A study of organic contaminant and *Escherichia coli* levels in stormwater runoff and their removal via biochar-based treatment systems

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ABSTRACT

Urban stormwater runoff is a major contributor of anthropogenic contaminants to receiving waters. In recent years, focus of stormwater best management practices has moved towards improving water quality using Low Impact Development (LID) systems such as filtration systems, due to the dual benefits of stormwater drainage and contaminant removal. However, conventional bioretention media are not effective for removal of all contaminants of concern. Amendment with sorbent materials such as biochar is a potential solution for remediation of bacterial contaminants such as *Escherichia coli* (*E. coli*) and dissolved contaminants of emerging concern (CECs) such as pesticides, which can easily pass through conventional treatment systems. The objectives of this study include verification of biochar amended filtration performance regarding simultaneous retention of CECs and *E. coli* from runoff under environmentally relevant conditions and predicting potential treatment effectiveness for a full-scale biochar amended system. Two Harbors, MN is used as a case study, where a biochar-amended filtration system will be installed to manage persistent *E. coli* contamination at Agate Bay in Lake Superior. We hypothesize that this system (construction in Fall 2024) will be effective for removal of CECs such as pesticides in addition to the target contaminant, given that both are known to interact with biochar surfaces via hydrophobic interactions. In the first research chapter (Chapter 2), intermittently dosed column tests were carried out to evaluate *E. coli* and CEC removal using the same biochar to be installed in the system in Agate Bay. Results showed that columns containing biochar amendments maintained effective removal of elevated levels of CECs, while rapid breakthrough was observed in columns containing only sand. No significant improvements in *E. coli* removal were observed for the biochar amended column, as all columns showed effective removal of *E. coli* throughout the experimental duration. This effect may have been due to (i) biofilm growth on the filter media, which has been shown to effect *E. coli* retention in sand filters (positively) and biochar amended filters(negatively), and/or (ii) reduced contact time for the biochar-amended columns, due to improved hydraulic performance relative to sand columns. In the second research (Chapter 3), passive samplers were deployed in a drainage system in Two Harbors throughout one field season to determine time-weighted concentrations of a suite of 13 analytes commonly detected in stormwater, including pesticides and compounds from vehicle fluids. Pesticides including atrazine, diuron, and imidacloprid were detected in nearly all samples, indicating time-weighted concentrations in runoff ranging from 0.1 – 50 ng/L. Based on the retention capacity of biochar amendment when calculated for a full-scale system (> 30 years) and the relatively short soil half-lives of these contaminants (e.g., maximum of 1.1 year for Atrazine), we predict breakthrough of CECs in a biochar-amended stormwater filtration system within a typical system lifetime to be unlikely, as contaminants will degrade prior to ever reaching breakthrough concentrations. The results of this study will inform the construction of a biochar amended treatment system in Agate Bay, and more

broadly, provide insights into the complexities of biochar-facilitated contaminant removal processes that can better inform material selection and design for future systems.

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CHAPTER 1

Literature Review

1.1.1. Urban runoff and Low Impact Development (LID)

As water pollution has become an issue of concern in the last century, one important pathway of contamination to receiving waters is through urban runoff[1]. Runoff from urban areas occurs after rain and storm events, as well as with snowmelt in colder climates. The water from these events can take up contaminants such as dirt, oils, and chemicals deposited on urban surfaces. Moreover, urban areas tend to have more impervious surfaces, preventing infiltration and increasing runoff. This leads to both flooding and degradation of receiving water quality. Conventional stormwater best management practices (BMPs) have primarily been focused on preventing flooding[2]; however, as concerns over water quality grow Low Impact Development Systems (LIDs) have been implemented to improve permeability of urban surfaces and also remove contaminants from runoff. These practices include but are not limited to increasing vegetation and urban forestry, setting limits on impervious surfaces, and establishing buffer zone standards.[3] These measures are designed with the intention of treating contaminants subject to state and local regulations, including *E. coli*, nutrients, suspended solids, and heavy metals.[4–6] For example, the Minnesota Pollution Control Agency (MPCA) has an *E. coli* water quality standard set for Lake Superior at no more than 235 organisms per 100 mL in more than 10% of all individual samples taken during a calendar month from April to October.[7] *E. coli* can be a serious concern in stormwater runoff because of its potential paths into drinking water and the environment.[8] Biological contaminants can be difficult to remove because they can use nutrients in stormwater to grow. They also tend to be released from traditional filter media when storm events are intermittent.[9]

Many contaminants are associated with small particles, which can be readily removed in conventional stormwater treatment systems.[10,11] However, *E. coli*, as well as dissolved compounds such as polar CECs, can more easily pass through both conventional BMPs and LID systems.[12,13] Biofiltration systems are one example of a popular LID system used for stormwater management and treatment. Biofiltration systems manage stormwater runoff in urbanized areas by allowing facile treatment through basic filtration mechanisms[14]. These systems include some mix of natural soils and materials such as sand and compost to promote contaminant removal as drainage occurs. They have proven effective in treating suspended solids,

heavy metals, and nutrients in stormwater[15]; however, they are less effective for removal of *E. coli* and CECs from runoff.

Organic contaminants of emerging concern (CEC) present in runoff include pesticides such as biocides, insecticides and herbicides[13], as well as pharmaceuticals, industrial chemicals, personal care products, polychlorinated biphenyls (PCBs), and polycyclic-aromatic hydrocarbons (PAHs).[12,16,17] A recent study conducted by Masoner et al. (2019) for the USGS examined contaminants in stormwater runoff from 21 urban sites across the United States. They found the most frequently detected classes of CECs to be pesticides, PAHs, industrial chemicals, household chemicals, pharmaceuticals, and plant/animal sterols; these contaminants accounted for 70% of the total detections during the course of the study[18]. Pesticides were the most detected contaminants, but PAHs accounted for the largest fraction of cumulative concentration. Detectable levels of CECs were found at every site, and 11 compounds were detected in all samples. These results are consistent with studies conducted by others in recent years.[16,19] Therefore, it is evident that new materials are needed to assist in the removal of these contaminants from stormwater runoff.

1.1. Biochar as a sorbent for stormwater treatment

One means of enhancing removal of contaminants in treatment systems is by amendment of filtration materials with sorbents. Sorption is a general term for the removal of a compound in solutions by a solid constituent, this can occur through mechanisms including adsorption and absorption.[20] Some natural materials such as soil and sand can be used as sorbents, but engineered sorbents are also available to improve contaminant removal thanks to the design of morphology and surface chemistry to enhance interactions with contaminants. However, these materials, such as activated carbon, can be expensive and are not typically used in applications with the size and flow conditions of stormwater treatment systems.[21] Therefore, alternative sorbent material are needed for stormwater treatment systems.

Biochar is a promising potential sorbent for stormwater treatment systems.[22] Filtration systems with biochar have been shown to reduce the concentration of various contaminants, although results vary based on biochar selection.[23–25] Biochar is a product of the pyrolysis of biomass, typically from plant materials such as grasses and wood. Pyrolysis occurs under oxygen-limited conditions and high temperatures ranging from 250°C to over 800°C. Biochar is a stable, solid carbon product which can have high surface area and tunable properties.[26,27] Various factors can affect the properties of a biochar, including the feedstock and the production temperature. Plant-derived biomass is composed of lignin and cellulose, with woody biomass having higher amounts of lignin and agricultural and grassy biomass containing more cellulose.[26] Lignin is

more aromatic in nature than cellulose and therefore will produce biochar with more aromatic surfaces. This means that the feedstock of a biochar strongly influences the final characteristics of a biochar surface. Additionally, lignin is more thermally stable and decomposes at higher temperatures relative to cellulose, so it can undergo pyrolysis at higher temperatures without structural decomposition. Increased pyrolysis temperatures decrease biochar yield but can also change the surface chemistry of the resulting biochar and increase the surface area of the material. This increase in surface area arises from the increase in intraparticle porosity, which is created from the condensation of organic materials at these high pyrolysis temperatures.[27] High surface area is a favorable characteristic, as it allows for greater adsorption capacities and aging potential. Generally, increasing the temperature during pyrolysis will also affect the relative elemental composition, with H and O content decreasing with increasing temperature and content of stable C increasing, causing biochar surfaces to become increasingly hydrophobic with increasing temerpature.[27] In other words, biochar produced at lower temperatures will contain more hydrophilic functional groups such as alcohols and carbonyls; whereas biochar produced at higher temperatures will have more aromatic surfaces due to both the feedstock and the pyrolysis temperature.[33] This means that depending on the application and analyte of interest, biochar with the most favorable surface chemistry can be selected.

These characteristics make biochar a promising alternative sorbent to activated carbon, potentially at a much lower cost.[21] Another benefit to the use of biochar is that the use and production of biochar is a carbon negative process, with pyrolysis essentially causing carbon sequestration in the formation of biochar. This is because the carbon in organic material that would otherwise be broken down into carbon dioxide and other carbon-containing compounds is instead made into a stable carbon material, biochar. This material can be used for contaminant removal in treatment systems, but it can also promote vegetation growth, increasing carbon dioxide removal via plant uptake.[28] This makes it an especially environmentally friendly option to be used in treatment systems. Biochar has been found to increase removal of *E. coli* in stormwater, and has been shown to perform preferentially over non-biochar-containing materials in column tests.[9,29] Physical straining is involved with the successful removal of *E. coli* by these systems, but the addition of a stronger sorbent such as biochar can improve its removal. Some factors that appear to affect the removal of these bacterial contaminants include using biochar with high surface area and porosity, high production temperatures, wood-based biomass sources, and with low ash contents.[30] Biochar with characteristics that improve removal of *E. coli* may also be effective for removal of polar CECs.[30] More specifically, it has been found that particle size and meso-porosity play an important role in removal of CECs.[31] Another advantage of biochar regarding organic contaminant removal is the tunable surface chemistry which can promote contaminant adsorption. Most neutral CECs like pesticides and PAHs have some level of

aromaticity. High temperature biochar, which have higher surface area, also have highly aromatic surfaces which allow for attraction of CECs via Van der Waals forces such as pi-pi interactions.[32] Additionally, polar groups such as carbonyls and alcohols can form hydrogen bonds with CECs when present on the biochar surface, further promoting adsorption and therefore contaminant removal[33]. Another potential advantage to the addition of biochar to filtration systems is that biochar can stimulate the growth of microbial communities which could facilitate biodegradation of CECs after adsorption.[34] This would help prevent leaching of contaminants after adsorption, and potentially increase the length of time a system would be effective.

Various studies have investigated the removal of *E. coli* with biochar at the laboratory scale.[9,30,31,35] It has been demonstrated that the presence of biochar enhances *E. coli* retention, primarily due to a combination of physical straining and hydrophobic interactions.[29,36] Additionally, Valenca et. al (2021) found that biochar characteristics including high fixed carbon content and surface area were positively correlated with *E. coli* retention, whereas high levels of volatile matter and ash were negatively correlated against retention.[37] Highly porous biochars with low particle sizes are often those with the highest surface area, but hydraulic conditions must be considered when selecting for particle size as very finer particles are more likely to be associated with clogging in biofilters.[38] There are various environmental conditions which have also been shown to significantly impact *E. coli* retention, including biofilm formation, flow rate, and intermittent vs. constant flow.[36,39] Because performance can be highly variable based on experimental conditions, it is important to consider what conditions are representative of those likely to be experienced by actual treatment systems when selecting conditions for laboratory studies.

Previous laboratory studies, while informative, lack the variability in conditions that is inevitable in implementing full-scale systems. For this reason, a next step is often to perform mesocosm level studies. These involve the construction of small-scale versions of systems with all or most components that would be present in a full-scale system, often done outside of a controlled laboratory setting. An example of a recent mesocosm study was published by Ulrich et al. in 2017. They conducted a study with intermittently dosed, vegetated columns simulating a scaled-down treatment system.[23] The study resulted in nearly 100% removal of trace CECs for 5 months in biochar amended filtration columns. They also evaluated *E. coli* removal as well as other contaminants (TOC, TN, nitrate, and metal ions), all of which showed some level of improved removal with biochar amended systems. Studies such as this, that evaluate not only larger systems, but also multiple contaminants are important to understand how materials may perform in a full-scale system. This is because the addition of varying environmental and water quality conditions can affect

how individual contaminants groups are removed. However, most studies only look at one contaminant or type of contaminant and do not conduct experiments under environmentally representative conditions.

1.2. Passive samplers for quantitative analysis of CECs in the environment

When studying contaminants that are found at trace concentrations, environmental sampling can be difficult. Method detection limits must be sufficiently low to detect and quantify trace contaminants. Conventionally, discrete or "grab" samples are used to conduct water quality and contaminant testing in runoff and other water samples. Grab samples are collected by filling a sample container directly from the sampling site at a single time point.[40] This means it acts as a snapshot of the concentration of contaminants at a specific time, but this is not ideal if concentrations of contaminants are fluctuating as can be the case with reservoirs, streams, and runoff. An alternative method of sample collection for monitoring CECs is passive sampling. Passive samplers are deployed directly in a waterbody for a defined period of time, during which contaminants are accumulated on to a receiving phase as water flows over the sampler,[40] an example of which is shown in Figure 1.1. This process concentrates the contaminants within the sampler, allowing for higher concentrations for analytical purposes. In contrast to grab samples, passive samplers are used to estimate the time-weighted concentrations of contaminants during the sampling period. Classic passive sampling devices are single-phase samplers, which include only the polymer binding surface which adsorbs analytes of interest. A popular example of this is the Polar Organic Chemical Integrative Sampler (POCIS), which as the name suggests, allows for the collection of polar organic compounds due to the copolymer binding material used. In single phase passive samplers, mass transfer rates must be accounted for, which is dependent on extensive calibration and various natural conditions.[41,42] Therefore, mathematical modeling in conjunction with site monitoring is needed to accurately estimate the concentration of contaminants at a given time.

Figure 1.1. A group of three passive samplers before deployment in a small stream of water. Image taken on 5/9/23 during sample collection at Agate Bay in Two Harbors, MN.

In recent years, passive samplers using organic diffusive gradients in thin films (o-DGT) have become a popular option. O-DGT allows for field deployment without the need for additional calibration, as contaminant uptake rate is dependent on fewer parameters.[43] This is because they contain a diffusive layer which controls the uptake of contaminants, allowing time-weighted concentrations to be estimated based on unique diffusion coefficients for each contaminant. After passing through the diffusion layer, analytes are then exposed to the binding phase to which they can adsorb and later be extracted in the laboratory after the sampling period. The principle of o-DGT is based on Fick's first law, so that the concentration of target compounds in solution can be determined via Equation 1:

$$C_{DGT} = \frac{M(\Delta g+\delta)}{D_e A t} \qquad \text{Eq. 1.1}$$

Where C_{DGT} is the o-DGT-measured concentration, M is the mass of analyte accumulated on the binding layer, Δg is the length of the diffusion layer before exposure to the binding phase, δ is the thickness of the diffusive boundary layer, D_e is the diffusion coefficient of the analyte, A is the sampling area of the o-DGT, and t is the deployment time of the system.[44] Therefore, time-weighted concentrations of individual analytes can be easily determined with information from the sampler parameters and the diffusion coefficient of the analyte.

Diffusion coefficients for analytes have been experimentally determined using diffusion cells.[43,45,46] These consist of two compartments connected by a cavity containing the diffusion layer matrix. One compartment is filled with water spiked with known concentrations of analytes; the other compartment is filled with the same media without analytes. Diffusion of analytes from compartment A to B is measured over time to determine diffusion coefficients using **equation 2**:

$$D_e = \frac{k\Delta g}{C_s A} \qquad \text{Eq. 1.2}$$

Where k is the first order diffusion rate constant (equal to the slope of a line plotting analyte mass as a function of time), Δg is the length of the diffusion layer, C_s is the initial concentration of the analyte, and A is the area of the connecting cavity.[45] Therefore, based on experimentally determined diffusion coefficients, parameters of the sampling apparatus, and deployment time, time-weighted average concentrations of individual analytes can be determined. These measurements can be conducted in conjunction with grab samples to inform contaminant levels and how they may vary over sampling periods.

