Biofiltration-based “green technology” as a techno-ecological nature-based solution for drinking water treatment and climate change resilience

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

Emma Blackburn was the sole author of Chapters 1 and 4 which were written under the co-supervision of Dr. Monica Emelko and Dr. Sarah Dickson-Anderson and not intended for publication. This thesis consists in part of two manuscripts prepared as refereed papers for publication that have either been accepted in or submitted to a peer-reviewed journal. Exceptions to sole authorship of material are as follows:

Research presented in Chapter 2:

This research was conducted at the University of Waterloo by Emma Blackburn under the co-supervision of Dr. Monica Emelko and Dr. Sarah Dickson-Anderson (McMaster University). Emma Blackburn developed the framework for assessment of green technologies in water supply & treatment collaboratively with Dr. Monica Emelko and Dr. Sarah Dickson-Anderson, with input from Dr. Michael Stone. Emma Blackburn drafted the manuscript and each author provided intellectual property on manuscript drafts.

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Abstract

While drinking water treatment process design is based on current and anticipated source water quality, changing climate makes it increasingly difficult to anticipate drinking water source quality and treatability. Although most climate change-exacerbated landscape disturbances can pose threats to drinking water security, wildfires can be especially concerning for drinking water treatment because they can episodically increase turbidity and alter dissolved organic matter (DOM)—key drivers of the design and optimization of drinking water treatment processes—in receiving source waters. Shifts in DOM concentration and character can be especially difficult to remove with conventional treatment technologies, as they can exert significant oxidant demand and increase disinfection by-product formation if not removed prior to disinfection. These impacts can challenge treatment plants beyond their design or operational capacity, ultimately resulting in increased infrastructure and operating costs, service disruptions or even service outages. Thus, they emphasize the need for new approaches to mitigate these threats. "Green" technologies or nature-based solutions (NBS) are increasingly proposed as climate change adaptation strategies for mitigating such threats. Perspectives on the factors that comprise green technology in the water industry are varied, however, and while biological filtration processes continue to emerge as some of the most promising green technologies in the drinking water industry, their reliability in responding to deteriorated or more variable source water quality after disturbances such as wildfires has not been investigated. Accordingly, the major goals of this research were to (1) develop a framework for characterizing green technologies relevant to the water industry and (2) evaluate biological filtration treatment technology resilience in buffering altered source water DOM after wildfire.

The green technology framework developed herein differentiates "greenness" by examining key attributes that may cause environmental impacts across technology life cycle through the lens of the environmental setting in which it is applied. It demonstrates that green technology used in the water industry can be described by four main attributes: natural-resource basis, energy consumption, waste production, and footprint. These attributes are closely linked and must be considered relative to the biophysical and human environments in which they are applied and the other technologies to which they are being compared. Biological filtration approaches emerged as key examples of green technologies in the drinking water treatment sector; however, case studies also underscored that operational control is often reduced as technology greenness increases.

Biological filtration treatment resilience in buffering elevated source water DOM after wildfire was also investigated. Elevated/altered post-fire DOM can be especially challenging to treat because it can be smaller and more aromatic after disturbance. More aromatic DOM is especially difficult to coagulate and may lead to greater formation of regulated disinfection by-products. Bench-scale biofiltration experiments were conducted using wildfire ash-amended source water (in duplicate at three levels: low, medium, and high ash content). Turbidity and DOM (measured as dissolved organic carbon [DOC]) were typically well-removed during periods of stable operation. These results indicated that the wildfire ash and associated DOM that it released to the water matrix did not reduce the DOM biodegradation capacity of the biofilters. DOM fractionation revealed that this was because low molecular weight neutrals (which are known to be readily biodegradable) and biopolymers fractions of DOM were reduced; however, humics were largely recalcitrant. Thus, this work provided a proof-of-concept demonstration that biological filtration may serve as a techno-ecological NBS for climate change adaptation. Notably, operational resilience may be compromised if the balance between readily removed and recalcitrant fractions of DOM change, as was observed when baseline source water quality fluctuated for brief periods during the investigation, underscoring the need to balance trade-offs of operational control and resilience to other types of source water quality change.

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List of Abbreviations

cm	centimeters
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DBP	Disinfection By-Product
DWTP	Drinking Water Treatment Plant
EBCT	Empty Bed Contact Time
EPA	Environmental Protection Agency
g	Grams
h	Hours
HLR	Hydraulic Loading Rate
HVAC	Heating, Ventilation, and Air Conditioning
L	Litres
LCA	Life Cycle Analysis
LC-OCD	Liquid Chromatography-Organic Carbon Detection
LMW	Low Molecular Weight
m	Metres
mm	Millimetres
mg	Milligrams
NBS	Nature-Based Solutions
nm	Nanometers
NTU	Nephelometric Turbidity Units
RBF	Riverbank Filtration
RPM	Revolutions per Minute
RRM	Rural, Remote, or Marginalized
SSF	Slow Sand Filtration
SUVA	Specific Ultraviolet Absorbance
SWP	Source Water Protection
TOC	Total Organic Carbon
UV	Ultraviolet
UVA_{254}	Ultraviolet Absorbance at Wavelength of 254 nm
WEOM	Water Extractable Organic Matter

Chapter 1 Introduction

1.1 Background

The paramount objective of drinking water treatment is the protection of public health. Treatment must therefore be fit for this purpose. While drinking water treatment process design is based on current and anticipated source water quality (Crittenden, 2012; Emelko et al., 2011), changing climate makes it increasingly difficult to anticipate changes in source water quality. Climate change shifts precipitation patterns, increases the rate and severity of snow and ice melt, and exacerbates natural disturbances such as fires, floods, hurricanes, and pests, ultimately resulting in increased runoff and more variable source water quality (IPCC, 2014). Although most climate change-exacerbated landscape disturbances can pose threats to drinking water security because of potential impacts to either water availability or quality (Milly et al., 2008), wildfires can be especially concerning for drinking water treatment because they can lead to a cascade of events that result in severely deteriorated and more variable source water quality (Emelko et al., 2011; Stone et al., 2011).

Wildfire threats to water supplies have been recognized in Canada and globally (Robinne et al., 2016; 2019; Mishra et al., 2021). Fire on the built landscape can lead to anthropogenic chemical contamination (e.g., benzene) of water supplies isolated in buried distribution networks (Proctor et al., 2020). After wildland fire, water temperature in impacted watersheds can increase and may impact sensitive ecosystems (Wagner et al., 2014). Vegetation is reduced or absent; as a result, more precipitation reaches the land surface (Williams et al., 2019). This results in increased erosion and runoff of solids (Silins et al., 2009; Murphy et al., 2012; Alessio et al., 2021), even at very large basin scales in systems with already deteriorated water quality (Emmerton et al., 2020). Accordingly, solid-associated metals (Abraham et al., 2017), nutrients including natural organic matter ([NOM]; Emelko et al., 2011; Silins et al., 2014; Gustine et al., 2019), and other contaminants (Crouch et al., 2006; Mansilha et al., 2019) also can be elevated in wildfire-impacted receiving waters. On landscapes rich in fine sediment, delivery to and storage within riverbeds can propagate over long distances and lead to longer-term releases of bioavailable phosphorus from those sediments to the water column (Stone et al., 2014; Emelko et al., 2016), promoting primary productivity (Silins et al., 2014) and the proliferation of algae that can produce toxins of human health concern and compromise the production of safe drinking water (Emelko et al., 2011). These effects fuel increases in abundance and diversity of macroinvertebrates (Martens et al., 2019) and are further exacerbated when they converge with those from anthropogenic landscape disturbances, leading to further increases in phosphorus bioavailability and potential for algae proliferation (Watt et al., 2021).

Suspended solids/turbidity and dissolved organic matter (DOM; typically described by measurement and characterization of dissolved organic carbon [DOC]) are key drivers of the design and optimization of drinking water treatment processes (Crittenden et al., 2012). Algae proliferation can reduce the efficiency of coagulation processes, clog filters, and require expensive treatment upgrades when they release cyanotoxins (Crittenden et al., 2012). Algae can further transform NOM and thus affect coagulant demands and disinfection by-product formation potential (Tsai et al., 2017). Collectively, these impacts underscore that wildfires challenge treatment plants beyond their design or operational capacity, ultimately resulting in increased infrastructure and operating costs, service disruptions, or potentially catastrophic service outages (Emelko et al., 2011; Price et al., 2017). The combination of source water quality shifts—especially those associated with DOM—and associated treatment costs that can result from wildfire have emphasized the need for water supply and treatment resilience to respectively mitigate these threats at the source and/or in treatment plants (Emelko & Shams, 2014; Blackburn et al., 2021).

Changing climate and an increased demand for water resources has resulted in increasingly unaffordable costs for drinking water utilities. In the United States, the price of distributed water has increased 41% from 2010 to 2017, with water rates expected to continue to rise such that many households will find this unaffordable on a full cost recovery basis (Mack & Wrase, 2017). Small drinking water systems, typically serving rural or remote communities, are expected to experience disproportionately higher costs since they do not fully benefit from economies of scale (Boisvert & Schmit, 1997), as treatment costs do not scale linearly with size (Randtke, 2012). Small systems also struggle with issues such as operation and maintenance, limited resources and funding, deteriorated infrastructure, and limited technical capacity (Kot et al., 2011; 2015). Thus, because of these inequalities between small and large systems—largely due to the structures that govern them—small systems experience a disproportionate number of drinking water advisories (NCCEH, 2021) and therefore disproportionately higher health risks associated with the provision of safe drinking water (Delpla et al., 2015; MacFarlane & Harris 2018), making them marginalized.

Low-cost and resilient solutions are needed to address these challenges. For instance, nature-based solutions (NBS) have been defined as "actions to protect, sustainably manage and restore natural or modified ecosystems…while simultaneously providing human well-being and biodiversity benefits"

(Cohen-Shacham et al. 2016). In the drinking water industry, the emergence of NBS is evident in industry-wide prioritization of source water protection (SWP) (AWWA, 2020; Emelko & Shams, 2014) and increasing promotion and public buy-in of "green" approaches (The Water Institute, 2017). While various "green" approaches exist in the broader water industry that are believed to offer environmentally conscientious and/or economically viable solutions, "green technologies" are mainly focused on engineering priorities such as energy efficiency, low waste, and having a natural resource basis. Arguably, one of the most readily recognized "green technologies" in the water industry is biological treatment because it harnesses natural microbial processes, does not generally require additional energy inputs, and does not typically produce significant waste relative to other treatment processes designed to achieve the same objectives (Fowler & Smets 2017). However, green technologies—including biological treatment processes—have not had much uptake in drinking water treatment as compared to other segments of the water sector due to the industry's aversion to real or perceived risks to public health that may be attributed to innovative technologies that are unproven, or require operational shifts for control, relative to conventional technologies (Brown et al., 2015; Blackburn et al., 2021).

Current opinions in biotechnology widely suggest that biofiltration technologies are "on the precipice of a revolution" because the increasing availability of modern biotechnological tools will drive biologically-mediated treatment process evaluation and customization (Kirisits et al., 2019). This will facilitate advancement of green technologies (including NBS) in the drinking water sector; however, the need to reliably protect public health in a changing climate will also necessitate the need for operational resilience. Investigations that intersect climate change-exacerbated landscape disturbance impacts on source water quality and green drinking water treatment technologies such as biological filtration are presently scant, however. As discussed above, they are especially needed to support drinking water security for small systems serving rural, remote, and marginalized communities that comprise the majority of drinking water treatment systems in the United States (EPA, n.d.) and Canada (NCCEH, 2021).

1.2 Research Objectives

The goal of this thesis was to advance the development of drinking water treatment and climate change adaptation strategies for the water industry broadly, but also with consideration of the challenges faced by small drinking water systems specifically. Thus, the specific focus of this research was biofiltration-based "green" technologies as techno-ecological NBS that have the potential to offer treatment resilience without high operational demand. The specific research objectives that were developed to address this goal were:

(1) Develop a framework to characterize green technologies relevant to the water industry,

(2) Develop an experimental method to pre-treat wildfire ash-impacted source water without chemical addition, and

(3) Evaluate "green" biological filtration treatment technology resilience in buffering elevated source water DOM after wildfire.

1.3 Research Approach

Techno-ecological NBS, such as biofiltration-based "green technologies," have the potential to offer drinking water treatment and climate change adaptaton solutions that can be especially benefial for small drinking water systems. Despite widespread use of the term "green" across the broader water sector and more specifically within the drinking water industry, however, there is no consistently applied definition or framework for what constitutes green technology or which aspects of greenness are valued. This makes it difficult for stakeholders to communicate values and implement these green approaches. The first research objective was to present a framework to evaluate green technology in the water industry, with specific focus and application to the drinking water treatment industry. An extensive literature review of green technologies was undertaken to distill recurring themes across several fields. Four factors contributing to technology greenness were identified: energy consumption, waste production, natural resource-based, and physical footprint. These factors were specifically applied to the drinking water treatment industry in hypothetical and actual case studies to demonstrate the importance of site-specific considerations in assessing technology greenness.

Biofiltration-based processes are increasingly emerging as some of the most promising green technologies or NBS for drinking water treatment. Their reliability in responding to deteriorated or more variable source water quality that may be experienced after climate change-exacerbated landscape disturbances has not yet been investigated, however. Given that wildfires can lead to some of the most challenging conditions associated with deterioration or fluctuation in source water quality, the biological filtration treatment technology resilience in buffering elevated source water DOM resulting from wildfire ash delivery to receiving waters was investigated. Bench-scale filtration experiments were conducted using wildfire ash-amended source water (in duplicate at three levels:

low, medium, and high ash content) from an agriculturally- and municipally-impacted watershed. Given that altered NOM concentrations and character that are episodically elevated comprise some of the most significant treatment challenges commonly observed after wildland fire, NOM removal was investigated here. To conduct these investigations, a roughing filtration method to pre-treat wildfire-impacted source water without chemical addition so that it could be subsequently treated by biological filtration processes was also developed.

1.4 Thesis Organization

This thesis is organized as a compendium of two papers, Chapters 2 and 3, formatted for submission to refereed journals. Some introductory material is thus repeated in Chapters 2 and 3.

Chapter 2 presents a framework to evaluate green technologies in the water supply and treatment sector, discussion of green biofiltration technologies, and specific application of the framework to both actual and hypothetical case studies. Chapter 3 presents background on wildfire impacts to water quality and biological filtration processes, experimental design of bench-scale biofilters, and discussion of experimental results. Chapter 3 concludes with discussion of resiliency of biological filtration in buffering elevated DOC in wildfire ash-impacted water. Finally, Chapter 4 presents key findings related to synthesis of the green technology framework and the results of the biological filtration experiments, in addition to implications for the drinking water treatment industry.

Chapter 2

Advancing on the Promises of Techno-ecological Nature-based Solutions: A Framework for Green Technology in Water Supply & Treatment

2.1 Summary

Nature-based solutions (NBS) are increasingly proposed for effectively and adaptively addressing societal challenges such as water security and natural disasters. However, NBS that are exclusively reliant on natural processes are not fit-for-purpose for the provision of safe drinking water—some range of built technology is required. There is a wide spectrum of techno-ecological NBS—"green technologies"—that are fit-for-purpose in the treatment and distribution of safe drinking water. A framework was developed to enable an accurate and transparent description of the "green" attributes of technology—including green infrastructure—in the water industry. The framework differentiates technology "greenness" by relatively examining key attributes that may cause environmental impacts across the technology's life cycle through the lens of the environmental setting in which it is applied. In the water industry, green technology can be described by four main attributes: natural-resource basis, energy consumption, waste production, and footprint. These attributes are closely linked and must be considered relative to the biophysical and human environments in which they are applied and the other technologies to which they are being compared. The use of the framework can facilitate techno-ecological decision-making that strives to address diverse stakeholder priorities—including the influence of sociocultural factors on the green technology preferences of individuals, groups, or communities.

2.2 Introduction

Nature-based solutions (NBS) are increasingly proposed for effectively and adaptively addressing societal challenges such as water security and natural disasters – they have been defined as "actions to protect, sustainably manage and restore natural or modified ecosystems … while simultaneously providing human well-being and biodiversity benefits" (Cohen-Shacham et al., 2016). NBS are growing in popularity globally; however, they are not a panacea to water security, climate change, or any other of society's grand challenges. The practical implementation of NBS can be challenging because of differences in what should be prioritized and the relative importance associated with those priorities. These challenges were recently highlighted by O'Sullivan et al. (2020) who cautioned that

NBS have sometimes been framed too idealistically, leading to undervaluation of biodiversity and unrealistic expectations of the capacity of natural processes to provide the “solutions” that are needed. Recognition that the value and limits of NBS must be understood, so that they are robust and resilient is also growing (Seddon et al., 2021). While rigid differentiation between nature- and technology-based approaches for managing some challenges has been suggested (Mustafa et al., 2019), efforts to describe the synergies between technological and ecological systems are growing (Bakshi et al., 2015) and discussions of NBS that are enhanced by or integrated with technology—"techno-ecological NBS”—are emerging.

In the drinking water industry, the emergence of techno-ecological NBS is evident in industry-wide prioritization of source water protection (SWP) (AWWA, 2020) and increasing the promotion of “green” approaches, such as the use of forest management-based strategies and other NBS for source water quality management and climate change adaptation (Ernst et al., 2004; Emelko et al., 2011; McLain et al., 2012; Robinne et al., 2019; Oral et al., 2020). Water managers are increasingly asked to integrate “green” approaches into water supply and treatment practices. Both “green infrastructure” and “green technology” terminologies are used in the water industry. They are also frequently integrated to yield techno-ecological concepts of natural resource-based treatment processes that reflect the technological aspects of natural landscape processes, such as low-cost cascade aeration systems that enhance the air–water transfer of atmospheric gases (e.g., oxygen and nitrogen) and volatile organic compounds (Figure 2-1).

The use of “green infrastructure” in the water industry is consistent with its common broader use, which reflects the practical application, preservation, and enhancement of natural capital using a management approach that “emphasizes the importance of environmental systems and networks for the direct provision of ecosystem services to human populations” (Chenoweth et al., 2018). Here, the term “natural capital” is also consistent with its broader use and refers to environmental assets that provide people with free goods and services that are often referred to as ecosystem services (Chenoweth et al., 2018). Thus, in the water industry, “green infrastructure” not only reflects natural capital, but also often encompasses natural resource-based management approaches to achieve engineering (i.e., treatment) targets—this inter-relationship between green infrastructure and natural capital directly aligns with the recognition that there is a spectrum of degrees of “naturalness” that ranges from environments with minimal human influence to those that have been built (Chenoweth et al., 2018).

In contrast, the use of “green technology” in the water industry tends to reflect approaches that may be linked to, but not necessarily reliant upon natural capital. Notably, while the “green” descriptor is frequently used interchangeably with “sustainable” (Ngo et al., 2016), sustainability analysis typically considers broad impacts on the environment, the economy, and society (Purvis et al., 2019). While life cycle analysis is regularly included in technology evaluation and selection in the water industry, all of the pillars of sustainability are not typically reflected in decision-making—even when they are discussed, trade-offs are of course required because of economic limitations.

The implementation of “green technologies” in the water industry tends to focus on the treatment processes themselves (Wu et al., 2015; Neoh et al., 2016) and reflects various engineering priorities such as energy efficiency and low waste production, which can be described as “green”. These technologies are generally understood to complement and sometimes replace more traditional “grey technologies”, which are human-engineered without reliance on the practical application, or prioritization of the preservation or enhancement, of natural capital. This is because “green technologies” are believed to offer environmentally conscientious, energy-efficient, and/or increasingly economically viable solutions to address challenges such as the need to concurrently protect human health, adapt to climate change-exacerbated threats to water security, and reduce the environmental impacts of water treatment and distribution (Gill et al., 2007; Emelko et al., 2011; Ngo et al., 2016).

Despite the widespread use of the term “green” across the broader water sector and within the drinking water industry specifically, there is no consistently applied definition or framework for what constitutes “green technology” or which aspects of “greenness” are valued. A framework for describing the “green” attributes of the broad range of technologies—including natural capital—relevant to the water industry is needed, as these attributes dictate how technologies are prioritized relative to others, and whether they are considered “green” at all. Such a framework will also enable stakeholders to better communicate the technical and engineering aspects of technology approaches that best align with community and individual sociocultural values, beliefs, and attitudes. In addition to the challenges associated with the lack of a framework to describe the “green” attributes of technologies or infrastructure options for meeting broader water industry objectives, it is important to recognize that “green technology” has not had much uptake in the drinking water industry, as compared to other segments of the water sector.

Figure 2-1 Low-cost cascade aeration system that enhances the air-water transfer of atmospheric gases (e.g., oxygen, nitrogen) and volatile organic compounds. The term "green technology" commonly invokes images of such technologies; however, green technologies span a broad spectrum of treatment typologies.

The drinking water industry is necessarily conservative and somewhat averse to real or perceived risks to public health that may be attributed to innovative technologies that are unproven, or require operational shifts for control, relative to conventional technologies. These challenges have been underscored for decades in the lack of widespread uptake of biological treatment processes because of concerns regarding health risks that might be attributable to microbially mediated treatment, difficulties in operation, and unlikely regulatory approvals (Brown et al., 2015). While such concerns are misplaced (Brown et al., 2015), well-known events such as the 1993 Milwaukee cryptosporidiosis outbreak, in which more than 50 people died and more than 400,000 people became ill (EPA, 1998), serve as stark reminders of the importance of public health protection through the provision of safe drinking water as the industry's paramount objective. Thus, any shifts in the fundamental way in which drinking water is treated and distributed must be approached with clarity in purpose and confidence that public health protection is not compromised.

Consistent with that recognition, it has been recently emphasized that the good science that is needed for meaningful advancement of sustainability goals such as the development of NBS requires clearly defined terminology rather than reliance on vague metaphors (Vos et al., 2007; Aronson, 2011). Fortunately, the promises of green technology can be advanced in the water supply and treatment sector with sound initial foundations in scientific and engineering principles. These begin with the foremost recognition that all drinking water treatment technologies must be effective for the protection of public health—these targets must be achievable in regular practice, not only at idealized conditions. Thus, any green technologies that would be considered for use within the drinking water industry must be "fit-for-purpose" for the protection of public health, meaning that they meet or exceed the drinking water treatment performance expectations and regulatory criteria that they are intended to address. For this reason, NBS that are exclusively reliant on natural processes are not fit-for-purpose for the provision of safe drinking water—some range of built technology is required. For example, recent work has demonstrated that viruses can be present in high-quality groundwater supplies and require substantial treatment even in situations where it has been historically believed that no treatment is required (Borchardt et al., 2012; Emelko et al., 2019). Additional built technologies would be required to indicate water safety and ensure its safe distribution. In contrast, it will be demonstrated herein that there is a wide spectrum of techno-ecological NBS— "green technologies"—that are fit-for-purpose in the treatment and distribution of safe drinking water.

Using the imperative fit-for-purpose criterion as a starting point, a framework is developed herein to enable an accurate and transparent description of the "green" attributes of technology—including green infrastructure—used in the water industry. It differentiates technology "greenness" by relatively examining key attributes that may cause environmental impacts across the technology's life cycle through the lens of the environmental setting in which it is applied. It is proposed that the framework developed herein can contribute to the development of more comprehensive techno-ecological NBS by providing clear and accurate description of the "green" attributes of technology options for the water industry, as well as a framework for their relative comparison, thereby facilitating techno-ecological decision-making that strives to address diverse stakeholder priorities. While a cost-benefit analysis would be essential for the ultimate selection of a treatment technology, the associated analysis is beyond the scope of the present work, which is focused on framework development. Microbiologically mediated biofiltration technologies are presented as obvious and effective examples of underutilized green technology opportunities in the drinking water industry. They are used to demonstrate that there is a wide spectrum of techno-ecological NBS— "green technologies"—that are fit-for-purpose in the treatment and distribution of safe drinking water. Finally, two case studies are briefly presented to highlight the benefits of green technologies in drinking water treatment, the use and limitations of the developed framework, and the influence of sociocultural factors on green technology preferences of individuals, groups, or communities.

2.3 Body

2.3.1 A framework for evaluating technology greenness

The most widely recognized "green" technologies in the broader water industry are likely found in stormwater management and include low-impact development practices such as vegetated rooftops, roadside plantings, absorbent gardens, and other measures. They are designed to mimic natural hydrological processes and landscape features to reduce stormwater flows and improve stormwater quality by filtration, adsorption, or other means before discharging to surface and groundwater supplies (Gill et al., 2007). In contrast, reductions in energy consumption and waste production are common green foci of wastewater treatment (Wu et al., 2015; Neoh et al., 2016). Here, many of the "green" technologies include biological treatment processes that remove or neutralize pollutants or other target compounds, often to yield less toxic or non-toxic materials at a lower cost than technologies that are not biologically mediated (Delgadillo-Mirquez et al., 2016). Membrane bioreactors are one such example; they combine biological, secondary, and tertiary wastewater treatment in one unit, thereby reducing carbon footprint relative to more conventional processes (Smith et al., 2012; Neoh et al., 2016). Groundwater treatment at contaminated sites increasingly involves the implementation of green in situ bioremediation technologies to reduce energy costs and largely eliminate excavation and incineration costs common to ex situ 'pump and treat' approaches (Haritash & Kaushik, 2009; Wang & Chen, 2009).

While the use of the term "green technology" is less common in the drinking water industry, its broader emergence is inevitable. For example, nature-based coagulants produced from renewable resources (Teixeira et al., 2017) are regularly referred to as "green" technologies. Reductions in energy consumption and waste production are already common goals in the industry, and biological filtration processes that "work for free" are referred to as either "natural" or "green" treatment technologies—their use in drinking water treatment plants (DWTPs) is increasingly described as "by design" rather than de facto (Basu et al., 2015; Brown et al., 2015; Petrescu-Mag et al., 2016; Kirisits et al., 2019). At the regional landscape scale, sophisticated watershed management techniques focused on maintaining high-quality source water are often relied upon to avoid the construction of costly filtration plants and are being increasingly implemented for the mitigation of climate change-exacerbated landscape disturbances such as severe wildfires (Emelko et al., 2011; Cristan et al., 2016; NAS, 2018; Robinne et al., 2019). Indeed, interest in the promise of "green tech" is growing across the water industry and to the general public who increasingly value it, and contribute to promoting it, as evident from public acceptance and willingness-to-pay for green tech implementation for water resource management and treatment (Newburn & Alberini, 2016; Brent et al., 2017; The Water Institute, 2017).

As highlighted by the examples above, green technologies in the field of drinking water supply and treatment have been most frequently described as "green" based on three key attributes or factors that are broadly associated with reducing environmental impacts: (1) nature- or natural resource-based origin (Spatari et al., 2011; Keeley et al., 2013; Liu et al., 2017), (2) relatively low-energy consumption (Wu et al., 2015; Ngo et al., 2016), and (3) relatively low waste production (Neoh et al., 2016; Ngo et al., 2016). Physical footprint is further proposed as a fourth key factor that contributes to technology greenness in the water supply and treatment field. The physical footprint of watershed management activities such as forest harvesting, DWTP construction, and associated residuals management infrastructure has the potential to adversely impact human health and ecosystems through fossil fuel emissions, destruction of sensitive habitat, habitat fragmentation, and biodiversity decline, to name a few. The impacts of physical footprint are generally understood to be linked to environmental impacts because they initiate a chain reaction of environmental impacts that can be broadly characterized as human health and ecosystem damage footprints. Thus, physical infrastructure footprints must be included in any evaluation of greenness to reflect these cumulative environmental impacts. Accordingly, a framework for characterizing water industry technology greenness based on four main key technology attributes is proposed. As illustrated in Figure 2-2, they are (1) natural-resource basis, (2) energy consumption, (3) waste production, and (4) footprint. Various fit-for-purpose drinking water treatment technology examples considered for application in the same environmental setting are presented in Figure 2-2 to demonstrate how the framework developed herein might be used. A more detailed description of the technology attributes that contribute to greenness follows, and opportunities to link the framework to more comprehensive evaluations of trade-offs between technological NBS in the water sector are briefly discussed.

