Drinking Water Treatment Technology Resilience for Management of Severely Deteriorated Water after Wildfire

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

Jesse Skwaruk was the primary author for all chapters included in this thesis. Chapters 1 and 7 were not written for publication; Chapters 2–6 of this thesis were prepared as manuscripts for publication. The manuscripts presented herein are at different stages of preparation for submission to peer-reviewed journals. Exceptions to sole authorship of material are described below.

Research presented in Chapter 2:

Research presented in Chapter 3:

Research presented in Chapter 4:

This research was conducted at two locations: the Glenmore WTP in Calgary, AB, and the Regional Municipality of Wood Buffalo (RMWB) WTP in Fort McMurray, AB. All research was completed by Jesse Skwaruk under the supervision of Dr. Monica Emelko. The overall study was designed by Dr. Monica Emelko and Jesse Skwaruk; additional pilot study coordination and operation were supported by Kelsey Kundert and Tyler Owl. The anticipated co-authors of the manuscript, including Dr. Monica Emelko, Dr. Uldis Silins, Dr. Micheal Stone, and Kelsey Kundert. This research was supported Alberta Innovates (AI 2385A and 3360-E086), the City of Calgary, NSERC (RGPIN-2016-04655), the *for*Water Network, and the Canada Research Chairs Program. The support of Veolia Water throughout this phase of research was invaluable and critical to achieving the research goals.

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The study design was conceived by Jesse Skwaruk and Dr. Monica Emelko. The research was completed by Jesse Skwaruk under the supervision of Dr. Monica Emelko. All experiments and data analysis were completed by Jesse Skwaruk. Draft manuscripts were prepared by Jesse Skwaruk anticipated co-authorship includes Dr. Monica Emelko, Dr. Uldis Silins, Dr. Micheal Stone, Dr. Fariba Amiri, and Soosan Baharamian. Additional support from Dr. Cristina Santín was crucial in acquiring ash samples. This research was supported by Alberta Innovates (AI 2385A and 3360-E086) and NSERC (RGPIN-2016-04655). Bench-scale laboratory analysis was also supported by Tyler Owl, Steven Ngo, and Celine Vandenberg.

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As the lead author of the aforementioned five chapters, I was responsible for: the contribution and conceptualization of all study designs; the implementation of experiments; the collection and analysis of data; and, the drafting of manuscripts. Guidance and feedback were provided by my co-authors during the various phases of research and the during the preparation of manuscripts. The authors declare that the

research was completed in the absence of any financial or commercial relationships which may be construed as a possible conflict of interest.

Abstract

Severe wildland fire is occurring with increased frequency in many regions and can be potentially catastrophic for the provision of safe drinking water due to increasingly variable or deteriorated source quality. Deteriorated water quality can have negative implications for drinking water treatment by challenging in-plant treatment technologies beyond design and operational response capacity as a result of elevated levels of carbon, turbidity and nutrients. While it is increasingly recognized that severe wildland fire can have long-lasting (i.e., decades or longer) impacts on source water quality, it is the short-lived, episodic impacts following major runoff events that can most challenge drinking water treatability. Although case studies are increasingly available regarding wildfire impacts on drinking water treatment, they typically provide limited or no information about treatment technology capabilities. While the presence of anthropogenic contaminants from the urbanized landscape may require specialized treatment after wildfire, this research strives to address the common belief that commonly available technologies are insufficient for treating severely deteriorated source water after wildland fire.

To date, the treatment of severely deteriorated, wildfire ash-impacted water representative of worst-case scenario "black water" that sometimes results from wildfire ash transport directly from hillslopes to source waters has not been investigated. Recognizing that the ability to treat the most severely deteriorated water that might be observed post-fire implies that less deteriorated water could also be treated, protocols were developed herein to collect fresh post-fire ash and prepare wildfire ash-impacted source water with high levels of turbidity and dissolved organic carbon (DOC) consistent with the most severely deteriorated levels that have been reported to date. These wildfire ash-impacted source waters were then used to evaluate the capacity to treat severely deteriorated, wildfire ash-impacted source water using commonly available water treatment technologies (e.g., conventional, high-rate treatment) at bench-scale. While turbidity was effectively reduced in all cases, reductions in DOC concentrations were often limited; however, powdered activated carbon (PAC) demonstrated potential for reducing DOC concentrations and disinfection by-product formation potential.

Pilot-scale investigations of focused on evaluating the capacity to treat severely deteriorated, wildfire ash-impacted source water was subsequently conducted using sand-ballasted flocculation (SBF) because this type of high rate clarification is designed to respond to rapid and large fluctuations in source water quality. The studies were conducted in two distinct ecozones with markedly different source water quality. The Montane Cordillera study in Calgary, Canada involved high quality source water (low turbidity and DOC) while the Boreal Plains study in Fort McMurray, Canada involved more deteriorated (higher turbidity and DOC) source water. SBF was investigated alone and in combination with enhanced coagulation or PAC for additional DOC removal and DBP management. These studies were critical to informing operational challenges associated with the various technologies. Consistent with the bench-scale outcomes, the studies indicated that while turbidity was again effectively reduced in all cases, reductions in DOC concentrations were often limited. PAC demonstrated potential for reducing DOC concentrations and disinfection by-product formation potential if needed, and without the challenges that were associated with fluctuating source water pH resulting from wildfire ash dissolution, which challenged the pH control required for effective enhanced coagulation at the conditions investigated.

The impacts of different vegetation types in different physiographic regions and wildfire burn severity on drinking water treatability after wildland fire were assessed to provide insight regarding the transferability of knowledge regarding wildfire impacts on drinking water treatment in different regions and after different types of wildfires. This work is novel in demonstrating that burn severity can significantly impact water treatability. In contrast, although the magnitudes of impacts on source water quality differed regionally when normalized to ash mass, similar treatment performance was achieved at consistent burn severity, regardless of regional differences between vegetation in wildland regions. Regardless of differences in wildland fire severity and setting, the key aspects of water quality that govern chemical pre-treatment

efficacy were also those that were consistently impacted by ash delivery to source water, namely: turbidity, DOC concentration and character, alkalinity and pH.