1.3. Thesis overview

The main objectives of this thesis are to (Objective 1) verify the performance of biochar-amended biofilters for simultaneous retention of *E. coli* and CECs from runoff under realistic environmental conditions, and (2) use the performance verification data to predict potential treatment effectiveness for a full-scale biochar-amended treatment system. We hypothesize that this system will also be effective for removal of CECs such as pesticides, given that both contaminants are known to interact with biochar surfaces via hydrophobic interactions.[30] Two Harbors, MN is used as a case study, where a biochar-amended filtration system will be installed in Fall 2024 to manage persistent *E. coli* contamination at Agate Bay in Lake Superior.

The first research chapter (Chapter 2: Simultaneous removal of *E. coli* and contaminants of emerging concern (CECs) from stormwater in biochar-amended sand filters) addresses objective 1, and describes a laboratory study involving intermittently dosed column filtration tests to simulate the performance of biochar-amended sand filters for simultaneous retention of CECs and *E. coli*, using the same biochar and sand to be installed in the treatment system at Agate Bay. We additionally investigated Specific Ultra-violet Analysis (SUVA) as a potential indicator for the ability of the biochar to facilitate hydrophobic interactions that have been associated with enhanced removal of both CECs and *E. coli*.

The second research chapter (Chapter 3: Assessment of the performance of stormwater treatment systems for organic contaminant retention using passive sampling) describes a study that explores the profile of CECs in urban runoff from Two Harbors, MN that drains into Agate Bay. The purpose of this work was to determine the existing concentrations of CECs in runoff to Agate Bay, such that potential CEC load reduction associated with installation of a biochar-amended filtration system could be estimated. Passive samplers were used to determine time-weighted concentrations of a suite of 6 CECs in the existing drainage system over one field season. These results were used to estimate the contaminant load to Agate Bay from runoff sources in Two Harbors, based on precipitation data and the size and composition of the catchment. We then estimated the potential CEC retention lifetime of the planned biochar-amended filtration system, based on results from chapters 2 and 3 as well as results from previous studies.

Conclusions of the from the first three chapters are summarized in Chapter 4. The findings of this work demonstrate that while biochar is a strong candidate for contaminant remediation via amendments in stormwater filtration, the removal performance of similar materials in terms of feedstock and production can vary greatly. We found that analysis of elemental composition and pore volume can give insights into the potential for removal of organic components present in natural waters, as indicated by SUVA. This work additionally highlights the complex chemical and biological processes which affect contaminant removal, and that environmental conditions are extremely relevant in predicting the retention of biological contaminants in biochar amended systems. Therefore, additional research will be needed to evaluate the comparison of laboratory and field-scale results to further inform the conditions which much be considered when predicting performance of contaminant removal.

CHAPTER 2

Simultaneous removal of *E. coli* and contaminants of emerging concern (CECs) from stormwater in biochar-amended sand filters

2.1 INTRODUCTION

Urban stormwater is an important and often overlooked source of environmental contamination, transporting contaminants to receiving waters and degrading water quality.[1] It has become a greater source in recent years due to increases in impervious surfaces in urban spaces. Stormwater best management practices (BMPs) focus on the prevention of flooding with a secondary goal of reducing contaminant transport.[2] Traditional low impact development (LID) systems prevent flooding and remove suspended contaminants and those bound to sediments, however they are ineffective at removing mobile and dissolved contaminants, including low level contaminants of concern.[3,4] An additional contaminant of concern is fecal indicator bacteria (FIB), such as *E. coli*. FIB can enter runoff through various sources including animal waste, failing sewer systems, and fertilizer runoff.[47] The presence of FIB in stormwater can cause concerns for environmental and public health, and it is often not sufficiently removed in existing filtration systems.[8,9]

The addition of sorbents to filtration systems, a type of LID system, is a promising method of improving the retention and removal of mobile contaminants from urban runoff. One such potential sorbent which has garnered increasing attention is biochar. Biochar is a product of the pyrolysis of biomass, a stable carbon product with high surface area and tunable surface chemistry.[26,27] While biochar has long been used as a soil amendment and has known carbon sequestration benefits, the use of biochar for stormwater treatment is a growing field of research.[28] Previous work has shown promising results regarding the removal capacity of biochar for a wide array of contaminants, including CECs (e.g., pesticides) and biological contaminants (e.g., *E. coli*)[9,23]. Regarding CECs, the adsorption of aromatic compounds is strongly driven by hydrophobic (pi-pi) interactions and the affinity of a compound with the biochar surface.[33] Surface chemistry can be inferred through biochar elemental ratios, as the hydrogen to carbon (H:C) and oxygen to carbon (O:C) ratios can indicate the level of hydrophobicity material. A low H:C is a sign of a highly aromatic surface, and a low O:C is indicative of few polar oxygen-containing functional groups. Both characteristics are therefore signs of a highly hydrophobic surface. Additionally, the availability and accessibility of carbonaceous sorption sites, affected by particle size and intraparticle porosity, plays an important role in organic contaminant sorption.[48] Various previous studies have demonstrated enhanced *E. coli* retention in the presence of biochar, which has been attributed to a combination of physical straining and hydrophobic interactions.[9,29,36] A recent study with several commercial biochars suggested that greater fixed carbon

content and surface area were beneficial to *E. coli* retention performance, while greater quantities of volatile matter and ash diminished performance.[43]

Commercially available biochars are often produced using wood feedstock at pyrolysis temperatures between 500 °C – 700 °C and are widely referenced as "high temperature" biochars. Valenca et. al (2021) conducted a study comparing various commercial high temperature biochars for *E. coli* removal and found that while all biochar improved removal performance, the removal capacity was positively correlated to surface area and carbon content and negatively related to ash content and volatile organic matter.[37] Biochars produced at very high temperatures (e.g., >900°C) have additionally been shown to be highly effective for adsorption of CECs, particularly biochars produced by gasification, which involves introduction of a controlled amount of oxygen during production.[31] This was attributed to more hydrophobic surface chemistry (lower H:C and O:C) and greater intraparticle pore volume relative to other commercial wood-based biochars produced at lower temperatures. While application of gasification biochars is of interest from an economic and sustainability perspective because the resulting biochar is a byproduct of a renewable energy generation process, biochars produced by gasification often have a higher ash content due to the presence of oxygen in the combustion process and can be less consistent on a batch-to-batch basis.[49] These "very high temperature" biochars can also be produced by pyrolysis using specialized production equipment, and can also be modified post-production to increase surface area (e.g., steam activation).

While previous studies have shown promise for the removal of CECs and *E. coli* in biochar-amended sand filtration systems, few studies have evaluated the simultaneous removal of these contaminants, particularly under intermittent flow conditions typical of actual treatment systems. Here, we evaluate the performance of biochar-amended sand columns for the simultaneous removal of CECs and *E. coli* during intermittent dosing tests. We hypothesize that effectiveness for removal of the aromatic portions of dissolved organic carbon (DOC), as indicated by specific ultraviolet analysis (SUVA), can be used to probe for the availability and accessibility of carbonaceous sorption sites that can facilitate hydrophobic interactions. We compared the performance of two commercial, high temperature wood-based biochars with highly hydrophobic surface chemistry but with different composition and intraparticle pore structure. Our findings provide insight into the complex biological and physiochemical processes that affect contaminant removal in biochar-amended stormwater filtration systems.

2.2 EXPERIMENTAL SECTION

2.2.1. Materials

2.2.1.1 Chemicals and reagents

Analytes measured in this study include atrazine, diuron, imidacloprid, and 5-methyl-1H-benzotriazole. These analytes were chosen because they have been widely detected at relatively high concentrations in urban runoff (ranging from 0.001 – 10 µg/L)[18]. Analytical standards for these analytes, as well as 1-(3,4-dichlorophenyl)-3-methylurea and isotope labelled standards for Atrazine-d4, Diuron-d6, Imidacloprid-d4, and Isoproturon-d6 were acquired from Millipore Sigma. Optima-grade water and methanol (Fischer Scientific) were used with trace organic samples and standards unless noted otherwise. PBS buffer for use with *E. coli* stocks and samples was made in the laboratory using deionized water and salts (Millipore Sigma). LB Miller broth from Fischer bioreagents was used for *E. coli* incubation.

2.2.1.2 Filter materials

Two wood-based commercial biochars were obtained from American Biochar Company (ABC, Niles, Michigan) and Wakefield Biochar (WFB, Valdosta, Georgia). The ABC biochar is a steam-activated biochar produced from Southern Yellow Pine with a maximum pyrolysis temperature of 900 °C (particle size ranging from 0.5 – 2.0 mm, see Table A2.2 for additional technical specifications). This biochar was selected because it was available regionally in cubic yard quantities, and because it demonstrated promising retention of *E. coli* in up-flow saturated column experiments in a previously publish laboratory study.[37] The WFB biochar was selected because it is widely available in bulk quantities, and initial characterization tests revealed substantial differences in elemental composition from the ABC biochar (see section 2.3.1.). This biochar is produced from Loblolly Pine waste wood from sawmill operations, with pyrolysis temperature of 600 °C or higher (particle size ranging from 0.3-2.4 mm, similar to the ABC biochar). Concrete sand was purchased from Plaisted Companies (Elk River, Minnesota), and technical specifications are provided in Tables A2.4-2.5. Gravel used as a drainage and topping layer (particle size ranging from approximately 2.38 – 4.76 mm) was obtained from Menards and was thoroughly washed with tap and deionized water prior to use.

2.2.2 Experimental Approach

2.2.2.1 Experimental apparatus

An image of the column apparatus is shown in Figure 2.1. Columns consisted of 2 x 24-inch PVC pipe with an open top and bottom cap with a 1 cm outlet, such that the drainage rate was controlled by the filter media

and back pressure within the column was minimized. Columns were packed with a lower gravel drainage layer, a filtration layer including sand or sand amended with biochar, and an upper gravel later to hold the filtration layer in place. This resulted in columns with approximately 8-10 cm of ponding space above the filter bed. Three different column configurations were evaluated in triplicate: sand-only (as a control), sand with the ABC biochar, and sand with the WFB biochar. Sand and biochar were mixed at a 70:30 ratio by volume prior to loading into columns, resulting in filtration layers with an empty bed volume (EBV) of approximately 700 mL. The bulk density of sand and sand/biochar mixtures were 1.6 g/cm^3 and 1.21 g/cm^3, respectively. Biochar has a typical bulk density of 0.3 6 g/cm^3. Porosities of the sand/biochar columns were similar (40% ± 2% v/v) as determined by the total pore volume of media mixtures.

Figure 2.1. A) An image of the column filtration experimental setup. B) A diagram of the makeup of column filters.

2.2.2.2 Preparation of dosing solution

Natural creek water (20 L) was collected from Tischer Creek (Duluth, MN) 24-72 hours prior to each test. To augment organic matter levels, dried leaves collected from urban leaf litter in fall of 2023 (approximately 5 grams) were added to the water following collection and the water was equilibrated at room temperature overnight. Prior to each test, equal volumes (2.1 L, equivalent to three empty bed volumes, EBVs) of creek water were added to nine separate influent containers, each of which were charged with equal amounts of CECs and *E. coli*. Atrazine, diuron, imidacloprid, and methyl benzotriazole were spiked into the creek water

immediately prior to each doing test via a methanol carrier solution to achieve contaminant concentrations between 10-20 µg/L. *E. coli* levels were also augmented in the creek water for a subset of dosing tests (three *E. coli* dosing periods, ranging between 2-5 tests during each period). A pure *E. coli* culture was prepared from stock *E. coli* in sterilized LB media and incubated at 35 °C and stored for the duration of the tests. Fresh *E. coli* subcultures were prepared one to two days prior to dosing tests by diluting *E. coli* cultures 100x in 1x PBS buffer. Immediately prior to dosing tests, 5 mL of dilute subculture were added to each influent reservoir to achieve *E. coli* levels between 10,000-20,000 / 100 mL. The concentrations of CECs and *E. coli* in the dosing solution were approximately one to two orders of magnitude greater than typically reported concentrations in runoff[18,47] to facilitate fast breakthrough and evaluate differences in treatment performance under high bacterial loading conditions.

2.2.2.3 Dosing procedure

A total of 34 dosing tests (3 EBV each, 102 EBV total) were performed over a six-month period, representative of 2.5 years of equivalent runoff volume for the Duluth, MN average annual rainfall (approximately 30 inches per year). The first 18 dosing tests were performed biweekly from August to October. To simulate a freeze-thaw cycle, the column manifold was then stored outside under a tarp for 6 weeks (average temperature of -6.1 °C, ranging from -22 to +6.9 °C), then thawed in the lab at room temperature for one week prior to performing an additional 18 dosing tests. Note that an unseasonably warm winter in Duluth, MN allowed collection of creek water from January to April, though the water was at near-freezing temperatures upon collection and did not reach room temperature following overnight equilibration during the second dosing period. During each test a multichannel peristaltic pump was used to deliver 3 EBVs (2.1L) of water (equivalent to a five-inch storm for a treatment system sized to 5% of the catchment area) from each influent reservoir to the ponding reservoir of each column, and the water was allowed to drain by gravity through each column into separate effluent reservoirs. In initial tests, it was noted that sorption of CECs to the influent and effluent containers was likely occurring throughout the testing period. To account for this slow loss of contaminants in influent water, samples were collected from each effluent reservoir once the reservoir volume reached approximately 1 L (i.e., after approximately half of the water had passed through the column for each dosing test). Influent water was also collected at approximately the halfway point for each dosing test for consistency. Samples for CECs were collected in 20 mL glass scintillation vials and frozen prior to analysis, and samples for UV 254 and *E. coli* analysis were collected in 50 mL falcon tubes and analyzed on the same day. Samples for dissolved organic carbon (DOC) analysis were collected in 250 mL poly bottles and submitted for analysis day of.

2.2.2.4 Hydraulic conductivity and flow rate measurements

Saturated hydraulic conductivity testing was performed periodically (during six tests) according to a previously published method[50] to evaluate changes in flow rate during periods of high *E. coli* loading. Briefly, while maintaining a constant height of water over the filter media, the discharge volume from each column was measured over 60 second increments. Saturated hydraulic conductivity was calculated using Darcy's law (Eq. 2.1):

$$k = \frac{Qd}{A(H+d)} \qquad \text{Eq. 2.1}$$

Where k is the saturated hydraulic conductivity (cm/s), Q is the flow rate (cm^3/s), d is the depth of substrate (cm), A is the cross-sectional area (cm^2), and H is the height of water over the substrate (cm). The average saturated hydraulic conductivity for each column was found from the average of individual measurements (n=6). Results of hydraulic conductivity testing for each column type are shown in Figure A2.3.

2.2.3 Analytical Methodology

2.2.3.1 Biochar characterization

Ultimate and Proximate analysis were carried out by Timber Products Inspection (Conyers, GA) following ISO standard methods (results in Table A2.3). While the two biochars appeared to be somewhat similar in terms of apparent surface chemistry as indicated by elemental analysis (ABC: 0.042 H/C, 0.031 O/C, WFB: 0.12 H/C, 0.047 O/C), the WFB biochar had a higher ash content (74.9 % vs. 9.4 %). The pH of the two selected biochars was measured following equilibration with deionized water using a Fisher Brand Accumet AB150 pH electrode.[51] ABC biochar was alkaline (pH = 9.67), while the WFB biochar was circumneutral (pH = 7.17). Dual N_2/CO_2 gas adsorption experiments were also performed for the two commercial biochars with a Micromeritics 3 Flex according to a previously published method[52]. Cumulative pore volumes were determined for the microporous (0.36 to 1.99 nm) and mesoporous (2.00 - 50 nm) ranges (Table A2.3), indicating that the ABC biochar had a much higher cumulative pore volume (0.443 cm^3/g) than the WFB biochar (0.0721).