*Technologies are assumed to be fit-for-purpose. Whether or not technologies are green is not absolute; they are more or less green relative to one another.

Figure 2-2 Framework for the evaluation of green attributes of water supply, treatment, and distribution technologies. (Photo credits bottom row from left to right: Humboldt Bay Municipal Water District; Reprinted from Nalwanga et al. (2014), with permission from Elsevier; Mount Carmel Ltd; DVGW, Water Technology Center, Karlsruhe).

Natural resource-based technology incorporates renewable or non-depletable materials that are either sourced from the surrounding environment or utilize natural processes to achieve treatment. Several of these technologies, such as biofiltration and solar disinfection, are intrinsically passive and do not require additional chemical inputs (McGuigan et al., 2012; Basu et al., 2015), which in turn contributes to their low-energy consumption and waste production. Some natural coagulants, such as moringa seeds, have been described as “green” (Teixeira et al., 2017); however, despite being natural resource-based, coagulants that are not sourced from the surrounding environment must still be transported to treatment facilities for use. As such, proximity of the material source and site of use should be considered, and those materials whose haulage has significant environmental costs should not be considered green in this context. Beyond drinking water treatment, natural resource-based technologies also include approaches such as forested watershed management practices that are applied for managing drinking water source quality (i.e., SWP technologies) (Cristan et al., 2016; NAS, 2018).

Energy consumption is often cited as an important and highly valued aspect of technology greenness (Bolla et al., 2011; Ngo et al., 2016; Barcelos et al., 2018). Energy-efficient technologies often offer a co-benefit of reduced long-term operational costs; this is mainly attributed to their passive nature and dependence on non-energy-intensive processes (e.g., naturally occurring biological activity) to achieve treatment goals (Wu et al., 2015; Neoh et al., 2016). Processes that require high energy inputs to operate, such as ozonation and UV disinfection, are relatively less green. High energy expenditures can also result from water conveyance through pumping. Therefore, the elevation of a DWTP site is an important design consideration and can impact overall energy consumption (Randtke & Horsley, 2012). For example, the need for pumping may be reduced if plant configuration follows natural topography. Even less major design choices, such as the selection of flocculator type, can also result in energy consumption changes. Although they offer substantively more operational control, mechanical flocculators require higher energy inputs compared to hydraulic mixers and are therefore less green in this respect (Crittenden et al., 2012). These types of decisions underscore the trade-offs that must be clearly articulated and considered in the selection and design of water treatment technologies.

Waste produced during water treatment has the potential to cause adverse environmental impacts as a result of its quantity and/or toxicity; thus, it is an important contributor to technology greenness. Treatment processes that produce large amounts of waste products, such as coagulation (i.e., sludge) and membrane technologies (i.e., brine, backwash, and residuals), can be generally considered as less green. However, some chemical additions may reduce waste production, such as the addition of polymers to alum or ferric chloride coagulants (Randtke & Horsley, 2012). Membrane technologies produce wastes in the form of backwash and cleaning-in-place residuals. Cleaning-in-place can increase both waste quantity and toxicity because it involves chemicals such as hypochlorite, citric acid, and caustic soda (Randtke & Horsley, 2012). Additionally, waste in the form of emissions implies that air stripping processes may be relatively less green due to exhaust fume emissions (Randtke & Horsley, 2012).

The physical footprint of infrastructure contributes to water treatment technology greenness because it can also readily result in adverse environmental impacts. Processes that require a large footprint, such as horizontal flow basins and slow sand filters, will tend to be less green in this respect. Additional infrastructures—such as residuals management plants, chemical storage, and pumping infrastructure—also increase footprint. This highlights the interplay between green attributes; for example, high waste-producing processes typically require the construction of a residuals management plant, which increases the footprint and contributes to the reduction in greenness of the process. Additionally, chemically-assisted processes require chemical storage infrastructure on-site, which increases footprint and can also increase energy consumption through the need for heating, ventilation, and air conditioning (HVAC) systems and hydraulic lifting (Randtke & Horsley, 2012). While this discussion generally suggests that larger environmental footprints are more disruptive, infrastructure footprints cannot be considered in a vacuum as they are intrinsically tied to the environmental setting in which they are to be applied. Thus, the inclusion of physical footprint in an evaluation of technology greenness necessarily requires consideration of the impacts to both the biophysical and human environments within that setting. For example, the optimal location and extent of DWTP footprint is dependent on several factors including distance from source water, elevation, and available space. Other environmental factors such as the presence of important fish habitat in a natural waterway receiving discharge from the waste stream of the DWTP also require consideration, however; as a result, limiting waste production may be ultimately prioritized in this setting to limit adverse impacts to biodiversity in the natural waterway.

The four attributes of water industry technology that impact greenness (natural-resource basis, energy consumption, waste production, and footprint) are closely linked and must be considered relative to both the specific environmental settings in which they are applied and the other technologies to which they are being compared. Thus, life cycles and supply chains should also be considered. Life cycle analysis (LCA) involves the evaluation of the environmental impacts of a product, process, or service over all of its stages of the life cycle; thus, it includes the environmental impacts of all relevant life cycle aspects, which may include raw material extraction or processing, manufacturing, distribution, use, regeneration, recycling, and final disposal (Ayres, 1995). For example, processes using activated carbon materials are generally less green since they require high energy inputs during the production and regeneration stages. Rigorous LCA will thus reflect several aspects of supply chain analysis including how risks can be reduced by bypassing certain suppliers and/or processes and reduce unnecessary inventories. Shipment of materials over long distances is a simple example of the importance of supply chains in evaluating technology greenness because of associated indirect increases in energy consumption and waste production via increased emissions. Co-benefits associated with certain technologies should also be considered. For example, some of the waste products from water treatment processes may be reused for various purposes such as land application, composting, cement manufacturing, and road subgrade (Randtke & Horsley, 2012; Márquez et al., 2019). While it could be argued that an absolute, quantitative index could be developed to measure the "greenness" of a given technology, this is not proposed herein because such a metric would require assumptions regarding both the relative value of the "greenness" attributes and the impacts of the technology on the biophysical and human environments relevant to the setting where it is to be applied.

It is at this point of greenness evaluation that the inter-connectedness of the choice between technology options and their relative greenness becomes iterative and complicated. The evaluation becomes iterative because of the chain reaction of environmental impacts that is initiated by these decisions, as demonstrated above. Approaches for characterizing these impacts are available, however. For example, they can be broadly characterized as human health and ecosystem damage footprints. Comprehensive damage assessments and LCAs have recently been applied to harmonized resource-based footprints (i.e., energy, material, land, and water) to demonstrate that resource footprints provide good proxies for environmental (i.e., human health and ecosystem) damage (Steinmann et al., 2017). Evaluations of technology greenness and ultimate implementation are also complicated, however, because of trade-offs between techno-ecological services. For example, the fail-safe provision of safe water may conflict with other techno-ecological services such as waste minimization. Conflicts may result from divergent sociocultural preferences among individuals, communities, or other stakeholders that are differently impacted by the techno-ecological services that can be provided by the technology that is ultimately implemented (King et al., 2015). Frameworks to characterize trade-offs in ecosystem services that reflect biophysical constraints and divergent values have been developed (Cavender-Bares et al., 2015; King et al., 2015) and offer further opportunities to advance on the promises of techno-ecological NBS in the water sector. While the explicit recognition of differences among stakeholder values and preferences is integral to ensuring that techno-ecological NBS achieve intended impacts, strategies for navigating such conflicts and evaluating the implications of trade-offs impacting biophysical and human environments are beyond the scope of the present work.

To illustrate the utility of the greenness framework shown in Figure 2-2 for identifying, naming, and describing the "green" attributes of treatment technology that may be valued in certain situations, the relatively simple selection of fit-for-purpose surface water treatment systems can be explored in two distinct environmental settings: remote and urban. Notably, technology typologies are excluded from the discussion; only key green attributes are discussed. A remote community may be challenged by accessibility and unreliable supply chains, unreliable power supplies, and institutional memory and staff retention (Hall, 2018; Chattha, 2020)—these challenges may not be as significant in an urban environment. In contrast, while available space and footprint may not be an issue in a rural or remote area, an urban community may be constrained by the available space. Despite these differences, both communities are likely challenged by competing demands between finances and treatment capacity, resilience, and redundancy, as well as operational burden. The remote community may, therefore, value technologies that are natural resource-based and easy to maintain, and reduce energy consumption and waste production as compared to those that reduce physical footprint. Natural resource-based technologies would address accessibility challenges as fewer components and chemicals would need to be sourced externally for operation, maintenance, and repairs, thereby reducing often high transportation costs. Additionally, natural resource-based technologies tend to be passive and therefore typically have lower energy demands and are associated with lower operational burdens and capacities than non-passive technologies. Thus, natural resource-based technologies may help to mitigate the challenges presented by power supply reliability, institutional memory and staff retention, finances, and operational burden and capacity. Technologies that generate relatively less waste might be prioritized, as the management of waste and hazardous substances add to both the operational burden and technical capacity requirements. Conversely, footprint may not be prioritized, as the small population and remote location imply lower water demand and more available space, respectively.

In contrast, an urban centre may value footprint, energy conservation, and low waste production as important green factors, with less importance placed on the passive quality of natural resource-based technologies. Technologies designed to reduce the footprint may minimize the environmental impact caused by the extent of infrastructure required to meet high production demands. Competition for financial resources may encourage a focus on reducing energy consumption, as this often represents a large fraction of a water utility's operational costs (Crittenden et al., 2012). Additionally, limiting waste production reduces the need for additional waste management infrastructure, further reducing footprint and energy demands.

It should be underscored that the framework illustrated in Figure 2-2 constitutes a simple organizational structure to identify, name, and describe the "green" attributes of the broad range of technologies—including natural capital—relevant to the water industry to enable stakeholders to clearly and accurately communicate the technical and engineering aspects of technology approaches that best align with their individual or community sociocultural values, beliefs, and attitudes. The framework necessarily requires consideration of the environmental setting in which the technology is to be applied and assessment of the technology's life cycle within that setting to provide structured discussion regarding techno-ecological trade-offs as a first step in facilitating techno-ecological decision-making that strives to address diverse stakeholder priorities.

2.3.2 Biofiltration as a key example of green technology for drinking water treatment

While minimizing waste production and energy consumption are somewhat obvious strategies for increasing the greenness of drinking water treatment and distribution approaches, the incorporation of natural resource-based green technologies as techno-ecological NBS is at the precipice of a revolution in the water industry. Biofiltration processes are arguably the most obvious and effective examples of underutilized green technology opportunities in the drinking water industry. They have not yet experienced as much uptake as conventional treatment technologies in some regions due to concerns regarding the health risk attributable to microbially mediated treatment, difficulties in operation, and unlikely regulatory approvals (Brown et al., 2015). However, such concerns are misplaced (Brown et al., 2015; Kirisits et al., 2019). Biofiltration technologies differ from conventional filtration in that biological activity is promoted and maintained within and on filter media—in built vessels or naturally in the subsurface—to remove suspended particles (including pathogens) and dissolved organics from the water phase (Basu et al., 2015; Kirisits et al., 2019). Biofiltration technologies harness natural microbial processes, do not generally require additional energy inputs, and do not typically produce significant waste relative to other treatment processes designed to achieve the same objectives (Fowler & Smets, 2017). However, when biofilters are operated passively at low flow rates, they often require large footprints to ensure targeted yields of drinking water. Notably, there are many types of biofiltration technologies; although they can also be considered green, they fall along a spectrum of greenness. Some common types of biofiltration used in drinking water treatment include:

- Classical biofiltration: biofiltration in an otherwise conventional DWTP (preceded by coagulation/flocculation/sedimentation);
- Classical direct biofiltration: biofiltration preceded by coagulation/flocculation;
- Biofiltration with pre-ozonation: biofiltration, either classical or classical direct, preceded by ozonation;
- Slow sand filtration (SSF): passively operated filtration through sand media; and
- Riverbank filtration (RBF): induced surface water infiltration to bankside abstraction wells.

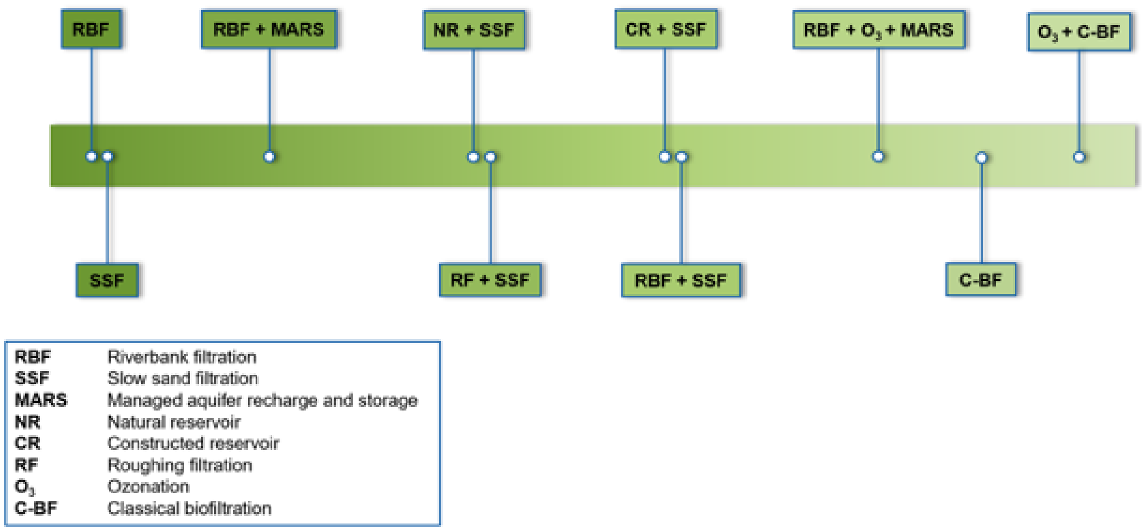


Figure 2-3 Greenness spectrum of biofiltration technologies for drinking water treatment.

The greener biofiltration technologies in this spectrum are generally operated passively and take advantage of natural processes in the surrounding environment to achieve treatment goals; such technologies include SSF and RBF. Combinations of biofiltration processes—such as roughing filters, managed aquifer recharge and storage, and reservoir storage—may provide additional treatment and can increase operational control, but increase footprint and energy requirements. As well, processes such as classical biofiltration indirectly contribute to waste production due to pre-treatment by coagulation and clarification processes prior to filtration; it is also more energy-intensive because it is not passively operated and requires backwashing to remove accumulated solids. Biofiltration technologies preceded by ozonation are especially effective in removing organics, but less green because of the energy-intensive nature of ozonation.

While not reflected in Figure 2-3, filter media are also an important factor contributing to biofiltration technology greenness. Biofiltration technologies employing a form of granular-activated carbon are intrinsically less green because of the high energy required to manufacture adsorptive media. The physical and chemical manufacturing processes involve carbonization, or conversion of the raw material to a char, and activation or oxidation to develop the internal pore structure—temperatures of 800–900°C are needed for the activation process (Edzwald, 2011). Readily available filtration media, such as anthracite coal and sand, are more green options, especially when they can be locally sourced.

2.3.3 Greenness assessment of drinking water treatment systems

In addition to the relative greenness ranking of biofiltration technologies, common drinking water treatment systems may also be relatively ranked according to their greenness. Figure 2-4 presents a relative ranking of common drinking water treatment system configurations; however, actual evaluation of technology greenness is case-specific, as discussed previously. Generally, treatment systems using biofiltration, such as classical biofiltration, SSF, or RBF (all followed by chlorine-based disinfection), are among the greenest treatment approaches relative to conventional (i.e., coagulation, flocculation, sedimentation, non-biological filtration, and chlorine-based disinfection) treatment because they are natural resource-based, require relatively lower energy inputs, and produce relatively less waste. It is important to note, however, that some key trade-offs exist between less energy-intensive technologies and operational control. Although energy-efficient technologies are generally more green, they often do not offer as much operational control as more conventional treatment systems because of factors such as the lack of design and operational (i.e., typically mechanical) controls over system components such as flow rates or microbially mediated degradation of contaminants. As such, some green technologies are less able to respond to sudden changes in source water quality, which can potentially compromise public health protection—this issue requires further investigation to ensure resilient treatment, especially in environments vulnerable to climate change-exacerbated landscape disturbances such as wildfires (Emelko et al., 2011; Stone et al., 2011).

Treatment system	Natural resources-basis	Energy consumption	Waste production	Footprint		
High-rate clarification plant*	Low	High	High	High	Less green	More operational control
Dissolved air flotation plant*	Low	High	High	High	Less green	More operational control
Direct filtration plant*	Moderate	Moderate to high	High	Moderate	Moderately green	Moderate operational control
Classical biofiltration plant*	Moderate	Moderate to high	Moderate to high	Moderate	Moderately green	Moderate operational control
Slow sand filtration & chlorine disinfection	High	Low	Low	Low to moderate	More green	Less operational control
Riverbank filtration & chlorine disinfection	High	Low	Low	Low	More green	Less operational control

* plant refers to an otherwise conventional treatment setting

Figure 2-4 General greenness assessment of common drinking water treatment typologies.

2.3.4 Applying the green technology framework to case studies

Two DWTP design case studies presented below highlight benefits of green technologies in drinking water treatment, use and limitations of the developed framework, and influence of sociocultural factors on the green technology preferences of individuals, groups, or communities.

CASE 1) Biofiltration to treat high ammonia groundwater for a small system (EPA, 2014)

The implementation of an innovative biofiltration system for a small drinking water system in Iowa highlights the promise of green tech to achieve a technologically fit-for-purpose treatment design. The EPA conducted pilot-scale and full-scale studies for implementation of a novel biofiltration treatment technology in Palo, Iowa, which did not have centralized water treatment prior to 2008. Palo is a small town of just over 1,000 people, with limited technical capacity as the utility relies solely on one treatment plant operator who is also responsible for other municipal operations such as snow plowing and landscaping. Source water for the DWTP is groundwater characterized by high ammonia and iron concentrations and is low in dissolved oxygen.

Breakpoint chlorination is a common treatment option to address high ammonia concentrations (Edzwald, 2011). However, the chlorine dose required to adequately oxidize ammonia and nitrogen species would be excessive for a small system. As an innovative alternative to breakpoint chlorination to treat ammonia-rich groundwater, the EPA designed a novel biofiltration treatment system. The treatment system, patented by the EPA, consists of aeration contactors, blowers, and dual media filters, with added chemical feeds of phosphate, chlorine, and sodium hydroxide. An aeration contactor was needed to ensure sufficient oxygen required for nitrification, as the groundwater source was low in dissolved oxygen. The main goal of the treatment plant is to remove ammonia and iron, which was consistently achieved in both the pilot- and full-scale systems.

An evaluation of all four green attributes discussed herein was not reported, as this is often not possible due to limited time or resources. Nonetheless, the biofiltration system may be described as green because it is natural resource-based and requires substantially less chemical input compared to breakpoint chlorination, the alternative treatment option. Because of these green aspects, the biofiltration system is operationally less demanding and thus also matches the operational (i.e., operator training and treatment processes supervision) capacity of a smaller system. Most importantly, the treatment system produces drinking water that consistently meets the regulatory targets set for contaminants of concern, thereby ensuring a fit-for-purpose treatment design for the protection of public health.

CASE 2) RBF for pre-treatment of municipally and industrially impacted surface water in Louisville, Kentucky (Ball, 2012)

Louisville Water Company in Louisville, Kentucky, implemented an RBF system as pre-treatment to address concerns of microbial contamination possibly not addressed by the city's conventional treatment system. The city is reliant upon the municipally and industrially impacted Ohio River for drinking water. The Ohio River is consistently ranked as the most polluted in the United States, with an estimated 30 million pounds of toxic chemicals illegally dumped into its waters each year (Kuhlman, 2019). Louisville is a relatively large, established city and thus has limited available space. The Louisville Water Company served a population of 764,769 in 2019 (EWG, 2019) and has a high level of technical capacity.

To address microbial contaminant concerns, the city launched a project to investigate the implementation of an RBF system on the Ohio River. The RBF system would also address challenges with water main breaks in the distribution system due to large variations in water temperature. As part of the project, the city investigated drilling options for the tunnel and wells. Ultimately, the city decided on a completely underground RBF system that includes a tunnel and collector wells.

Although an above-ground system would have been much easier and less expensive to construct, the public did not want any above-ground structures to impact the aesthetic value of the Ohio River. Additionally, while vertical wells would be much easier to maintain than collector wells, collector wells were chosen due to the possibility for construction complications with vertical wells. Additionally, the city's high technical capacity was able to address the increased maintenance requirements associated with collector wells.

Similar to the previous case study in Palo, information detailing the green attributes of the treatment process was not reported. Nonetheless, it is clear that Louisville's RBF system is relatively natural resource-based, as it utilizes the natural subsurface to eliminate taste and odour compounds, provides an additional barrier for waterborne pathogen removal, and creates a stable water temperature that results in fewer main breaks in the distribution system. Despite this, the physical footprint of the RBF system is relatively large due to the footprint needed during the construction of an underground system.

This case study highlights the importance of discussing stakeholder priorities accurately and transparently to achieve fit-for-purpose and socioculturally appropriate treatment design. Louisville Water Company considered stakeholder priorities after ensuring treatment design met regulatory requirements to uphold the protection of public health. While the public held sociocultural values that aligned with preserving the aesthetic quality of the Ohio River, the Louisville Water Company sought to minimize risk of construction complications. These needs were ultimately met by the selection of an underground RBF system equipped with collector wells.

2.4 Conclusions

The main conclusions of the analysis presented herein are briefly summarized below. They are:

1. While the concept of green technology is widely recognized, its meaning varies considerably. In the water industry, green technology can be described by four main attributes: natural resource-basis, energy consumption, waste production, and footprint.
2. The greenness of a technology can be evaluated with respect to each of the above-mentioned attributes and is therefore relative to both the environmental setting and the other technologies to which it is being compared.
3. The paramount objective of treatment is public health protection and thus technologies must be fit-for-purpose with respect to their use and meet regulated performance targets regardless of their greenness.

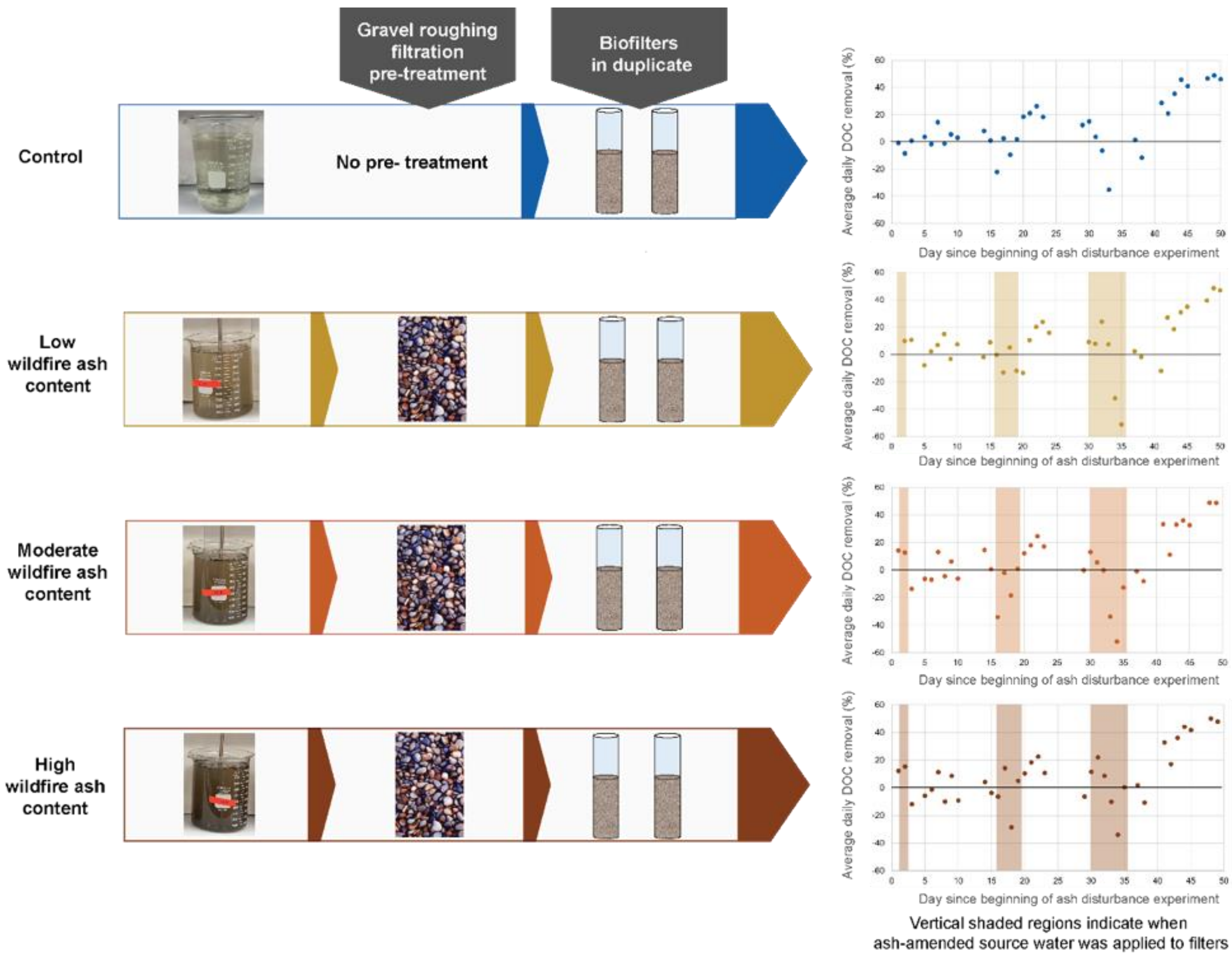
4. Operational control is often reduced as the greenness of a technology is increased.
5. In the water sector, environmental setting (i.e., location-specific factors including hydroclimate, sensitive habitat(s), water quality, temperature, etc.) is a critical consideration that can limit the practical application of some technologies.
6. Biofiltration processes are arguably the most obvious and effective examples of underutilized green technology opportunities in the drinking water industry. These technologies can be differentiated along a spectrum of greenness.
7. Prioritization of the factors contributing to technology greenness varies based on sociocultural considerations of individuals, groups, and communities, as identified based on their collective knowledge, values, attitudes, beliefs, feelings, and behaviours.
8. The framework developed herein enables an accurate and transparent description of the "green" attributes of technology—including green infrastructure—used in the water industry. It differentiates technology "greenness" by relatively examining key attributes that may cause environmental impacts across the technology's life cycle through the lens of the environmental setting in which it is applied. It can contribute to the development of more comprehensive techno-ecological NBS by providing a clear and accurate description of the "green" attributes of technology options for the water industry, as well as a framework for their relative comparison, thereby facilitating techno-ecological decision-making that strives to address diverse stakeholder priorities.