The novel insights described above were synthesized in conjunction with a literature review to develop a framework to detail watershed- and plant-scale operational response actions for describing and mitigating the potential impacts of wildfire on drinking water treatment (Chapter 6). Thus collectively, this dissertation (1) provides an in-depth analysis of the treatment challenges and potential solutions that may be implemented to effectively treat severely deteriorated, wildfire ash-impacted source water following wildfire and (2) contributes to advancing risk management, operational resilience, and climate change adaptation planning for drinking water utilities in fire-prone regions.

Acknowledgements

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List of Abbreviations

ANOVA	Analysis of Variance
BDCM	Bromodichloromethane
CFSTR	Continuous Flow Stirred Tank Reactor
DBAA	Dibromoacetic Acid
DBCM	Dibromochloromethane
DBP	Disinfection By-product
DBP-FP	Disinfection By-product Formation Potential
DCAA	Dichloroacetic Acid
DOC	Dissolved Organic Carbon
FMWTP	Fort McMurray Water Treatment Plant
GMWTP	Glenmore Water Treatment Plant
HAA	Haloacetic Acid
HAA5	Total Haloacetic Acids
HCl	Hydrochloric Acid
LC-OCD	Liquid Chromatography – Organic Carbon Detection
LMW	Low Molecular Weight
MBAA	Monobromoacetic Acid
MCAA	Monochloroacetic Acid
NOM	Natural Organic Matter
NTU	Nephelometric Turbidity Units
PAC	Powdered Activated Carbon
PACl	Polyhydroxy Aluminum Chloride
RSD	Relative Standard Deviation
SBF	Sand-ballasted Flocculation
SBF+EC	Sand-ballasted Flocculation with Enhanced Coagulation
SBF+PAC	Sand-ballasted Flocculation with Powdered Activated Carbon
SCR	Scottie Creek Road
SD	Standard Deviation
SE	Standard Error
SUVA	Specific Ultraviolet Absorbance
TBM	Tribromomethane
TCAA	Trichloroacetic Acid
TCM	Trichloromethane
THM	Trihalomethane
TLR	Thuya Lake Road
TOC	Total Organic Carbon
TTHMs	Total Trihalomethanes
UVA_{254}	Ultraviolet Absorbance at 254 nm
WEOM	Water Extractable Organic Matter
WTP	Water Treatment Plant

Chapter 1: Introduction

1.1 Background: wildfire and drinking water treatment

Global increases in the frequency and severity of wildfire are one of the clearest manifestations of climate change. They are expected to continue throughout the 21st century because of increased extreme rainfall events that lead to vegetation growth followed by longer, hotter periods and droughts during which ground and vegetation moisture content is reduced, leading to more fuel for wildfires (Flannigan et al., 2013; Westerling et al., 2006). Wildfire can substantially alter water quality (Bladon et al., 2014) and impact drinking water treatment efficacy, thereby affecting regional drinking water security (Emelko et al., 2011). The recent devastation in the United States that resulted from the 2017 Tubbs Fire in Sonoma and Napa Counties in California and the 2018 Camp Fire in Butte County, California underscored the risks that wildfire poses in wildland–urban interfaces in which combustion and pyrolysis of the built environment can lead to hazardous chemical (e.g., benzene) contamination of water supplies isolated in buried distribution networks (Proctor et al., 2020).

It is critical to recognize that wildfire can significantly challenge the provision of safe drinking water in absence of anthropogenic contaminants. In 2014, an international expert panel comprised of leading scientists and practitioners was assembled by the Water Research Foundation and the Canadian Water Network to discuss wildfire impacts on water supply and treatment and the potential for mitigation. The panel concluded that wildfire on the natural, unurbanized landscape (i.e., wildland fire) can be catastrophic for drinking water treatment because "water treatment plants and processes are not always designed to treat the range of changes in the character and/or magnitude of source water quality parameters (e.g., peak values of turbidity, dissolved organic carbon, nutrients, or heavy metals) after wildfire, and some of these fluctuations may render existing treatment capacity inadequate" (Emelko & Sham, 2014).

Severe wildland fire can result in periodically deteriorated and more variable water quality (Stone et al., 2011) that can challenge conventional and advanced drinking water treatment processes; small systems are especially vulnerable (Emelko et al., 2011; Emelko & Sham, 2014). Following wildfire, more precipitation reaches the landscape (Williams et al., 2019) and burned material can be rapidly mobilized from the landscape to receiving streams by erosion from wind or runoff (Moody & Martin, 2001; Santín et al., 2015). Vegetation loss can lead to bank instability and erosion, also increasing sediment loads to receiving streams (Silins et al., 2009; 2016; Tecle & Neary, 2015); hydrophobic soil conditions reduce permeability and further increase overland runoff (Certini, 2005; Doerr et al., 2000; Neary et al., 2005). Such conditions can have significant impacts on key water quality characteristics relevant to drinking water treatment, including suspended solids/turbidity (Silins et al., 2009; Stone et al., 2014), nutrients (Bladon et al., 2008; Emelko et al., 2011; Silins et al., 2014), and dissolved organic carbon (DOC) (Emelko et al., 2011; Writer et al., 2014), which typically drive the selection, design, and operation of drinking water infrastructure (Emelko et al.,

2011). Thus, even in absence of toxic anthropogenic contaminants, degraded water quality following severe wildfire can challenge drinking water treatment and operational response capacities, leading to an inability to meet demands, service disruptions or even outages (Emelko et al. 2011). Rapid changes in raw water quality are especially challenging for water providers because they require treatment infrastructure that is resilient in response to source water quality change, continuous raw water quality evaluation to enable the appropriate response, and highly trained operators capable of rapidly optimizing treatment process performance as raw water quality changes; these needs leave small systems especially vulnerable because operator training and availability in rural, remote, and marginalized communities is especially challenging (Emelko & Sham, 2014).

The impacts of wildfire on source water quality may last for many years after wildfire (Emelko et al., 2016); some of the greatest challenges to drinking water treatment during those periods may be associated with deteriorated source water quality following major runoff events, which may persist for short periods of time, lasting anywhere from one day to one week (Dahm et al., 2015; Leak et al., 2003; Lyon & O'Connor, 2008; Mast et al., 2016; Murphy et al., 2015; Writer & Murphy, 2012). While anecdotal and retrospective case studies about wildfire impacts on drinking water treatment are available (White et al., 2006; Writer et al., 2014), they typically provide limited information about treatment technology capabilities because of factors such as inadequate time available to source materials (e.g., alternative coagulants), or implement alternative treatment approaches (e.g., enhanced coagulation) or technologies (e.g., powdered activated carbon). Thus, it is not surprising that there is widespread belief that treatment of severely deteriorated water may not always be possible after wildfire (Emelko & Sham, 2014; Sham et al., 2013).