2.2.3.2 Specific ultraviolet absorbance (SUVA)

Filtered (0.45 µm, nylon) influent and effluent samples were analyzed by ultraviolet visible absorbance spectroscopy at 254 nm (UVA 254, indicator of absorbance in the aromatic region) immediately following dosing tests using a Perking Elmer Lambda 25 Spectrophotometer. DOC (mg/L) was also measured for select samples to determine the specific ultraviolet absorbance (SUVA, UVA 254/DOC, mg/L*m). DOC

analysis was conducted by the Central Analytical Laboratory at the Natural Resources Research Institute following a high temperature combustion method (SM 5310-B 2014) on a Shimadzu TOC-L Total Carbon Analyzer.

2.2.3.3 *E. coli* measurements

Plating and quantification of *E. coli* were performed using Coliscan® Easygel® kits (Micrology Laboratories, Granger, Indiana) according to manufacturer-recommended procedures. Briefly, Easygel media containing 1-5 mL aliquots of sample were incubated in sterile petri dishes at 35°C in an incubator for 24 hours. Highly concentrated samples (e.g., influent samples during *E. coli* dosing periods) were diluted with PBS buffer before being added to the media. Following incubation, plates were documented photographically, and colonies were counted based on the images using the pen feature in PowerPoint. *E. coli* concentrations (colony forming units, CFU, per 100 mL) were calculated according to equation 2.2:

$$CFU\ per\ 100\ mL = \#\ colonies\ counted * \frac{100mL}{volume\ of\ sample\ added} \quad \text{Eq. 2.2}$$

2.2.3.4 Organic contaminant analysis

Samples for organic contaminant analysis were stored frozen and thawed in the refrigerator overnight prior to preparation for analysis by liquid chromatography quadrupole time of flight mass spectrometry (LC-QTOF-MS) analysis. Aliquots (180 µL) of aqueous samples were spiked with isotope-labelled extraction surrogates, diluted 10x in Optima Methanol/Water (80:20), and filtered through 0.22 µm glass fiber filters, spiked with isotope-labelled internal standard solution, and stored refrigerated for up to 7 days prior to analysis. Extraction surrogates used include Atrazine-d4, Diuron-d6, and Imidacloprid-d5 (final concentration of 1 – 1.5 µg/L in extracted samples) and the internal standard used was Isoproturon-d6 (concentration of 0.5 µg/L in sample vials). Laboratory blanks consisting of Optima water were also analyzed periodically (completed in two of five sample batches) to confirm that the measured analyte concentrations were not affected by contamination from the sample preparation process. Effluent samples were processed as experimental duplicates or triplicates (i.e., replicate effluent samples from different columns of the same configuration). LC-QTOF-MS analysis was performed with an AB Sciex X500R QTOF coupled to a Sciex ExionLC AD liquid chromatography system equipped a 50 µL sample loop (25 µL injection volume), a reverse phase chromatography column (Luna C18, 5µm, 100 x 3 mm; Phenomenex) and a column oven (40 ˚C). Chromatography was performed at a flow rate of 0.4 mL/min using aqueous and organic mobile phases of Optima grade water and Optima methanol, both containing 2mM formic acid. The gradient method proceeded as follows: ramp from 5% organic to 60% organic from 0.5 to 5 minutes,

ramp from 60% organic to 90% organic from 5 to 10 minutes, hold at 90% organic until 15 minutes, then drop to 10% organic to equilibrate for the final 3 minutes (18 minutes total). Mass spectrometry analysis was performed in positive electrospray ionization mode with a spray voltage at 5500 V, ion source gasses at 55 psi, and curtain gas at 35 psi. A multiple-reaction-monitoring high resolution (MRM^{HR}) acquisition method was used to monitor two transitions per analyte (one quantitative, one qualitative). TOF mass scanning ranged from 100 - 1000 *m/z*. Additional details regarding the MS method, including the ionization parameters, designated internal standards, and monitored ions for each analyte are provided in Table A2.1. Quantification was performed according to 9-point calibration curves with analyte concentrations ranging from 0.050-53.08 µg/L (Table A2.1) with an R^2 value of 0.99 as the linearity criteria, an accuracy criterion of ±30%, and a signal to noise (S/N) threshold of 10. Data are reported for cases where analytes were measured at concentrations above the limit of quantification (LOQ, the lowest calibration level that passed the acceptance criteria).

2.3 RESULTS AND DISCUSSION

2.3.1 Effects of biochar on DOC quality

Results of DOC and UVA 254 analysis for three column configurations (sand only, WFB biochar amended, and ABC biochar amended) are shown in Figure 2.2A and 2.2B, with the calculated SUVA values for column effluents shown in Figure 2.2C. The influent UVA 254 values varied over time and were highest during the first dosing period (conducted during the fall) than during the second dosing period (conducted during the winter). This apparent seasonal difference may have been due to the water temperature, as the water would not fully equilibrate to room temperature overnight during winter months, causing organic matter from the leaves to leach more slowly into the influent. However, the reduction in absorbance at 254 nm maintained consistent trends through the 36 filtration tests, as shown by the difference in UVA 254 reduction between column types in Figure 2.2A. Interestingly, though minimal variations were observed in the effluent DOC concentrations between the sand columns (54.8 ± 4.2 mg/L, n = 21) and the biochar-amended columns (ABC 47.0 ± 2.2 mg/L, WFB 48.4 ± 3.6 mg/L, n = 21), large differences in UVA 254 and SUVA values were observed between the column effluents during both dosing periods. Notably, the effluent from the ABC biochar columns had the lowest SUVA values during the first dosing period when influent UVA-254 values were high, while there was no significant difference between the effluent SUVA values for sand and WFB biochar columns (as indicated by standard deviations for triplicate measurements). These differences were also visually apparent during experiments, as there were distinct color differences among the influent and effluents.

These results suggest that while both biochars showed minimal improvements for retention of the total DOC, the SUVA effluents results suggest that the ABC biochar preferentially retained the aromatic portion of DOC. This was likely due to differences in the material properties of the two biochars (Table A2.3). Adsorption of aromatic compounds to the biochar surface is primarily driven by hydrophobic interactions such as pi-pi stacking.[32] The retention of these compounds is dependent on the affinity with the surface, the aromaticity of which can be characterized by the carbon content and surface chemistry.[53] However, elemental analysis of the two biochars suggest that the surface chemistries are similarly hydrophobic. One difference in that was observed with elemental analysis was in fixed carbon levels. ABC biochar has a much higher fixed carbon content and much lower ash content (71.19% and 9.42%) than WFB biochar (14.63% and 74.90%). While these differences would not necessarily explain the difference in observed SUVA levels, it is a likely sign that partial combustion occurred during the production of the WFB biochar (leading to ash formation).

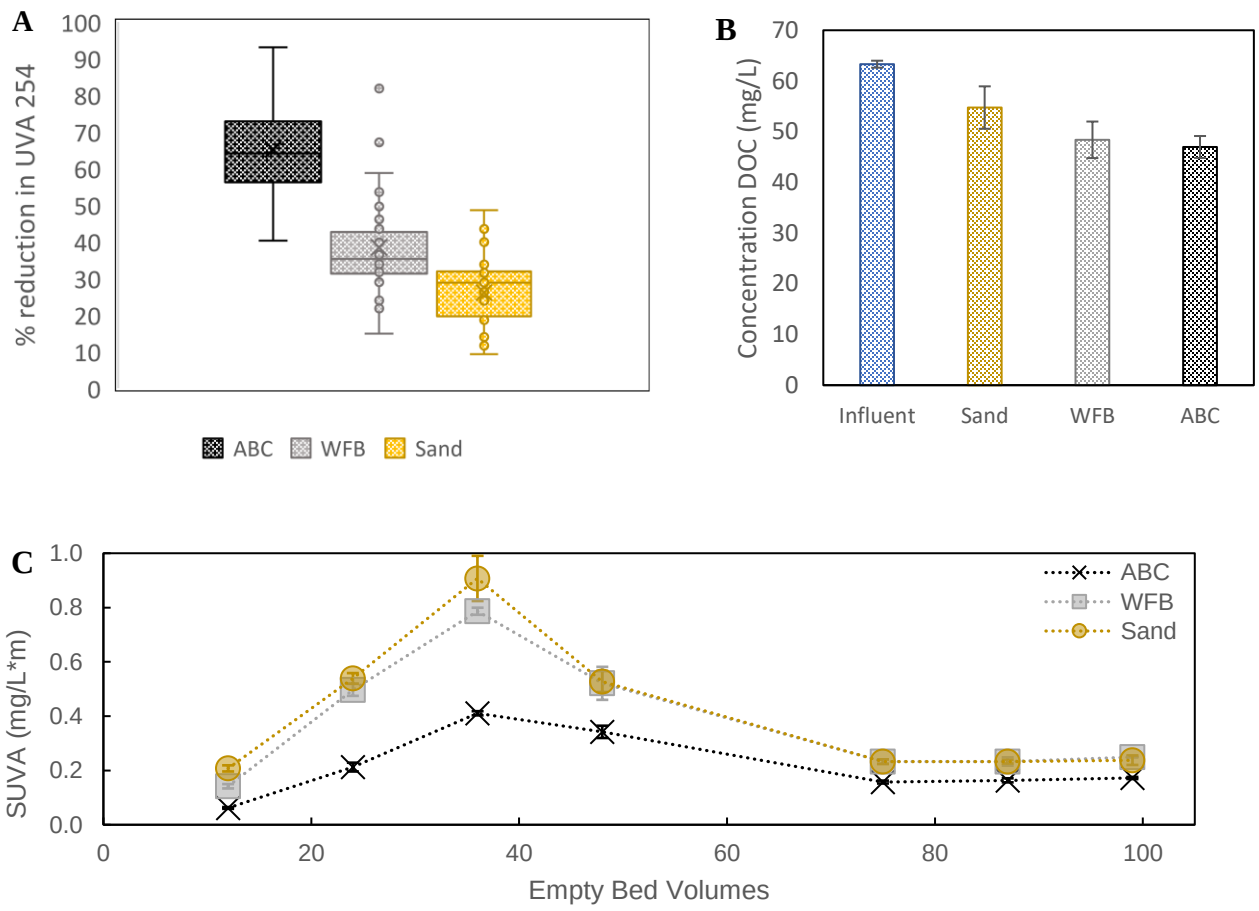

Figure 2.2. A) Reduction in UVA 254 from influent levels for each column types over the duration of dosing tests. B) Average measured DOC concentrations from intermittent testing. Error bars indicate standard deviations for all measurements. C) Calculated SUVA values for column effluents. Error bars indicate standard deviations for experimental triplicates.

The formation of ash suggests that another consequence of partial combustion is possible: the collapse of intraparticle pore structures, which make biochar such a promising sorbent material. This is confirmed by comparison of the cumulative pore volume between the two materials, which is composed of micro- to mesopores. ABC biochar has over six times the cumulative pore volume than WFB biochar (0.443 vs 0.0721 cm^3/g), which likely contributed to its superior performance by providing a greater surface area with more intraparticle sorption sites. The measured pore volume for WFB biochar is particularly low for wood-based biochars. One study observed a pore volume range of 0.074 – 0.623 cm^3/g for wood-based biochars, where a majority were around 0.2 - 0.3 cm^3/g.[31] This further suggests that the feedstock for the WFB biochar

was partially combusted during production, such that the intraparticle pore structure collapsed, causing a loss of functional biochar materials and a decrease in overall intraparticle surface area.

The size fractions of organic matter and biochar pore size distribution may have also affected the accessibility of sorption sites. DOC consists of components with vary sizes, including humic (1 - 50 nm) and fulvic (0.2 - 1 nm) acids,[54] while the pore diameter ranges for micropores and mesopores are <2 nm and 2-50 nm, respectively. Humic substances also tend to contain more aromatic character than fulvic acids. Therefore, the higher mesopore volume of ABC biochar (approximately 50% of the cumulative pore volume) may have contributed to higher retention of humic components present in the DOC, given that the humic components of the DOC are too large to enter the micropores. These results suggest that SUVA may be a simple and effective indicator for probing biochars for intraparticle aromatic sorption sites in the mesoporous region, but that it may be less effective for probing differences in microporosity.

2.3.2 Effects of biochar on organic contaminant removal

The influent and effluent concentrations of the four CECs augmented in the column influent (i.e., atrazine, imidacloprid, methyl-benzotriazole, and diuron) are compiled according to column configuration in the box and whisker plot in Figure 2.3A (analyte-specific concentrations versus EBV are shown in the Appendix in Figure A2.6). Influent and effluent compositions were similar for the sand-only columns, indicating minimal retention of the CECs by the sand filters. Interestingly, 1-(3,4-dichlorophenyl)-3-methylurea (DCP-MU) was detected periodically in the effluent from sand columns at low concentrations (Figure A2.2, $\leq$ 2.5 µg/L). The aerobic biodegradation of diuron is well documented, with a reported degradation half-life in soil of 30-365 days (typical time reported as 90 days). [55,56] This suggests that partial degradation of diuron in sand filtration systems may lead to release of DCPMU, which is both more mobile in the environment and more toxic to aquatic organisms relative to its parent compound.[57] This result reflects findings from previous studies showing the formation of DCPMU in soils and provides additional incentive to include sorbent materials in filtration systems to prevent the generation and release of potentially harmful transformation products.[58]

Both the WFB and ABC biochars demonstrated substantially improved retention of CECs relative to the sand-only columns, reflecting results from previous studies evaluating different high temperature, wood-based biochars.[23,31,59] Interestingly, while none of the monitored CECs were observed in the effluent samples from the ABC biochar columns (i.e., no peaks observed with S:N > 3), initial breakthrough of atrazine in WFB biochar-amended columns was observed near the end of the dosing experiment, with

atrazine concentrations reaching 0.29 µg/L after dosing with 102 EBVs (C_{out}/C_{in} = 0.03). These results are shown in Figure 3B. The weaker retention of atrazine relative to the other contaminants may have been caused by reduced pi-pi interactions with biochar surface caused due to less planar configuration, as has been reported previously.[60] As the elemental analysis results suggest that the ABC biochar and WFB biochars have similarly hydrophobic surface chemistries as indicated by low H:C and O:C ratios (0.04 vs 0.12 H:C and 0.03 vs 0.04 O:C, respectively), the difference in performance is related to differences in the intraparticle pore volumes between the biochar materials (0.443 vs 0.0721 cm^3/g, respectively).