Chapter 3
Biological filtration is resilient to wildfire ash-associated organic carbon threats to drinking water treatment

3.1 Summary

Elevated/altered levels of dissolved organic matter (DOM) in water can be challenging to treat after wildfire. Biologically-mediated treatment removes some DOM; its ability to remove elevated/altered post-fire dissolved organic carbon (DOC) resulting from wildfire ash was therefore investigated. The treatment of low, medium, and high wildfire ash-amended source waters by bench-scale biofilters was evaluated in duplicate. Turbidity and DOC were typically well-removed during periods of stable operation (effluent turbidity ≤ 0.3 NTU in 93% of samples, average DOC removal ~20% in all biofilters during periods of non-impaired DOC removal). Daily DOC removal across all biofilters was generally consistent, suggesting that the wildfire ash and associated water extractable organic matter did not reduce the DOC biodegradation capacity of the biofilters. DOM fractionation indicated that this was because the low molecular weight neutral (which are known to be readily biodegradable) and biopolymer fractions of DOM were reduced; however, humics were largely recalcitrant. Thus, biological filtration may be resilient to wildfire ash-associated DOM threats to drinking water treatment. However, operational resilience may be compromised if the balance between readily removed and recalcitrant fractions of DOM change, as was observed when baseline source water quality fluctuated for brief periods during the investigation.

3.2 Graphical abstract



3.3 Introduction

Wildfire threats to water supplies are recognized globally (Robinne et al., 2016; 2019; Mishra et al., 2021). After wildland fire, vegetation is reduced or absent and more precipitation reaches the land surface (Williams et al., 2019), leading to increased erosion and solids runoff (Silins et al., 2009; Alessio et al., 2021); even at large basin scales in systems with already deteriorated water quality (Emmerton et al., 2020). Accordingly, solid-associated metals (Abraham et al., 2017), nutrients (Emelko et al., 2011; Silins et al., 2014; Gustine et al., 2021), and other contaminants (Crouch et al., 2006; Mansilha et al., 2017) also can be elevated—or transformed in the case of natural organic matter (NOM)—in wildfire-impacted waters (Hohner et al., 2019). Longer-term releases of bioavailable phosphorus from sediments to the water column also have been observed in some areas (Stone et al., 2014; Emelko et al., 2016). They promote primary productivity (Silins et al., 2014) and the proliferation of algae that can produce toxins of human health concern—these effects are magnified when they converge with those from anthropogenic landscape disturbances (Watt et al., 2021). Collectively, these impacts underscore that wildfires can challenge treatment plants beyond their operational capacity, ultimately resulting in increased infrastructure and operating costs, service disruptions, or outages (Emelko et al., 2011; Price et al., 2017).

While elevated turbidity can be treated with conventional technologies, elevated/altered NOM can be challenging. It is typically described by characterization of dissolved organic carbon (DOC) concentrations and aromaticity that can challenge treatment, especially when rapidly fluctuating (Kundert et al., 2014; Skwaruk, 2021). Although DOC is not a regulated "contaminant", elevated source water DOC increases coagulant demand (Sharp et al., 2006) and is a precursor for potentially harmful disinfection by-products (Kitis et al., 2002; Kraus et al., 2010). Moreover, smaller, more aromatic, and thus more difficult to coagulate post-fire DOC has been suggested (Chow et al., 1999; Emelko et al., 2011; Hohner et al., 2019); more aromatic DOC also tends to lead to greater formation of regulated disinfection by-products (Singer, 1999; Hua et al., 2015). These DOC-associated post-fire treatment concerns emphasize the need for water supply and treatment resilience, potentially in the form of techno-ecological approaches, to respectively mitigate these threats at the source and/or in treatment plants (Emelko & Shams, 2014; Blackburn et al., 2021).

Biologically-mediated drinking water treatment technologies may offer treatment resilience in buffering altered aquatic DOC concentrations and character after wildfire. While conventional filtration focuses solely on achieving particle and pathogen removal and requires pre-treatment by chemical coagulants for effective operation even when source water quality is high (Lee et al., 2018), biological filtration offers additional treatment benefits, including reductions of taste and odor compounds, NOM, and therefore regulated disinfection by-products (Bouwer & Crowe 1988, Emelko et al. 2006, Kirisits et al., 2019; Brown et al., 2020). Biological filtration also improves the biological stability of drinking water in distribution systems (Brown et al., 2017). Particle, pathogen, and DOC removal by biological filtration depends on biofilm formation and biodegradation (Kirisits et al., 2019; Brown et al., 2020). Biological filtration processes range from classical—biofiltration in an otherwise conventional treatment plant (i.e., preceded by coagulation/flocculation/clarification and sometimes advanced oxidation processes such as pre-ozonation)—to slow sand filtration (SSF) that is typically operated without chemical or other types of pre-treatments (Kirisits et al., 2019; Blackburn et al., 2021). Thus, while they may include physico-chemical filtration that relies on synergies between particle size, media depth, media size, particle destabilization by coagulation, and media roughness (Tobiason et al., 1988; Pernitsky & Edzwald 2006; Jin et al., 2015a,b; 2016; 2017), biodegradation, biotransformation, adsorption, and bioregeneration may also contribute to treatment. Critically, however, biological filtration performance is not directly proportional to the amount of biomass present (Urfer et al., 1997; Huck et al., 2000; Emelko et al., 2006); thus, lab- and pilot-scale assessments remain critical to demonstrating biological treatment capabilities.

Biological filtration preferentially removes low molecular weight (LMW) compounds (Shin & Lim, 1996; So et al., 2017) that may be present in wildfire-impacted source waters (Hohner et al., 2019). Accordingly, it may offer treatment resilience in buffering elevated source water DOM after wildfire. Thus, biological treatment is a reasonable option for the management of wildfire ash-associated organic carbon threats to the provision of safe drinking water. Treatment by SSF is a logical starting point because it is differentiated from other types of biological filtration in that particles and dissolved constituents are predominantly removed in a layer of biologically active material associated with and atop the filter media, called the schmutzdecke, rather than throughout the depth of the filter (Fox et al., 1984; Bellamy et al., 1985; Barrett et al., 1991). Low hydraulic loading rates (HLRs) and extended contact times (relative to classical biofiltration) promote biodegradation of DOC, even without chemical or energy-intensive pre-treatments such as coagulation or pre-ozonation (Collins et al., 1996; Lodgson et al., 2002). Thus, biological filtration with relatively long contact times is the most likely design configuration to enable demonstration of treatment resilience in buffering elevated source water DOM resulting from wildfire ash because kinetic limitation is practically precluded—a proof-of-concept evaluation was the focus of this investigation. Specifically, the resilience of biological filtration treatment in reducing elevated/altered post-fire DOC resulting from wildfire ash was investigated.

3.4 Methodology & Methods

3.4.1 Overview of experimental approach

Bench-scale biological filtration experiments were conducted using wildfire ash-amended source water (in duplicate at three levels: low, medium, and high ash content) from an agriculturally- and municipally-impacted watershed (GRCA, 2021a). This water was pre-treated by roughing filtration to removed suspended solids to a level ($\leq$ 5 NTU; Barrett et al., 1991) appropriate for subsequent treatment by biological filtration. Given that altered NOM (measured as DOC concentrations and/or character that are episodically altered) results in some of the most significant treatment challenges commonly observed after wildland fire, DOC removal was investigated here. Two-, four-, and seven-day disturbances were investigated because they are consistent with or longer than many observations of episodically elevated DOC after wildfire (Lyon & O'Connor, 2008; Emelko et al., 2011, 2016; Writer & Murphy, 2012; Dahm et al., 2015; Murphy et al., 2015; Mast et al., 2016). Each DOC pulse was followed by a one-week return to “baseline” source water without ash amendment. Figure 3-1 depicts the operational conditions during bench-scale experimental evaluations.

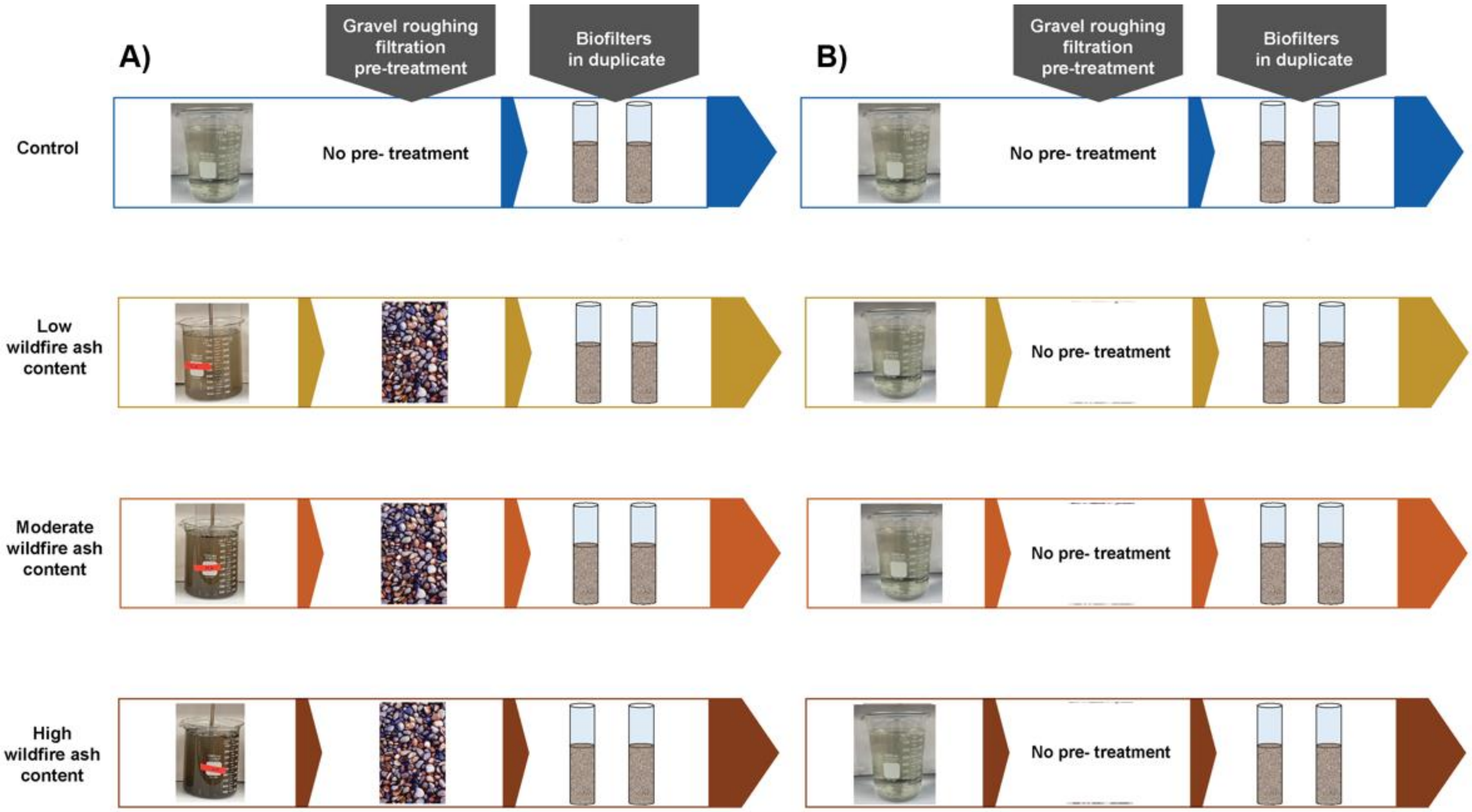


Figure 3-1 Operational conditions during the bench-scale experimental evaluation (Days 1 to 50, 8 biofilters) of biofilter treatment resilience in (A) buffering elevated aquatic NOM resulting from low, moderate, and high wildfire ash content (for 2-, 4-, and 7-days periods), followed by a (B) return to baseline source water quality conditions for approximate one week after each disturbance. Biofilters were acclimatized for 103 days prior to start of 50-day experiments.

3.4.2 “Baseline” source water and preparation of ash disturbance-impacted source water

Baseline source water samples were collected from flowing Grand River water approximately five feet from shore, directly below water surface, every 7-10 days in Kitchener, Ontario (43°25'21.8"N 80°24'48.1"W). Water quality was subsequently characterized (section 3.4.4). Raw water was acclimatized to room temperature for a period of between one to 7 days before being fed to the biofilters or used to prepare the disturbance-impacted source water as described below.

Wildfire ash-impacted source water was created by amending the river water with ash collected on September 22, 2020 from the 2020 Doctor Creek wildfire (N21257, high burn severity) in British Columbia, Canada (50°05'00.2"N 116°03'52.6"W) (BC Wildfire Service, 2021). Disturbance-impacted source waters were created at three levels of ash content intended to correspond to disturbance “severity” and associated source water quality deterioration: low (0.25 g of ash/L of Grand River source water), moderate (0.50 g of ash/L of Grand River source water), and high (1.00 g of ash/L of Grand River source water; detailed water quality in Appendix A). To ensure water extractable organic matter (WEOM) was adequately leached from the ash, each ash matrix was mixed for 18 hours at a rate of 200 RPM for two hours, followed by mixing for 16 hours at a rate of 180 RPM (Phipps & Bird, PB-900 Series Programmable 6-Paddle Jar Tester). Following mixing and a subsequent three hours settling period to reduce turbidity, settled water quality was analyzed (Appendix A).

3.4.3 Bench-scale filter design and operation

Bench-scale SSF-like biofilters with low HLRs and extended contact times (relative to classical biofiltration) were used because they represent operational scenarios in which maximal biodegradation of DOC would be expected (Collins et al., 1996; Logdson et al., 2002). The suitability of using bench-scale biofilters to reasonably represent aspects of pilot- and full-scale biological filtration performance such as the ability to remove dissolved contaminants is generally understood (Manem & Rittmann, 1990; Huck et al., 1995; Liu et al., 2001) and has gained renewed interest in recent years (McKie et al., 2019; Terry, 2019). Thus, this approach was used here and enabled duplicate evaluation of several source water quality ash content scenarios and disturbance periods.

The biofilters were designed to ensure that porosity oscillations caused by small column diameter relative to grain size—wall effects—were negligible (Bear, 1972). Consideration of mass transfer dynamics was also incorporated. Lower HLRs at a given empty bed contact time (EBCT) may result in lower DOC removal if external mass transfer—rather than the reaction rate—is rate-limiting (Terry et al., 2019). To confirm that the reaction rate is rate-limiting, the Damkohler number II (i.e., the ratio of reaction rate to mass transfer rate) was estimated for the bench-scale biofilter design specifications (Appendix E). Non-adsorptive filter media were used to ensure that only biotic DOC removal in the biofilters was evaluated.

Eight bench-scale filters were used. They had an inner diameter of 26 mm and a bed depth of 70 cm, which is in the recommended range of filter depths for SSF (Barrett et al., 1991). The filter media consisted of clean quartz sand with an effective size of 0.20 mm and uniformity coefficient of 1.5, which are also consistent with typical SSF design (Crittenden et al., 2012). The filters were continuously operated in down-flow mode for approximately five months, with 103 days of acclimation and a 50-day experimental period. The filters were operated at room temperature (19-22^{o}C) with an extended EBCT of approximately 10 hours (corresponding HLR of 0.07 m/h), which represents the upper ranges of previously reported EBCTs in full-scale SSF (Rachwal et al., 1986; Collins et al., 1996). They were covered in aluminum foil to prevent photosynthesis. When maximum headloss was reached, they were maintained by scraping the schmutzdecke so that the underlying filter media were visible (Barrett et al., 1991). This was done immediately prior to each period of ash disturbance so that biofilter performance and treatment resilience were evaluated during filter ripening when performance is most vulnerable (Barrett et al., 1991; Arora, 2018;).

Pre-treatment of disturbance-impacted water was limited to settling (section 4.4.2) and gravel roughing filtration to target an influent turbidity of $\leq$ 5 NTU to prevent filter clogging and shortened run times. The roughing filters had an inner diameter of 5 cm and a bed depth of 30 cm; they were operated intermittently at an HLR of 0.31 m/h. To ensure that DOC removal only within the biofilters was evaluated, the gravel media within the roughing filters were rinsed and the filters were re-packed after no more than 24 hours of run-time. Roughing filter effluent water quality was analyzed as described in section 3.4.4.

3.4.4 Water quality analyses

Standard methods (Baird & Bridgewater, 2017) were used to evaluate turbidity (Method 2130B; Hach 2100 N turbidimeter, Loveland, CO), pH (4500-H+B Electrometric method; Orion 720A pH meter, Thermo Fisher Scientific, Waltham, MA), alkalinity (Method 2320; titration method with pH endpoint of 4.5), DOC concentration (filtration through pre-rinsed 0.45 µm Nylaflo membranes, Pall, Port Washington, NY; Method 5310B; Shimadzu TOC-V CPH analyzer, Kyoto, Japan), and ultraviolet absorbance (UVA_{254}; Method 5910B; 1 cm quartz cell; Hach DR 5000 Spectrophotometer, Loveland, CO). Specific ultraviolet absorbance at 254 nm (SUVA) was calculated by dividing UVA_{254} absorbance by the DOC concentration (Weishaar et al., 2003).

Liquid chromatography in combination with organic carbon detection (LC-OCD) was used to fractionate DOC (as biopolymers [BPs], humic substances [HS], building blocks [BB], low molecular-weight [LMW] neutrals, LMW acids) as described in Huber et al. (2011). Samples were first filtered through a pre-rinsed 0.45 µm polyethersulfone membrane (Millipore Express® PLUS; Merck Millipore, Burlington, MA). Chromatographic separation was completed using a weak cationic exchange column (Toyopearl, TSK HW 50S, Tosoh, Japan).

3.4.5 Statistical analyses

A paired-samples t-test was conducted to compare the influent and effluent DOC concentrations and UVA_{254} measurements between all filters throughout the experimental period. The assumptions of a paired t-test are that (1) the differences between the matched pairs follows a roughly normal distribution and (2) that the variance between the two data sets is approximately equal. These assumptions were tested by visually inspecting normal scores plots for the differences between the matched pairs. Additionally, a heteroscedastic t-test for the difference between the means of control and disturbance severity conditions with respect to DOC % removal was also conducted. Two-tailed tests were conducted using the p-value approach. All assumptions, normal scores plots, and t-test equations are presented in Appendix C.

3.5 Results & Discussion

3.5.1 Performance of bench-scale biofilters

Turbidity was effectively reduced in all biofilters (effluent turbidity $\leq$ 0.3 NTU in 93% of samples throughout 153 days of filter operation, never exceeding 1.0 NTU) (Figures B-1 through B-8) and pH and alkalinity remained stable through the biofilters (Figures B-17 through B-32). Thus, filter performance met or exceeded performance expectations (Barrett et al., 1991; Health Canada, 2017). DOC removal varied considerably throughout the 50-day experimental period, ranging from negative to approximately 40% removal. DOC concentrations typically decreased significantly from influent to effluent across all biofilters ($p \leq 0.026$ for all filters; Appendix C) and were consistent with those reported for various types of biological filtration. For example, Collins et al. (1996) reported 12-33% removal of DOC in several full-scale SSF plants with EBCTs ranging from 3.8 to 21.9 hours, while Vines & Terry (2020) reported only 7-8% DOC removal in bench-scale anthracite biofilters (EBCTs of 5 to 30 minutes). DOC removals of 12-38% by classical biological activated carbon filtration (i.e., preceded by coagulation/flocculation/clarification) with pre-ozonation also have been reported (So et al.; 2017). Full-scale classical biofiltration treating Grand River water achieved average total organic carbon removals of 14% with anthracite filter media and 23% with granular activated carbon filter media (Emelko et al., 2006). Here, the use of an SSF-based approach that did not include absorptive filter media or pre-treatment to remove or enhance the removal of more hydrophobic DOM (i.e., coagulation) or more recalcitrant DOM (i.e., post-clarification ozonation) resulted in DOC removals that were generally consistent with previous reports describing both classical biofiltration and SSF performance. It should be highlighted that despite the average to high overall extent of DOC removal observed herein, episodic impairment of DOC removal was also observed in all biofilters (regardless of wildfire ash amendment) in association with seasonal changes in source water quality that are known to occur during the fall. These periods are discussed below in section 3.5.2.

A small but significant decrease in UVA_{254} from biofilter influent to effluent was observed across all experimental conditions ($p \leq 1.16E\text{-}05$, average change in daily UVA_{254} measurements ≤ 0.012 cm^{-1}). The observation of limited capacity to reduce UVA_{254} is consistent with other reports of biological filtration performance (So et al., 2017; Vines & Terry, 2020) and common understanding of associated treatment mechanisms. Substantial reductions in UVA_{254} across the biofilters were not expected because (i) UVA_{254} reflects both DOC concentration and aromaticity (Weishaar et al., 2003), (ii) WEOM is typically more aromatic when an impact of wildland fire on source water DOM is observed (Hohner et al., 2019), and (iii) aromatic DOC is less biodegradable than more aliphatic DOC (Shin & Lim, 1996; Hozalski et al., 1999; So et al., 2017). Thus, while the biofilters were able to reduce UVA_{254} somewhat, the extent of removal diminished as more of the influent UVA_{254} was derived from wildfire ash addition (i.e., higher ash content). Importantly, the biofilter DOC, UVA_{254}, and LC-OCD removal data collectively demonstrate that while the biofilters were not designed to mimic all aspects of full-scale biofiltration (especially not operational aspects such as headloss accumulation), they provided representative and therefore reasonable indication of the biodegradation capabilities of biological filtration processes. Thus, the bench-scale biofilter design was suitable for evaluating DOM removal by biological filtration and the potential for treatment resilience in buffering elevated source water DOM resulting from wildfire ash.

3.5.2 Impact of wildfire ash on DOC removal by biofilters

DOC removal across all biofilters was generally consistent (Figures 3-2 and 3-3); significant differences in average DOC removals were not observed between biofilters treating baseline or ash-amended waters during the study ($p \geq 0.489$ in all cases). Moreover, DOC removal in biofilters treating ash-amended source water remained consistent with that in the control biofilters. For a brief period immediately after the return to baseline source water after the two-day period of ash amendment, DOC removal was significantly lower in the biofilters treating high ash content-impacted water than in control biofilters ($p \leq 0.0271$)—this type of performance difference was not observed after the other experiments involving ash addition to the source water ($p \geq 0.146$) (Figure 3-2). These data may suggest that while the biofilters are adjusting from high nutrient (i.e., LMW neutral DOC) availability to lower availability, biofilters may release some DOC while communities adjust to these shifts. Moona et al. (2019) suggested such shifts when periods of low biological activity coincided with negative concentration gradients and attributed their observations to organic matter desorption from filter media. While these brief periods of performance difference cannot be elucidated mechanistically herein, they underscore the need to better understand DOC removal mechanisms (e.g., adsorption, biodegradation, bioregeneration) in biological filtration processes.

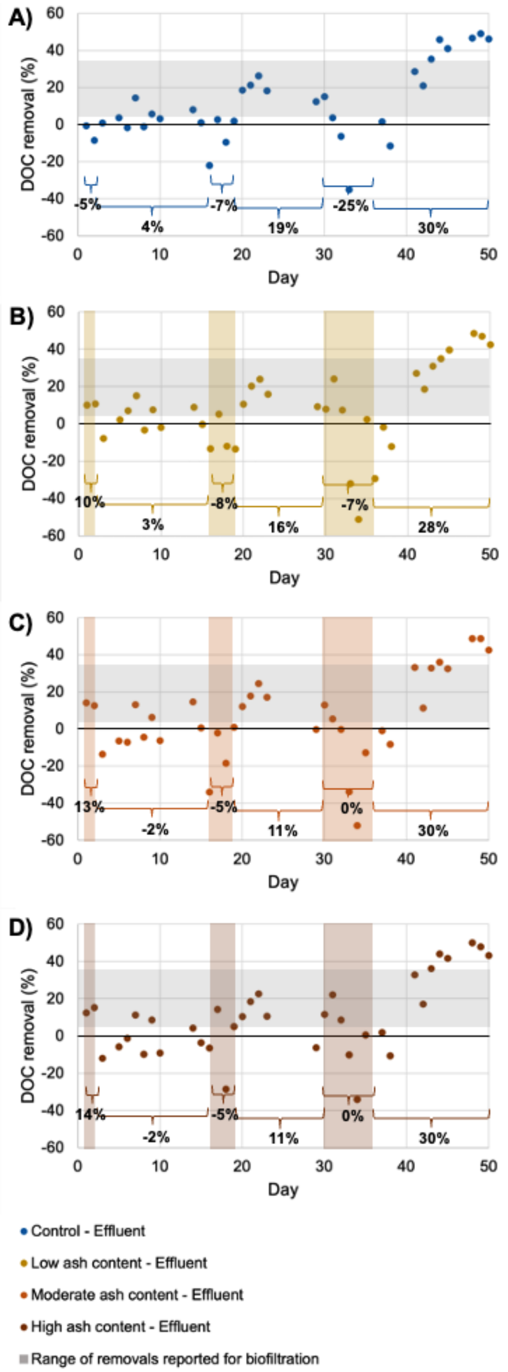


Figure 3-2 Daily DOC removal (%) by biofilters treating (A) control and (B) low, (C) moderate, and (D) high wildfire ash content Grand River water. Vertical shaded regions indicate when ash-amended source water entered filters, and braces correspond to average DOC removals for the periods indicated. Biofilters were acclimated for 103 days prior to start of 50-day ash experiments.

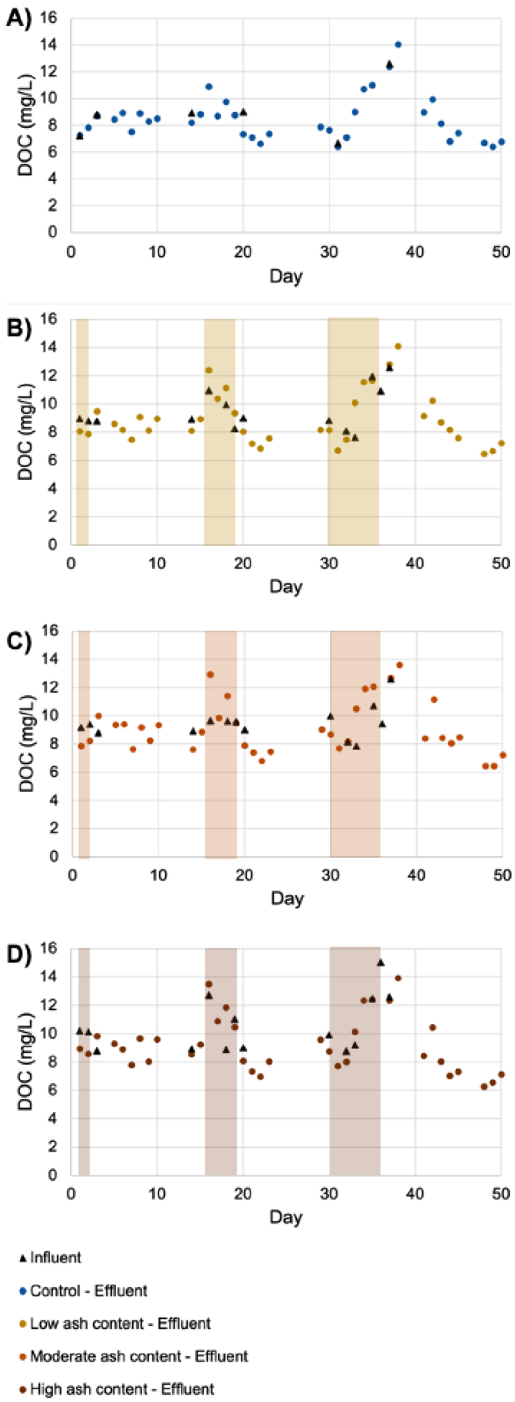


Figure 3-3 Daily change in DOC concentrations across biofilters treating (A) control and (B) low, (C) moderate, and (D) high wildfire ash content source water. Vertical shaded regions indicate when ash-amended source water was fed to filters. Biofilters were acclimated for 103 days prior to start of 50-day ash experiments.