Although evaluations of the impacts of deteriorated post-fire water quality on drinking water treatability are increasingly available, they typically provide limited or no information about either treatment technology capabilities or operational response for minimizing the probability of service disruption occurrence. Furthermore, most studies to date have assumed some pre-treatment of wildfire-impacted water by settling or filtration; therefore, they have not informed the ability to treat severely deteriorated water resulting from direct delivery of wildfire ash to source water after major runoff events. Accordingly, guidance for evaluating wildfire effects on drinking water treatment has not been developed (Knowledge Gap 1) and associated treatment performance evaluations have not been formally conducted (Knowledge Gap 2).

Of course, not all wildland fires become catastrophic megafires and there may be regional differences between wildfire impacts on water quality and treatability. Differences in wildfire burn severity and physiographic setting may further lead to a range of regionally variable impacts of wildfire on hydrology and water quality and treatability. The impacts of wildfire burn severity and burned vegetation type in

different physiographic regions on drinking water treatability have not been reported to date, however, making it difficult for water managers to extrapolate between investigations (Knowledge Gap 3). As a result, action-based guidance for risk management, operational resilience, and climate change adaptation planning for drinking water utilities in fire-prone regions is also lacking (Knowledge Gap 4).

1.2 Research objectives

The overall goal of this research was to enable risk management, operational resilience, and climate change adaptation planning for drinking water utilities in fire-prone regions. To address this goal, the four key knowledge gaps identified above were broadly addressed by evaluating common drinking water treatment technology capacity for treating severely deteriorated water following wildfire and developing actionable guidance to drinking water providers in fire-prone regions to safeguard the provision of potable water. The specific research objectives that were identified to address this goal were:

(1) Develop protocols for (i) post-fire ash collection and (ii) wildfire ash-impacted source water preparation (addressing Knowledge Gap 1);

(2) Evaluate the capacity to treat severely deteriorated, wildfire ash-impacted source water using commonly available water treatment technologies (addressing Knowledge Gap 2);

(3) Evaluate the capacity to treat severely deteriorated, wildfire ash-impacted source water at pilot-scale in regions of markedly different source water quality (addressing Knowledge Gap 2);

(4) Assess the impacts of vegetation type and wildfire burn severity on drinking water treatability after wildfire (addressing Knowledge Gap 3); and

(5) Develop a framework to detail watershed- and plant-scale operational response actions for describing and mitigating the potential impacts of wildfire on drinking water treatment (addressing Knowledge Gap 4).

1.3 Research approach

To address the objectives above, a research program comprised of four phases was developed. Each research phase addressed one of the key knowledge gaps detailed above (from which the research objectives were developed). Outputs from some of the initial phases were necessarily required to complete subsequent research phases. The research phases comprising this program of thesis research are presented in Figure 1.1, in which the interconnectivity between them is also indicated. Collectively, these research phases advance the body of available science and practice to enable improved risk management, operational resilience, and climate change adaptation planning for drinking water utilities in fire-prone regions.

Phase 1: Protocol Development

Develop protocols for: (1) post-fire ash collection and (2) synthetic wildfire ash-impacted source water preparation

(Objective 1)

Protocols developed in Phase 1 used in Phases 2 & 3

Phase 2: Treatment Evaluation

Evaluate treatment of severely deteriorated, wildfire ash-impacted source water at <u>bench-scale</u> using commonly available technologies

(Objective 2)

Evaluate treatment of severely deteriorated, wildfire ash-impacted source water at <u>pilot-scale in different source regions</u>

(Objective 3)

Bench-scale study provided preliminary insight regarding chemical dosing requirements and technology performance

Phase 3: Wildfire/Region Impacts Assessment

Assess impacts of: (1) burn severity and (2) vegetation type on drinking water treatability using conventional technology

(Objective 4)

Phase 2 & 3 findings were combined with literature review to develop Phase 4 framework

Phase 4: Planning/Response Framework Development

Develop framework to detail: (1) watershed- and (2) plant-scale operational response actions for describing and mitigating the potential impacts of wildfire on drinking water treatment

(Objective 5)

Figure 1.1: Overview of research approach indicating the relationship between research objectives. Blue arrows indicate the interrelationship between specific research objectives and outputs that informed subsequent research.

Phase 1 of this research involved the development of a protocol for post-fire ash collection and preparation of wildfire ash-impacted source water (Chapter 2). A review of the relevant literature regarding wildfire ash characterization and its impacts on water quality was completed. Bench-scale investigations of the impacts of wildfire ash and thermally-altered forest floor materials were reviewed, and the approaches used in the preparation wildfire ash-impacted water were summarized. A protocol for post-fire ash collection that includes simple differentiation of burn severity was then developed and implemented. Pyrogenic material (i.e., ash) was collected from newly burned sites prior to any precipitation events to ensure that water-extractable organic matter had not leached from the ash. To ensure that enough ash was available for the completion of Phases 1 to 3, 101 19-L pails (i.e., more than a tonne) of ash were collected. Following collection, different quantities of ash were added to river water and a suite of water qualities characteristics that are known drivers of drinking water coagulation and clarification was evaluated, including turbidity,

dissolved organic carbon (DOC) concentration, ultraviolet absorbance at 254 nm (UVA_{254}), specific UV absorbance (SUVA), alkalinity, and pH (Pernitsky & Edzwald, 2006). A protocol was then developed to enable reproduceable preparation of wildfire ash-impacted source water. The ability to prepare wildfire ash-impacted source water with targeted levels of turbidity, DOC concentration, and DOC aromaticity (i.e., SUVA) because of ash addition was not expected due to differences in the composition of various forest floor and pyrogenic materials (Bodi et al., 2011). Thus, given that DOC typically drives coagulant dosing requirements during drinking water treatment, consistency in DOC concentrations was targeted. As indicated in Figure 1.1, the ash collection and wildfire ash-impacted source water preparation protocols that were developed during Phase 1 were used during subsequent phases of the research; specifically, Phases 2 and 3.