Overall, these results reflect the observations from the SUVA tests and support the utility of SUVA as probe for hydrophobic surface chemistry and mesoporous surface area that affect the ability of biochar to retain CECs. It is important to note that while this similarity in SUVA results and CEC removal was noted between biochar columns, SUVA results were similar for sand and WFB columns which showed significantly difference CEC removal results. This may highlight the importance of aromaticity in CEC removal, whereas intraparticle porosity plays a more important role regarding SUVA analysis. Though higher microporosity is associated with a greater proportion of intraparticle surface area, mesopores still have important contributions to organic contaminant sorption. For example, mesopores can act as a conduit for CECs to access intraparticle microporous sorption sites, improving sorption kinetics. Further, the presence of DOC may block access to micropores, such that sorption sites within mesopores may be more resilient to fouling.[48,61]

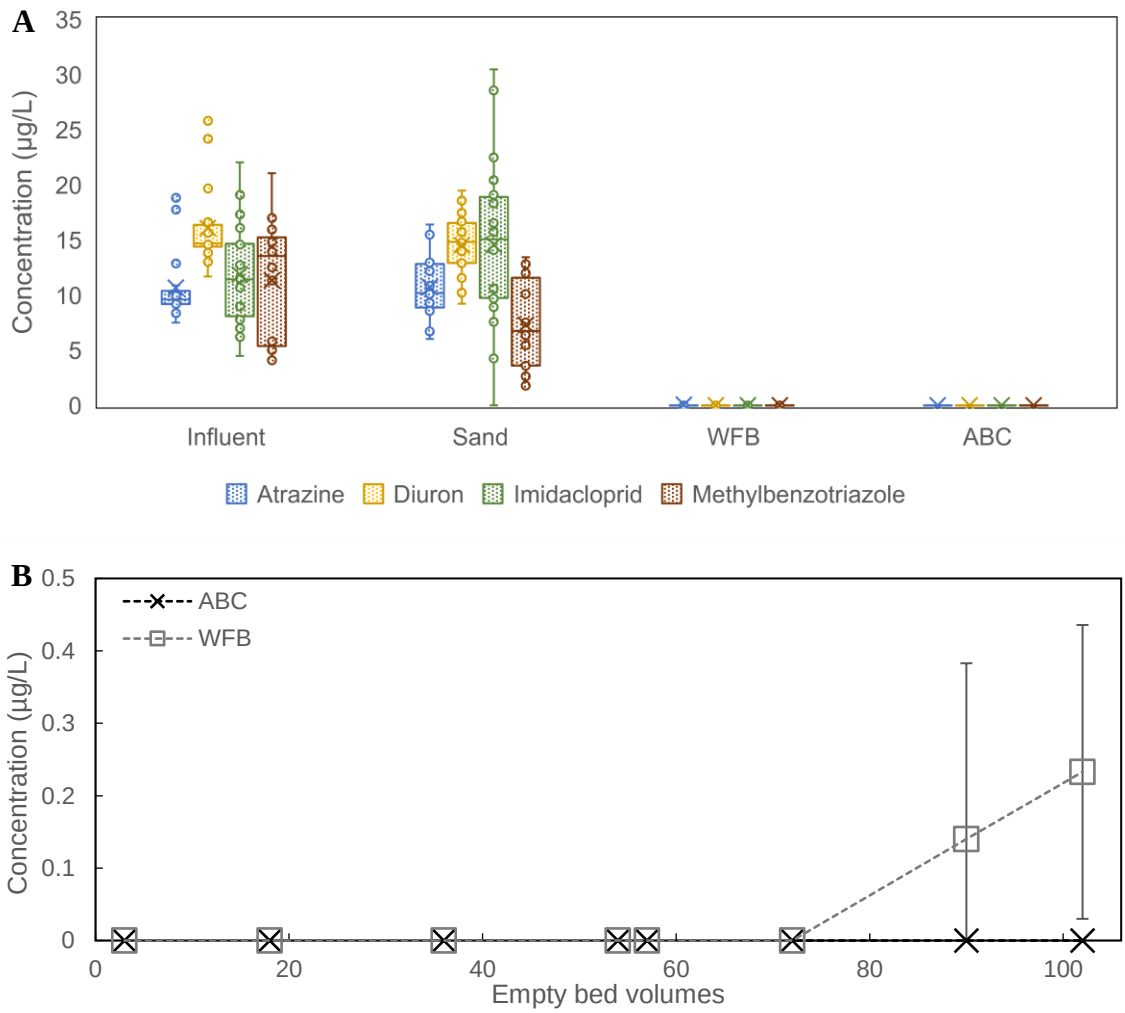

Figure 2.3. Organic contaminant concentrations in column influents and effluents: A) Box and whisker plot showing influent and effluent concentration data, for all CECs added to the influent (atrazine, methyl benzotriazole, imidacloprid, and diuron). B) Atrazine concentrations in effluents from the biochar-amended columns. Error bars indicate standard deviations of triplicate measurements.

2.3.3 Effects of biochar on *E. coli* retention

Figure 2.4A shows the *E. coli* concentrations in the column influent and effluents over the duration of the dosing tests. No statistically significant differences in effluent *E. coli* concentrations (as indicated by standard deviations for experimental triplicates) were observed between the different column configurations for individual dosing tests during the three *E. coli* loading periods. Inconsistent *E. coli*

retention was observed for all column configurations during the first loading period (log removal range of < 0 to 1.4), which was conducted at the beginning of the dosing experiment. Following equilibration over a dosing period of 40 EBVs, all column configurations showed similarly effective *E. coli* retention during a prolonged period of high *E. coli* loading. The average influent concentration in this period was 23,589 +/- 8250 *E. coli*/100 mL, and the average effluent concentrations were 3907 +/- 2318 *E. coli*/100 mL (average log removals were 0.73, 0.92, and 0.80 for ABC, WFB, and Sand), which occurred over a total of 15 EBVs during this second *E. coli* loading period. All columns continued to perform similarly during the final *E. coli* loading test conducted following the freeze-thaw cycle, though removal was overall somewhat lower relative to the previous loading test (influent concentration of 50333 *E. coli* / 100 mL) with log removals of 0.42 (ABC), 0.48 (WFB) and 0.29 (Sand). This may have been due to changes in the filters associated with the freeze-thaw cycle (e.g., channeling due to expansion and re-compaction)[62], though other factors (e.g., biofilm development) may have also contributed to reduced *E. coli* retention performance.

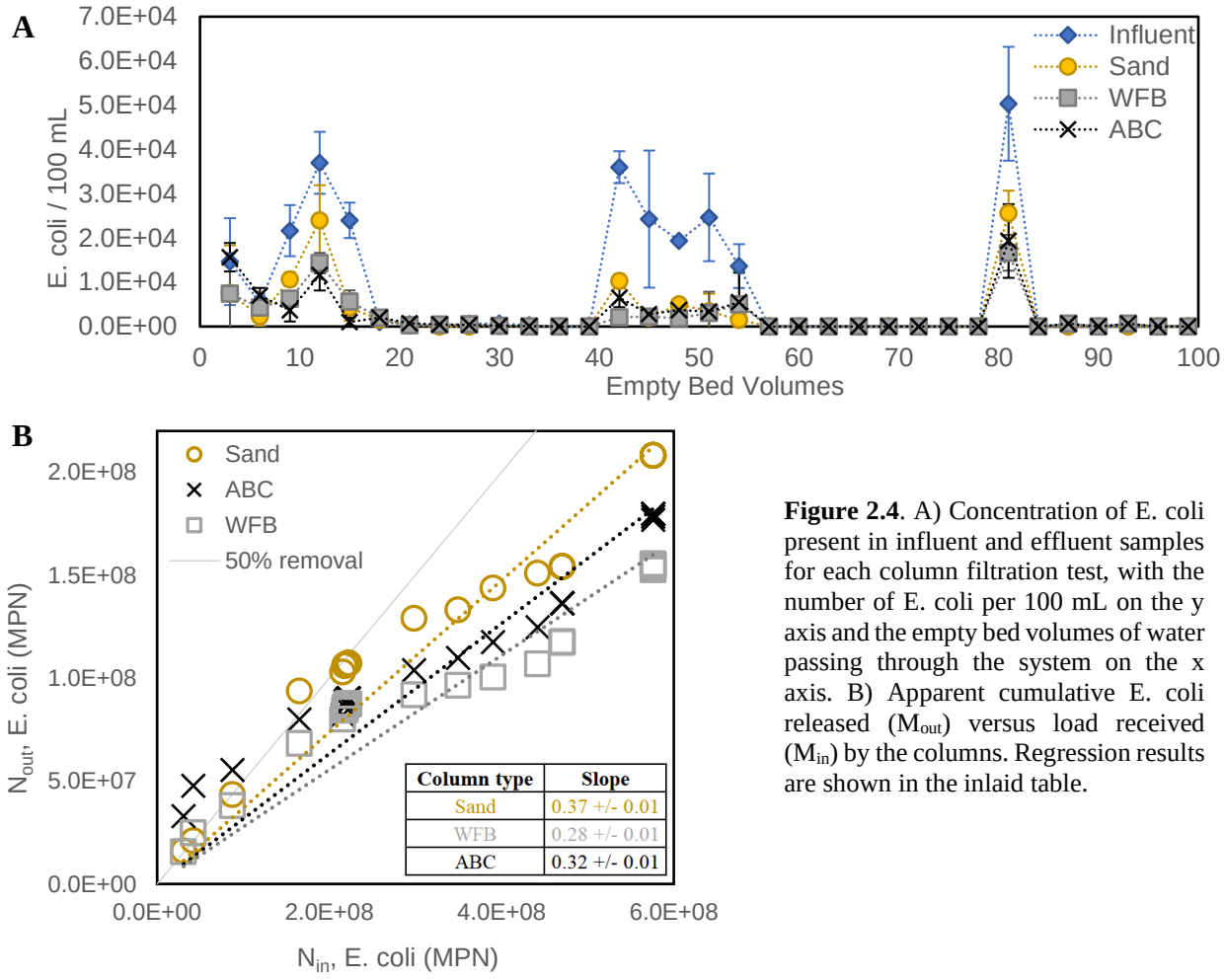

Figure 2.4. A) Concentration of E. coli present in influent and effluent samples for each column filtration test, with the number of E. coli per 100 mL on the y axis and the empty bed volumes of water passing through the system on the x axis. B) Apparent cumulative E. coli released (M_{out}) versus load received (M_{in}) by the columns. Regression results are shown in the inlaid table.

Figure 2.4B shows the cumulative *E. coli* retention performance (cumulative *E. coli* cells released from each filter versus the cumulative cells entering each filter at each dosing tests) for each column configuration over the duration of the dosing experiment. Note that by this analysis, the slope is reflective of an inverse of the average retention performance over time. Overall, while the biochar-amended columns achieved a somewhat greater cumulative *E. coli* retention by the end of the dosing experiment, as reflected by difference in the slopes for linear regressions of the retention data, these differences were primarily due to just three individual high concentration dosing tests. Therefore, these small differences in *E. coli* performance between the three different column configurations do not appear to be statistically significant.

Saturated hydraulic conductivity tests (Figure A2.3) revealed that the biochar-amended columns maintained higher hydraulic conductivity during periods of high *E. coli* loading relative to the sand filters, with the ABC biochar columns demonstrating the highest hydraulic conductivity overall (1.41 cm/hr average vs 0.71

cm/hr and 0.74 cm/hr for sand and WFB biochar columns, 66% and 62% difference). While previous studies have largely been conducted with upflow saturated columns to achieve controlled flow rates,[9,36,37] the intermittently dosed downflow column tests conducted here were allowed to drain by gravity at rates controlled by the hydraulic conductivity of the filter media. Therefore, potential improvements in *E. coli* retention associated with the presence of biochar may have been diminished due to reduced contact times. However, these results also suggest that biochar may enhance performance overall by better maintaining hydraulic performance during periods of high bacterial loading.

The development of biofilms may also account for these observations. For example, Afrooz and Boehm (2016) found that biochar-amended columns facilitated much greater biofilm growth than sand columns alone, but the benefit of biochar amendment to *E. coli* retention decreased when biofilms were present. This was compounded when DOC was present in synthetic stormwater (1.5 log removal without biofilm or DOC, 0.6 log removal with both)[39]. However, biofilm growth was associated with improved *E. coli* retention during sand filtration[63]. These differences were attributed to surface chemistry, considering that the biofilm was less hydrophobic than the biochar surfaces but more hydrophobic than the sand alone[39,64]. Additionally, biofilms can fill pore space, decreasing available surface area for *E. coli* interactions. The presence of DOC has been shown to facilitate bacteria transport through saturated porous media and therefore decreases its removal performance[65,66]. It interacts with surfaces via both hydrophobic and hydrophilic interactions and can compete for surface sites and provide a physical barrier via steric interactions[67]. Our results and experimental conditions suggest that these factors influenced the *E. coli* removal of all column types and may suggest that *E. coli* removal in field scale systems will be lower than observed in previous laboratory experiments with controlled conditions.

2.4 CONCLUSIONS

The findings of this study, some of which were unexpected, provide insights into the complex biological and physiochemical processes affecting contaminant removal in biochar-amended filtration systems. While no significant improvements in *E. coli* retention could be attributed to the presence of biochar, we observed improved hydraulic performance with biochar amendment, suggesting that biochar amendment may improve overall filtration function and limit clogging due to high levels of biological communities. A notable result was the promise of SUVA as a potential probe for biochar aromatic intraparticle sorption sites in the mesoporous region. As the analysis of CECs is costly and time consuming, SUVA presents a simple methodology for screening biochars ability to adsorb CECs based on site availability. Our results

for organic contaminant retention also indicate the importance of intraparticle pores in addition to hydrophobic surface chemistry for the enhancement of biochar sorption of CECs. Overall, these findings highlight the importance of evaluating treatment performance under conditions that are representative of those expected for field systems. Moreover, simultaneous evaluation of multiple contaminant types can provide substantial insights into how systems will function more broadly.

CHAPTER 3

Assessment of the CEC retention performance of stormwater management systems using passive samplers

3.1. INTRODUCTION

Urban stormwater is an important source of environmental contamination, transporting contaminants to receiving waters and degrading water quality.[1] It has become a greater source in recent years due to increases in impervious surfaces in urban spaces. In 2019, a USGS/USEPA study conducted by Masoner et. al surveyed 50 Urban sites across 21 US states to improve understanding of the contaminant profile of urban stormwater, specifically regarding organic and inorganic chemicals. They found concentrations of organic chemicals to be much higher than inorganic chemicals and suggest that the levels of contaminants of emerging concern (CECs) present in runoff are cause for concern for potential environmental effects. While polyaromatic hydrocarbons (PAHs) were detected at the highest concentrations, they found that organic compounds classified as pesticides were the most commonly detected in stormwater.[18] Many pesticides are highly water soluble and therefore exist in runoff as dissolved compounds, which are known to be poorly removed with conventional stormwater best management practices (BMPs) compared to nonpolar compounds like PAHs which can be easily removal through filtration as they are most often bound to sediment and particles.[13,68] Because pesticides and other polar CECs are not well removed from runoff, they pose a high risk to ecological health.

In the fields of environmental research and regulation of contaminants of concern, passive sampling approaches represent a valuable data collection method.[69] Passive sampling techniques involve the movement of analytes from a sampling medium to a receiving phase in a sampling device, allowing for uptake of analytes to occur. Passive sampling results in a composite sample of analytes, which accumulate on the receiving phase over time.[40] The use of passive samplers in tandem with discrete or "grab" samples can improve the detection of trace analytes overcoming insufficient method detection limits by concentrating analyte onto the receiving phase, which can be extracted in a laboratory setting for analysis. Another advantage of composite sampling with passive samplers is the ability to gain an average concentration over a long deployment period, which gives more accurate long-term information on analyte concentration than the snapshot of a discrete sample. While passive sampling is not able to identify short term periods where contaminant concentrations exceed acute toxicity levels, it can serve as a highly

complementary sampling method to grab sampling for monitoring initiatives seeking to understand potential toxicity concerns.

The use of passive samplers utilizing organic diffusive gradients in thin films (o-DGT) is gaining popularity in recent years. These devices contain a diffusive layer which controls the uptake of analytes through which any contaminant has a unique diffusion coefficient which can be easily experimentally determined.[43] This characteristic allows for concentrations to be estimated with little field monitoring and no additional calibration, making these devices a strong alternative to devices such as Polar Organic Chemical Integrative Samplers (POCIS).[41,42] Diffusive gradients in thin films are based on Fick's first law, a variation of which is used to determine the concentration of target compounds.[44] .