In the water industry, it is widely recognized that brief periods of treated water quality fluctuation occur regularly (e.g., filter ripening, hydraulic surges) but are not necessarily indicative of process failure (Emelko & Huck, 2004). It is for this reason that regulatory compliance monitoring for demonstrating well-operated treatment relies on synoptic sampling (e.g., EPA, 2003) and 95th percentile water quality performance thresholds (e.g., EPA, 1998) rather than imposing absolute criteria. Here, despite brief periods of performance difference in some cases, the biofilters promptly recovered from "shock loads" associated with wildland fire ash delivery to source water and did not exhibit long-lasting DOC removal performance deterioration as a result of the rapid change in source water quality (including increased influent DOC concentrations) relative to baseline source water quality. Thus, these data indicate that biological filtration processes such as SSF offer resilience in buffering elevated source water DOM after wildfire. They also suggest that the wildfire ash and associated WEOM and any other materials that the ash released to the water matrix did not reduce/inhibit the DOC biodegradation capacity of the biofilters because differences in DOC removal by the biofilters treating wildfire ash-impacted water and the control biofilters were not observed.

Interestingly, the present investigation suggests enhanced DOC removal (on a per cent basis) in biofilters treating wildfire ash-impacted water relative to control biofilters treating baseline source water. Average DOC removal during the 2-day ash disturbance period was significantly higher in each of biofilters treating wildfire ash-impacted water relative to the control biofilters (p = 0.0044, 0.0012, and 0.0012 for biofilters receiving low, moderate, and high ash content-amended water, respectively). DOC fractionation by size exclusion chromatography (i.e., LC-OCD analysis) revealed that biopolymers were most effectively removed by biofilters compared to other LC-OCD components (Tables B-1 through B-4), consistent with other studies (Halle et al., 2009; Huang et al., 2011; Pramanik et al., 2014; Pharand et al., 2015; Chen et al., 2016; Elsayed, 2016). In contrast, So et al. (2017) reported that building blocks and LMW neutrals were removed more efficiently than biopolymers and humic substances. A possible explanation for divergent observation could be that biofiltration in this study was in the context of otherwise conventional treatment with pre-ozonation, which can impact biodegradability of DOC (Urfer et al., 1997). Even during periods of impaired DOC removal, such as in the week following the two-day ash disturbance period, biopolymers were typically still well removed, while LMW neutrals increased from the influent to the effluent, indicating transformation or incomplete degradation (Figure 3-4 C vs D).

DOC fractionation also revealed that the enhanced DOC removal was likely attributable to the greater proportion of LMW neutrals comprising WEOM in wildfire ash-impacted filter influent streams compared to control biofilters treating only baseline source water (Figure 3-4 A vs B). LMW neutrals are readily biodegradable, and their removal during biofiltration has been well-documented (Pharand et al., 2014; Elsayed, 2016; So et al., 2017); they tend to be removed even more effectively in biofiltration preceded by ozonation (Pharand et al., 2014; So et al., 2017). This behaviour was observed again in biofilters receiving source water amended with high ash content during the 7-day ash disturbance period ($p = 0.0187$), where LMW neutrals were elevated in the ash-amended source water relative to the control (0.74 mg/L and 1.19 mg/L, respectively; Tables B-1 through B-4). In contrast, enhanced DOC removal in biofilters treating ash-amended source water was not observed during the four-day ash disturbance period ($p \geq 0.344$ for all cases)—this was likely because of the shift in baseline source water quality during this period, discussed below. Collectively, these results underscore that the extent of DOC removal that can be achieved by biofiltration depends on its character and associated bioavailability.

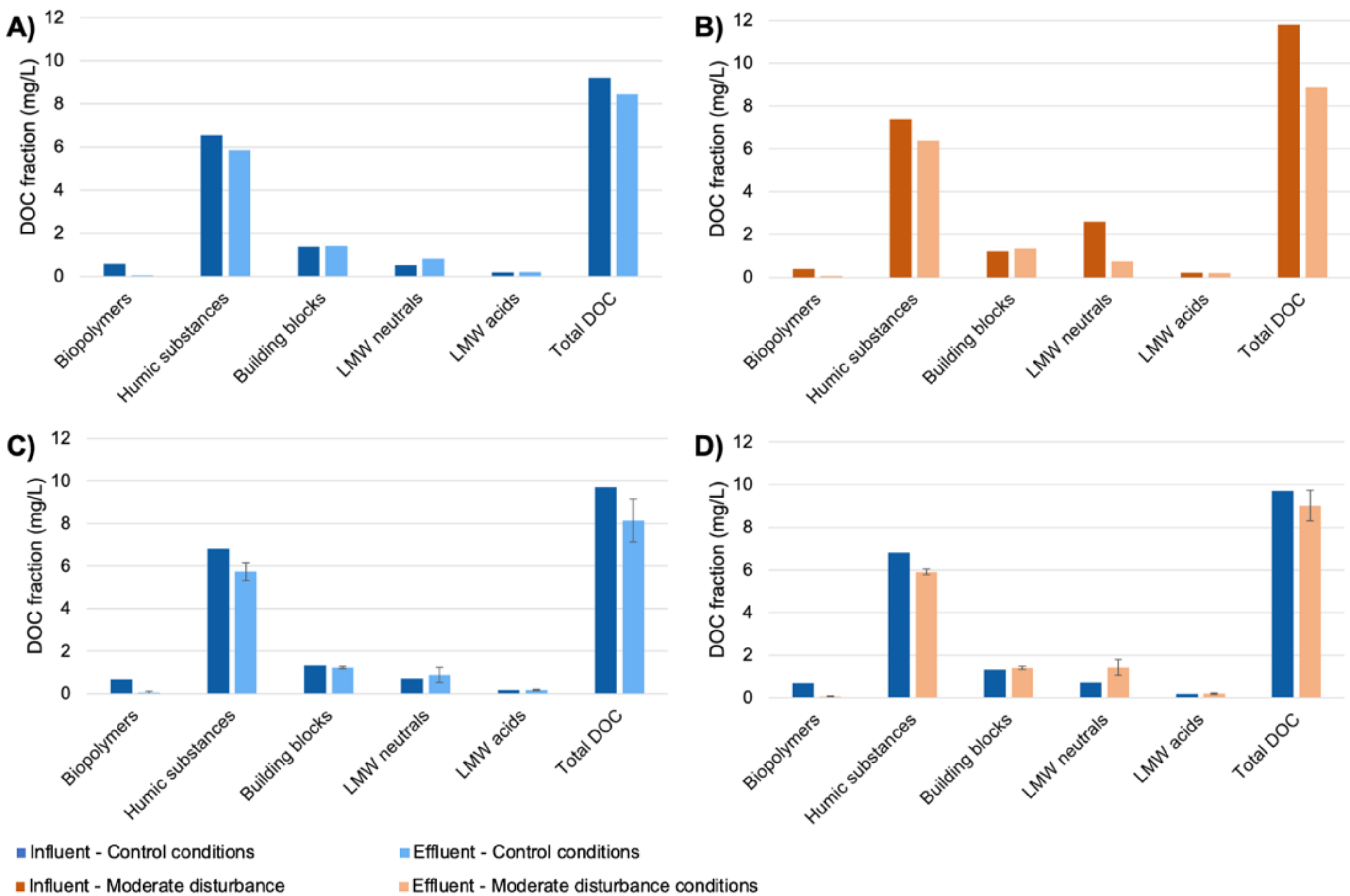


Figure 3-4 LC-OCD fractionation of influent and effluent DOC in (A) control biofilters during two-day ash trial (day 1 and 2), (B) biofilters treating moderate ash content water during two-day ash trial (day 1 and 2), (C) control biofilters during return to baseline period following two-day ash trial (days 3 to 15; n=4), and (D) biofilters treating moderate ash content water during return to baseline source water following two-day ash trial (days 3 to 15; n=4). Error bars indicate standard deviations where mean LC-OCD results are presented.

As indicated above, while DOC removal across experimental conditions was generally consistent, it did vary over the course of the study. All of the biofilters (regardless of ash amendment to the baseline source water) exhibited a few brief periods of biofilter performance decline, likely in association with seasonal fluctuations in source water quality (Figures 3-2 through 3-4). Seasonal water quality changes, including those in DOM, in the Grand River have been well documented. In the summer, primary production is at its highest and discharge is at its lowest. During the fall, nutrient and dissolved oxygen concentrations shift (GRCA, 2021b; Cummings, 2015; Huck et al., 2000). For a relatively brief period, DOM in the Grand River is more allochthonous in the fall than in the summer, as indicated by DOC fractionation analyses by LC-OCD during the present study (Table B-5), and substantial increases in humic-like fluorescence/DOC and larger sizes of DOC molecules observed in other investigations (Hutchins, 2011). Higher DOC/DON ratios and lower protein content consistent with more allochthonous organic matter have also been observed during this period (Hutchins, 2011). Accordingly, it is not surprising that DOC removal by the biofilters was severely reduced during these brief periods (Figures 3-2 through 3-4) because a greater proportion of DOC is known to be less biodegradable during these transitional periods (Table B-5; Cummings, 2015; Hutchins, 2011; Huck et al., 2000). Although no significant changes in bulk water quality were observed during the present study, historical data and accounts including full-scale plant data corroborate reduced biological filtration performance during the fall "transitional" period (Camper et al., 2000; Emelko et al., 2006). Although biomass was not quantified herein because it is not directly indicative of biological activity (Urfer et al., 1997; Huck et al., 2000; Emelko et al., 2006), breakthrough of biopolymers during the return to baseline period following the four-day ash disturbance period (Tables B-1 through B-4) suggests the passage of extracellular polymeric substances from stressed or dead bacterial cells. Further evaluation of the source water quality and ecohydrological factors contributing to these periods of biofilter performance decline merits investigation but was beyond the scope of the present investigation. While these periods of biofilter performance decline did not preclude demonstration of biofilter resilience in buffering elevated source water DOM after wildfire, they did underscore the need to (i) further evaluate biofilter resilience during a variety of operational conditions, including periods of seasonal change in source water quality and (ii) develop watershed monitoring programs to better understand how shifts in source water quality affect drinking water treatability, especially in a changing climate.

UVA_{254} measurements complement LC-OCD analyses to provide additional insight into biodegradability of WEOM derived from wildfire ash used in the present study. UVA_{254} of the ash-amended source water consistently increased with higher contents of ash added (i.e., from low to high ash content, Figure 3-5), despite inconsistent increases in DOC with sequentially higher ash content (Figure 3-3). Relatively lower influent UVA_{254} during the 7-day ash disturbance relative to other ash-disturbance periods was expected given the lower baseline source water UVA_{254}. This good correlation of wildfire ash content with UVA_{254} (rather than DOC concentration) is consistent with previous wildfire ash studies (Skwaruk, 2021). As discussed above, LC-OCD analyses revealed that LMW neutrals and smaller amounts of humics by mass were added to source water with ash-amendment (Figure 3-4 A vs B; Tables B-1 through B-4). Since LMW neutrals do not contribute to UVA_{254} (Huber et al., 2011), the observed increase in UVA_{254} in ash-amended source waters is likely driven by the relatively small addition of humics. Humics are not typically well-removed by biofiltration (Pramanik et al., 2014; Chen et al., 2016; Peleato et al., 2017) since they are not readily biodegradable (Shin & Lim, 1996; Namour & Muller, 1998); thus, it is not surprising that average daily change in UVA_{254} measurements throughout the 50-day experiment was significantly lower in all biofilters treating ash-amended water relative to control biofilters ($p \leq 0.034$) and thus emphasizes the insights obtained from DOC characterization by fractionation.

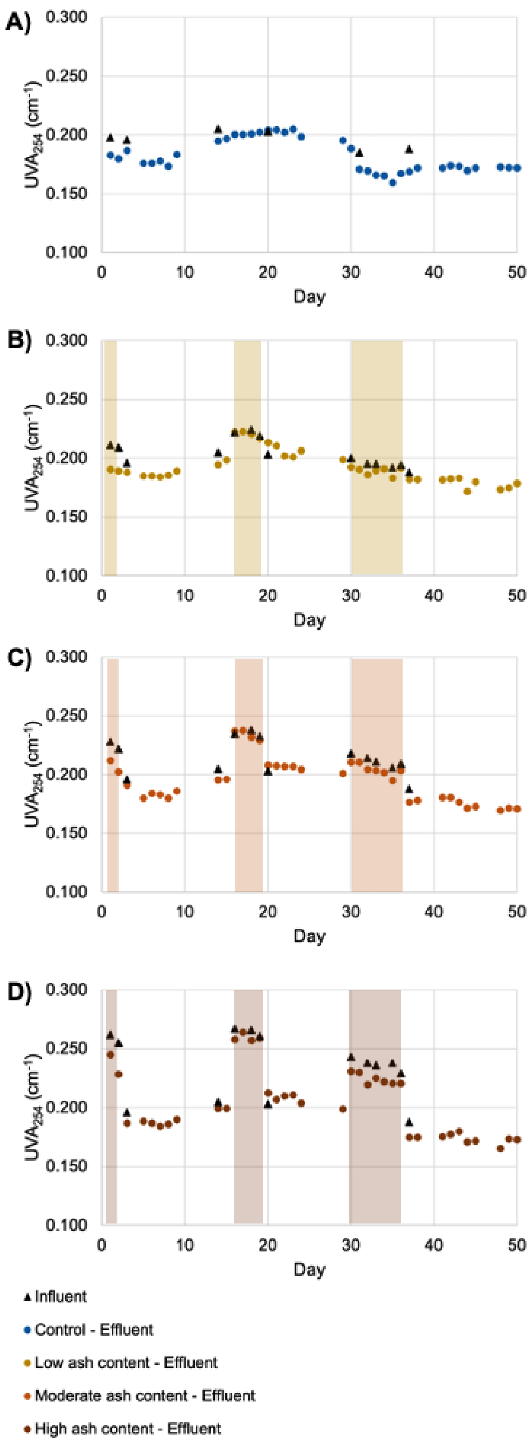


Figure 3-5 Daily change in UVA_{254} measurements across biofilters treating (A) control and (B) low, (C) moderate, and (D) high wildfire ash content source water. Vertical shaded regions indicate when ash-amended source water was fed to filters.

Collectively, the UVA_{254} and the DOC concentration and fractionation data provide a proof-of-concept demonstration that is supported by mechanistic insights regarding wildland fire ash-associated changes to DOM character that enable reductions in DOM by biofiltration. These results can likely be extended beyond SSF configurations (i.e., those with extended contact times) to other biological filtration processes with shorter contact times because it has been widely shown that most removal of DOC occurs at the top of the filter media (Emelko et al., 2006; Basu et al., 2016), corresponding to shorter contact times. The importance of contact time (typically reflected as EBCT) for DOC removal in biological filtration processes has been well-documented at relatively short timescales (i.e., minutes) (Basu et al., 2016). It is unlikely that extended contact times would result in enhanced DOC removal, as less readily biodegradable DOC is also less likely to be removed by biofiltration (Hozalski et al., 1999; Leenheer & Croue, 2003; So et al., 2017), regardless of contact time. Notably, the extended contact time of 10 hours employed herein did not improve removal of aromatic or humic substances relative to their removal in more typical biofiltration configurations (with contact times ranging from 10-30 minutes) (Pharand et al., 2014; Basu et al., 2016; So et al., 2017). Increased EBCT is not likely to further enhance DOC removal of elevated, wildfire ash-associated WEOM because (i) only the biodegradable fractions of DOC are removed by biological filtration and (ii) it is the removal of those fractions that was reflected in biofilter buffering of elevated source water DOM leached from wildland fire ash. Thus, this work suggests that implementation of biological filtration processes for enhanced NOM removal or as climate change adaptation strategies is not advisable in situations where NOM is especially aromatic or largely comprised of humic substances unless it is preceded by coagulation optimized for NOM removal or oxidation by ozonation for increased biodegradability (and subsequent removal by biofiltration). Additionally, brief periods of decline in biofilter performance observed herein underscore that there can be periods in which source water DOM is less biodegradable (Huck et al., 2000; Hutchins, 2011; Cummings, 2015). Overall, this work underscores the need for improved aquatic carbon characterization in response to increasing climate- exacerbated landscape disturbances and integration of that understanding into treatment prioritization and design. Further research is also needed to evaluate water treatment by biological filtration of source water impacted by ash rich in heavy metals such as mercury that may lead to elevated concentrations in impacted receiving waters (Kelly et al., 2006; Emelko et al., 2011) and possibly inhibit biological activity (Sadler & Trudinger, 1967), thereby compromising biofilter performance. Such evaluation was beyond the scope of the present investigation.

3.6 Conclusions

Overall, this investigation demonstrated that biological filtration processes offer resilience in buffering elevated source water DOM after wildfire. Notably, all of the biofilters (regardless of ash amendment to the baseline source water) exhibited brief periods of biofilter performance decline, likely in association with seasonal fluctuations in source water quality, not ash delivery to the source water matrix. While these periods of biofilter performance decline did not preclude demonstration of biofilter resilience in buffering elevated source water DOM after wildfire, they did underscore the need to (i) further evaluate biofilter resilience during a variety of operational conditions, including periods of seasonal change in source water quality and (ii) develop watershed monitoring programs to better understand how shifts in source water quality affect drinking water treatability, especially in a changing climate.

UVA_{254} measurements and LC-OCD analyses revealed that WEOM derived from ash resulted in increased relative mass of LMW neutrals and, to a lesser degree, humics fractions in ash-amended source waters. There was evidence of increased DOC removal in biofilters treating wildfire ash-impacted water relative to the control biofilters during the two-day ash disturbance period, although this observation was weak or absent during other disturbance periods when DOC removal was impaired in all biofilters. LC-OCD analyses revealed that the enhanced DOC removal was likely attributable to the greater proportion of readily biodegradable LMW neutrals comprising WEOM in wildfire ash-impacted filter influent streams compared to control biofilters treating only baseline source water. UVA_{254} measurements and LC-OCD analyses revealed that humics, which are a main driver of UVA_{254} (Huber et al., 2011), were less effectively removed by biofilters treating ash-amended water relative to control biofilters. These observations highlight the importance of DOC characterization when evaluating biological filtration resilience in buffering elevated source water DOM, especially given that more aromatic DOM tends to result in greater formation of regulated DBPs (Singer, 1999; Hua et al., 2015). They also suggest that resilience of biological filtration may be compromised if the balance between readily removed and recalcitrant fractions of DOM change, as was observed when baseline source water quality fluctuated for brief periods during the investigation.

Chapter 4
Conclusions, implications, and recommendations

4.1 Conclusions

The goal of this research was to advance the development of drinking water treatment and climate change adaptation strategies for the water industry broadly, but also with consideration of the challenges faced by small drinking water systems specifically. Thus, the specific focus of this research was biofiltration-based "green" technologies as techno-ecological NBS that have the potential to offer treatment resilience without high operational demand. The key conclusions of this work are:

1. While the concept of green technology is widely recognized, its meaning varies considerably. In the water industry, green technology can be described by four main attributes: natural resource-basis, energy consumption, waste production, and footprint.

   The greenness of a technology can be evaluated with respect to each of the above-mentioned attributes and is therefore relative to both the environmental setting and the other technologies to which it is being compared. In the water sector, environmental setting (i.e., location-specific factors including hydroclimate, sensitive habitat(s), water quality, temperature, etc.) is a critical consideration that can limit the practical application of some technologies. Prioritization of the factors contributing to technology greenness varies based on sociocultural considerations of individuals, groups, and communities, as identified based on their collective knowledge, values, attitudes, beliefs, feelings, and behaviours. The framework developed herein enables an accurate and transparent description of the "green" attributes of technology—including green infrastructure—used in the water industry. It differentiates technology "greenness" by relatively examining key attributes that may cause environmental impacts across the technology's life cycle through the lens of the environmental setting in which it is applied.

2. Technologies must be (i) fit-for-purpose with respect to their use and (ii) meet regulated performance targets regardless of their greenness because the paramount objective of drinking water treatment is the protection of public health.

This perspective on “fit-for-purpose” treatment is obvious, but has not yet been described in the context of “fitting” drinking water treatment technologies with how they are intended to be used and the goals they are intended to meet.

3. Operational control is often reduced as the greenness of a technology is increased.

4. Biofiltration processes are arguably the most obvious and effective examples of underutilized green technology opportunities in the drinking water industry. These technologies can be differentiated along a spectrum of greenness.

5. Biological filtration is resilient to wildfire ash-associated organic carbon threats to drinking water treatment. This is supported by several key observations:
    - DOC removal across all biofilters receiving both ash-amended source water and control source water (i.e., not amended with ash) was generally consistent, suggesting that the wildfire ash and associated WEOM it released to the water matrix did not reduce the DOC biodegradation capacity of the biofilters.
    - The biofilters promptly recovered from “shock loads” associated with wildland fire ash delivery to source water and did not exhibit long-lasting DOC removal performance impacts as a result of the rapid change in source water quality that included increased influent DOC concentrations relative to baseline source water quality.
    - There was some evidence of increased DOC removal in biofilters treating wildfire ash-impacted water relative to the control biofilters during periods of ash disturbance in which DOC removal performance was not impaired, although this observation was weak or absent during disturbance periods during which DOC removal was impaired in all biofilters. LC-OCD analysis revealed that the enhanced DOC removal was likely attributable to the greater proportion of readily biodegradable LMW neutrals comprising WEOM in wildfire ash-impacted filter influent streams compared to control biofilters treating only baseline source water.

6. Biological filtration may not be resilient to other types of source water quality fluctuations. Evidence for this in the present study include:

- All of the biofilters (regardless of ash amendment to the baseline source water) exhibited brief periods of biofilter performance decline, likely in association with seasonal fluctuations in source water quality.
- For a brief period immediately after the return to baseline source water after the two-day period of ash amendment, DOC removal was high in all of the biofilters but significantly lower in the biofilters treating high ash content-impacted water than in control biofilters—this type of performance difference was not observed after the other experiments involving ash addition to the source water. These data may suggest that while the biofilters are adjusting from high nutrient (i.e., LMW neutral DOC) availability to lower availability, biofilters may release some DOC while communities adjust to these shifts.
- UVA_{254} measurements and LC-OCD analyses revealed that humics, which contribute to UVA_{254}, were less effectively removed by biofilters treating ash-amended water relative to control biofilters. Resilience of biological filtration to wildfire ash-impacts are thus dependent on both the concentration and character of WEOM derived from ash material.

4.2 Implications & Recommendations

1. The green technology framework developed in Chapter 2 can contribute to the development of more comprehensive techno-ecological NBS by providing a clear and accurate description of the ‘green’ attributes of technology options for the water industry, as well as a framework for their relative comparison, thereby facilitating techno-ecological decision-making that strives to address diverse stakeholder priorities.

2. Biological filtration can be an attractive alternative to conventional treatment, especially for small systems, since it is less operationally demanding and more cost-effective compared to conventional treatment technologies because of its lower energy demand and reduced or eliminated need for chemical pre-treatment (Brown et al., 2015).

3. Roughing filtration can be an effective pre-treatment for turbidity reduction following wildfire-ash disturbance to source water and can be especially beneficial for small systems due to its simplicity and low cost.

4. Although the importance of contact time (typically reflected as EBCT) for DOC removal in biological filtration processes has been well-documented at relatively short timescales (i.e., minutes) (Basu et al., 2016), the data reported herein are consistent with those insights and indicate that extended EBCTs (i.e., on the scale of hours) are not likely to further enhance DOC removal of elevated, wildfire ash-associated WEOM because (i) only the biodegradable fractions of DOC are removed by biological filtration and (ii) it is the removal of those fractions that is largely reflected in biofilter buffering of elevated source water DOM after wildfire. Given this observation, EBCTs as typical with SSF (i.e., on the scale of hours) may possibly be shortened to increase yield, although further investigation is necessary.

5. Periods of biofilter performance decline during experiments in Chapter 3 underscored the need to (i) further evaluate biofilter resilience during a variety of operational conditions, including periods of seasonal change in source water quality and (ii) develop watershed monitoring programs to better understand how shifts in source water quality affect drinking water treatability, especially in a changing climate.

6. Evaluation of resilience of biological filtration in buffering elevated source water DOM must include DOC characterization, as UVA_{254} measurements and LC-OCD analyses revealed that WEOM derived from ash resulted in increases of various DOM components, which were not equally removed by biofilters. Additionally, these observations also highlight that biofiltration may not always be resilient to wildfire disturbance impacts on the natural landscape, depending on both the concentration and character of WEOM derived from ash material, and how these materials might be altered in the natural environment before entering a DWTP. Not only is DOM characterization important for evaluating the effectiveness of biofiltration to treatment of wildfire-impacted source water, but it can also provide insight on the potential formation of regulated DBPs.

7. While treatment technology greenness was maximized with the design of bench-scale biofilters investigated in Chapter 3, brief periods of unanticipated DOC removal impairment throughout the experiment highlighted that biological treatment technologies are not always reliable, especially when they are accompanied by limited or no operational control. Water providers must therefore transparently assess the trade-offs between aspects of greenness that customers and water providers value, and operational control of any treatment technology, including techno-ecological NBS. These considerations are system specific.

8. While recognition that technologies must be fit-for-purpose with respect to their use and meet regulated performance targets regardless of their greenness because the paramount objective of drinking water treatment is the protection of public health may seem obvious to the drinking water industry, it is nonetheless critical to state because global enthusiasm for the development of NBS for managing climate change-associated threats to water supplies is rapidly growing (Cohen-Shacham et al., 2016; O'Sullivan et al., 2020; Oral et al., 2020). While the experimental work in Chapter 3 provides concrete evidence that this zeal may be warranted in some cases, it also emphasizes that—especially for the provision of safe drinking water—NBS, like any other drinking water treatment technologies, cannot be implemented in absence of performance monitoring technology and associated establishment of operational protocols. Thus, the collective implications of Chapters 2 and 3 of this thesis research for the water industry are that approaches that are exclusively nature-based are insufficient for the water industry. Instead, the water industry should communicate and advocate for the need for techno-ecological NBS and associated operational strategies and tools (including those for performance monitoring) to ensure the protection of public health through the provision of safe drinking water.