Phase 2 of this research involved an evaluation of the ability to treat worst-case scenario source water quality associated with wildland fire ash runoff directly from hillslopes to source waters using current commercially available drinking water treatment technologies. First, the treatment performance of conventional chemical pre-treatment and high-rate clarification processes that are specifically designed to treat large fluctuations in influent water quality (sand-ballasted flocculation [SBF], SBF with enhanced coagulation, and SBF with powdered activated carbon [PAC]) was evaluated at bench-scale (Chapter 3) and then a subset of these approaches was investigated at pilot-scale (Chapter 4). Conventional chemical pre-treatment (i.e., coagulation, flocculation, sedimentation) efficacy in reducing turbidity, but not DOC, was expected given the widely recognized, frequently challenging nature of DOC removal by conventional treatment (Crittenden et al., 2012; Pernitsky & Edzwald, 2006)—this challenge has been previously reported after wildfire (Emelko et al., 2011; Hohner et al., 2017). SBF alone was also expected to effectively reduce turbidity because it is designed and able to respond to rapid fluctuations in source water turbidity (Crittenden et al., 2012; Desjardins et al., 2002). Consistent with previous reports not focused on wildfire, challenges in reducing DOC concentrations were expected (Plum et al., 1998). Accordingly, SBF coupled with enhanced coagulation or PAC addition were also investigated because those approaches are recognized as the best available technologies for removing DOC from water (Crittenden et al., 2012; Edzwald, 2011; USEPA, 1999).

The pilot-scale investigations were conducted in two distinct ecozones with markedly different source water quality. The Montane Cordillera study in Calgary, Canada involved high quality source water (low turbidity and DOC) while the Boreal Plains study in Fort McMurray, Canada involved more deteriorated (higher turbidity and DOC) source water (Chapter 4). SBF was investigated alone and in combination with enhanced coagulation or PAC for additional DOC removal and DBP management. These studies built on the bench-scale outcomes (Chapter 3) and were critical to informing operational challenges such as

difficulties in maintaining pH control with fluctuating source water pH resulting from wildfire ash dissolution.

The ability to treat sufficiently treat water with chemical commonly available chemical pre-treatment technologies was expected given that this ability has been observed after severe, catastrophic wildfires such as the 2016 Horse River wildfire in Fort McMurray, Alberta, Canada (Emelko et al., 2020). The present investigation thus also considered operational challenges associated with ensuring sufficient treatment performance during periods of extreme source water quality change due to wildfire ash. Both the bench- (Chapter 3) and pilot-scale (Chapter 4) investigations conducted during Phase 2 were designed as proof-of-concept, as opposed to process optimization, which is necessarily system specific (e.g., water quality, process configuration, etc.). Notably, although they would be desirable, investigations focused on optimizing the treatment of severely deteriorated, wildfire ash-impacted water were not feasible because of the significant mass (i.e., multiple tonnes) of post-fire ash that would be required to conduct the studies. Rather, the pilot-scale work conducted herein (which involved the use of approximately one tonne of ash) focused on (i) demonstrating how key aspects of water quality change can most challenge water treatment after severe wildfire, and (ii) highlighting that while technology is available to treat even the most severely deteriorated water, the highly uncertain and typically episodic nature of wildfire-associated shifts in source water quality require particular consideration in treatment infrastructure design, planning, and operation. Notably, these investigations comprise the first pilot-scale evaluations of the ability to treat wildfire ash-impacted water globally.

In Phase 3 of this research, the impacts of vegetation type and wildfire burn severity on drinking water treatability after wildland fire were assessed to provide insight regarding the transferability of knowledge regarding wildfire impacts on drinking water treatment in different regions and after varying burn severities (Chapter 5). While the water quality impacts of ash derived from different vegetation types on water quality have been previously reported, the drinking water treatability implications of ash deliver to source water after wildfires of differing severity or in different physiographic regions with different predominant vegetation types have not been directly contrasted and reported. Here, wildfire ash-impacted source water was prepared using unburned, moderately burned, and severely burned material from a single wildfire site. Notably, this work comprises the first reported investigation of the impacts of burn severity on drinking water treatability based on the use of actual post-fire ash. Conventional chemical pre-treatment was investigated at bench-scale because it is the most common approach implemented for surface water treatment (Crittenden et al., 2012). Next, the treatment (i.e., conventional chemical pre-treatment) of wildfire ash-impacted source water prepared with ash collected after severe wildfire in chaparral, moorland, grassland, and montane regions was investigated at bench-scale.

Burn severity was expected to impact treatment efficacy because of associated impacts on water quality, especially DOC concentration and character (e.g., Almendros et al., 1992; Fernandez et al., 1997; Norwood et al., 2013; Ulery et al., 1993), which is a key factor governing coagulation (Crittenden et al., 2012; Edzwald, 2011). Organic matter is generally amenable to conventional water treatment due to the hydrophobic character and high molecular weight of these compounds (MWH, 2012); however, it has been suggested that water impacted by severe wildfire may be less amenable to chemical pre-treatment because of a shift toward lower-molecular weight dissolved organic matter as a result of wildfire (Hohner et al., 2017; Hohner et al., 2018; Hohner et al., 2019b). Although the composition (e.g., quality and quantity of carbon, pH, alkalinity) of ash derived from wildland fire on different vegetated landscapes can vary considerably (Bodi et al., 2011; Certini 2005; Harper et al., 2019; Plumlee et al., 2007), the treatment implications of the release of these materials to source water should be generally consistent because many of these constituents result in water quality change in the factors that govern coagulation (Crittenden et al., 2012; Edzwald, 2011) and thus increase coagulant demand and challenge chemical pre-treatment.

Lastly, in Phase 4, a framework was developed to provide practical guidance to drinking water utilities in fire-prone regions. The novel insights from the first three research phases described above were synthesized in conjunction with a literature review to develop a framework to detail watershed- and plant-scale operational response actions for describing and mitigating the potential impacts of wildfire on drinking water treatment (Chapter 6). Although wildfire impacts on source water quality and drinking water treatment have been described, the framework summarizes potential wildfire impacts on source water quality with current understanding of the potential treatment implications of those changes to recommend watershed- and plant-scale operational response strategies focused on the monitoring and mitigation of potential wildfire impacts on the provision of safe drinking water.