The objective of this study was to determine representative levels of CECs present in runoff at from an urban space, such that the potential load that could be prevented from being discharged to receiving waters with a biochar-amended filtration system could be estimated. Two Harbors, MN is used as a case study, where a biochar-amended filtration system is being installed in Fall 2024 to manage *E. coli* contamination at Agate Bay in Lake Superior. To complete these objectives, passive samplers were deployed in a drainage system that will be modified in the future to include a biochar-amended treatment system, and time-weighted concentrations of a suite of 13 CECs at the inlet and outlet of the drainage system were quantified over one field season. These concentration results, in combination with the CEC retention performance observed during column experiments from Chapter 2, were then used to predict the potential load of CECs that could be prevented from being discharged to Agate Bay following installation of the biochar-amended filtration system. Our results demonstrate the importance of considering the actual CEC concentrations in runoff, the effectiveness of the selected biochar for CEC sorption, and the size of the treatment system when making estimations of CEC retention lifetimes in biochar-amended filtration systems.

3.2. EXPERIMENTAL SECTION

3.2.1. Materials

3.2.1.1. Chemicals and Reagents

A suite of 13 representative stormwater CEC that are frequently present in urban runoff at relative high concentrations (ranging from 0.001 – 10 µg/L)[18] were selected for targeted analysis, a table of which can be found in Table A3.1. This list is primarily composed of urban-use pesticides (e.g., atrazine, diuron, and imidacloprid) as well as methyl benzotriazole, a commonly detected tire additive. Analytical standards for each analyte, as well as isotope labelled surrogates for select standards are described in Table A3.1. Optima-

grade water and methanol (Fischer Scientific) were used for all standards and analyses unless noted otherwise.

3.2.1.2. Passive sampler devices

Organic diffusive gradient thin film (o-DGT) based passive samplers were obtained from DGT Research (Lancaster, United Kingdom). The samplers (model LSND-AG) were composed of a 0.8 mm agarose diffusive gel, a 0.14 mm hydrophilic polypropylene (GHP) filter membrane, and a 0.5 mm HLB binding layer. Unique diffusion coefficients have been experimentally determined with these specific devices for various pesticides and herbicides, including several analytes from the suite used in this study (Atrazine, Clothianidin, Diuron, Imidacloprid, Thiabendazole, Thiamethoxam, Isoproturon*).[70] A table of these compounds with the determined diffusion coefficients can be seen in Table A3.2. Samplers were deployed in triplicate using acrylic device holders also obtained from DGT Research.

3.2.2. Experimental approach

3.2.2.1. Field site

The field study was conducted in Two Harbors, MN in an existing drainage system which flows into Agate Bay. A map indicating the location of a future biochar-amended filtration system to be constructed at the site are depicted in Figure 3.1. The treatment train will include a two-stage sedimentation ditch leading to bioretention and biochar-amended filtration basins. The catchment area of the system is primarily composed of residential space and is approximately 100 acres in size. Samples were collected at the inlet and outlet of the current drainage system such that future sampling following system installation can be used to identify improvements in contaminant discharge. The main sample collection sites are marked in yellow and blue in Figure 3.1, which are easily accessible inlet (yellow) and outlet (blue) locations in the pre-existing drainage system. An additional inlet site, marked in green, was also sampled intermittently to identify any potential differences in concentration between the two inlets.

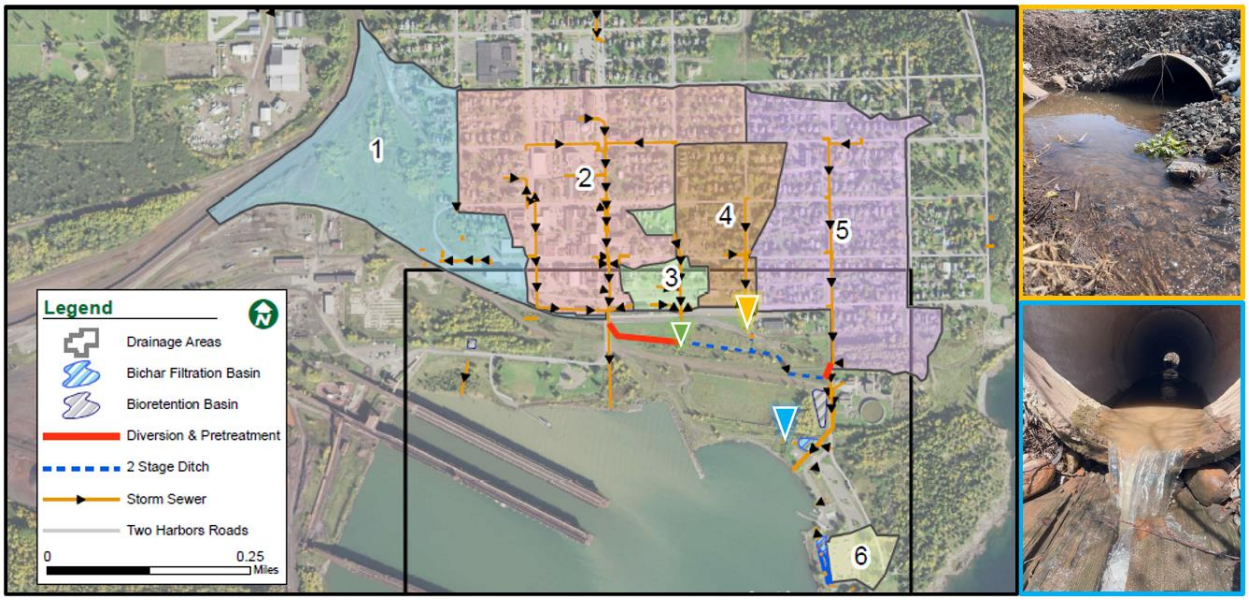

Figure 3.1. A map of the Agate Bay area with drainage areas, location installation of the treatment train, and the inlet (yellow) and outlet (blue) sampling sites marked. An additional "west inlet" site is marked in green. Plans for a to-be-installed treatment train are indicated in the legend. Images of the sampling location for each site are outlined with the corresponding color of the points on the map.

3.2.2.2. Grab sample collection

Initial grab sampling was performed to gain insight into the comparability between concentration data from CECs from individual grab samples versus passive samplers. Grab sampling was conducted weekly for four weeks starting in April 2023, during which snowmelt enabled consistent and predictable flow conditions. Ashed 300 mL glass amber bottles were used to collect samples for CEC analysis, with field blanks consisting of identical bottles filled with Optima water. Individual samples were collected at each site for each date. Samples for additional water quality analyses (TOC, TN/TP, TSS, Cl^-) performed at the NRRI Central Analytical Lab were collected in 4-liter cubitainers were filled at each site (see Table A3.3). *E. coli* sampling was also performed during this initial grab sampling period but was not continued beyond May 2023 due to logistical constraints associated with transporting *E. coli* samples to NRRI for analysis within 24 hours of collection during unpredictable flow conditions. Grab sampling results are provided in Table A 3. 4.

3.2.2.3. Passive sampler deployment

Deployment of passive samplers was also initiated in April 2023 and continued through October 2023. Devices were deployed in triplicate at the main inlet and outlet sites noted in Figure 3.1 for periods ranging from 3 days to 4 weeks at a time over 7 deployment periods (individual deployment periods shown in Table A3.6), with the length of deployment depending on precipitation trends and the resulting duration of flow within the channel system (the system would intermittently run dry during extended dry periods). Field blanks, consisting clean sampler devices which were exposed to air during the deployment process (approximately 2 minutes) were conducted at each deployment. During two sampling periods, devices were additionally deployed at the west inlet site in green to identify any potential differences in organic contaminant concentrations between the two inlets. Temperature loggers (Onset HOBO MX2201 Pendant Temperature Data Loggers) were attached to samplers to track the water temperature throughout each deployment period, as recommended by the manufacturer if temperature fluctuations of greater than 2 °C are expected. Upon collection samplers were immediately rinsed with Optima LC-MS grade water and stored in air-tight containers for transportation back to the lab. Devices were stored frozen until analysis. Further information on passive sampler deployments can be found in Table A3.6.

3.2.3. Analytical methods

3.2.3.1. Solid phase extraction of grab samples.

Grab samples for analysis of CECs were processed by solid phase extraction (SPE). Grab samples were initially spiked with a methanol carrier solution containing isotope-labelled extraction surrogates (Atrazine-d5, Diuron-d6, Imidacloprid-d4, Pendimethalin-d5, Simazine-d5) and then filtered using a vacuum filtration setup with 37 mm glass fiber filters. Automated SPE was performed using a Promochrom SPE-400 Automated SPE apparatus loaded with HLB oasis (6cc, 200mg) SPE cartridges. This method was adapted from manufacturer-recommended protocols for HLB oasis SPE cartridges.[71] The SPE method consisted of the following steps: (i) pre-condition with methanol (5 mL) followed by water (5mL), (ii) load 100 mL of sample, (iii) rinse containers with 15 mL water, with the rinsate passed through the cartridge (repeated 2x), and (iv) rinse containers with 80:20 water/methanol mixture and pass through cartridge, followed by purging the lines with nitrogen, then elute with 10 mL of methanol and collect extracts into 12 mL glass vials. Extracts were evaporated to dryness and reconstituted to 1 mL in an 80:20 LC-MS grade

methanol and water (Fischer Chemical) mix containing internal standard at 0.5 µg/L and stored refrigerated until analysis by liquid chromatography quadrupole time of flight mass spectrometry (LC-QTOF-MS).

3.2.3.2. Extraction of passive samplers.

Passive samplers were processed according to manufacturer-recommended protocols[72]. Briefly, the devices were rinsed with Optima water, and then the binding-gel layer was removed and placed in an amber vial containing 5 mL of methanol containing isotope-labeled surrogates. Following ultra-sonication for 30 minutes (at room temperature) the initial extract was decanted into a separate glass vial and the extraction process was repeated with an additional 5 mL of methanol, resulting in a pooled extract of 10 mL. Extracts were then evaporated and reconstituted as described for the SPE extracts, filtered using 0.22 µm glass fiber syringe filters, and then internal standard was added before storing in the refrigerator prior to analysis.

3.2.3.3. LC-QTOF-MS Analysis

LC-QTOF-MS analysis was carried out using an AB Sciex X500R QTOF in combination with a Sciex ExionLC AD liquid chromatography system. The system was equipped with a 50 µL sample loop (25 µL injection volume), a reverse phase chromatography column (Luna C18, 5µm, 100 x 3 mm; Phenomenex) and a column oven (40 ˚C). Chromatography was performed at a flow rate of 0.4 mL/min using Optima grade water and Optima methanol, both containing 2mM formic acid, as the aqueous and organic mobile phases. The gradient method was as follows: ramp from 5% organic to 60% organic from 0.5 to 5 minutes, ramp from 60% organic to 90% organic from 5 to 10 minutes, hold at 90% organic until 15 minutes, then drop to 10% organic to equilibrate for the final 3 minutes (total run time of 18 minutes). Mass spectrometry analysis was performed in positive electrospray ionization mode with a spray voltage at 5500 V, ion source gasses at 55 psi, and curtain gas at 35 psi. A multiple-reaction-monitoring high resolution (MRM^{HR}) acquisition method was used, monitoring two transitions per analyte (one quantitative, one qualitative). The TOF mass scan ranged from 100 - 1000 *m/z*. Additional details regarding the MS method, including the ionization parameters, designated internal standards, and monitored ions for each analyte are provided in Table A3.1. Quantification was based on a 9-point calibration curves with analyte concentrations ranging from 0.025-53.08 µg/L (Table A3.1) with an R^2 value of 0.99 as the linearity criterion, an accuracy criterion of ±30%, and a signal to noise (S/N) threshold of 10. Surrogate recovery was low in passive sampler extracts, samples which showed recoveries outside of the determined interquartile range for the given surrogate were excluded. Data are reported for cases where analytes were measured at concentrations above the limit of quantification (LOQ), defined as the lowest calibration level that met the acceptance criteria.

3.2.4. Data analysis

3.2.4.1. Calculation of time-weighted concentrations

The concentrations measured in the sampler extracts were converted to time-weighted average concentration over the deployment duration according to Equation 3.1, adapted from manufacturer recommendations[72,73]:

$$C_{DGT} = \frac{M\Delta g}{D_T A_p t} \quad \text{Eq. 3.1}$$

Where C_{DGT} (ng/mL) is the time-weighted concentration of analyte at the collection site, M (ng) is the mass of analyte accumulated in the binding layer, Δg (0.094 cm) is the total thickness of the materials in the diffusion layer, D_T ($cm^2 s^{-1}$) is the diffusion coefficient of the analyte in the diffusion layer at average water temperature, A_p (3.14 cm^2) is the area of exposed filter membrane, and t (s) is the deployment time. M is calculated according to Equation 3.2:

$$M = \frac{c_e V_{re}}{f_e} \quad \text{Eq. 3.2}$$

Where c_e is the analyte concentration measured in the extract, V_{re} is the extract volume, and f_e is the elution efficiency (the efficiency at which a compound can be extracted from the binding phase, determined previously).[74] D_T is calculated by correcting diffusion coefficients previously determined at 25 °C (D, Table A3.2) for the average water temperature during deployment (T, °C) according to Equation 3.3:

$$\log D_T = \frac{1.37023(T-25)+0.00836(T-25)^2}{109+T} + \log\frac{D_{25}(237+T)}{298} \quad \text{Eq. 3.3}$$

3.2.4.2. Calculation of contaminant load to Agate Bay

The estimated volume of runoff, V_R, discharged to Agate Bay from the test site was calculated according to Equation 3.4:

$$V_R = D_p A_c R \quad \text{Eq. 3.4}$$

where D_p is the depth of precipitation over a selected period (31-inch annual average). A_c is the catchment area (95.3 acres), and R is the runoff coefficient based on the amount of impervious surface of the catchment area (value ranges from 0.83 to 0.90 for the catchment area of this system). The load of each contaminant (M_{in}) discharged to Agate Bay was then estimated according to the time-weighted concentrations determined from the passive samplers (C_{DGT}) according to Equation 3.5:

$$M_{in} = V_R C_{DGT} \quad \text{Eq. 3.5}$$

3.3. RESULTS AND DISCUSSION

3.3.1. CEC concentrations in grab samples from spring runoff

Results for analyte concentrations determined for individual grab samples collected during spring snowmelt (i.e., instantaneous concentrations) at the primary inlet (A) and outlet (B) sites are shown in Figure 3.2. Five consecutive weeks of sampling are depicted. The variation of concentrations is inconsistent between analytes and is generally more consistent with the inlet site – besides values for Methyl Benzotriazole. Methyl benzotriazole and Atrazine were detected at the highest concentrations, with average influent concentrations of 64.48 and 7.16 ng/L, and outlet concentrations of 1.80 and 7.21 ng/L respectively. Diuron and 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU), a main degradation product of Diuron, were also detected in every sample, ranging from 0.28 to 5.02 ng/L. This indicates some degradation of Diuron is occurring in runoff, but before reaching the existing drainage system as levels are comparable for both compounds. Imidacloprid was found intermittently in outlet samples but was not detected in any inlet grabs samples, which may suggest an alternative source of Imidacloprid to the drainage system. Other compounds, including Thiabendazole, Simazine, and Clothianidin were found at low levels intermittently. Methyl benzotriazole was present in field blanks at low concentrations (< 2 ng/L).