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Appendix A

Chapter 3: Ash amended water quality prior to pre-treatment

Table A - 1 Water quality of ash-amended water for each after 18 hours of mixing and three hours of settling during each ash disturbance period

Ash disturbance period	Severity of ash amendment	Turbidity (NTU)	pH	Alkalinity (mg/L $CaCO_3$)	UVA_{254} (cm^{-1})	DOC (mg/L)	SUVA (L/mg-M)
Two-day	Low ash content	15.2	8.7	Not recorded	0.216	8.98	2.41
	Moderate ash content	31.4	8.7	Not recorded	0.234	9.35	2.50
	High ash content	56.9	8.7	Not recorded	0.270	9.28	2.91
Four-day	Low ash content	18.0	8.7	285	0.223	9.19	2.43
	Moderate ash content	30.2	8.7	285	0.237	8.98	2.64
	High ash content	58.6	8.6	275	0.271	9.94	2.73
Seven-day	Low ash content	16.6	8.7	286	0.199	8.16	2.44
	Moderate ash content	25.3	8.7	245	0.214	8.85	2.42
	High ash content	49.0	8.7	265	0.248	9.66	2.57

Appendix B

Chapter 3: Additional water quality analyses

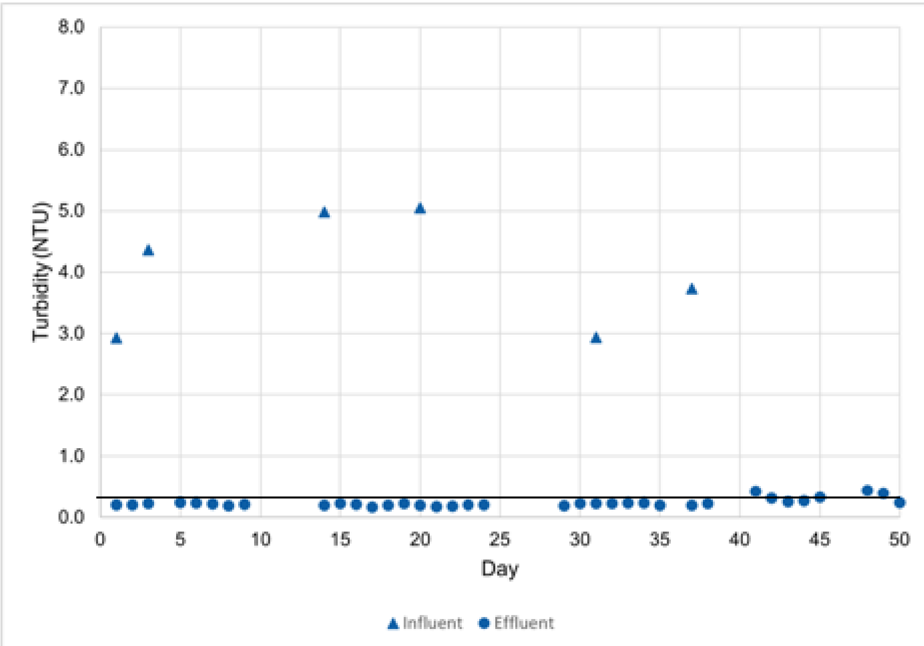

Figure B- 1 Influent and effluent turbidity, Biofilter #1 (control)

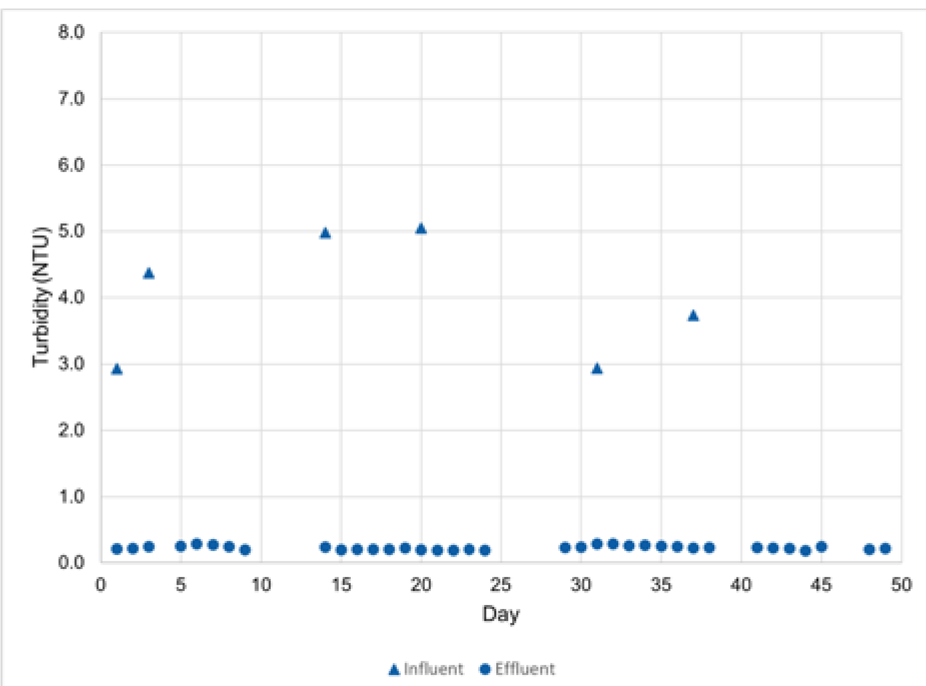

Figure B- 2 Influent and effluent turbidity, Biofilter #2 (control)

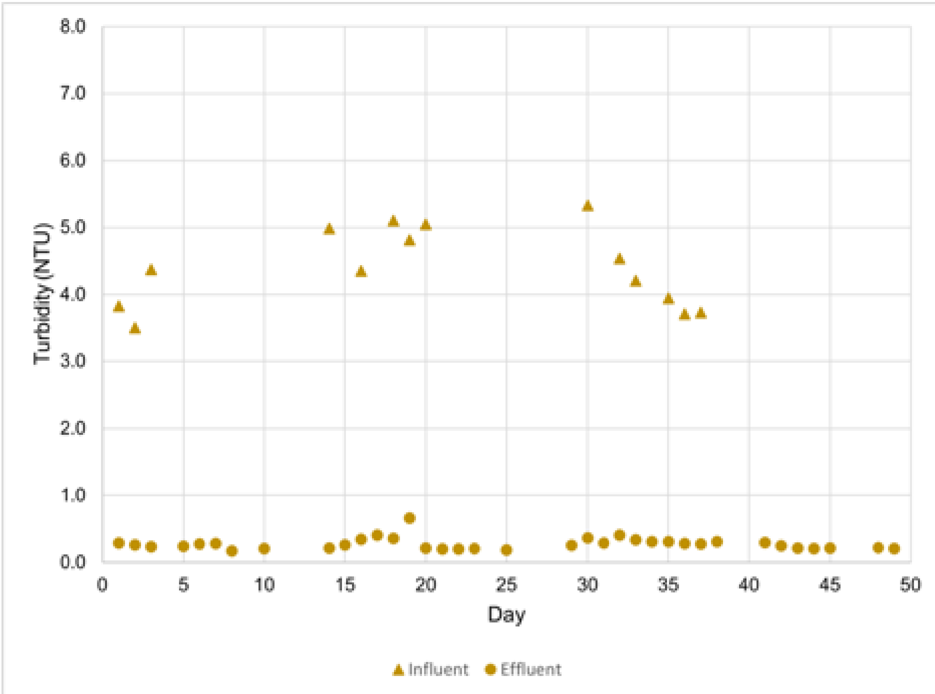

Figure B- 3 Influent and effluent turbidity, Biofilter #3 (treating low ash content water)

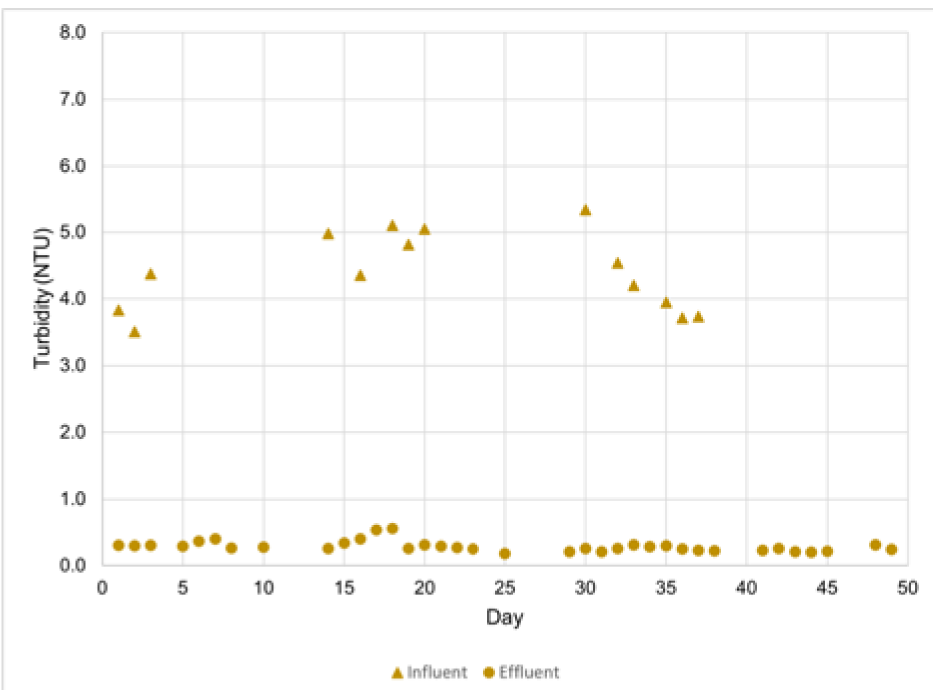

Figure B- 4 Influent and effluent turbidity, Biofilter #4 (treating low ash content water)

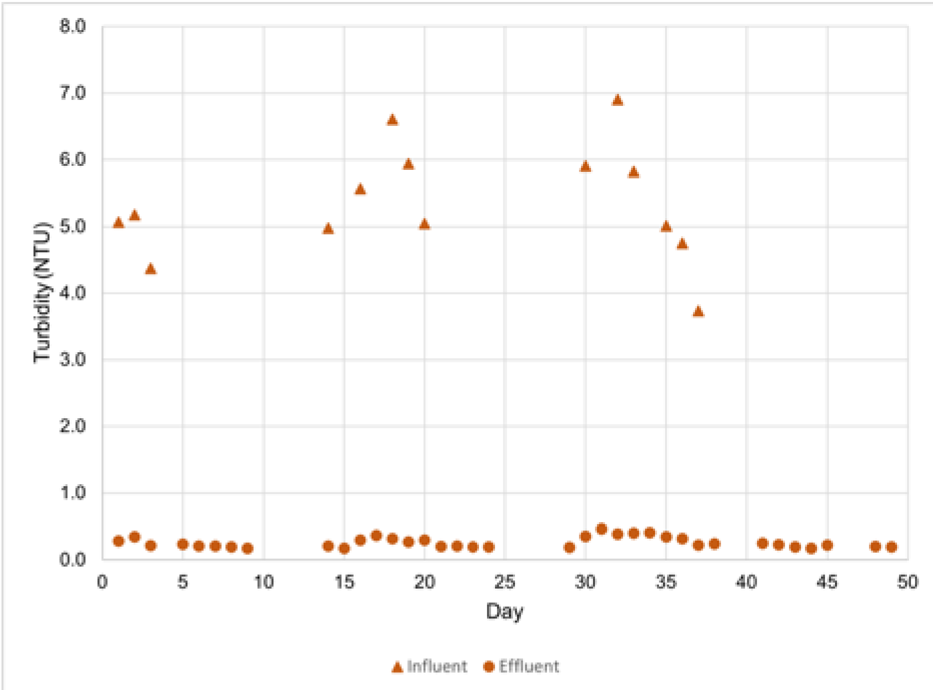

Figure B- 5 Influent and effluent turbidity, Biofilter #5 (treating moderate ash content water)

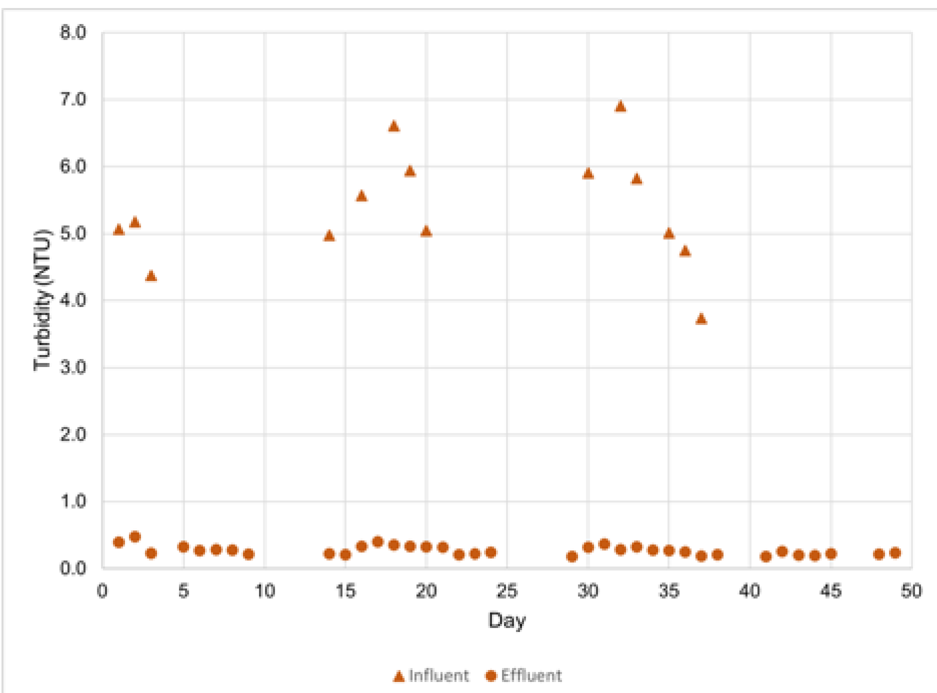

Figure B- 6 Influent and effluent turbidity, Biofilter #6 (treating moderate ash content water)

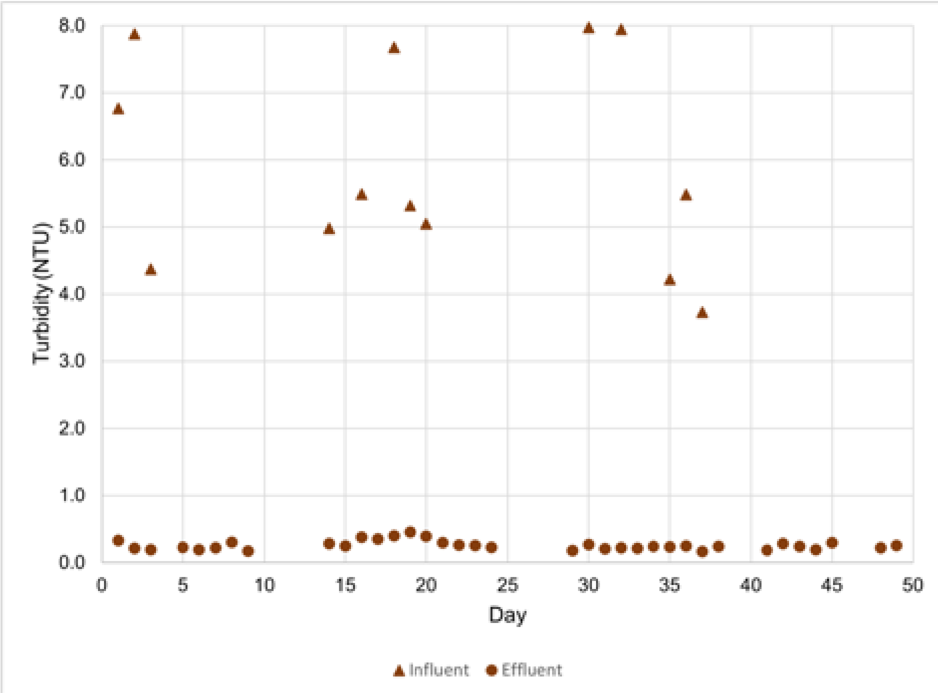

Figure B- 7 Influent and effluent turbidity, Biofilter #7 (treating high ash content water)

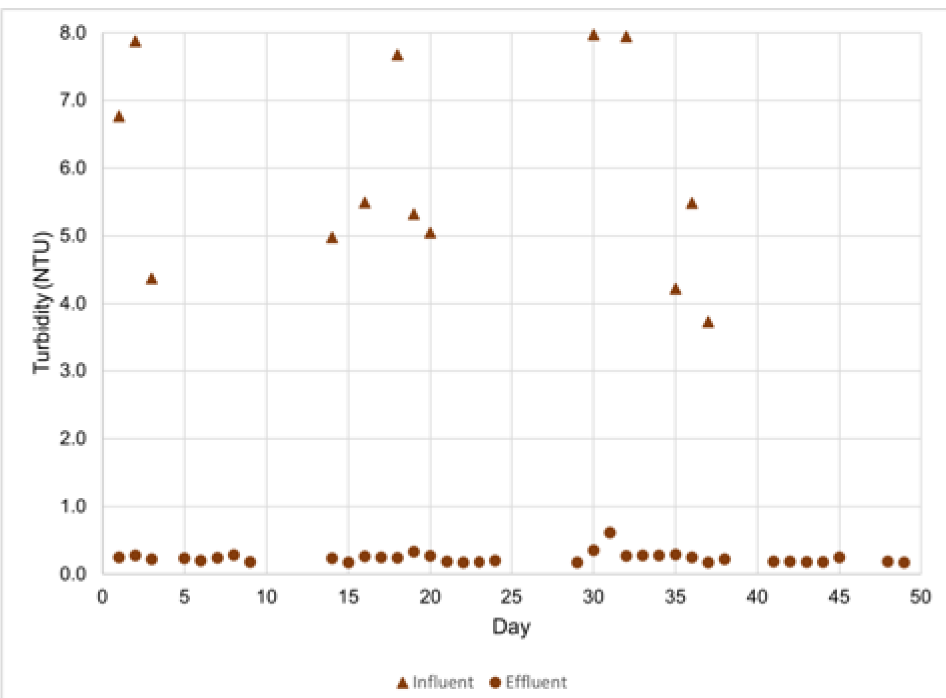

Figure B- 8 Influent and effluent turbidity, Biofilter #8 (treating high content ash water)

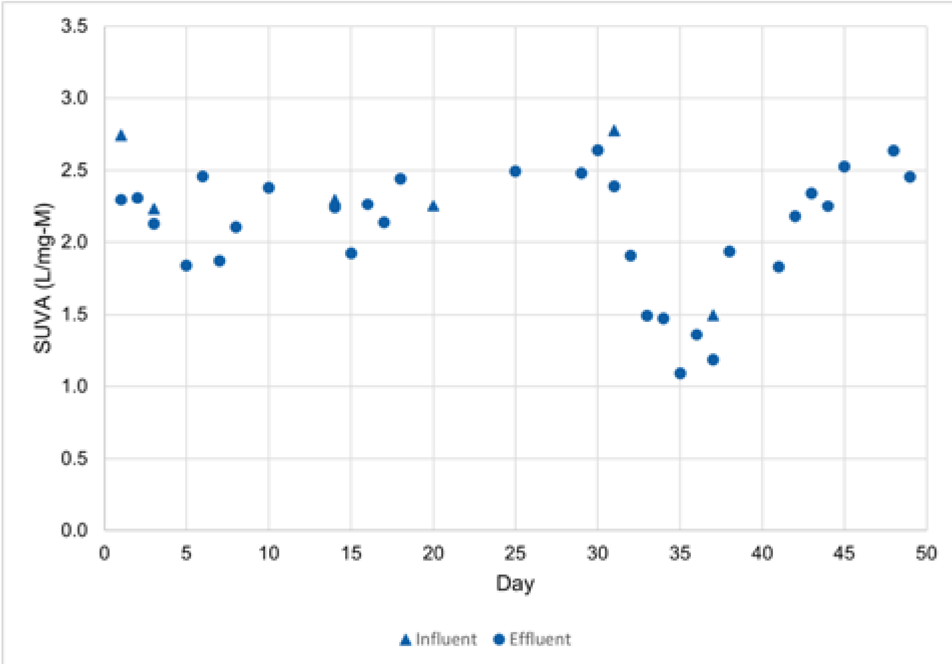

Figure B- 9 Influent and effluent SUVA, Biofilter #1 (control)

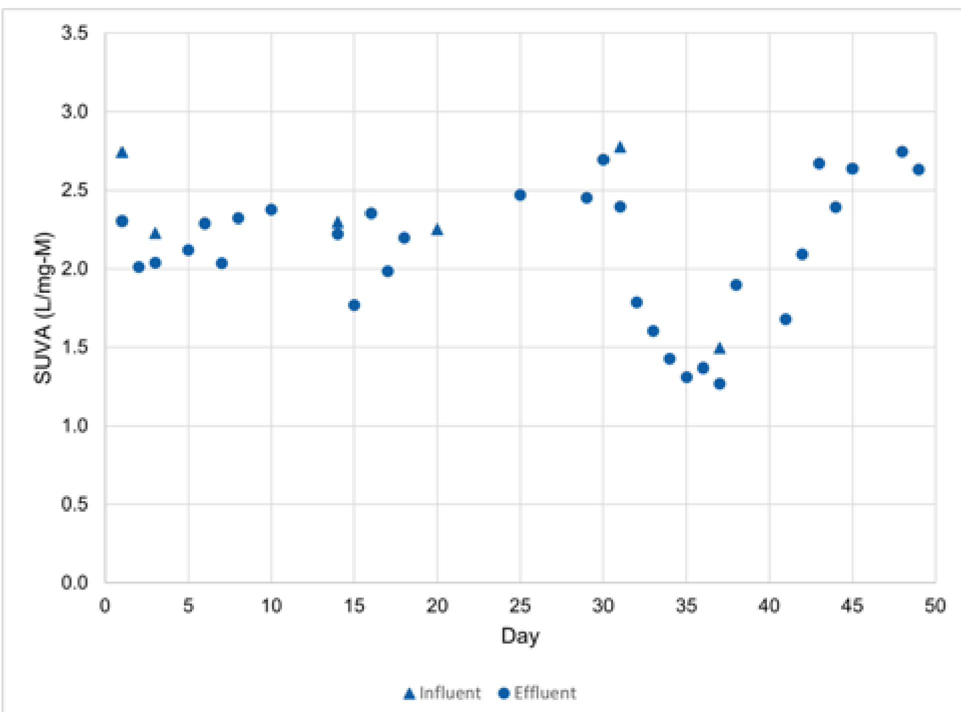

Figure B- 10 Influent and effluent SUVA, Biofilter #2 (control)

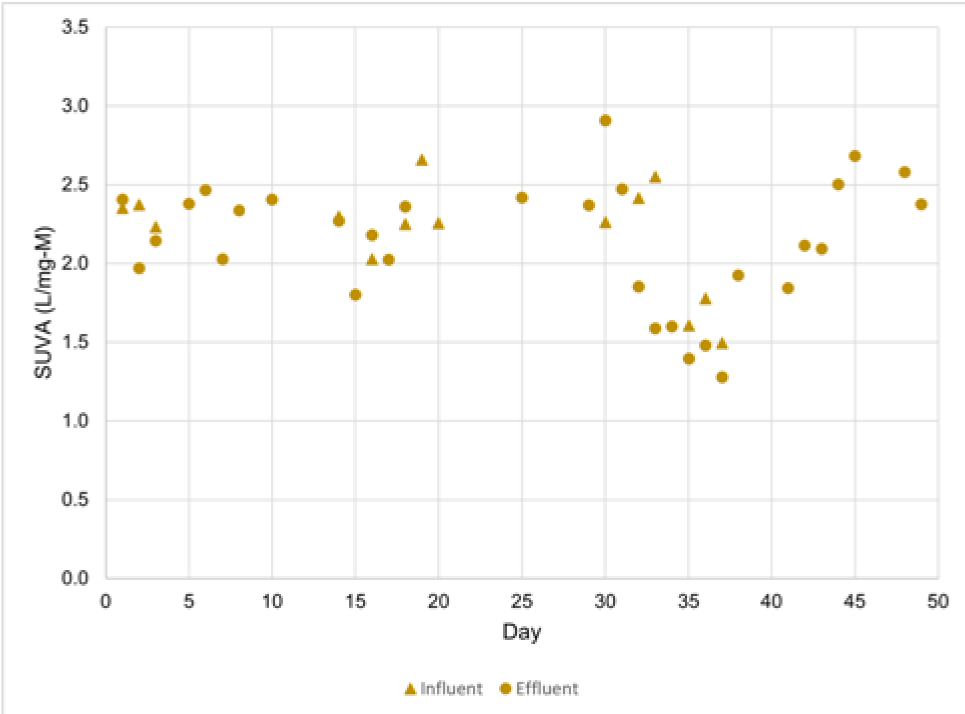

Figure B- 11 Influent and effluent SUVA, Biofilter #3 (treating low ash content water)

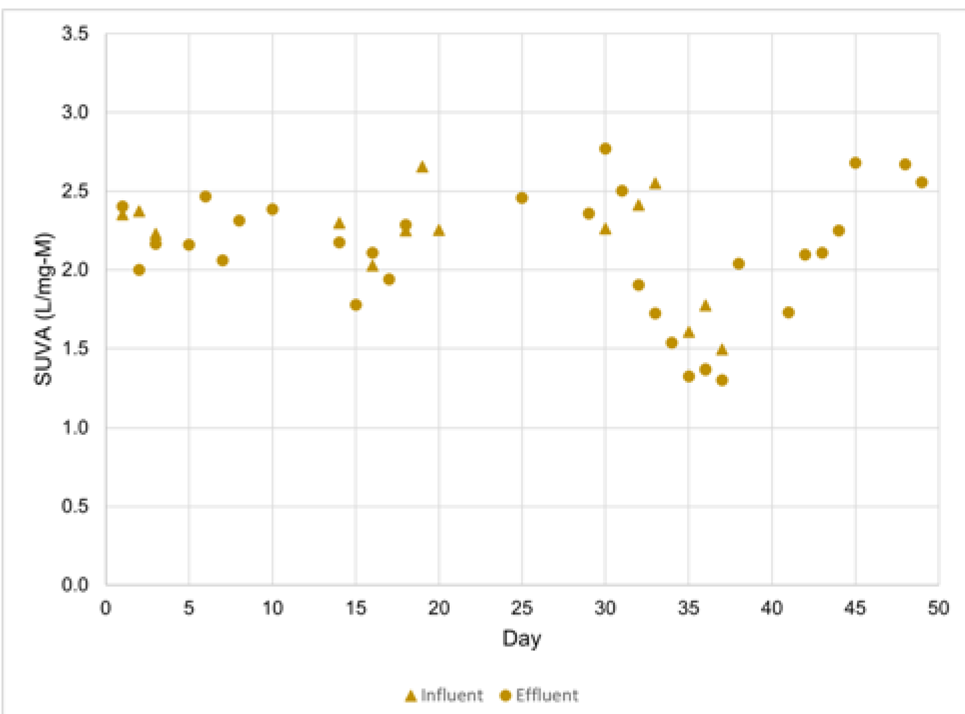

Figure B- 12 Influent and effluent SUVA, Biofilter #4 (treating low ash content water)

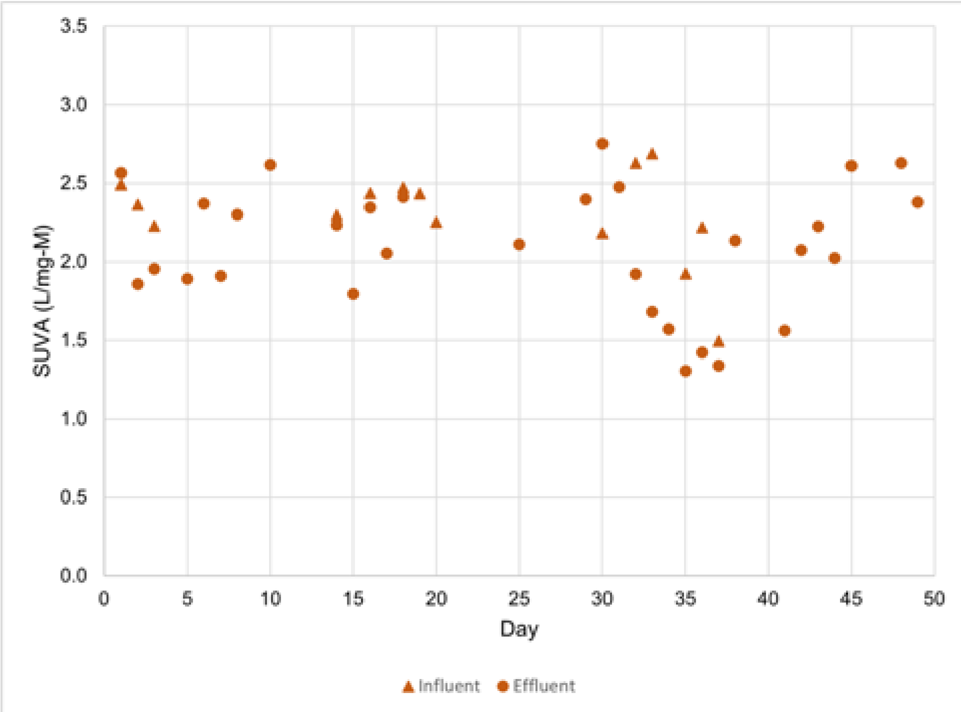

Figure B- 13 Influent and effluent SUVA, Biofilter #5 (treating moderate ash content water)