Collectively, this dissertation research (1) provides an in-depth analysis of the treatment challenges and potential solutions that may be implemented to effectively treat severely deteriorated, wildfire ash-impacted source water following wildfire and (2) contributes to advancing risk management, operational resilience, and climate change adaptation planning for drinking water utilities in fire-prone regions.

1.4 Thesis organization

This thesis consists of seven chapters, where Chapters 2, 3, 4, 5, and 6 are formatted as journal articles that are intended for submission to refereed journals. Chapter 2 details the protocols developed for post-fire ash collection and the preparation of wildfire ash-impacted source water. Chapter 3 describes the results of bench-scale drinking water treatability studies in which the efficacy of an array of commercially available

technologies for treating severely deteriorated water after wildfire was evaluated. In Chapter 4, three pilot-scale studies are presented in which high-rate clarification of severely deteriorated, wildfire ash-impacted source water was evaluated in two regions of markedly different source water quality. Chapter 5 provides an evaluation of the impacts of vegetation type and wildfire burn severity on drinking water treatability after wildfire. A proposed framework detailing watershed- and plant-scale operational response actions for describing and mitigating the potential impacts of wildfire on drinking water treatment is described in Chapter 6. Lastly, Chapter 7 provides a summary of the conclusions, major contributions, implications, and recommendations of this work. This is followed by a reference list from all chapters and several appendices are included to provide additional details. Appendices A, B, C, and D provide supporting information for Chapters 2, 3, 4, and 5 respectively.

Chapter 2:

Evaluating wildfire impacts on drinking water treatment: Guidance for post-fire ash collection and preparation of wildfire ash-impacted water

2.1 Summary

Global increases in the frequency and severity of wildfire have the potential to dramatically alter the quality of source waters used for the provision of drinking water. The transport of post-fire materials from hillslopes to receiving waters can deliver solids and pyrogenic organic matter which may challenge drinking water treatment. To rigorously and safely evaluate the impacts of wildfire-impacted source water on drinking water treatment, a method for simulating deteriorated source water quality after wildfire is needed. While wildfire impacts on drinking water treatability have been assessed in numerous studies in which a wide range of approaches have been used to generate wildfire ash-impacted source waters that are intended to reflect deteriorated water quality after wildfire, guidance for the preparation of water with deteriorated quality representative of that which could be expected after wildfire is currently unavailable. Such methods are needed to meaningfully evaluate implications of wildfire to drinking water treatability at bench- and pilot-scales and to investigate treatment performance capacity. Thus, the objective of this work was to provide guidance regarding (1) post-fire ash collection and (2) wildfire ash-impacted source water preparation. Field approaches for ash characterization and collection were synthesized. Various factors that should be considered when preparing a wildfire ash-impacted source water are discussed and previously reported methods of wildfire ash-impacted water preparation were then identified and synthesized; this included review and discussion of methods that have been used to evaluate effects wildfire effects on drinking water treatability to date. Thereafter, the available information was synthesized to propose guidance regarding (1) post-fire ash collection and (2) wildfire ash-impacted source water preparation for evaluating of wildfire effects on drinking water treatment. Limitations of these approaches are discussed. Finally, a detailed case study demonstrating the preparation of severely deteriorated, wildfire ash-impacted water with quality that might be expected following major runoff events after severe wildfire is provided to show that wildfire ash-impacted water with consistent quality (e.g., relative standard deviation of dissolved organic carbon (DOC) concentration <10%).

2.2 Introduction

The severity and frequency of wildfire have substantially increased in recent decades as a result of warmer climate promoting drought conditions (Flannigan et al., 2009; Westerling et al., 2006). Such conditions have the potential to adversely impact water sources that challenge the provision of safe drinking water (Bladon et al., 2014; Emelko et al., 2011; Robinne et al., 2021). Pyrogenic materials remaining on the landscape after wildfire may be rapidly mobilized into surface water following major runoff events, such as storm or snow melt, thereby degrading the quality of surface water (Moody & Martin, 2001; Shakeby & Doerr, 2006). Various water quality parameters can be impacted following wildfire, including increased

levels of suspended solids and turbidity (Silins et al., 2009; Stone et al., 2014), high concentrations of DOC (Emelko et al., 2011; Emelko & Sham, 2014; Writer et al., 2014), elevated levels of heavy metals (Kelly et al., 2006; Wolf et al., 2008), and excessive quantities of nutrients, such as nitrogen and phosphorus (Bladon et al., 2008; Emelko et al., 2011; Silins et al., 2014). Wildfire impacting urban environments may also lead to health concerns when anthropogenic contaminants (e.g., benzene) enter treated water supplies because of pyrolysis of distribution system materials (Isaacson et al., 2021; Macler et al., 2020; Proctor et al., 2020). Although wildfire may impact both wildland (i.e., non-urban) and urban areas, the focus of this work is the collection of ash and generation of wildfire ash-impacted water after wildfire in non-urbanized areas (i.e., wildland fire) because the potential range of anthropogenic contaminants running off the urbanized landscape would be highly diverse and wildfire/landscape specific.

Wildfire is a significant threat to the provision of safe drinking water even in absence of anthropogenic contaminants. Severe wildland fire can result more variable source water quality (Stone et al., 2011) that makes operational response with respect to chemical dosing in both conventional and advanced drinking water treatment systems more challenging; as a result, small systems with relatively limited operator and financial resources are especially vulnerable (Emelko et al., 2011; Emelko & Sham, 2014). Following wildfire, more precipitation reaches the landscape (Williams et al., 2019) and burned material can be rapidly mobilized from the landscape to receiving streams by erosion from wind or runoff (Moody & Martin, 2001; Santín et al., 2015). Increased erosion follows wildfire, resulting in increased sediment loads to receiving streams (Silins et al., 2009; 2016; Tecle & Neary, 2015); hydrophobic soil conditions reduce permeability and further increase overland runoff (Doerr et al., 2000; Certini, 2005; Neary et al., 2005). These changes on the landscape often impact the quality and treatability of receiving waters. For example, increases in suspended solids/turbidity (Silins et al., 2009; Stone et al., 2014), nutrients (Bladon et al., 2008; Emelko et al., 2011; Silins et al., 2014), and dissolved organic carbon (DOC) (Emelko et al., 2011; Writer et al., 2014), which typically drive the selection, design, and operation of drinking water infrastructure (Emelko et al., 2011) are frequently reported after wildland fire. Thus, even in absence of toxic anthropogenic contaminants, degraded water quality following severe wildfire can challenge drinking water treatment and operational response capacities, leading to an inability to meet demands, service disruptions or even outages (Emelko et al. 2011).