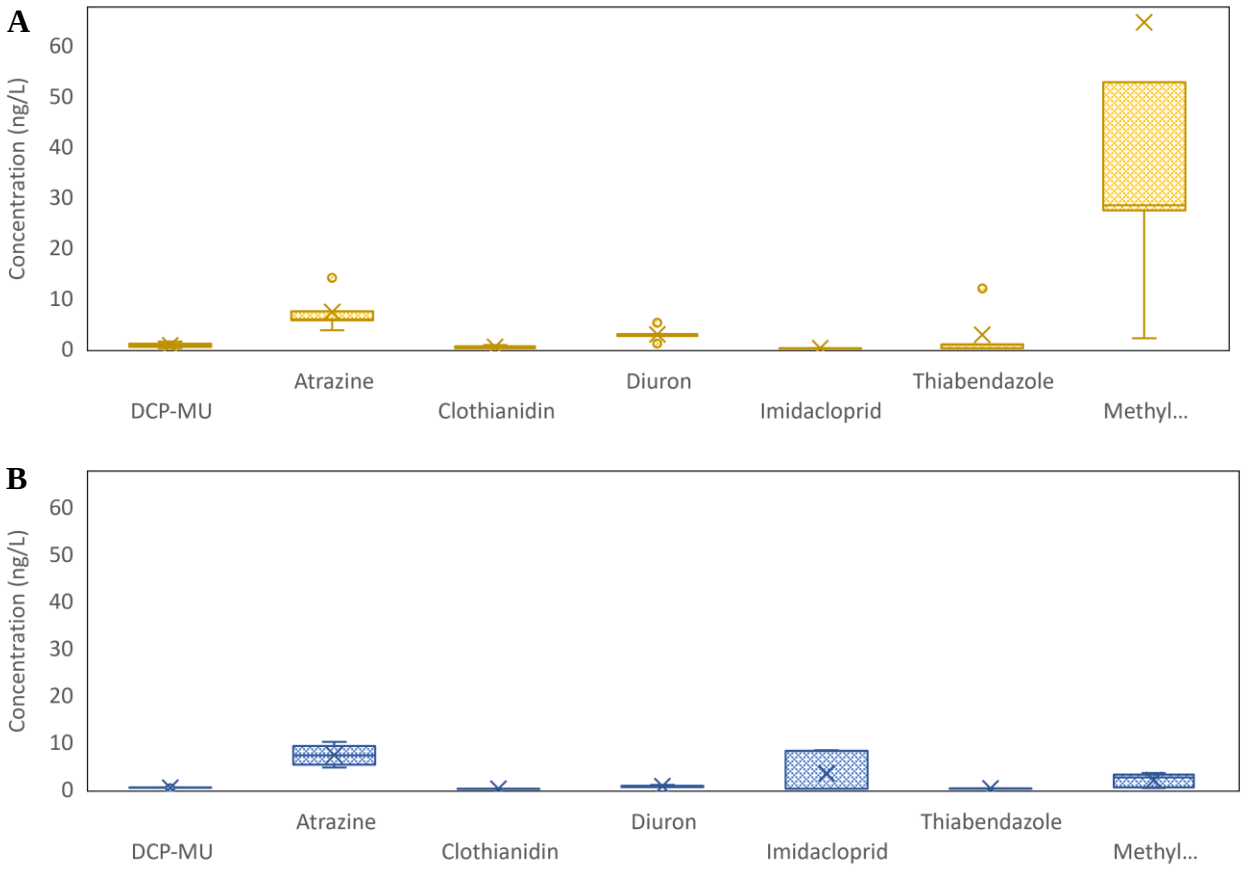

Figure 3.2. Box and whisker plots showing the distribution of individual concentrations determined in runoff from spring snowmelt (n=5) at inlet (A) and outlet (B) sites over four weeks. Inclusive means were used to determine interquartile range

3.3.2. Time-weighted CEC concentrations

Results for time-weighted contaminant concentrations over sampler deployment periods are compiled in the box-and-whisker plots in Figure 3.3, with results for the four-week period of snowmelt in Figure 3.3A and results over a complete field season in Figure 3.3B. Date-specific concentration data for all analytes are shown in the Appendix. Data collected during deployments in which only one of the sampling sites (inlet/outlet) had samplers deployed is also located here. Additionally, compounds which cannot be quantified with passive samplers due to a lack diffusion coefficients but were detected in extracts are listed in this table (Methyl benzotriazole, DCPMU). For consistency, data from four deployment periods was included in Figure 3.3B, where data was successfully collected for both sampling sites.

Figure 3.3A shows the contaminant concentration results from passive samplers during the initial sampling period when grab sampling was also being conducted. In results from passive samplers, Atrazine was found to have the highest concentration with a 4.43 ng/L average inlet concentration and 6.07 ng/L average outlet concentration. It was detected throughout this entire period in both grab samples and passive samplers, as was Diuron (1.33 ng/L and 3.43 ng/L inlet and outlet averages). Imidacloprid was detected intermittently in the outlet but was not detected in the inlet samples. Clothianidin and Thiabendazole were also detected intermittently at low concentrations (0.3 to 0.5 ng/L). In general, the time-weighted (Figure 3.3A) and instantaneous concentrations (Figure 3.2) were similar on average, but there was a wider range in the instantaneous concentrations for analytes detected at higher concentrations (e.g., atrazine and thiabendazole, which were both detected at above 10 ng/L in individual grab samples from the main inlet location). These results overall reflect a known trade-off between grab sampling versus passive sampling, as contaminant concentrations will inherently fluctuate throughout the deployment period, even during periods of relatively consistent flow (e.g., spring snowmelt).

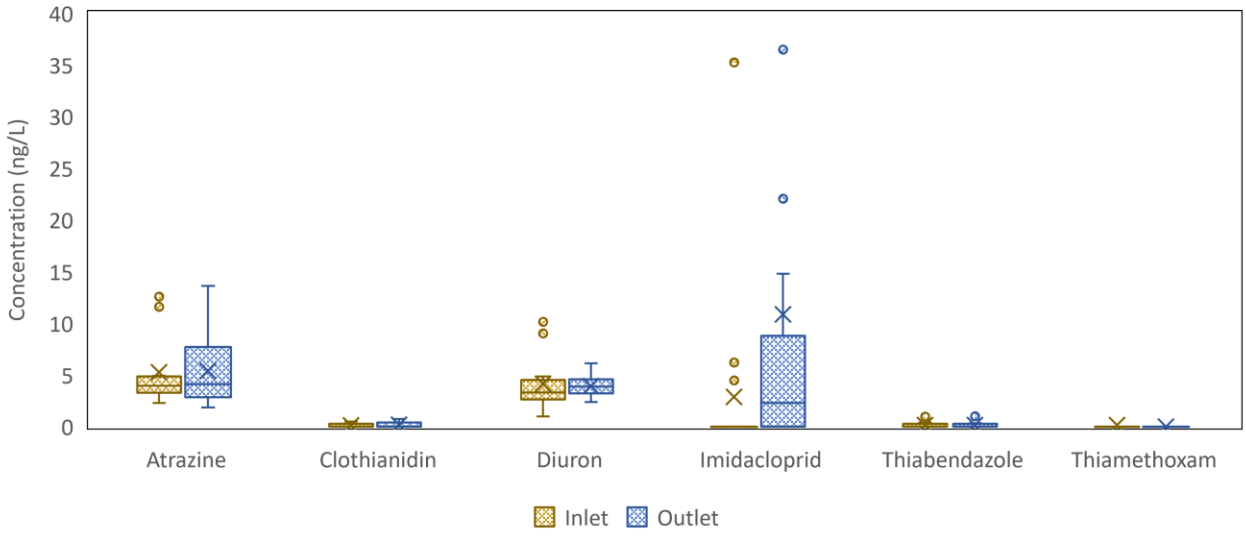

Figure 3.3. The distribution of analyte concentrations determined via passive samplers in runoff from at inlet (yellow) and outlet (blue) sites over one field season (April – October 2023). Concentrations are shown for detected contaminants with known diffusion coefficients and which pass all quality control measures. Inclusive means were used to determine interquartile range.

Figure 3.3 shows the range of calculated concentrations from passive samplers over a field season. The relative concentration ranges agree those from the shorter period indicated in Figure 3.2, with Atrazine, Diuron, and Clothianidin at similar levels. Imidacloprid again is present at much higher concentrations in

the outlet site than the inlet, suggesting there is another source of this contaminant to the system. The west inlet site which was periodically monitored showed much higher levels of Imidacloprid (0-23 ng/L), suggesting residential areas which supply runoff to the main inlet are not a significant contributor to the Imidacloprid in this runoff. The primary difference between data from spring and the whole year appears to be an increase in maximum concentrations when including data from the complete field season. A potential explanation for this is record snow levels which occurred over the 2022-2023 winter (140.1 inches in Duluth, MN) which may have diluted the typical concentrations of contaminants during snowmelt. Additionally, summer data was collected during / after rain events in a drought setting (>30 days between rainfalls). The combination of these conditions could cause compounding differences associated with seasonal changes. Finally, concentrations for all contaminants over the field season at the inlet and outlet sites were similar, which suggests contaminants easily flushed through the current drainage trench. This agrees with previous reports of high mobility of these contaminants (polar dissolved CECs) in conventional stormwater BMPs.[13] It additionally supports the implementation of treatment systems that are capable of the removal of these contaminants.

Results from both grab sample and passive sampler collection are lower than average concentrations reported by Masoner et. al. (2019) but are generally near the minimum concentrations reported[18]. For example, the median concentrations of Atrazine, Diuron, and Imidacloprid were in the range of 20 – 50 ng/L in that study, while we observed average concentrations between 4-10 ng/L, five times lower. This trend was consistent in all analytes monitored in both studies. The differences observed are not surprising due to the difference in sampling sites, as Two Harbors, MN is a relatively small urban space with much developed open space including lawns and grasses. By comparison, many urban sites monitored by Masoner et. al (2019) had high levels of medium to high intensity developed land cover. One would therefore expect higher levels of anthropogenic contaminants in more highly developed urban spaces.

3.3.3. Estimation of CEC load discharged to Agate Bay

The runoff volume to Agate Bay for a typical 1-inch rain event is 8.16×10^6 L. This was calculated using Equation 5, with values supplied in Table A4.1. The average concentration of combined pesticides found in runoff to Agate Bay based on data from the 2023 field season is 18.85 ng/L. Therefore, the load of total contaminants (M_{in}) into Agate Bay is 154 mg for a 1-inch rain event (Eq 6). In 2023, 35.5 inches of precipitation were recorded (NOAA NOWData) in Two Harbors, MN. This is higher than the average annual precipitation of approximately 30 inches. Using the average combined pesticide concentration for the 2023 field season, the cumulative contaminant load to Agate Bay in 2023 would be 5.46 g. The annual

load to Agate Bay for individual contaminants as well: Atrazine (0.52 – 2.57 g, 1.54 g average), Diuron (0.55 – 1.79 g, 1.17 g average), and Imidacloprid (0 – 6.65 g, 1.99 g average) were pesticides found at the highest concentrations and therefore would contribute the highest contaminant loads. Atrazine and Diuron were found in every measurement, Imidacloprid was detected inconsistently resulting in much higher uncertainty in load predictions. Annual contaminant loads can be normalized to the catchment area for runoff into Agate Bay, which has an area of 95.3 acres. The average values for contaminant mass per acre which contributes to the annual load can be seen in Figure 3.4. Average values for individual pesticides range from 12.3 to 20.9 ng/acre/yr within the total catchment area. The load of cumulative pesticides monitored in this study was found to be 57.3 ng/acre/yr (± 21.8 ng/acre/yr).

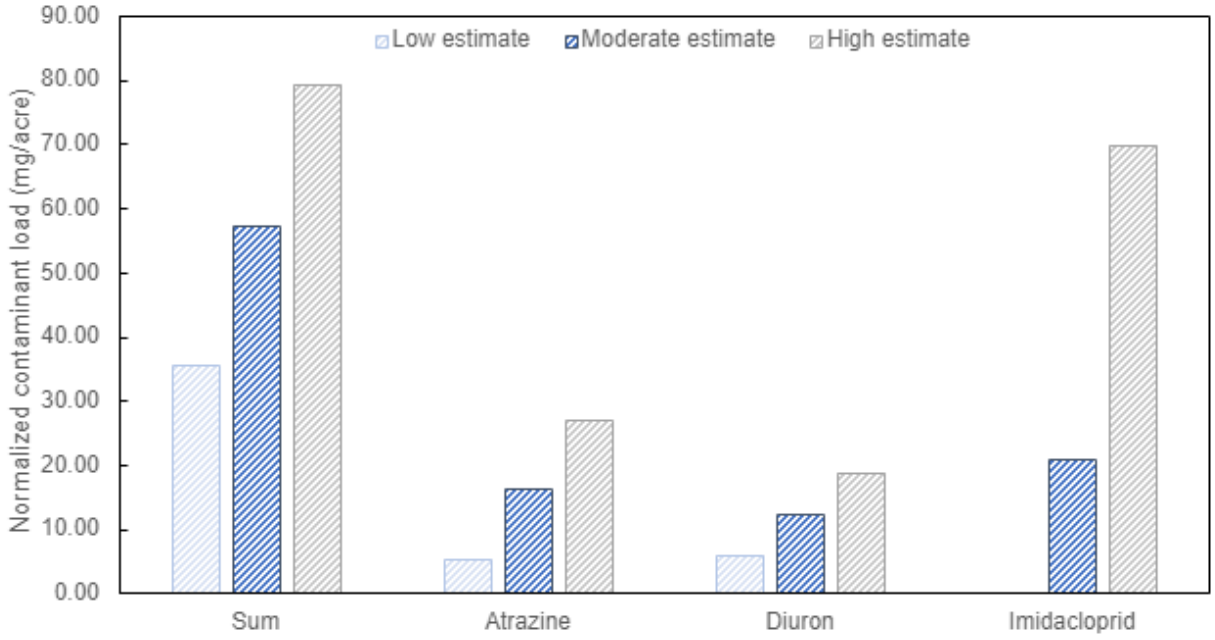

Figure 3.4. The estimated annual contaminant load into Agate Bay, normalized to catchment area. Low, moderate, and high estimates are shown for cumulative contaminants (based on 2023 field season data) and three individual contaminants based on uncertainty of calculated contaminant levels through the field season. Estimations are based on the average and standard deviation of concentration values.

3.3.4. Estimation of CEC retention lifetime in biochar-amended biofilters

In laboratory column tests (Chapter 2), breakthrough of one spiked organic contaminant (Atrazine) was observed in sand columns amended with WFB biochar. At the end of 34 individual tests, atrazine was detected at 3.1% of the average concentration in spiked influent water. While breakthrough is typically considered to occur at 5% detection in effluent, we can nonetheless compare results of these tests to previous

studies. The calculated atrazine removed at 3% breakthrough was 7.08 µg/g sorbent. This is representative of greater removal longevity than that observed previously with a similar pinewood biochar material produced with high temperature pyrolysis[59]. In this study, conducted by Ulrich et. al (2017), they observed faster breakthrough with triazines compared to other CECs including benzotriazoles and diuron, which confirms our results of observing only breakthrough of atrazine at the end of this study[31]. Experimental conditions such as the dosing frequency and contact time with influent water differ between the studies which could contribute to differences in results. An aspect which potentially improved the removal capacity in this study is the intermittent dosing, allowing for potential degradation of bound contaminants which could extend the removal capacity of a biochar amended system. Biochar amendment has been shown to improve the growth of microbial communities that can facilitate biodegradation of bound contaminants and increase the lifetime of sorbent material regarding removal of CECs[30].

In the column tests, 104 EBV prior to atrazine breakthrough for the WFB biochar is equivalent to approximately 2.5 years of equivalent runoff volume based on the average annual precipitation for the area of Duluth, MN. However, the CEC concentrations in the column tests were significantly higher than those measured in runoff to Agate Bay (10 µg/L vs 5 ng/L in Chapter 3). Using the ratio of experimental concentrations to actual runoff concentrations observed at Two Harbors, our results suggest that breakthrough would not be observed for nearly 5000 years of intermittent dosing. These results can be used to predict the performance of a full-scale system; assuming the system is built with a similar 5% ratio of filtration media to catchment area, we would expect to observe similar performance. However, this is not always the case.