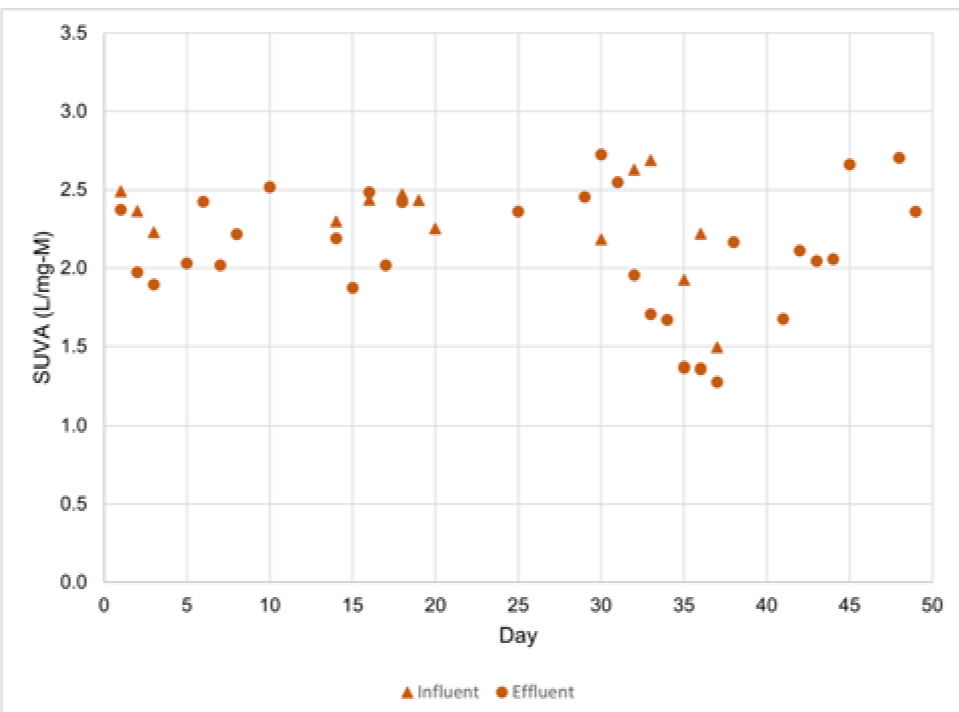

Figure B- 14 Influent and effluent SUVA, Biofilter #6 (treating moderate ash content water)

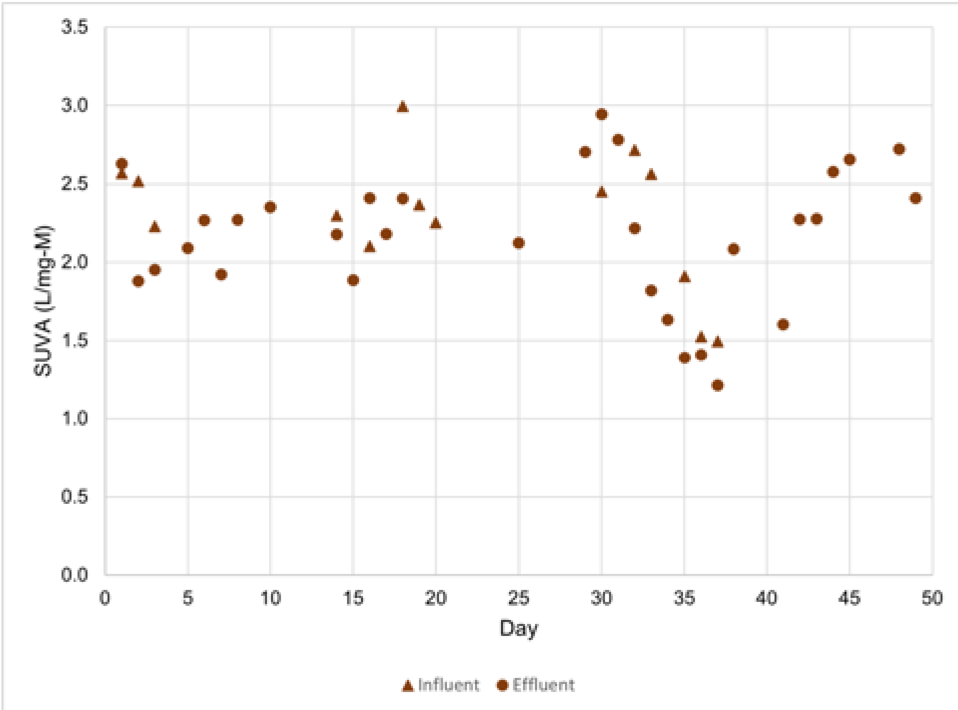

Figure B- 15 Influent and effluent SUVA, Biofilter #7 (treating high ash content water)

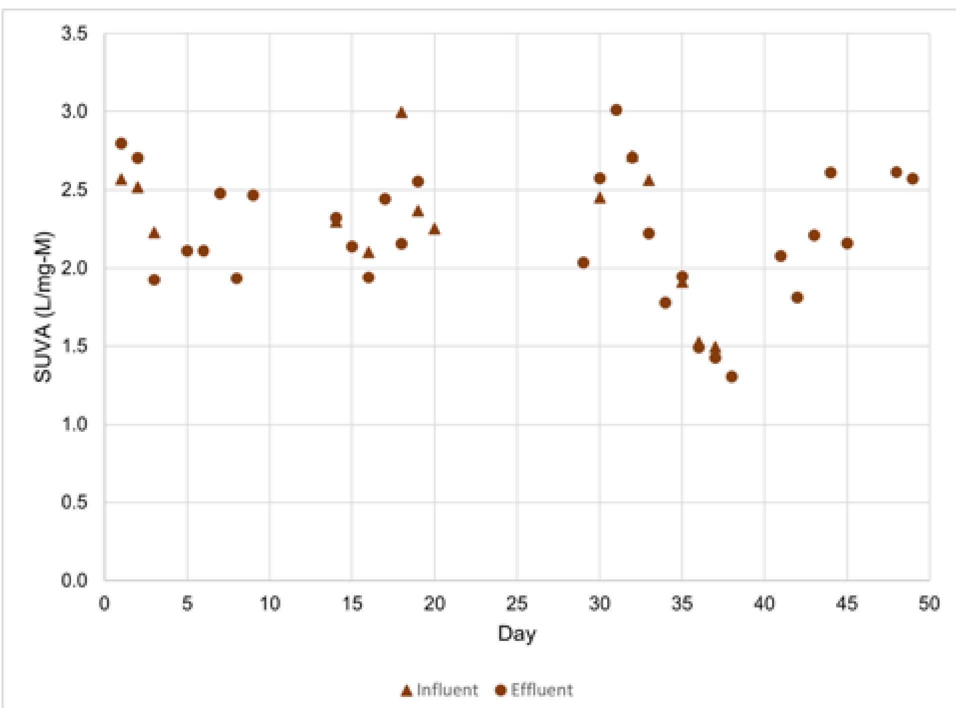

Figure B- 16 Influent and effluent SUVA, Biofilter #8 (treating high ash content water)

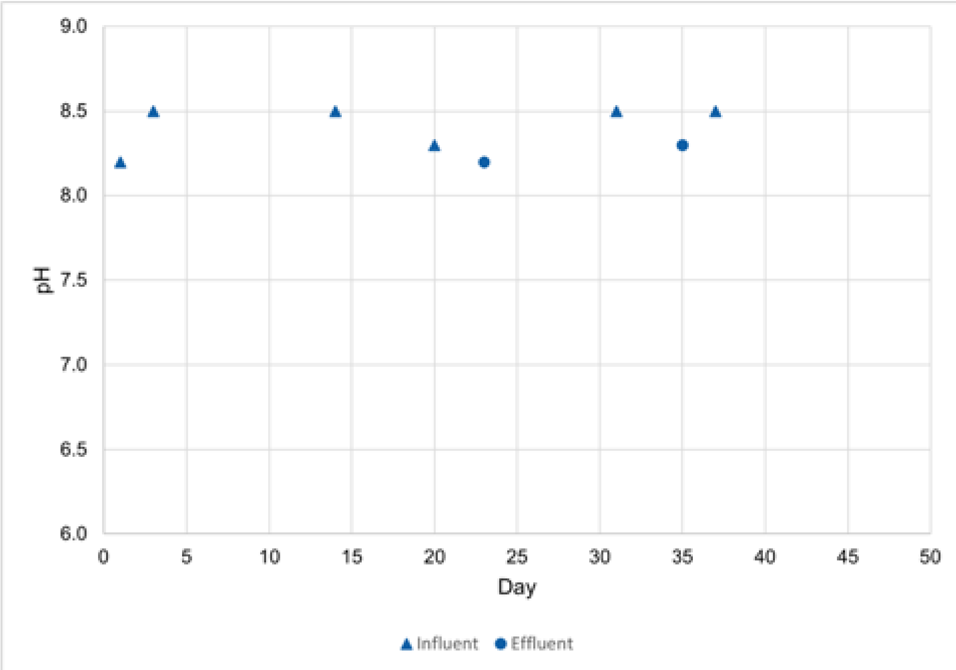

Figure B- 17 Influent and effluent pH, Biofilter #1 (control)

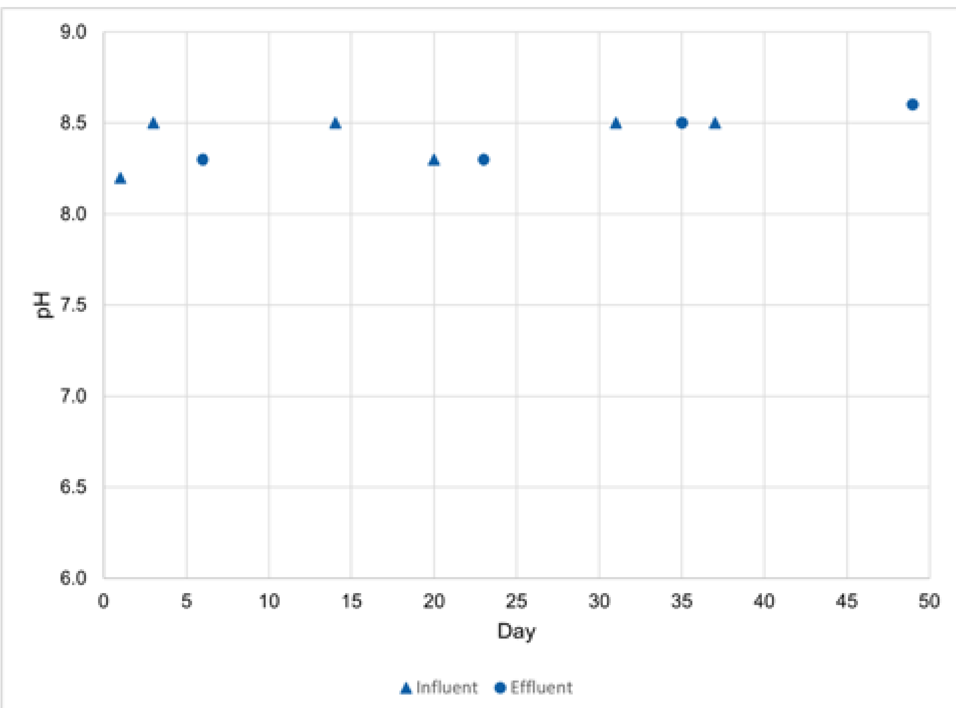

Figure B- 18 Influent and effluent pH, Biofilter #2 (control)

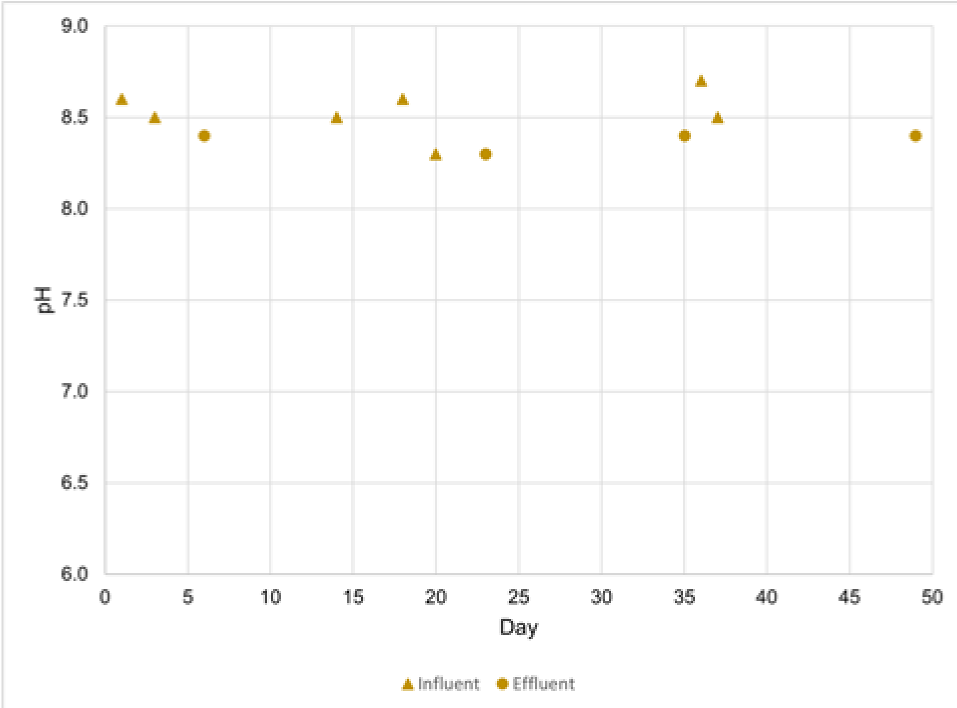

Figure B- 19 Influent and effluent pH, Biofilter #3 (treating low ash content water)

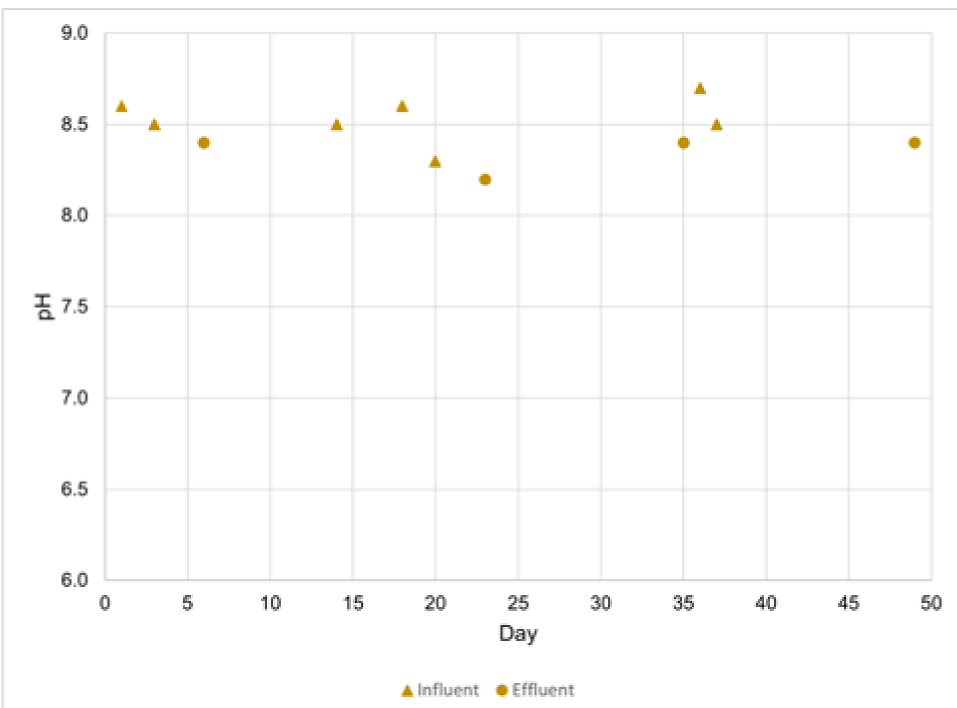

Figure B- 20 Influent and effluent pH, Biofilter #4 (treating low ash content water)

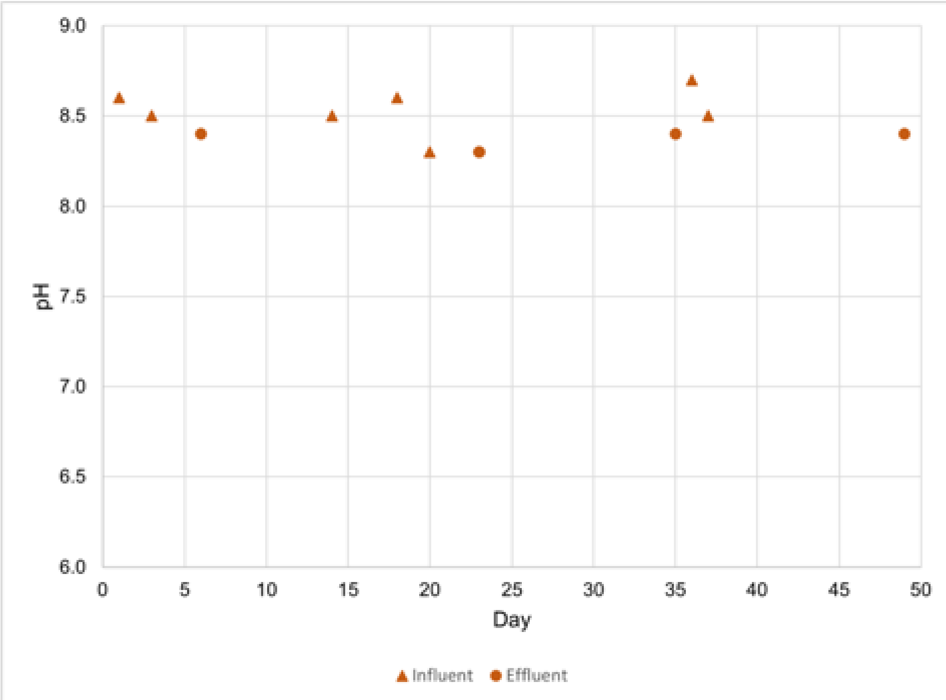

Figure B- 21 Influent and effluent pH, Biofilter #5 (treating moderate ash content water)

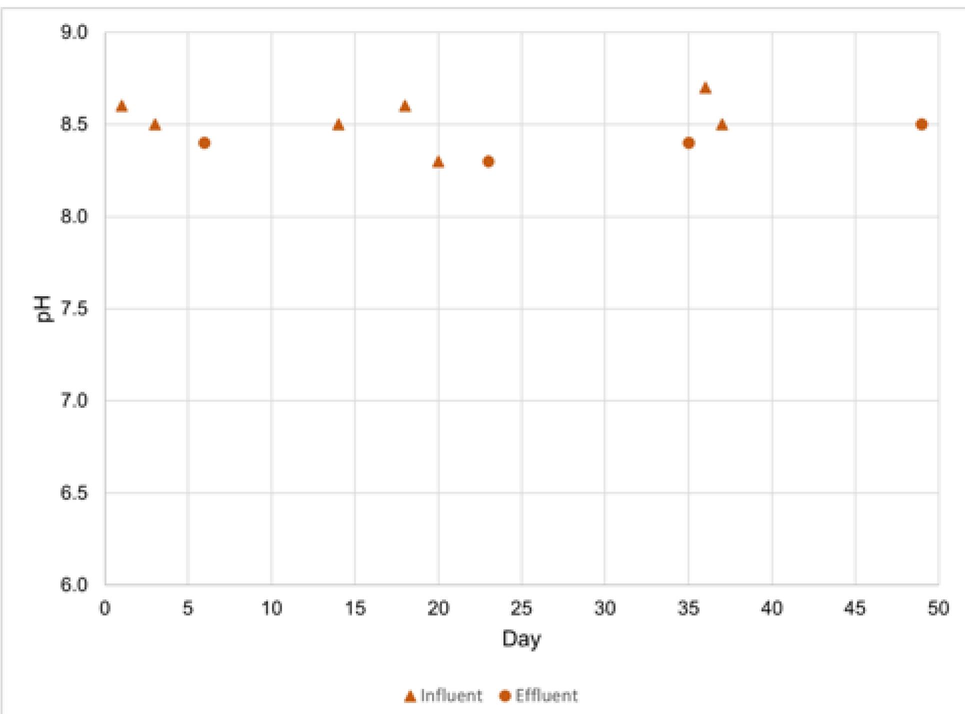

Figure B- 22 Influent and effluent pH, Biofilter #6 (treating moderate ash content water)

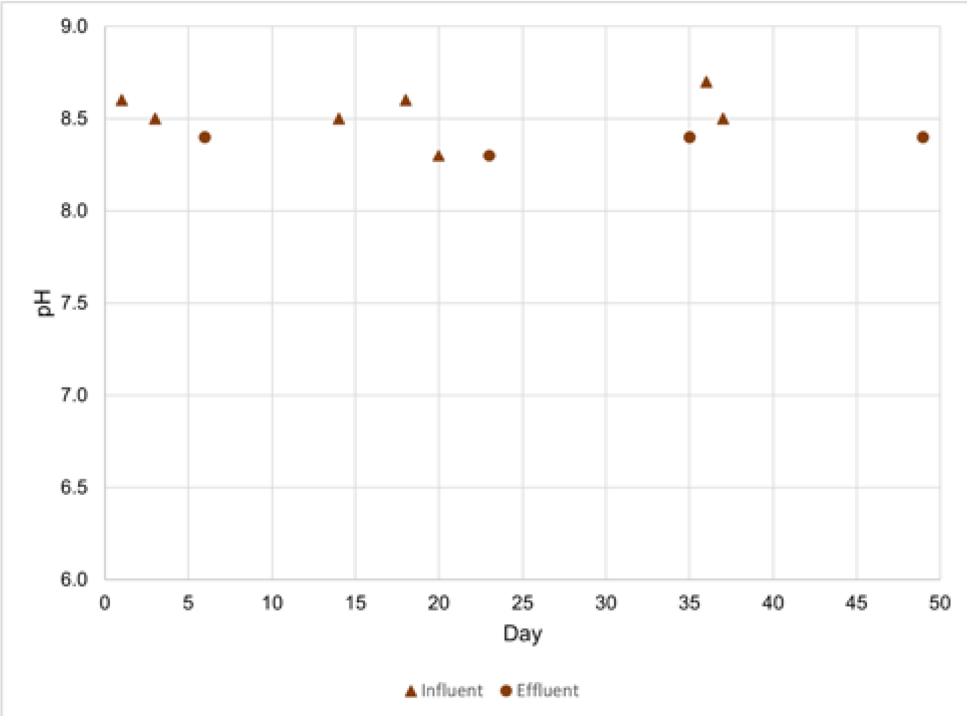

Figure B- 23 Influent and effluent pH, Biofilter #7 (treating high ash content water)

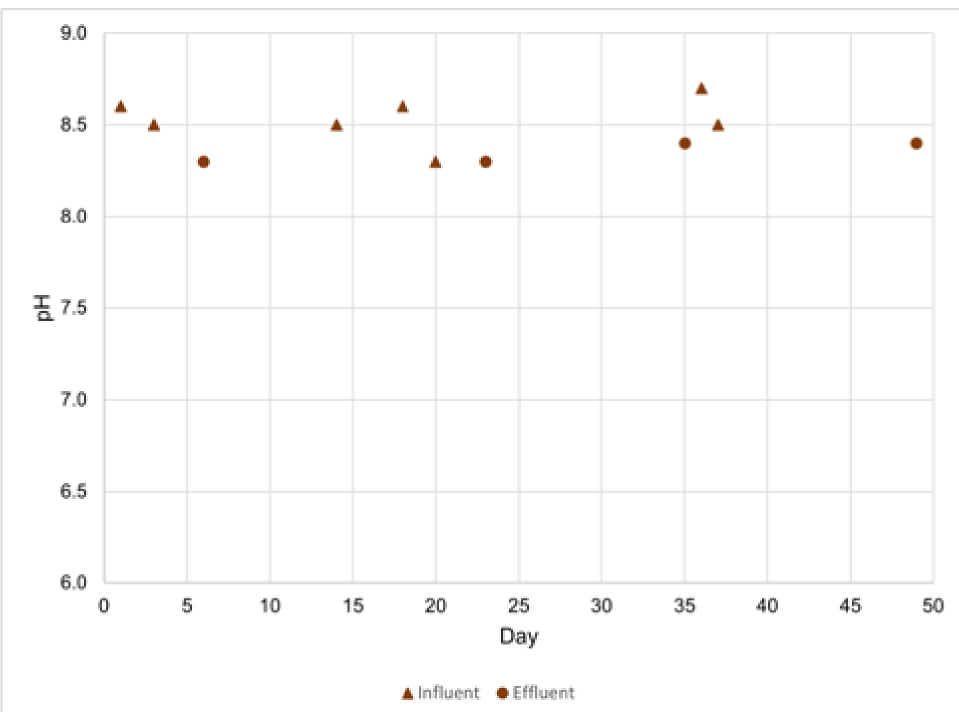

Figure B- 24 Influent and effluent pH, Biofilter #8 (treating high ash content water)

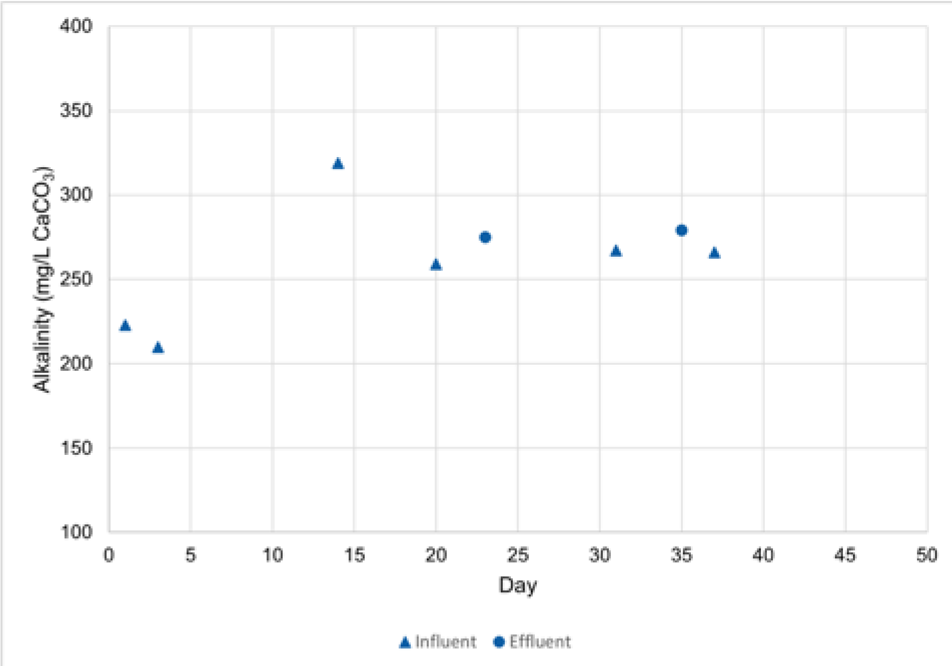

Figure B- 25 Influent and effluent alkalinity, Biofilter #1 (control)