The impacts of wildfire on source water quality may last for many years after wildfire (Emelko et al., 2016). While anecdotal and retrospective case studies about wildfire impacts on drinking water treatment are available (White et al., 2006; Writer et al., 2014), they typically provide limited information about treatment technology capabilities; thus, it is not surprising that there is widespread belief that treatment of severely deteriorated source water may not always be possible after wildfire (Sham et al., 2013; Emelko & Sham,

2014). In 2014, an international expert panel comprised of leading scientists and practitioners was assembled by the Water Research Foundation and the Canadian Water Network to discuss wildfire impacts on water supply and treatment and the potential for mitigation. The panel concluded that wildfire on the natural, unurbanized landscape (i.e., wildland fire) can be catastrophic for drinking water treatment because "water treatment plants and processes are not always designed to treat the range of changes in the character and/or magnitude of source water quality parameters (e.g., peak values of turbidity, dissolved organic carbon, nutrients, or heavy metals) after wildfire, and some of these fluctuations may render existing treatment capacity inadequate" (Emelko & Sham, 2014).

To investigate the treatment of wildfire-impacted water, both the extent and duration of source water quality change must be considered. Evaluation of the effects of wildfire on drinking water treatment processes using water flowing from naturally burned landscapes (Emelko et al., 2011; Writer et al., 2014) is especially ideal for case-specific information; however, the collection of large volumes of wildfire-impacted, deteriorated water can be logistically and financially prohibitive, especially for pilot-scale investigation that are critical for treatment technology feasibility assessment (Crittenden et al., 2012). Wildfire-impacted source water collection can be especially challenging when extremes in quality deterioration are of interest because the timing and duration of these periods of source water quality deterioration depends on numerous factors such as storm events, erosion processes, hysteresis, biogeochemical transformation, etc. (Lintern et al. 2018) and is therefore difficult to predict. As such, it can be advantageous and necessary to prepare water indictive of the environmental conditions which are being investigated, with the same major composition as the natural water being studied when performing experiments (Smith et al., 2002). In spite of the array of drinking water treatment studies focused on evaluating wildfire impacts on drinking water treatability, guidance for the preparation of wildfire ash-impacted source water which that is representative of that which could be expected after wildfire is not currently available. Accordingly, the objective of this work is to provide a general framework and guidance for the (i) post-fire ash collection, and (ii) preparation of source water with deteriorated quality consistent with what might be experienced after wildfire so that it can be used to investigate drinking water treatability at either bench- or pilot-scales.

2.3 Materials & Methods

Ash can be considered one of the major by-products resulting from the transformation of biomass, necromass, and soil organic matter by wildfire; comprised of mineral materials and charred organic constituents, it is the particulate residue that remains after wildfire (Bodí et al., 2014). Ash may be incorporated into soil profiles or redistributed by direct delivery to water supplies via atmospheric deposition or runoff to surface water, or dissolution, leaching, and infiltration to groundwater. Ash delivered to surface water supplies may further undergo dissolution, leaching, or transformation prior to treatment.

Thus, water type and environmental setting must be considered when collecting ash and preparing wildfire ash-impacted source water. When wildfire impacted source water is not available, wildfire-impacted source water can be generated by (i) adding post-fire ash to source water and (ii) pre-treating the water so that its quality is more consistent with that which would be expected after wildfire in the specific environmental setting being investigated.