To make predictions with varied system and environmental conditions, we calculated the predicted breakthrough time of Atrazine (years of equivalent runoff) for three different biochar amendments at variable filtration basin size (0.2%, 1%, and 5% of catchment area) and comparing the average Two Harbors concentration (5 ng/L) to the median concentration in Masoner (approximately 35 ng/L). The biochars are denoted by the approximately Atrazine load at breakthrough: Biochar A (2 ng/g) and Biochar B (100 ng/g) from Ulrich et. al (2017) and WFB (7 ng/g,).[35,59] Biochar A was produced via pine wood pyrolysis and B was produced via pine wood gasification and therefore should have similar characteristics to the WFB biochar. These variable conditions will affect the performance of a theoretical treatment system, as smaller systems will likely result in shorter retention times as there is a higher comparative contaminant load than to a larger system. Additionally, small systems are more likely to overflow due to high volumes of water passing through the system, allowing water to bypass the filter. The level of contamination within a

catchment area will also affect the retention time of CECs, as more highly developed urban spaces (as monitored by Masoner et al (2019)) will have a comparatively higher load of contaminants which a system will be subject to.

The typical maximum design lifetime of these systems is 30 years.[75] This lifetime is inherently limited by the accumulation of non-degradable contaminants such as metals and represents a timeline at which the materials must be replaced. All combinations of conditions besides two (WFB and Biochar A, with a system size at 0.2% of the catchment area and with a higher contaminant load, represented by concentrations from Masoner et al (2019)) resulted in an estimated breakthrough time greater than this average lifetime of a treatment system. This means that any of those configurations would likely retain dissolved CECs such as pesticides throughout the lifetime of the system. The breakthrough prediction for the remaining configurations (9 years using Biochar A, 30 years using WFB) may not exceed the lifetime of the system, but they far exceed the maximum biodegradation half-life of Atrazine (approximately 1.1 years).[76,77] Additionally, biochar amendment has been previously shown to increase the rate of biodegradation of organic compounds through the facilitation of microbial community growth.[35] This makes breakthrough of CECs such as Atrazine even less likely to occur with similar environmental conditions as those observed in laboratory column filtration tests.

A treatment train utilizing a biochar-amended filtration step is to be implemented to treat runoff into Agate Bay, using ABC biochar. Although we did not observe breakthrough of any CECs in column tests, we can assume the scaled-up system would have better performance than WFB amended filtration. The system will implement biochar amended filtration basins at approximately 0.2% of the system catchment area. Based on predictions from biochar B at 0.2% catchment area and Two Harbors concentration, we would not expect to observe a breakthrough of CECs represented by Atrazine in the lifetime of this system. It should be noted, however, that this would not necessarily be the case for CECs which are more mobile or more persistent than pesticides (e.g., per- and polyfluoroalkyl substances). More research is needed to determine how filtration with biochar amended media would perform in retaining these alternative contaminants.

3.4. CONCLUSIONS

The results of this work demonstrate the utility of passive sampling techniques for the monitoring of urban stormwater runoff. Passive sampling results indicate that the concentrations of CECs at Agate Bay are low relative to other, more highly urbanized areas. As performance monitoring using grab sampling often requires collecting numerous samples to characterize concentrations throughout the hydrograph, passive sampling offers a simpler approach to assess system performance over time, though this simplification

comes with some assumptions and challenges. Our results support the use of these alternative sampling techniques2, as the concentration ranges determined by passive samplers agreed with discreet concentrations detected in grab samples. The occurrence of contaminant detection in both sample types reflects the pervasive nature of CECs in stormwater, as several analytes were detected in every sample. This agrees with previous studies which have demonstrated that CECs are ubiquitous in urban runoff. Little to no removal of CECs was observed in the existing drainage system at Two Harbors. This was expected, as previous literature has reported poor removal of dissolved CECs in conventional stormwater systems. Estimated discharge loads of pesticides provide insight into the potential benefits of installation of a treatment system regarding pollution prevention. The results of this study suggest that ubiquitous dissolved CECs, such as pesticides, can be successfully removed from runoff with treatment system installation, and that these systems should be considered as a tool to prevent pollution of environmental and receiving waters.

CHAPTER 4

Conclusions

Results from chapter 2 (Simultaneous removal of *E. coli* and contaminants of emerging concern (CECs) from stormwater in biochar-amended sand filters) indicate several key findings on the removal performance of biochar for DOC, CECs, and *E. coli*. Notably, columns with biochar amendments showed improved retention of DOC and CECs, with characteristics including high hydrophobicity and high surface area significantly improving this retention. The differences between the biochars highlight the importance of material properties, such as pore volume and carbon content, in determining their effectiveness. While no significant improvements in *E. coli* retention were observed with the addition of biochar, improvements in hydraulic performance were observed. The presence of both DOC and biofilm growth have been associated with reduced *E. coli* removal. Biochar facilitates greater biofilm growth than sand alone, potentially leading to a decrease in the removal capacity of *E. coli* due to decreases in available surface area. This highlights the complexities involved with removal processes of biological contaminants. Overall, results of this study indicate that while biochar amendments may not significantly improve *E. coli* retention, they can enhance the retention of specific CECs and improve hydraulic performance under high bacterial loads which may be relevant to field conditions. Moreover, simultaneous evaluation of the removal of multiple contaminant types can provide insights into how field systems will function more broadly.

Main findings from chapter 3 (Assessment of the CEC retention performance of stormwater management systems using passive samplers) include that passive sampling is an effective method for investigating the contaminant profile of CECs in stormwater. As previously observed, CECs including pesticides proved ubiquitous in stormwater runoff, with multiple analytes detected in all samples. Additionally, results confirmed that existing drainage systems are ineffective in reducing the load of CECs in runoff or inhibiting their release into receiving waters. The estimation of pesticide discharge loads provides insights into benefits of treatment system installation. Consulting results from column tests in Chapter 2, the contaminant load reduction of a biochar amended system was estimated. Based on the contaminant load detected in runoff and the removal capacity observed in laboratory tests, we predict near complete reduction of contaminant load with the installation of biochar amended systems through system lifetimes due to the relative retention time as compared to degradation half-lives of CECs in this study.

This study will inform future use biochar amendment in treatment systems, specifically biochar amended filtration. We have demonstrated various strengths of biochar, including but not limited to increased contaminant retention (CECs) and improved hydraulic performance. Additionally, we have shown that even

the use of biochar with poor contaminant retention (comparatively) can significantly decrease the contaminant load of CECs to environmentally relevant receiving waters. As an economically and environmentally viable sorbent material, biochar's use in pollution prevention measures is promising. More research is needed to probe the efficacy of biochar amended filtration for further combinations of contaminants under environmentally relevant conditions to further understand its potential. Our results suggest that biochar amended systems can and should be considered as a tool to limit environmental pollution through reduction of contaminant loads. The use of these systems not only increases public and environmental safety through pollution prevention, but also has potential to capture future CECs and therefore limit the needs for future remediation measures, which can be costly and often too late to prevent all consequences of contaminant release. As stormwater is a known source of current CECs to the environment, the treatment of this contaminant source will help in preventing future crises associated with their spread.

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CHAPTER 2 - Appendix

Table A2.1. Mass spectrometry method for analytes, isotope-labelled extraction surrogates*, and isotope-labelled internal standard**

Analyte	Parent ion mass (Da)	Quantitative fragment ion mass (Da)	Qualitative fragment ion mass (Da)	Collision Energy (V)	Declustering Potential (V)	Low reporting limit (µg/L)	High reporting limit (µg/L)
1-(3,4-dichlorophenyl)-3-methylurea	219.01	127.0182	174.0541	30	60	0.025	25.11
acetamiprid	223.07	126.0110	90.0340	20	50	0.025	25.15
Atrazine	216.10	104.0013	174.0406	34	40	0.025	25.00
Clothianidin	250.02	131.9670	169.0420	18	40	0.127	25.43
Diuron	233.02	72.0449	159.9734	22	45	0.025	24.98
Imidacloprid	256.06	126.0103	175.0813	30	40	0.126	25.20
Methyl-1H-benzotriazole	134.07	79.0543	77.0386	20	60	0.106	53.08
Nitenpyram	271.10	225.1000	126.1000	10	45	0.025	25.20
Pendimethalin	282.14	212.0539	194.0525	10	45	0.125	25.00
Simazine	202.09	132.0330	104.0009	22	40	0.025	25.00
Thiabendazole	202.04	175.0295	131.0584	28	60	0.025	25.00
Thiacloprid	253.03	126.0107	99.9928	22	70	0.025	24.85
Thiamethoxam	292.03	211.0663	181.0385	10	45	0.025	25.35
Atrazine-d5*	221.12	179.0866	-	22	45	-	-
Diuron-d6*	239.06	78.0815	-	20	45	-	-
Imidacloprid-[illegible]	260.09	179.1240	-	22	45	-	-
Isoproturon-[illegible]	213.19	78.0800	-	22	55	-	-
Pendimethalin-[illegible]	287.18	213.0740	-	10	45	-	-
Simazine-d5*	207.12	129.1178	-	22	40	-	-

Table A2.2. Technical specifications of NAKED Char biochar from American Biochar Company (ABC).

General Information	
Composition	100% Wood BioChar
Feedstock	Southern Yellow Pine Species
Production Method	Pyrolysis, temp. range of 550-900° C
Pore Surface Area	557 acres/cf (225 hectares/cf)
Carbon Content	77.6% (USDA 95%)
Particle Size	.5mm – 2.0mm
Bulk Density	15.1 lbs/cu ft
Moisture Content	25 – 46%

TYPICAL ANALYSIS	
pH	7.5-9.0
Hydrogen:Carbon Ratio (H:C)	1:3 (.37)
Nitrogen (N)	.40% tdm
Phosphorous (P)	837 mg/kg
Potassium (K)	1215 mg/kg
Iron (Fe)	1014 mg/kg
Manganese (Mn)	457 mg/kg
Sodium (Na)	nd
Magnesium (Mg)	.36% dwt
Calcium (Ca)	2.22% dwt
Zinc (Zn)	14.1 mg/kg

Table A2.3. Elemental analysis, cumulative pore volumes, and pH results for both commercial biochars (ABC, WFB).

Parameter	Method	ABC	WFB
Moisture total (wt%)	ISO 18134-1	13.52	2.12
Ash (wt%)	ISO 18122	9.42	74.90
Volatile matter (wt%)	ISO 18123	5.86	8.29
Fixed Carbon (wt%)	By difference	71.19	14.63
Sulfur (wt%)	ISO 16994	0.01	0.06
Carbon (C) (wt%)	ISO 16948	73.54	21.27
Hydrogen (H) (wt%)	ISO 16948	0.26	0.21
Nitrogen (N) (wt%)	ISO 16948	0.22	0.11
O (O) (wt%)	ISO 16948	3.01	1.33
H/C	NA	0.0421	0.118
O/C	NA	0.0307	0.0472
(O+N)/C	NA	0.0333	0.0516
pH in DI water (biochar/water)	NA	9.67	7.17
Cumulative pore vol. (cm^3/g)	NA	0.443	0.0721
Micropore vol. (cm^3/g)	NA	0.214	0.0405
Mesopore vol. (cm^3/g)	NA	0.222	0.0316

Table A2.4. Concrete Sand Particle Size Distribution. Particle size distribution information was provided by Plaisted Companies.

Sieve Size	Passing (%)
9.5 mm (3/8 inch)	100
4.75 mm (No. 4)	100
2.36 mm (No. 8)	96
1.18 mm (No. 16)	83
600 μm (No. 30)	60
300 μm (No. 50)	23
150 μm (No. 100)	4
75 μm (No. 200)	0.7

Table A2.5. Mineral Composition of concrete sand determined by X-ray diffraction (includes illite, mica, kaolinite, and chlorite). Data was provided by Plaisted Companies.

Mineral	**Weight percent**
Quartz	65.7
K-feldspar	9.8
Plagioclase	17.6
Calcite	1.3
Dolomite	1.1
Pyrite	0.2
Total Clay Minerals	4.3

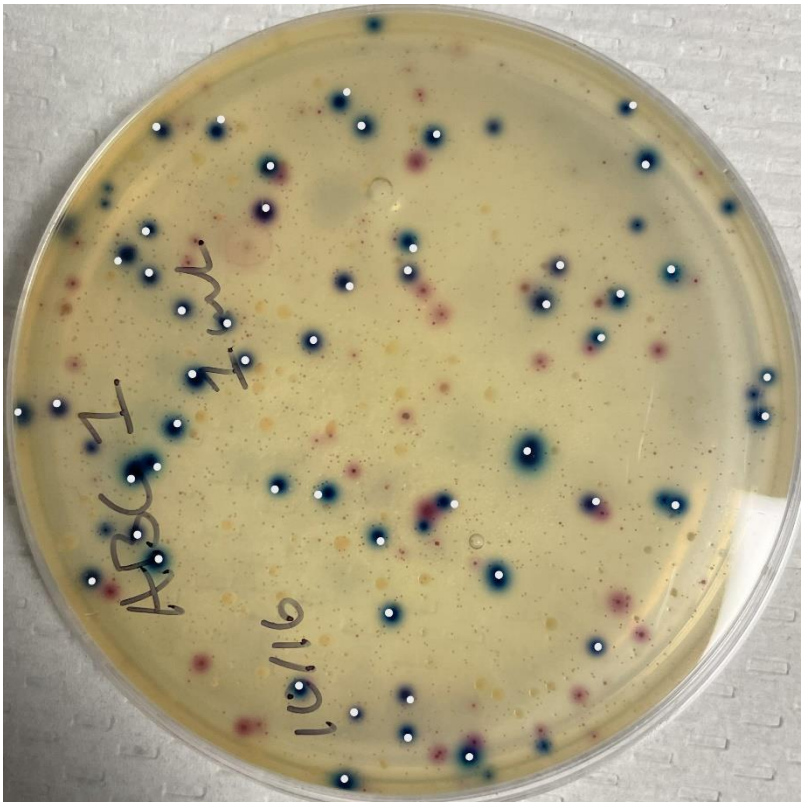

Figure A2.1. Image of incubated plate on which colonies are counted for quantification of *E. coli*. Colonies of *E. coli* grow a dark blue to purple color, while colonies of other coliforms will grow a pink color. *E. coli* colonies larger than the head of a pin are counted as full colonies for quantification purposes.

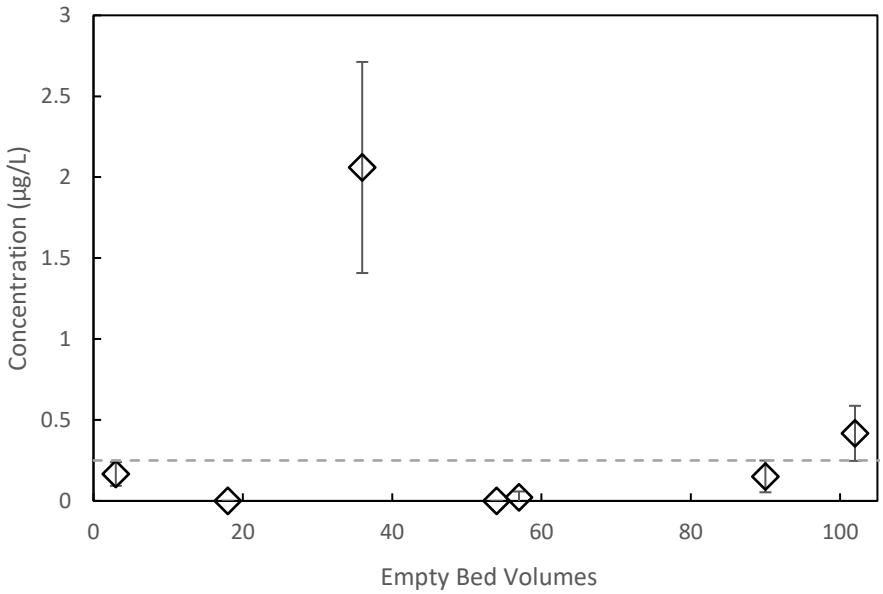

Figure A2.2. Concentrations of DCP-MU in effluent of sand columns. The horizontal line represents the lower limit of the linear calibration curve used to quantify analyte concentrations.

Table A2.6. Analyte specific concentration values at each empty bed volume measurement in column filtration tests. Bolded data include values lower than the method calibration range. Data in italics are suspected to be due to contamination of column effluent.