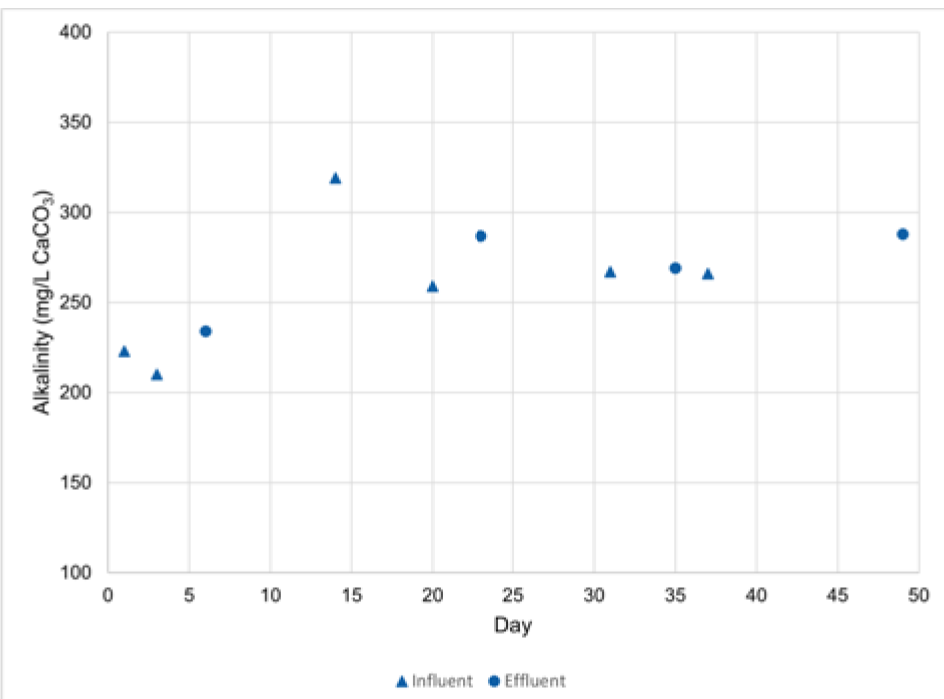

Figure B- 26 Influent and effluent alkalinity, Biofilter #2 (control)

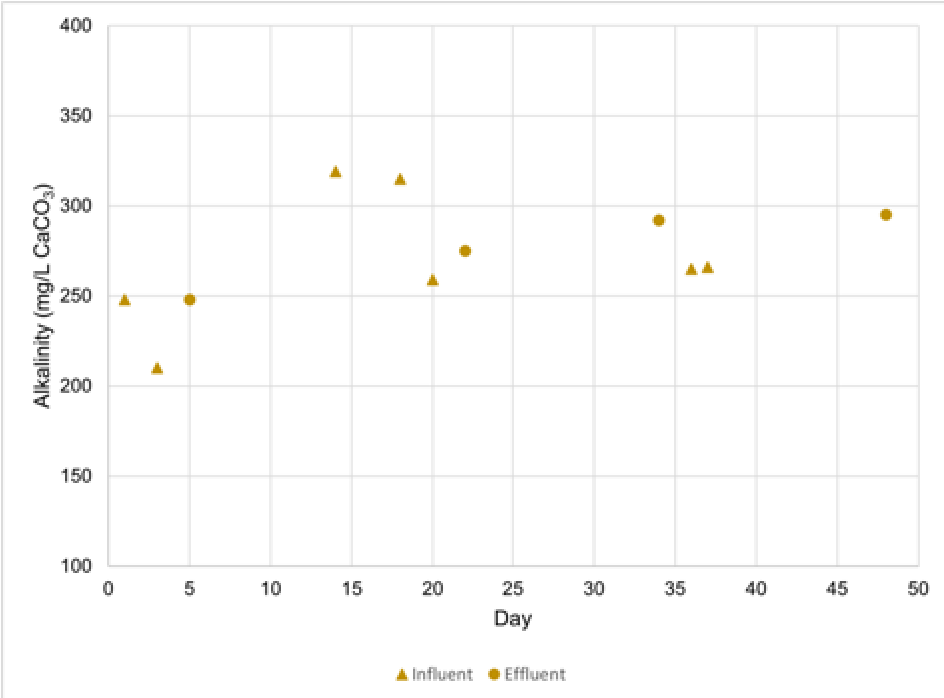

Figure B- 27 Influent and effluent alkalinity, Biofilter #3 (treating low ash content water)

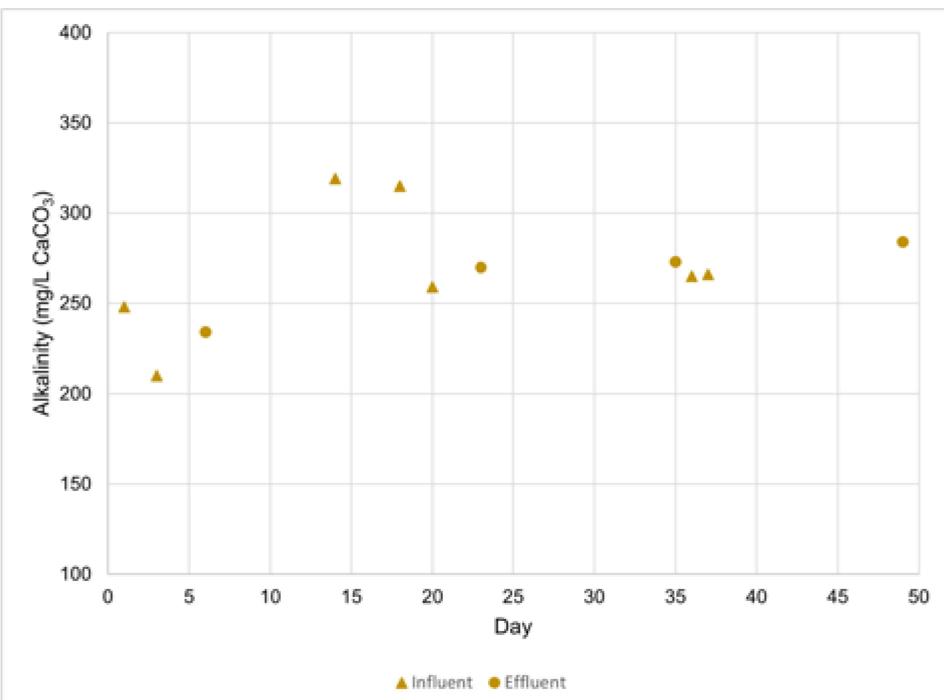

Figure B- 28 Influent and effluent alkalinity, Biofilter #4 (treating low ash content water)

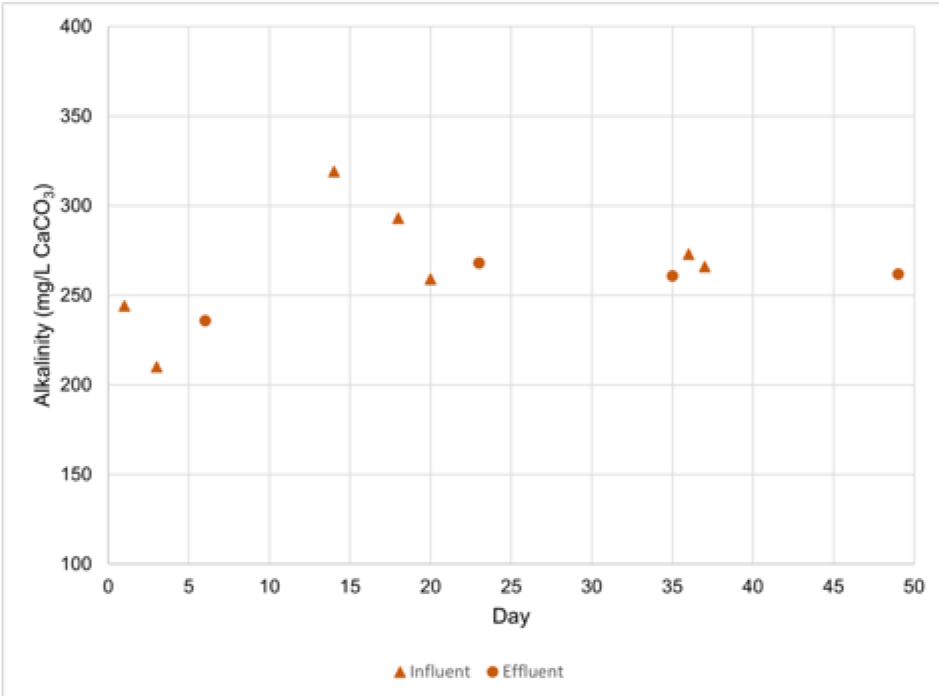

Figure B- 29 Influent and effluent alkalinity, Biofilter #5 (treating moderate ash content water)

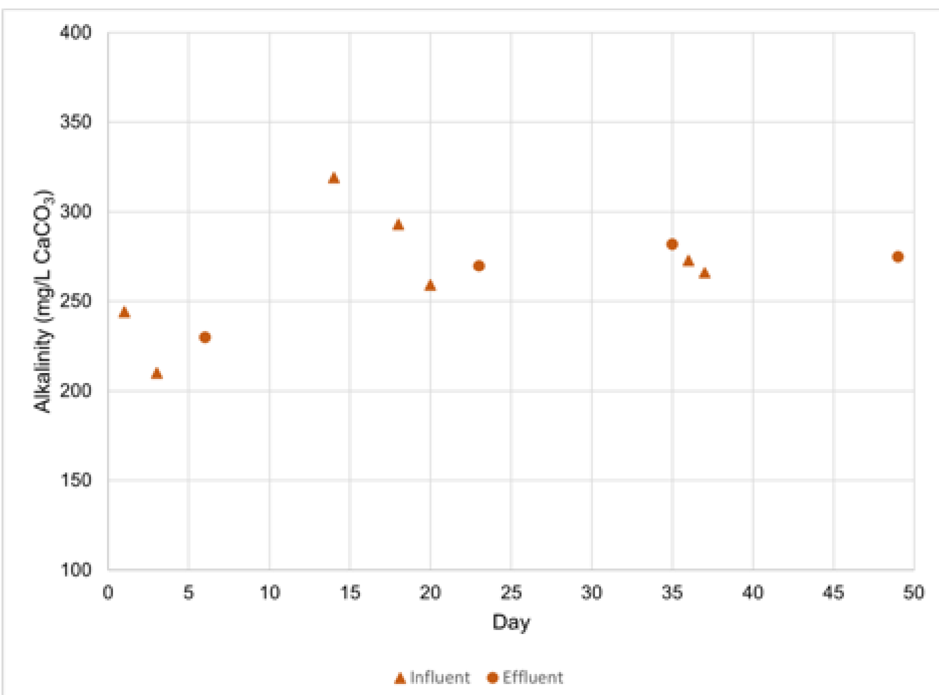

Figure B- 30 Influent and effluent alkalinity, Biofilter #6 (treating moderate ash content water)

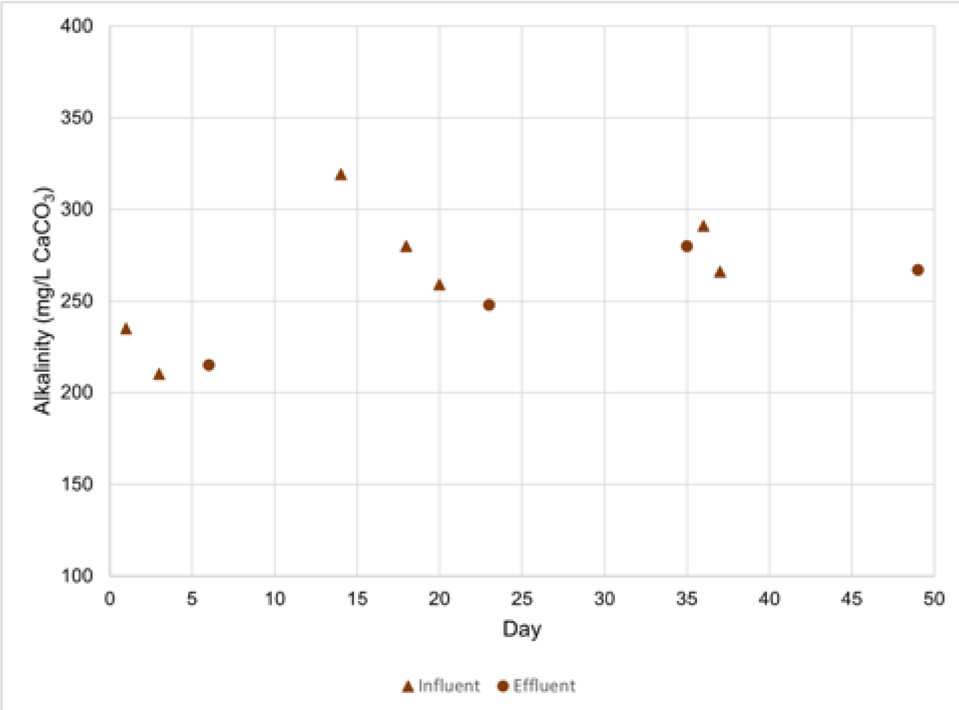

Figure B- 31 Influent and effluent alkalinity, Biofilter #7 (treating high ash content water)

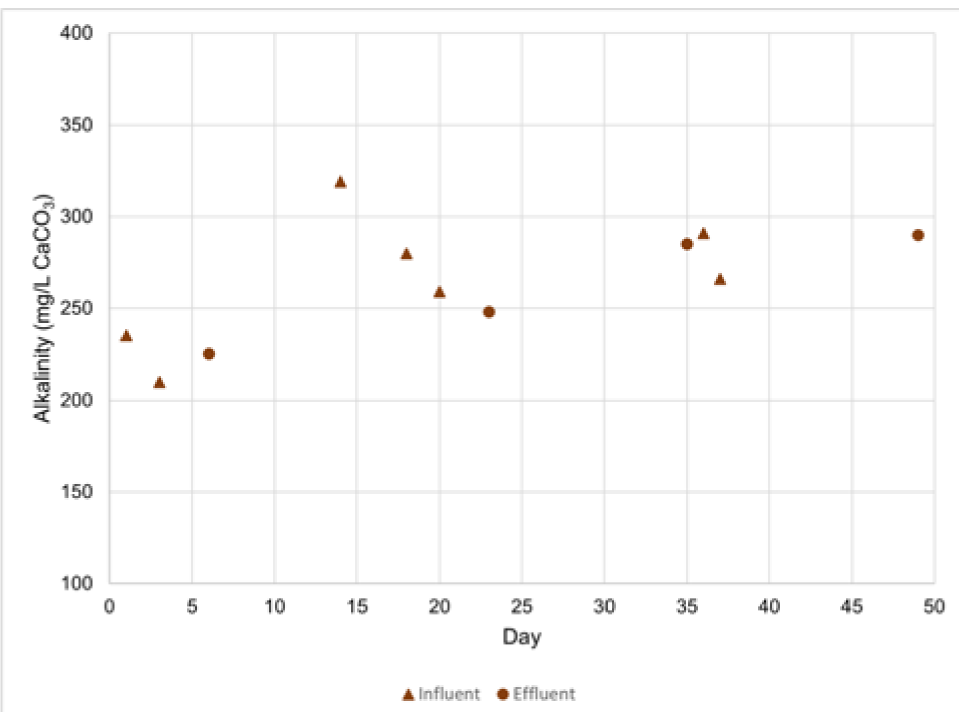

Figure B- 32 Influent and effluent alkalinity, Biofilter #8 (treating high ash content water)

Table B - 1 LC-OCD results for control biofilters (#1 and #2)

Phase of experiment	Influent or effluent type	Total DOC (mg/L	Biopolymers (mg/L)	Humics (mg/L)	Building blocks (mg/L)	LMW neutrals (mg/L)	LMW acids (mg/L)
Two-day ash disturbance period	Influent	8.35	0.58	6.54	1.39	0.52	0.18
	Day 1 – Biofilter #2	8.59	0.05	5.83	1.47	0.84	0.18
	Day 2 – Biofilter #1	7.87	0.05	5.86	1.39	0.80	0.24
Return to baseline from two-day ash disturbance period	Influent	8.90	0.68	6.81	1.32	0.72	0.18
	Day 3 – Biofilter #2	9.38	0.13	6.31	1.24	1.35	0.21
	Day 4 – Biofilter #1	7.10	0.01	5.35	1.26	0.50	0.17
	Day 6 – Biofilter #2	8.11	0.06	5.75	1.15	0.88	0.17
	Day 8 – Biofilter #1	7.44	0.02	5.55	1.27	0.79	0.16
Four-day ash disturbance period	Influent	8.67	0.47	6.76	1.37	0.45	0.22
	Day 16 Biofilter #1	9.08	0.02	5.89	1.22	0.74	n.d.
	Day 18 Biofilter #2	8.95	0.09	6.78	1.40	0.98	n.d.
	Day 19 Biofilter #1	8.73	0.09	6.47	1.51	0.70	n.d.
Return to baseline from four-day ash disturbance period	Influent	8.03	0.20	7.09	1.65	0.94	0.02
	Day 20 Biofilter #2	7.51	0.06	7.22	1.52	0.94	n.d.
	Day 22 Biofilter #1	9.63	0.02	6.80	1.61	0.42	0.04
Seven-day ash disturbance period	Influent	8.24	0.61	6.02	1.59	0.74	0.01
	Day 30 Biofilter #2	5.58	0.04	4.47	0.81	0.52	0.04

	Day 31 Biofilter #1	6.04	0.02	4.12	0.91	1.35	0.01
	Day 33 Biofilter #1	7.13	0.01	5.48	1.34	0.56	0.05
	Day 35 Biofilter #2	7.28	0.01	5.79	1.40	0.66	0.03
	Day 36 Biofilter #2	7.54	0.07	5.63	1.21	0.84	0.07
Return to baseline from seven-day ash disturbance period	Influent	12.01	0.85	9.28	2.03	0.92	0.09
	Day 37 Biofilter #2	13.54	0.03	9.53	2.30	1.92	0.08
	Day 41 Biofilter #1	8.03	0.09	6.72	1.47	1.27	0.02

Table B - 2 LC-OCD results for biofilters treating low ash content water (biofilters #3 and #4)

Phase of experiment	Influent or effluent type	Total DOC (mg/L	Biopolymers (mg/L)	Humics (mg/L)	Building blocks (mg/L)	LMW neutrals (mg/L)	LMW acids (mg/L)
Two-day ash disturbance period	Influent (low ash content)	8.69	0.44	6.46	1.47	1.00	0.22
	Day 1 – Biofilter #4	8.54	0.08	6.43	1.14	0.73	0.18
	Day 2 – Biofilter #3	9.12	0.02	6.07	1.31	1.28	0.20
Return to baseline from two-day ash disturbance period	Influent	8.90	0.68	6.81	1.32	0.72	0.18
	Day 3 – Biofilter #4	9.21	0.14	5.80	1.24	1.43	0.54
	Day 4 – Biofilter #3	7.97	0.11	6.10	1.23	1.09	0.15
	Day 6 – Biofilter #3	9.54	0.04	5.75	1.46	2.14	0.20
	Day 8 – Biofilter #3	7.80	0.06	5.71	1.47	1.01	0.17
Four-day ash disturbance period	Influent (low ash content)	9.68	0.41	6.39	1.47	1.22	0.07
	Day 16 Biofilter #3	13.28	n.d.	9.26	1.91	1.43	0.04
	Day 18 Biofilter #4	10.20	0.70	7.09	1.66	0.97	0.03
	Day 19 Biofilter #3	8.88	0.34	6.87	1.77	1.54	0.02
Return to baseline from four-day ash disturbance period	Influent	8.03	0.20	7.09	1.65	0.94	0.02
	Day 20 Biofilter #4	8.52	0.39	7.30	1.51	0.73	n.d.
	Day 22 Biofilter #4	9.02	0.45	6.97	1.62	0.76	n.d.

Seven-day ash disturbance period	Influent (low ash content)	8.64	0.49	6.39	1.41	0.96	n.d.
	Day 30 Biofilter #4	5.84	0.08	4.23	0.92	0.77	0.02
	Day 31 Biofilter #3	5.75	0.21	4.23	1.04	0.62	n.d.
	Day 33 Biofilter #3	8.39	0.46	6.37	1.41	0.95	0.02
	Day 35 Biofilter #3	10.84	0.52	6.18	1.71	1.25	0.52
	Day 36 Biofilter #4	9.05	0.41	6.22	1.61	1.39	n.d.
Return to baseline from seven-day ash disturbance period	Influent	12.01	0.85	9.28	2.03	0.92	0.09
	Day 37 Biofilter #4	13.06	0.50	9.91	2.47	1.99	0.11
	Day 41 Biofilter #3	9.76	0.32	6.69	1.29	0.71	0.08

Table B - 3 LC-OCD results for biofilters treating moderate ash content water (biofilters #5 and #6)

Phase of experiment	Influent or effluent type	Total DOC (mg/L	Biopolymers (mg/L)	Humics (mg/L)	Building blocks (mg/L)	LMW neutrals (mg/L)	LMW acids (mg/L)
Two-day ash disturbance period	Influent (moderate ash content)	11.80	0.38	7.37	1.20	2.58	0.22
	Day 1 – Biofilter #6	8.87	0.07	6.69	1.33	0.78	0.20
	Day 2 – Biofilter #5	8.67	0.05	6.08	1.37	0.73	0.20
Return to baseline from two-day ash disturbance period	Influent	8.90	0.68	6.81	1.32	0.72	0.18
	Day 3 – Biofilter #6	9.20	0.10	6.08	1.52	1.43	0.22
	Day 4 – Biofilter #5	8.74	0.09	5.86	1.42	1.81	0.21
	Day 6 – Biofilter #5	7.60	0.07	5.75	1.34	0.93	0.16
	Day 8 – Biofilter #5	8.99	0.04	5.95	1.36	1.55	0.22
Four-day ash disturbance period	Influent (moderate ash content)	9.62	0.42	6.77	1.31	1.94	0.08
	Day 16 Biofilter #5	10.98	0.06	6.23	1.40	0.74	n.d.
	Day 18 Biofilter #6	11.82	0.21	6.93	1.52	0.89	n.d.
	Day 19 Biofilter #5	8.73	0.24	7.02	1.68	1.25	n.d.
Return to baseline from four-day ash disturbance period	Influent	8.03	0.20	7.09	1.65	0.94	0.02
	Day 20 Biofilter #6	9.05	0.22	7.24	1.63	0.91	n.d.

Seven-day ash disturbance period	Influent (moderate ash content)	9.12	0.46	6.32	1.38	0.98	n.d.
	Day 30 Biofilter #6	6.14	0.14	4.52	0.99	0.74	0.01
	Day 31 Biofilter #5	6.15	0.26	4.40	1.10	0.72	n.d.
	Day 33 Biofilter #5	8.85	0.41	6.65	1.38	1.32	0.01
	Day 35 Biofilter #5	9.96	0.49	6.24	1.75	1.41	n.d.
	Day 36 Biofilter #6	10.81	0.26	6.17	1.52	1.13	n.d.
Return to baseline from seven-day ash disturbance period	Influent	12.01	0.85	9.28	2.03	0.92	0.09
	Day 37 Biofilter #6	12.55	0.05	9.40	2.15	0.96	0.01
	Day 41 Biofilter #5	8.42	0.21	6.47	1.56	0.55	0.11

Table B - 4 LC-OCD results for biofilters treating high ash content water (biofilters #7 and #8)

Phase of experiment	Influent or effluent type	Total DOC (mg/L	Biopolymers (mg/L)	Humics (mg/L)	Building blocks (mg/L)	LMW neutrals (mg/L)	LMW acids (mg/L)
Two-day ash disturbance period	Influent (high ash content)	10.75	0.44	6.56	1.74	1.59	0.22
	Day 1 – Biofilter #8	10.17	0.06	6.50	1.64	1.07	0.19
	Day 2 – Biofilter #7	8.28	0.12	6.33	1.46	1.01	0.21
Return to baseline from two-day ash disturbance period	Influent	8.90	0.68	6.81	1.32	0.72	0.18
	Day 3 – Biofilter #8	10.13	0.15	6.27	1.37	1.08	0.17
	Day 4 – Biofilter #7	7.92	0.20	5.70	1.27	0.73	0.17
	Day 6 – Biofilter #7	8.95	0.09	5.72	1.31	0.81	0.14
	Day 8 – Biofilter #7	8.22	0.09	6.41	1.46	1.43	0.14
Four-day ash disturbance period	Influent (high ash content)	9.67	0.15	6.21	1.43	1.46	n.d.
	Day 16 Biofilter #7	10.70	0.51	6.87	1.46	1.34	n.d.
	Day 18 Biofilter #8	10.12	0.13	6.79	1.76	1.21	n.d.
	Day 19 Biofilter #7	10.10	0.49	7.27	1.86	1.21	n.d.
Return to baseline from four-day ash disturbance period	Influent	8.03	0.20	7.09	1.65	0.94	0.02
	Day 20 Biofilter #8	8.85	0.19	7.02	1.80	1.00	0.01
Seven-day ash	Influent (high ash content)	9.24	0.37	6.75	1.73	1.19	n.d.

disturbance period	Day 30 Biofilter #8	6.04	0.13	4.45	1.02	0.63	0.02
	Day 31 Biofilter #7	6.25	0.08	4.48	0.93	1.04	n.d.
	Day 33 Biofilter #7	7.72	0.04	6.18	1.56	0.89	n.d.
	Day 35 Biofilter #7	10.62	0.10	6.56	1.65	0.97	n.d.
	Day 36 Biofilter #8	10.85	0.33	7.48	2.14	1.86	n.d.
Return to baseline from seven-day ash disturbance period	Influent	12.01	0.85	9.28	2.03	0.92	0.09
	Day 37 Biofilter #8	8.38	0.08	6.11	1.50	1.14	n.d.
	Day 41 Biofilter #7	8.04	0.02	6.47	1.51	0.67	0.03

Table B - 5 LC-OCD results for raw Grand River Water samples from Summer and Fall 2021

Date of Raw Grand River water Sampling	Total DOC (mg/L)	Biopoly-mers (mg/L)	Humics (mg/L)	Building blocks (mg/L)	LMW neutrals (mg/L)	LMW acids (mg/L)
September 2	7.62	0.71	4.29	0.96	0.51	n.d.
September 14	10.2	0.64	3.84	1.06	3.98	n.d.
October 14	8.35	0.58	6.54	1.39	0.52	0.18
October 20	8.90	0.68	6.81	1.32	0.72	0.18
October 29	8.67	0.47	6.76	1.37	0.45	0.22
November 4	8.03	0.20	7.09	1.65	0.94	0.02
November 16	8.24	0.61	6.02	1.59	0.74	0.01
November 14	12.01	0.85	9.28	2.03	0.92	0.09

Appendix C

Chapter 3: Statistical analyses

Paired comparisons t-test

$$t_{calc} = \frac{\overline{D} - d_o}{S_d \big/ \sqrt{n}} \, , \nu = n - 1 \qquad (C.1, C.2)$$

Assumptions:

1) Differences are approximately normally distributed (see normal scores plots below).
2) Data is collected in independent pairs.