An overview of the process developed herein to produce wildfire ash-impacted water for use in drinking water treatment evaluations is provided in Figure 2.1. In brief, it is critical to recognize that the collection of fresh ash after wildfire and prior to precipitation is often desirable because it will not have undergone any changes in composition (e.g., due to leaching, dissolution, biological transformation, etc.); however, the collection of fresh ash can be dangerous because it often involves obtaining access to active wildfire sites. Though not discussed further herein, access to active wildfire sites typically requires coordination with regional and federal government agencies responsible for wildfire response and management. The amount of ash required for analysis is a key factor for consideration because it may range from grams to kilograms for bench-scale work (depending on the number of analyses to be conducted) and hundreds of kilograms to multiple tonnes for pilot-scale work. As burn severity can impact water quality (Santín et al., 2015), and water quality impacts water treatability (Emelko et al., 2011), burn severity should also be considered. When possible, wildfire ash collection should include representative composite samples collected from multiple locations so that variability in the impacts on water quality can be assessed. It is at this point that differentiation in burn severity may be considered and reflected in sample collection and separation, depending on the objectives of the study. While there is a wide range of possible interactions between wildfire ash and water resources, three simplified source water scenarios (groundwater, surface runoff to surface water, and surface runoff to surface water with subsequent settling) were identified herein because the associated source water types would require different pre-treatment approaches (i.e., filtration for solids removal, continuous mixing, or settling, respectively) prior to use in drinking water treatment investigations.
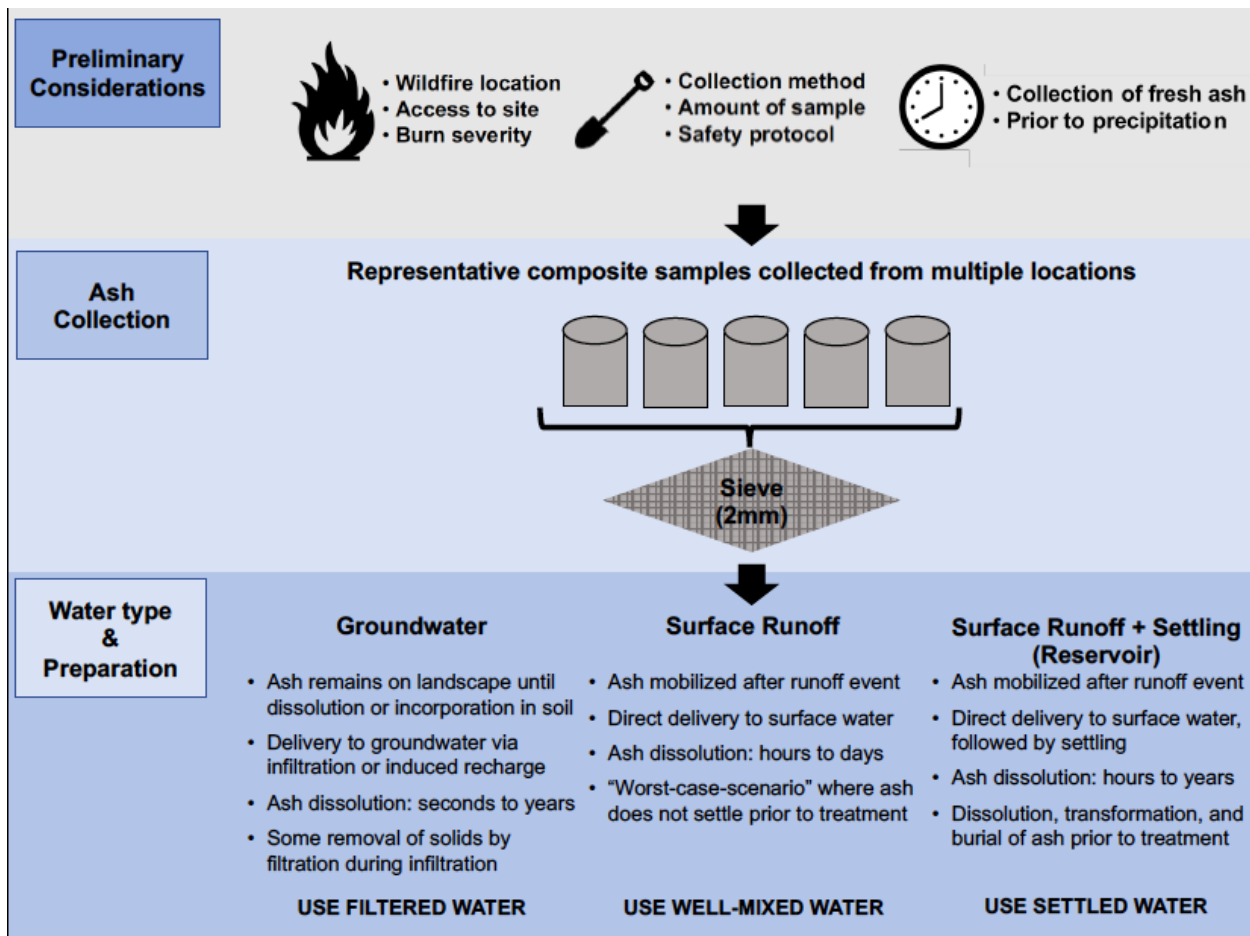
Figure 2.1: Overview of the process followed to produce wildfire ash-impacted water for use in drinking water treatment evaluations.

2.4 Wildfire ash collection

2.4.1 General considerations

The collection wildfire ash requires preliminary planning to ensure collection can be effectively executed. To be most efficient and effective, it is essential to collaborate with wildfire authorities so that sample locations may be identified based on ease of accessibility (e.g., near road access) and severity of fire (e.g., severe wildfire where large amounts of ash will be available). Additionally, partnering with wildfire authorities is crucial to ensure ash can be collected safely, as post-wildfire landscapes are extremely hazardous environments, especially in cases where active fires are still burning in surrounding areas. In such situations, only limited access periods may be granted to enter active burn zones; this will impact the methods used and the amount of ash that is collected. In addition to safety, key guidance for wildfire ash collection is summarized in Table 2.1.

Table 2.1: Guidance for wildfire ash collection.

- **Site Accessibility:** Is the site near an accessible road? This is important for facilitating ash transport.

- **Transportation:** Consider the type of vehicle required to access the site and transport the collected materials. A pick-up truck with 4-wheel drive is preferable; ATVs and/or cargo vans may also be considered. A typical cargo van can hold 80, 20L pails. A tarp and rope or bungee cords may be required to cover sample pails.

- **Ash Availability:** Wildfires do not uniformly burn the landscape. Ensure that sufficient quantities of ash are available. Ash often collects in depressions on hillslopes, on hummocky terrain, and in erosion features such as drainage ditches or under burned logs or stumps.

  Ash collection: Use soft bristled kitchen brooms or brushes with dustpans to collect ash. A snow shovel or spade may be beneficial in some circumstances; brush the surface lightly to collect light, low-density material on surface; avoid upsetting soil below ash layer. Ensure representative sampling by collecting ash samples at several locations, if possible. Separation of ash samples according to type of ash and burn severity may be desirable—detailed guidance is provided below in section 2.4.2. in brief, in addition to differentiating by burn severity, different sample types may be collected, depending on the objectives of the work. They include:
  - **Burned vegetation (ash layer)**: burned canopy, understory, and duff layer that remains on the ground surface after wildfire,
  - **Burned soil (surface/subsurface)**: collected below the ash layer, and
  - **Composite (i.e., burned vegetation and soil)**: collected from the upper ~5 cm of material remaining on the landscape; it includes the material mobilized from the landscape after major runoff events.

- **Weather:** Is rain forecasted and/or has it already rained? While the weather forecast is important for safety, collection of fresh ash after wildfire and prior to precipitation is often desirable because it will not have undergone any changes in composition (e.g., due to leaching, dissolution, biological transformation, etc.).

- **Preparedness:** Complete Safe Work Plan in advance and bring copies for every team member. Confirm objectives and methodology prior to meeting with wildfire field staff. Determine if additional samples/information will be collected in the field, such as water samples, soil samples, soil profiles, unburned samples, low/moderate burn samples, etc. Ensure that all necessary supplies/equipment are brought into field sample area.

- **Documentation:** Record all relevant site information. This should include:
  - GPS coordinates should be recorded at every ash collection site.
  - Pin the sampling location on the GPS and write latitude and longitude on sampling bags and pails. Labelling pails and bags is extremely important (use sharpees to write on lids and sides of pails; ensure pail lids are free from dust when labelling or sharpee will rub off; consider covering sharpee labels with epoxy to prevent rubbing off).
  - Measure depth of ash at all sampling points.
  - Photo- and/or video-document the deposition and spatial variability of ash. Close-up images can help to inform burn severity, as can landscape images.
  - Record all site characteristics: slope, burn severity, vegetation type(s), etc.

