Cu effluent 60L(µg/l)	Cu effluent 70L(µg/l)	Cu effluent 80L(µg/l)

1	7.62	1.01	1.38	0.4	0.13	0.8	1.53	1.67	0.67
2	9.73	1.25	1.48	0.42	1.93	1.3	3.23	1.67	1.57
3	5.72	1.4	1.21	1.25	1.26	1.54	1.02	1.3	1.86
4	4.79	1.42	0.9	2.03	1.13	1.28	1.48	2.36	1.79
5	4.39	1.47	1.67	2.64	1.87	1.46	1.36	1	0.66
6	8.03	1.05	1.23	0.12	0.9	1.7	0.56	1.2	1.48
7	5.01	1.5	1.02	0.4	1.03	1.26	1.84	0.65	1.9