Heteroscedastic t-test

$$t_{calc} = \frac{(\overline{X}_1 - \overline{X}_2) - \delta}{\sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}}}, \nu = \frac{(S_1^2/n_1 + S_2^2/n_2)}{\left[\frac{(S_1^2/n_1)^2}{(n_1 - 1)}\right] + \left[\frac{(S_2^2/n_2)^2}{(n_2 - 1)}\right]} \qquad (C.3, C.4)$$

Assumptions:

1) Variances are unequal.

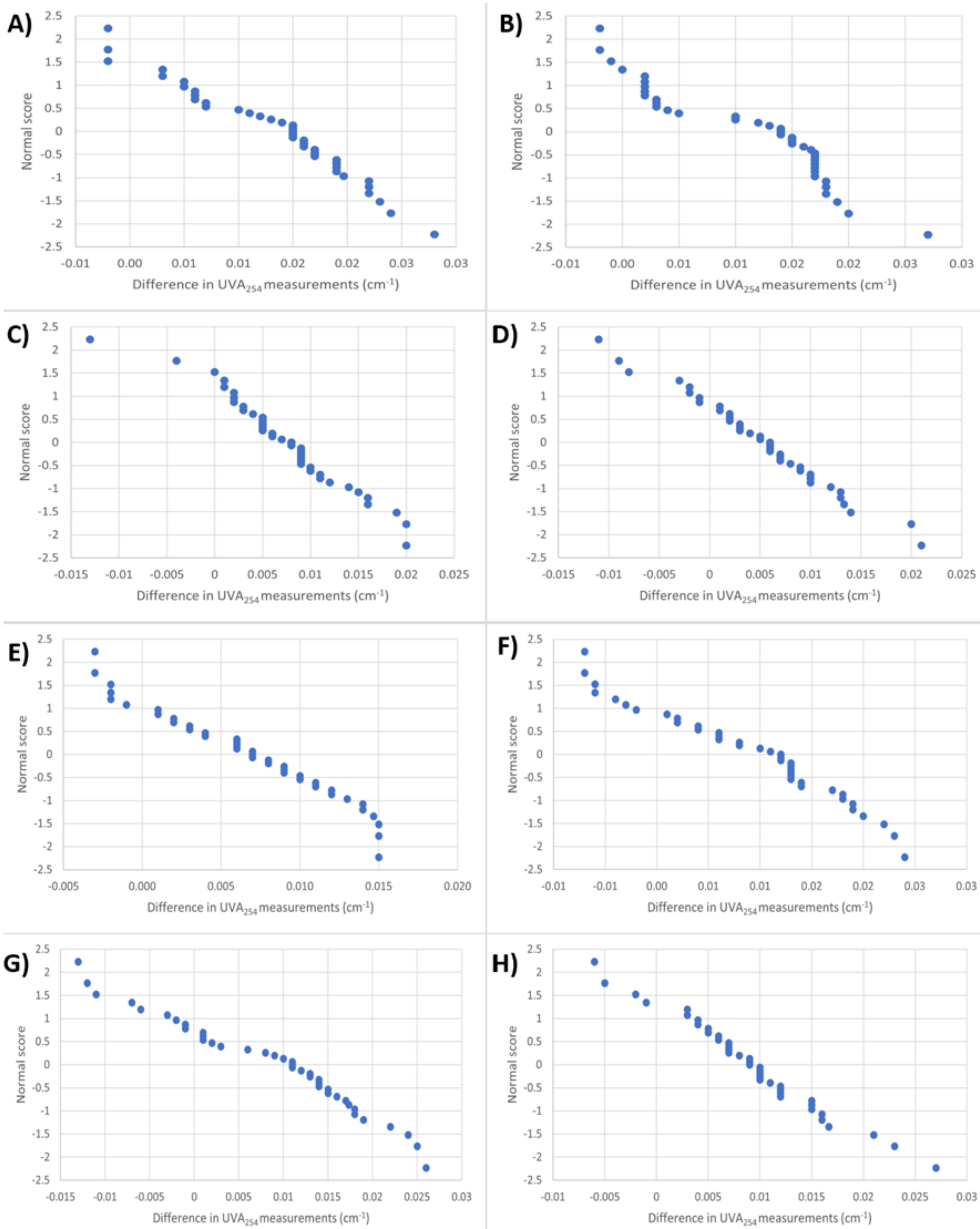

Figure C - 1 Normal scores plots for assumption of normality between paired influent and effluent UVA_{254} measurements in biofilters A) #1, B) #2, C) #3, D) #4, E) #5, F) #6, G) #7, and H) #8

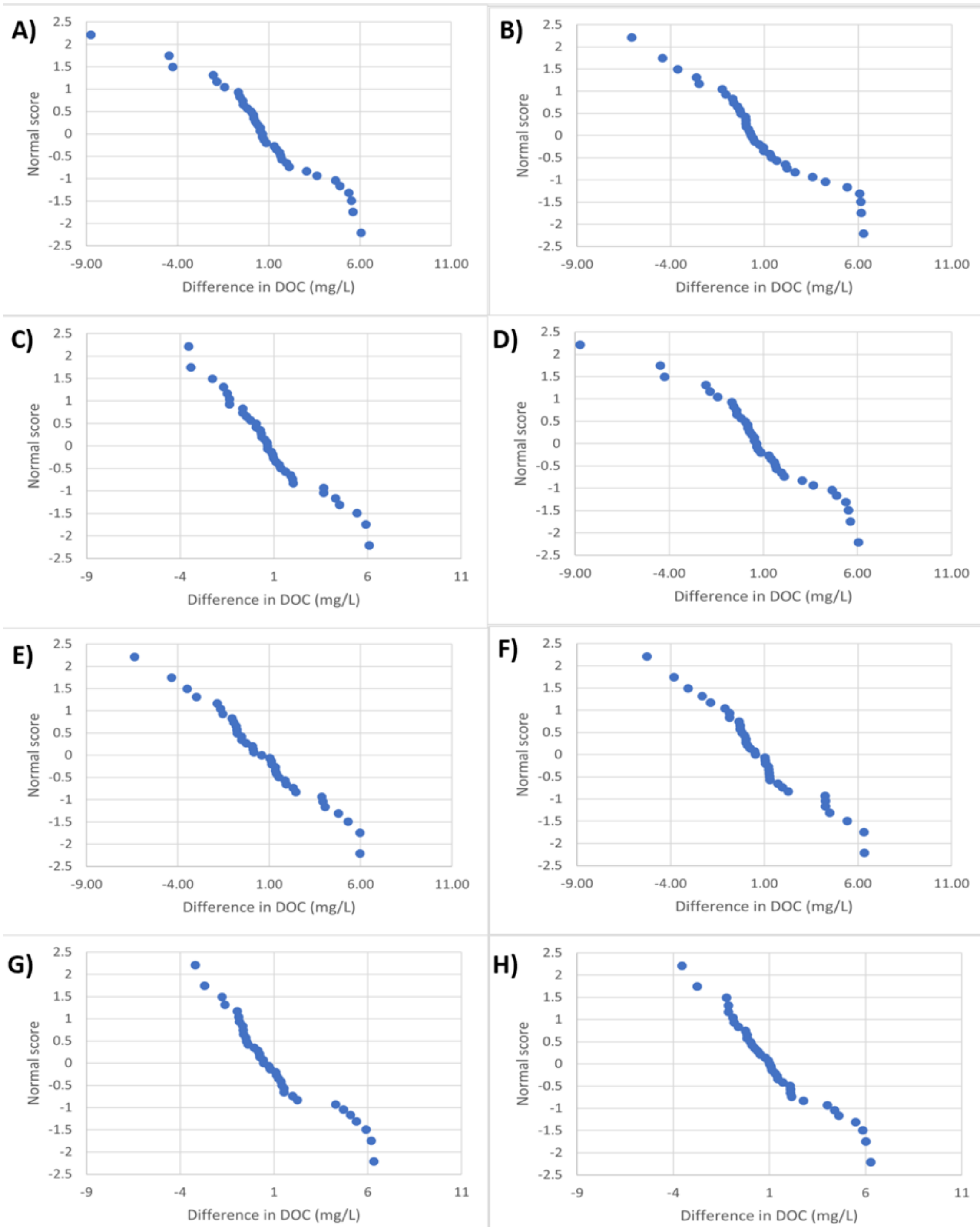

Figure C - 2 Normal scores plots for assumption of normality between paired influent and effluent DOC concentrations in biofilters A) #1, B) #2, C) #3, D) #4, E) #5, F) #6, G) #7, and H) #8

Table C - 1 Paired comparison tests for influent DOC > effluent DOC for each biofilter during the 50-day experiment

Filter #	p-values
1	0.00705
2	0.01672
3	0.00198
4	0.00447
5	0.02550
6	0.00734
7	0.00560
8	0.00118

Table C - 2 Paired comparison tests for influent UVA_{254} > effluent UVA_{254} for each biofilter during the 50-day experiment

Filter #	p-values
1	4.197E-13
2	7.177E-11
3	2.023E-08
4	4.590E-05
5	4.862E-09
6	1.377E-07
7	1.057E-05
8	4.136E-10

Table C - 3 p-values of two-tailed heteroscedastic t-tests for differences in average DOC removals between experimental conditions throughout the 50-day experiments. Values in red indicate where one-tailed tests were completed

	Individual periods of 50-day experiments						
Comparison between experimental conditions	Two-day disturbance period	Return to baseline from two-day disturbance period	Four-day disturbance period	Return to baseline from four-day disturbance period	Seven-day disturbance period	Return to baseline from seven-day disturbance period	Overall
Control and biofilters treating low ash content water	0.0044	0.7454	0.7572	0.2205	0.1602	0.6602	0.5825
Control and biofilters treating moderate ash content water	0.0012	0.1460	0.3437	0.1635	0.2554	0.6793	0.9659
Control and biofilters treating high ash content water	0.0012	0.0148	0.8502	0.0271	0.0187	0.9920	0.4888

Table C – 4 p-values of one-tailed heteroscedastic t-tests for differences in overall average daily change in UVA_{254} removals between experimental conditions throughout the 50-day experiments.

Comparison between experimental condition	p-values
Control and biofilters treating low ash content water	0.0002
Control and biofilters treating moderate ash content water	0.0063
Control and biofilters treating high ash content water	0.0339

Appendix D

Chapter 3: Images of experimental set-up

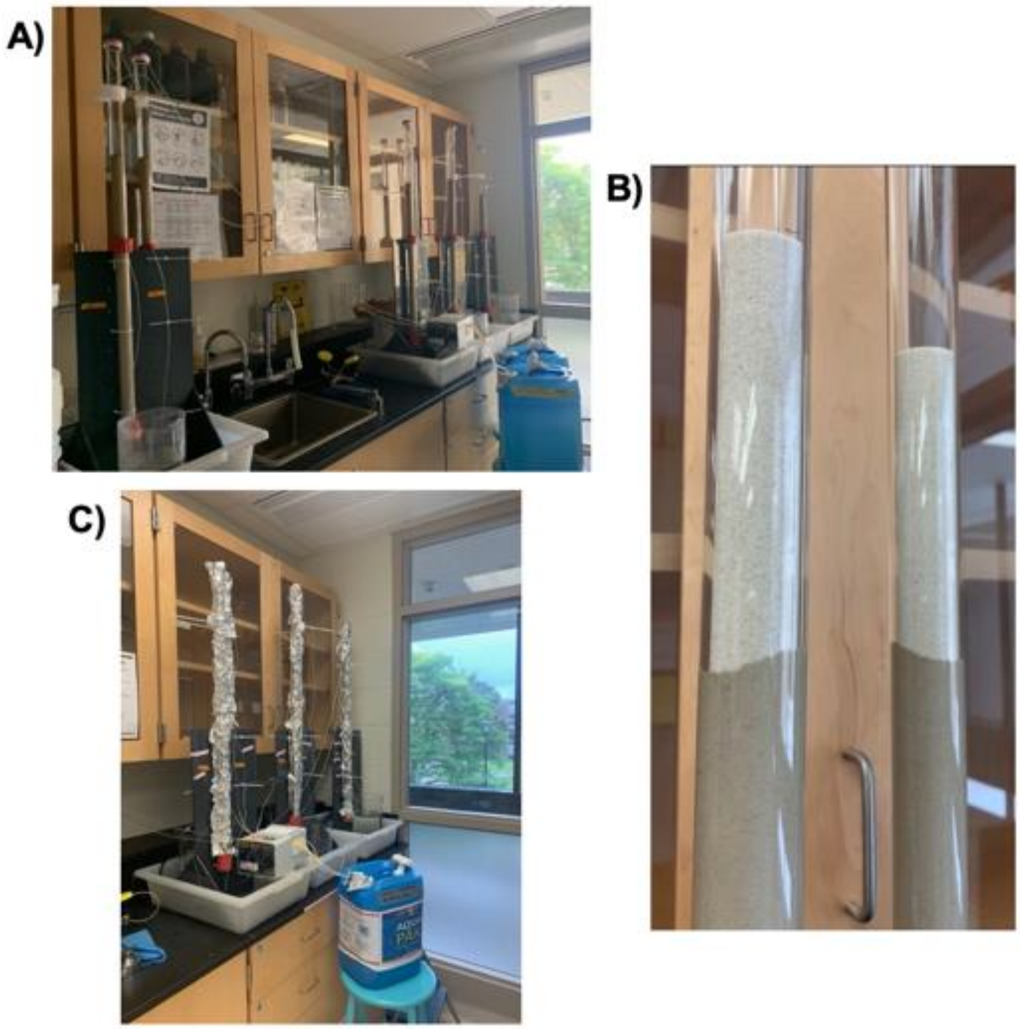

Figure D - 1 A) Biofilter set-up (down-flow mode) with blue influent container, 16 August 2021 (Day -65 of experiment). B) Sand bed saturation with de-gassed water following purging of sand bed with carbon dioxide gas. C) Biofilters #3 through #8 with aluminum foil covering to prevent photosynthesis. Flow rate of influent water into biofilters is controlled with 8-channel low-flow peristaltic pump pictured here.

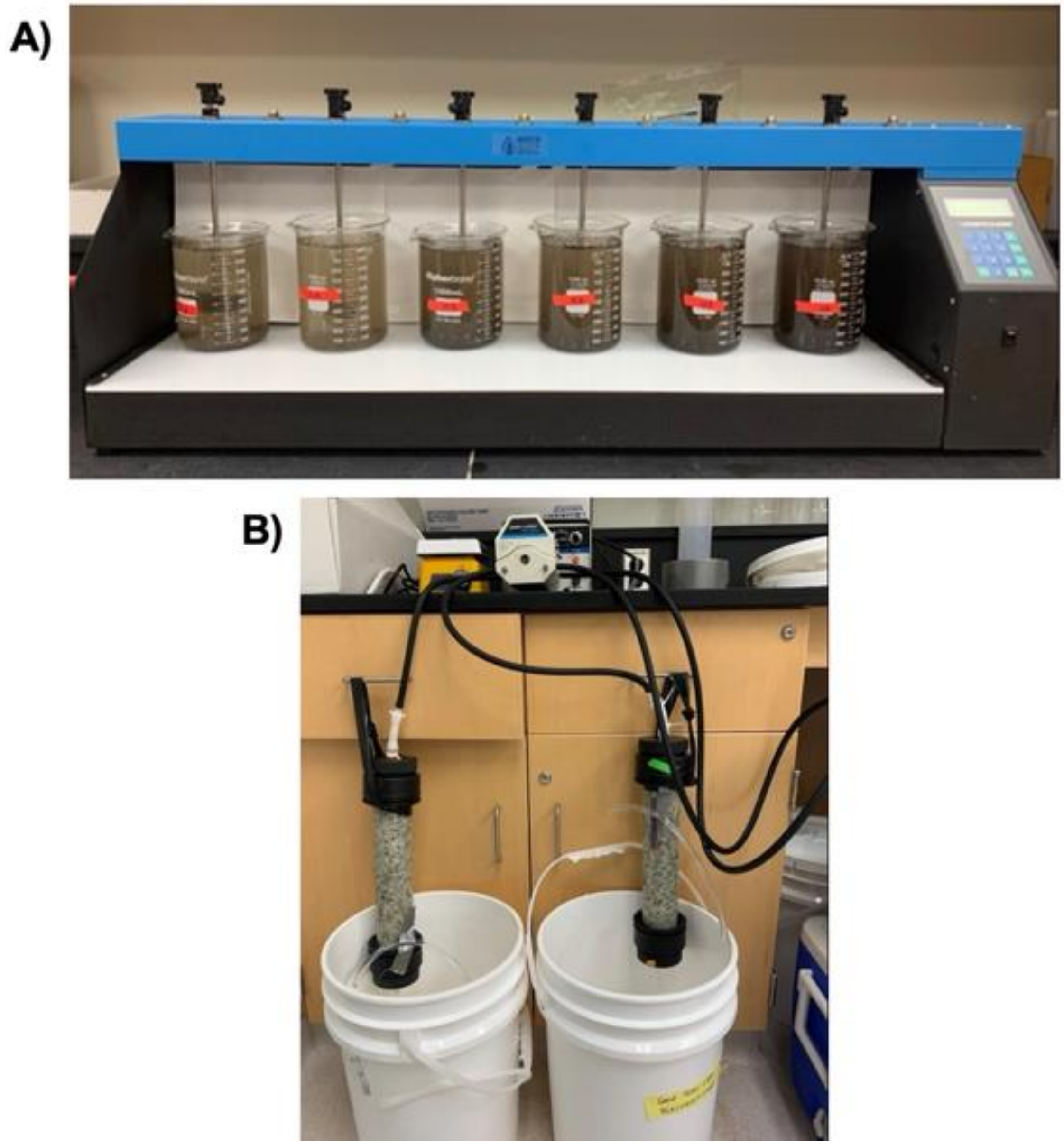

Figure D - 2 A) Mixing of wildfire ash and raw Grand River water to create low (two leftmost beakers), moderate (two middle beakers), and high (two rightmost beakers) ash content water. B) Roughing filtration pre-treatment set-up. Influent is controlled with peristaltic pump pictured here on lab bench.

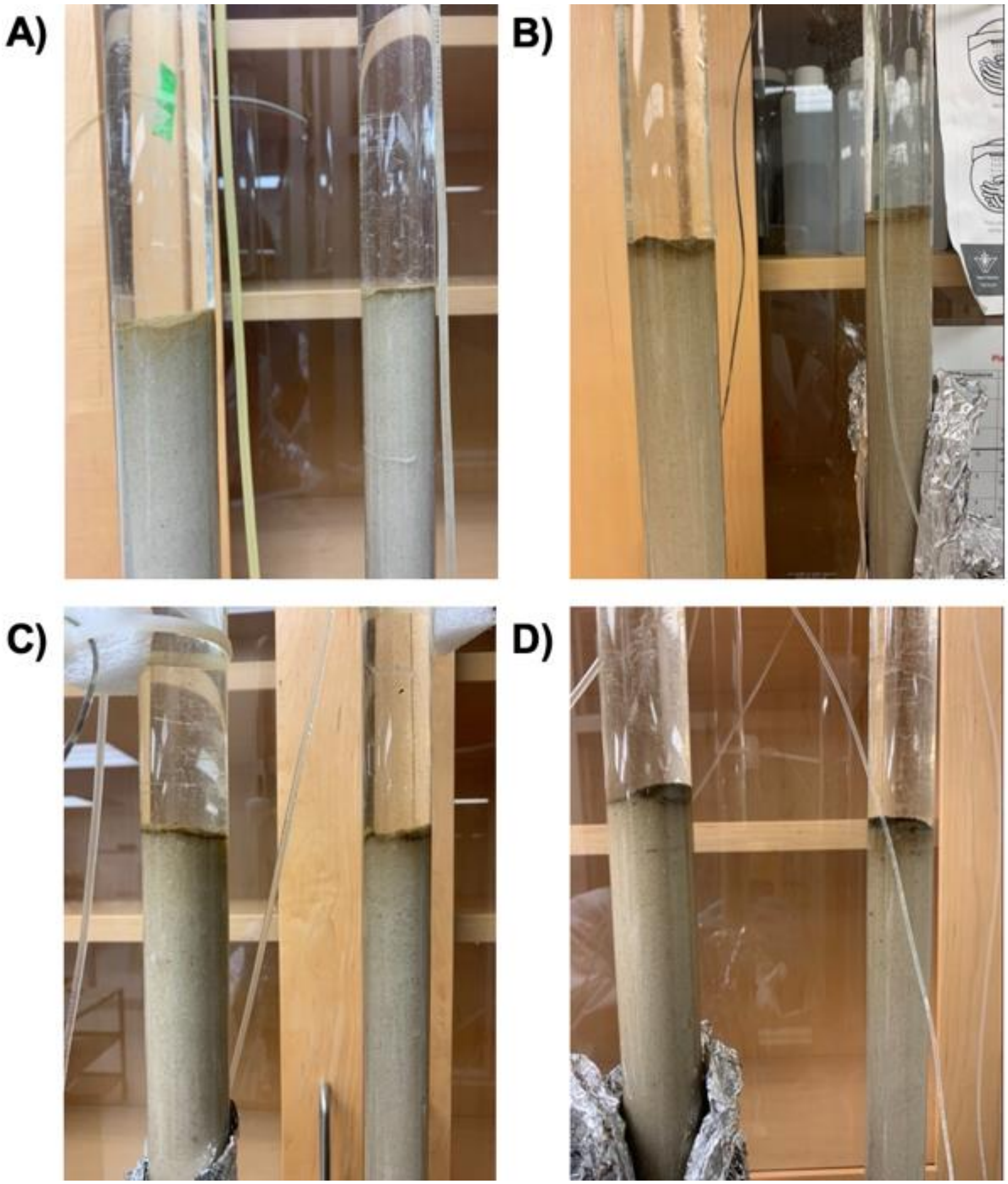

Figure D - 3 Schmutzdecke of A) biofilters #1 and #2 (control), B) biofilters #3 and #4 (treating low ash content water), C) biofilters #5 and #6 (treating moderate ash content water), D) biofilters #7 and #8 (treating high ash content water) prior to scraping, 8 November 2021 (Day 20 of experiment)

Figure D – 4 Grand River sampling location, Schneider Park, Kitchener, Waterloo, Ontario, 30 September 2021

Appendix E

Chapter 3: Biofilter design considerations and calculations

Equations for EBCT and HLR

$$EBCT = \frac{Volume\ of\ empty\ bed}{Flow\ rate} \qquad (E.1)$$

$$HLR = \frac{Bed\ depth}{EBCT} \qquad (E.2)$$

Damkohler number II estimation (variables progressively defined throughout)

Estimated bulk diffusion coefficient (DL) for low molecular weight NOM (Cornel et al., 1986b) (note: low molecular weight NOM have lower DL, resulting in a more conservative estimate for Da_{II})

$$DL = 2.0\ x\ 10^{-10}\,\frac{m^2}{s} \qquad (E.3)$$

Estimated bed porosity (ε)

$$\varepsilon = 0.45 \qquad (E.4)$$

Estimated interstitial velocity (u)

$$u = \frac{HLR}{\varepsilon} \qquad (E.5)$$

Particle diameter (dp)

$$dp = 0.20\ mm \qquad (E.6)$$

Kinematic viscosity (ν) of water at 20°C

$$\upsilon = 1.004\ x\ 10^{-6}\,\frac{m^2}{s} \qquad (E.7)$$

Sphericity (S) of fresh sand

$$S = 0.65 \qquad (E.8)$$

Specific surface area (as)

$$as = \frac{6(1-\varepsilon)}{S(dp)} \qquad (E.9)$$

Estimated reaction rate (k') (maximum reported reaction rate in literature for un-ozonated waters at $\leq$ 20°C to ensure a conservative estimate of Da_{II}) (Terry & Summers, 2018)

$$k' = 0.18/min \qquad (E.10)$$

Estimated surface reaction rate (k_0)

$$k_o = \frac{k'}{as} \qquad (E.11)$$

Reynolds Number (Re)

$$Re = \frac{u(dp)}{\upsilon} \qquad (E.12)$$

Schmidt Number (Sc)

$$Sc = \frac{\upsilon}{DL} \qquad (E.13)$$

Gnielinski Equation (Roberts et al., 1985, Cornel, et al 1986a, Sontheimer et al., 1988)

$$Sh = 2\psi + 0.644\psi[(Re^{0.5})(Sc^{0.33})]; where\ Sh = Sherwood\ Number, \psi = 1 + 1.5(1-\varepsilon) \qquad (E.14, E.15)$$

External mass transfer coefficient (k_f)

$$k_f = \frac{Sh(DL)}{dp} \qquad (E.16)$$

Sherwood Number (Sh)

$$Sh = \frac{k_f(dp)}{DL} \qquad (E.17)$$

Damkohler Number II (Da_{II})

$$Da_{II} = \frac{k_o}{k_f} \qquad (E.18)$$

Table E - 1 Calculated values for Damkohler number II estimation

u (m/s)	4.32E-05
as (/m)	2.54E+04
k_o (m/s)	1.18E-07
Re	0.00861
ψ	1.83
Sc	5020
Sh	5.46
k_f (m/s)	5.46E-06
Da_{II}	**0.0216**
Mass limiting Da_{II} value	**0.1**

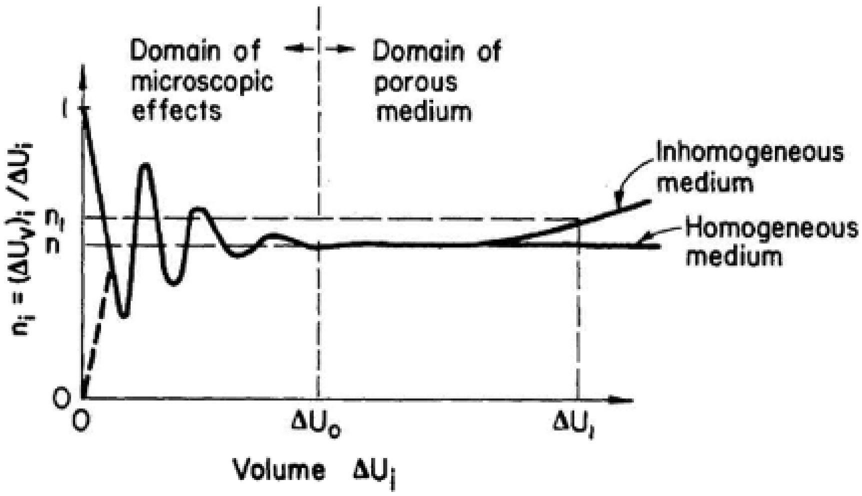

Figure E - 1 Porosity oscillations at small porous media volumes (Bear, 1972)

Procedure for packing sand columns

1. Clean quartz sand, first autoclaved to ensure sterility, was dry packed slowly with the use of a funnel and a hand-held massager to a total depth of 70 cm to ensure sand was evenly packed.
2. Air-tight dry packed sand columns were then purged up-flow with carbon dioxide gas at a maximum flow rate of 1.7 cm^3/min until at least six empty bed volumes of carbon dioxide gas were purged (approximately 30 min). Six empty bed volumes were assumed to be sufficient to adequately fill the air-filled pore spaces of the sand bed with carbon dioxide gas.

   Raw Grand River water was then de-gassed by bubbling helium gas for approximately 20 minutes in a 500 ml Kimble bottle. The de-gassed water was then used to saturate the sand column up-flow at a maximum flow rate of 0.15 ml/min. Since carbon dioxide gas is very soluble in water, and de-gassed water does not contain air bubbles, this procedure ensures a low likelihood of entrapped air bubbles in the sand bed.