EBV	Influent average (µg/L)	Influent standard deviation	Sand average (µg/L)	Sand standard deviation	WFB average (µg/L)	WFB standard deviation	ABC average (µg/L)	ABC standard deviation
Atrazine								
3	9.5	0.7	12.6	0.5	0.0	0.0	0.0	0.0
18	9.9	0.7	12.8	0.4	0.0	0.0	0.0	0.0
36	9.8	0.2	10.0	0.3	0.0	0.0	0.0	0.0
54	18.2	0.6	15.8	0.5	0.0	0.0	0.0	0.0
57	9.4	0.5	8.9	0.1	**0.1**	**0.0**	0.0	0.0
72	11.0	1.7	10.3	1.0	**0.1**	**0.1**	0.0	0.0
90	8.2	0.7	6.6	0.6	**0.4**	**0.0**	0.0	0.0
102	9.3	0.1	8.9	0.4	**0.2**	**0.0**	0.0	0.0
Diuron								
3	13.7	1.3	17.8	2.6	0.0	0.0	0.0	0.0
18	15.6	0.1	15.2	1.7	0.0	0.0	0.0	0.0
36	15.2	1.2	15.4	1.3	0.0	0.0	0.0	0.0
54	27.6	2.2	19.5	1.4	0.0	0.0	0.0	0.0
57	12.7	0.9	11.1	1.3	0.0	0.0	0.0	0.0
72	14.4	2.8	14.1	2.2	0.0	0.0	0.0	0.0
90	13.0	3.2	7.6	1.0	0.0	0.0	0.0	0.0
102	15.5	5.3	12.2	0.9	0.0	0.0	0.0	0.0
Imidacloprid								
3	8.8	1.0	14.3	0.8	0.0	0.0	0.0	0.0
18	9.7	0.4	20.1	12.0	0.0	0.0	0.0	0.0
36	10.1	1.6	10.1	0.9	0.0	0.0	0.0	0.0
54	14.3	2.8	13.3	0.5	0.0	0.0	0.0	0.0
57	12.6	0.6	11.7	0.8	0.0	0.0	0.0	0.0
72	15.0	2.2	13.6	0.4	0.0	0.0	0.0	0.0
90	11.7	2.0	9.1	0.7	0.0	0.0	0.0	0.0
102	15.1	2.0	12.2	3.1	0.0	0.0	0.0	0.0
Methyl benzotriazole								
3	4.4	0.5	5.3	1.2	0.0	0.0	0.0	0.0
18	5.8	0.3	2.4	1.1	0.0	0.0	0.0	0.0
36	5.0	0.4	7.4	0.4	0.0	0.0	0.0	0.0
54	14.7	1.9	12.1	1.7	0.0	0.0	0.0	0.0
57	15.2	0.3	12.6	0.5	0.0	*0.1*	0.0	0.0
72	17.1	3.9	11.0	1.6	0.0	0.0	0.0	0.0
90	13.7	2.3	3.3	0.9	0.0	0.0	0.0	0.0
102	15.0	0.2	4.3	1.9	0.0	0.0	0.0	0.0

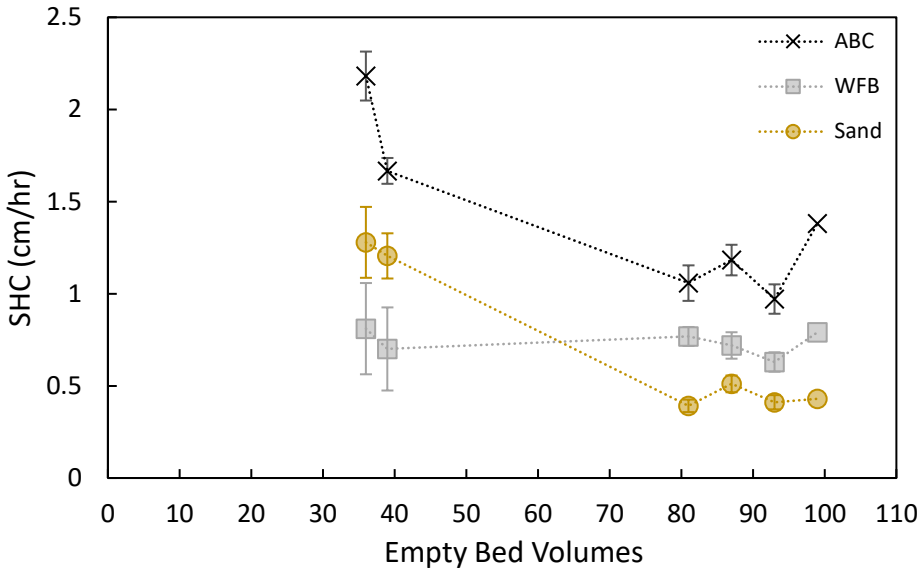

Figure A2.3. Average saturated hydraulic conductivity of each column type over 34 tests with the average saturated hydraulic conductivity on the y axis and empty bed volumes of influent passing through the columns on the x axis. Error bars represent one standard deviation.

CHAPTER 3 - Appendix

Table A3.1. Mass spectrometry method for analytes, isotope-labelled extraction surrogates*, and isotope-labelled internal standard**

Analyte	Parent ion mass (Da)	Quantitative fragment ion mass (Da)	Qualitative fragment ion mass (Da)	Collision Energy (V)	Declustering Potential (V)	Low reporting limit (µg/L)	High reporting limit (µg/L)
1-(3,4-dichlorophenyl)-3-methylurea	219.01	127.0182	174.0541	30	60	0.025	25.11
acetamiprid	223.07	126.0110	90.0340	20	50	0.025	25.15
Atrazine	216.10	104.0013	174.0406	34	40	0.025	25.00
Clothianidin	250.02	131.9670	169.0420	18	40	0.127	25.43
Diuron	233.02	72.0449	159.9734	22	45	0.025	24.98
Imidacloprid	256.06	126.0103	175.0813	30	40	0.126	25.20
Methyl-1H-benzotriazole	134.07	79.0543	77.0386	20	60	0.106	53.08
Nitenpyram	271.10	225.1000	126.1000	10	45	0.025	25.20
Pendimethalin	282.14	212.0539	194.0525	10	45	0.125	25.00
Simazine	202.09	132.0330	104.0009	22	40	0.025	25.00
Thiabendazole	202.04	175.0295	131.0584	28	60	0.025	25.00
Thiacloprid	253.03	126.0107	99.9928	22	70	0.025	24.85
Thiamethoxam	292.03	211.0663	181.0385	10	45	0.025	25.35
Atrazine-d5*	221.12	179.0866	-	22	45	-	-
Diuron-d6*	239.06	78.0815	-	20	45	-	-
Imidacloprid-d4*	260.09	179.1240	-	22	45	-	-
Isoproturon-d6**	213.19	78.0800	-	22	55	-	-
Pendimethalin-[illegible]	287.18	213.0740	-	10	45	-	-
Simazine-d5*	207.12	129.1178	-	22	40	-	-

Table A3.2. Method analytes with known diffusion coefficients for use with LSND-AG o-DGT devices.

Analyte	Diffusion Coefficient, D (10^{-6} cm^2/s) at 25˚C
Atrazine	5.67
Clothianidin	4.22
Diuron	5.24
Imidacloprid	4.59
Thiabendazole	6.17
Thiamethoxam	4.17
Isoproturon**	4.93

Table A3.3. Water quality analyses conducted on runoff samples from spring snowmelt by the CAL at the NRRI

Analysis	Collection vessel	Number of replicates	method
Total organic carbon (TOC)	4-liter cubitainer	2	SM 5310 B 2014
Total Nitrogen, Phosphorus (TN/TP)	4-liter cubitainer	2	SM 4500 PJ / SM 4500 PE-11 / SM 4500 NO3 F-16
Total suspended solids (TSS)	4-liter cubitainer	2	SM 2540 D 2015
Chloride (Cl-)	4-liter cubitainer	2	SM 4500 Cl-E2011

Table A3.4. Results of water quality analysis conducted on spring snowmelt samples

Inlet

Date Sampled	**TP (ppb)**	**TN (ppb)**	**Cl- (mg/L)**	**TSS (mg/L)**	**TOC (ppm)**	**Total Coliforms (mpn/100 ml)**	**E coli (mpn/100 mL)**
4/11/2023	288.5	1618.5	46.22	43.1	5.89	1178.10	101.2
4/18/2023	160.5	1128	88.28	40.9	6.435	5241.50	419.5
4/25/2023	41	903	55.825	7.2	4.99	104.90	22.5
5/2/2023	54	702.5	69.255	9.4	4.66	161.40	1.3
5/9/2023	40.5	496.5	71.515	7.1	4.58	213.00	1.5

Outlet

Date Sampled	**TP (ppb)**	**TN (ppb)**	**Cl- (mg/L)**	**TSS (mg/L)**	**TOC (ppm)**	**Total Coliforms (mpn/100 ml)**	**E coli (mpn/100 mL)**
4/11/2023	188	913	29.475	51.6	5.37	1787.20	107.9
4/18/2023	192.5	891	67.765	65.4	5.545	2228.60	67
4/25/2023	253	912	38.705	100.9	4.885	277.00	25.5
5/2/2023	34.5	371.5	48.135	6.4	5.135	126.70	3.4
5/9/2023	28	304.5	52.415	5.9	5.335	170.05	3.6

Table A3.5. Complete data for grab samples, depicting the calculated concentration values of analytes in grab samples in ng/L for each site at various collection dates. Data which is italicized indicates values that fall below the linear range of the calibration curve but were still detected.

	DCPMU	Acetamiprid	Atrazine	Clothianidin	Diuron	Imidacloprid	Methyl benzotriazole
Inlet							
4/11/2023	0	0	3.50	0	2.39	0	212.37
4/18/2023	0.47	0	13.88	*0.36*	5.02	0	52.58
4/25/2023	*0.24*	0	5.49	0	0.88	0	1.95
5/2/2023	1.29	0	5.66	0	2.39	0	28.25
5/9/2023	0.84	0	7.26	*0.63*	2.76	0	27.24
Outlet							
4/11/2023	1.63	0	5.07	0	2.78	8.16	29.53
4/18/2023	2.12	0	9.94	0	7.74	0	33.15
4/25/2023	0.71	0	7.08	0	3.09	0	*1.05*
5/2/2023	2.15	0	4.49	0	4.63	8.00	23.72
5/9/2023	2.09	0	9.02	0	6.14	0	2.31

	Nitenpyram	Pendimethalin	Simazine	Thiabendazole	Thiacloprid	Thiamethoxam
Inlet						
4/11/2023	0	0	0	0	0	0
4/18/2023	0	0	0	11.82	0	0
4/25/2023	0	0	0	0	0	0
5/2/2023	0	0	0.31	0.73	0	0
5/9/2023	0	0	0.43	0.69	0	0
Outlet						
4/11/2023	0	0	0	0	0	0
4/18/2023	0	0	0	0	0	0
4/25/2023	0	0	0	0.25	0	0
5/2/2023	0	0	0	1.05	0	0
5/9/2023	0	0	0	0	0	0

Table A3.6. Passive sampler deployment data. Precipitation depths do not account for runoff volumes coming from spring snowmelt. Temperature data for period 7 was calculated from the average lake temperature in Agate Bay as logging devices were not deployed.

Deployment period	Deployment Dates	Average Inlet temperature (°C)	Average Outlet temperature (°C)	Total precipitation depth (in)
1	4/11/23 – 4/18/23	7.5	4.2	0.62
2	4/18/23 – 5/9/23	5.0	5.3	2.25
3	5/9/23 – 5/30/23	9.6	9.1	0.20
4	6/23/23 – 6/29/23	15.8	14.8	3.18
5	7/26/23 – 7/28/23	18.8	17.1	0.17
~~6~~	8/10/23 – 8/17/23	17.3	-	0.86
7	9/29/23 – 10/27/23	15.5*	15.5*	1.51

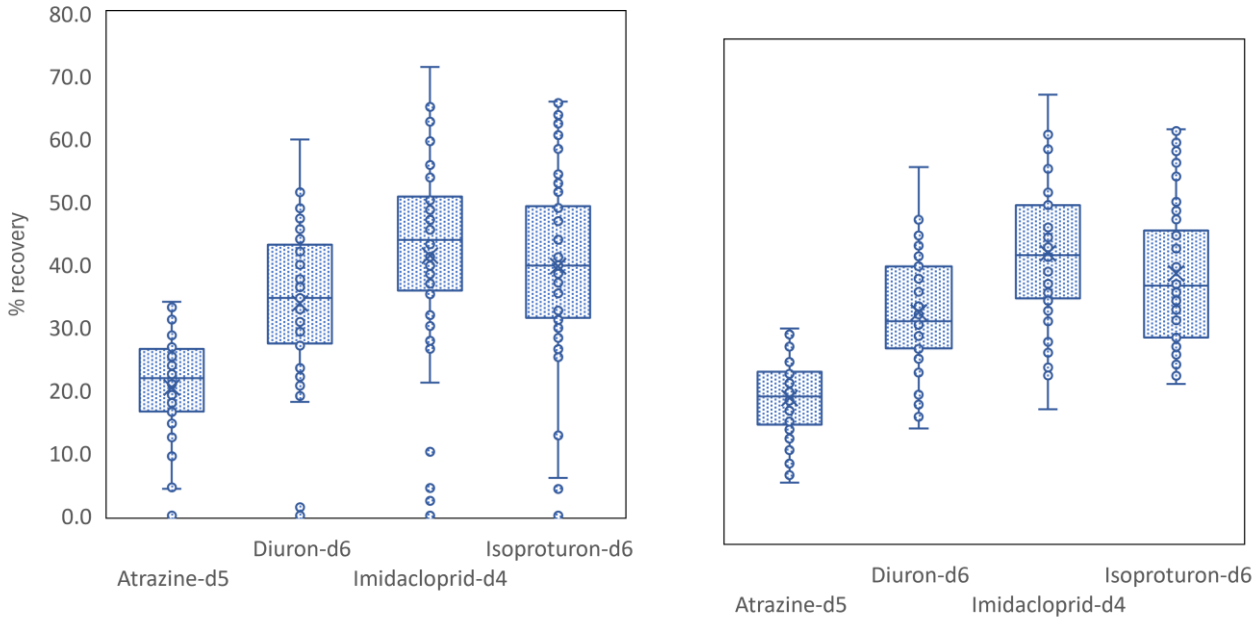

Figure A3.1. Distribution of recovery for isotope-labelled surrogates and internal standard for passive sampler data. A) before the exclusion of data points considered outliers and B) after the exclusion of outlier points. Outliers were not used for data analysis. Interquartile ranges were determined using an inclusive mean.

Table A3.7. Values used to calculate runoff volume into agate bay, for a 1-inch rainfall event (top) and for an average year of rainfall (bottom 31inches).

Zone #	A_C (acres)	A_C (m^2)	D_P (m)	R	V_R (m^3)	V_R (L)	Cumulative V_R (L)
2	41.8	169159	0.0254	0.83	3.6E+03	3.6E+06	8.2E+06
3	4.7	19020	0.0254	0.9	4.3E+02	4.3E+05	
4	13.3	53823	0.0254	0.83	1.1E+03	1.1E+06	
5	35.5	143663	0.0254	0.83	3.0E+03	3.0E+06	

Zone #	A_C (acres)	A_C (m^2)	D_P (m)	R	V_R (m^3)	V_R (L)	Cumulative V_R (L)
2	41.8	169159	0.787	0.83	1.1E+05	1.1E+08	2.5E+08
3	4.7	19020	0.787	0.9	1.3E+04	1.3E+07	
4	13.3	53823	0.787	0.83	3.5E+04	3.5E+07	
5	35.5	143663	0.787	0.83	9.4E+04	9.4E+07	