- **Fitness:** Ash collection is physically demanding, and all team members must be physically fit and prepared to work under challenging conditions (i.e., hot weather, dust, steep slopes, long work days, etc.). Hydration and nourishment are critical.

- **Situational Awareness:** Work must be completed as cautiously and quickly as possible: conditions in wildfire mountain regions can change rapidly and evacuating an area may be required at a moment's notice. Park vehicles facing toward the road to facilitate rapid evacuation. Stop work every few minutes to scan surroundings to ensure that the environment is safe (i.e., no leaning trees, no bears, no nearby flames, no holes, no potential for mass wasting or debris flows).

Detailed guidance regarding type of ash and burn severity determination is provided below in section 2.4.2.

Ash should be collected at several locations across a burn site to provide a reasonable representation of the post-fire conditions on the landscape. The number of samples will be determined by experimental design and environmental conditions, such as ash availability on the landscape. Collecting samples from multiple locations is important as ash will not be ubiquitously dispersed across the landscape and will be in deposited in low depressions on the landscape and under logs (Neary et al., 2005). The timing of when samples are collected is another import consideration and must be indicative of the environmental conditions which are being experimentally replicated with regards to impacts on water quality. For instance, while many studies have collected fresh ash immediately after a wildfire and prior to any precipitation events (e.g., Bodí et al., 2014; Pereira et al., 2012; Pereira et al., 2014), other studies have prepared wildfire-impacted source water with samples collected months (Ferrer et al., 2021; Revchuck & Suffet, 2014) or even years after a fire (Majidzadeh et al., 2019; Revchuck & Suffet, 2014). The amount of time between when a wildfire occurs and when ash is collected ash will impact the character of the material collected, as more exposure to precipitation and wind will alter the nature of the ash, such as leaching of water-soluble organic matter following storms immediately after a fire (Olivares et al., 2019).

Selecting the appropriate equipment to collect ash must also be considered. In previous studies various methods have been used to collect ash, including brushes (Pereira et al., 2014; Santín et al., 2015), shovels or trowels (Brye et al., 2002; Hohner et al., 2019b), spoons (Pereira et al., 2010; Pereira et al., 2014), or portable field vacuums (Hughes et al., 2000). The method of collection will be determined by the landscape and type of material that is desired; for instance, light, low density material which resides on the surface, should be collected using a soft-bristled brush or broom to avoid collecting soil below the ash layer. However, in cases where soil samples impacted by wildfire are desired, a shovel or trowel will likely be the most appropriate tool for the task. Randomized sampling grids have been used in some investigations to systematically collect ash samples (Hohner 2019b; Majidzadeh et al., 2019; Pereira et al., 2012; Pereira et al., 2014; Santín et al., 2015), which can be very useful depending on the information being sought and/or if adequate access time is permitted to collect ash at a burn site. The method selected for sample collection should also be based on the amount of ash required, where, for example, using a spoon or trowel may not be appropriate for collecting large quantities.

2.4.2 Type of ash and burn severity

Ash has been collected immediately after a wildland fire has burned (e.g., Bodí et al., 2011; Harper et al., 2019; Pereira et al., 2014; Tsai et al., 2017; Wang et al., 2015a), following prescribed or experimental burns (Pereira et al., 2011b; Ulery et al., 1993; Uzun et al., 2020b), collected from river bank sediment samples from post-fire streams (Cawley et al., 2017; Hohner et al., 2017), or produced in a laboratory furnace

(Hohner et al., 2019b; Majidzadeh et al., 2015; Tsai & Chow, 2016; Ubeda et al., 2009; Wang et al., 2015b; Wilkerson & Rosario-Ortiz, 2021). While the production of thermally-altered material in laboratory furnaces can control heat, these conditions do not adequately mimic natural burning conditions, regardless of the temperatures used (Bodí et al., 2011; Santín et al., 2017). The use of natural wildfire ash provides a more realistic indication of wildfire impacts. The methods presented here specifically focus on post-fire material collected from natural wildfires that is referred to herein as ash, defined as the residual particulate matter remaining on the landscape following the burning of wildland fuels which consist of charred organic and mineral materials (Bodí et al., 2014) and is easily transported from hillslopes to source waters following major runoff events.

The term "burn severity" is somewhat subjective as there is no universal approach for characterizing or quantifying burn severity due to the variability between ecosystems and the specific metrics (e.g., vegetation type and cover) which may be assessed (DeBano et al., 1998). In general, burn severity is largely based on the loss of organic matter above ground and in soil that is converted to ash (Keeley, 2009). Burn severity can have profoundly different impacts on landscape conditions (e.g., extent of vegetation loss; extent of soil heating) which in turn can have differential impacts on water quality (Norwood et al., 2013; Pereira et al., 2011a; Santín et al., 2015; Uzun et al., 2020b). In spite of this, there are guidelines which aid in determining burn severity in forested ecosystems; they are based on specific post-fire impacts, such as canopy burn, duff layer consumption, and level of charring on branches (e.g., Chafer et al., 2004; Ryan & Noste, 1985; Ryan, 2002; Stockdale et al., 2016). Although ash colour has been used as a parameter to evaluate burn severity (e.g., Pereira et al., 2014; Robichaud et al., 2007; Ubeda et al., 2009; Ulery & Graham, 1993), this method may result in an inaccurate indication of burn severity (Bodí et al., 2011). A visual assessment of a burn site is a simple approach that can be used for evaluating wildfire burn severity (Figure 2.2). It involves identifying various impacts of wildfire on vegetation, such as duff layer charring and the extent to which trees are burned, such as the presence or absence crown burning (Keeley, 2009). In addition to burn severity, the specific type of material that was burned, such as vegetation (e.g., Pereira et al., 2014), soil (e.g., Cawley et al., 2017), or composited vegetation and soil (e.g., Santín et al., 2015; Wang et al., 2016) should also be considered. While there are benefits to studying either burned vegetation or soil independently, using composite samples that include both burned vegetation and soil are most indicative of the actual ash remaining on the landscape post-fire that are most likely impact water quality.
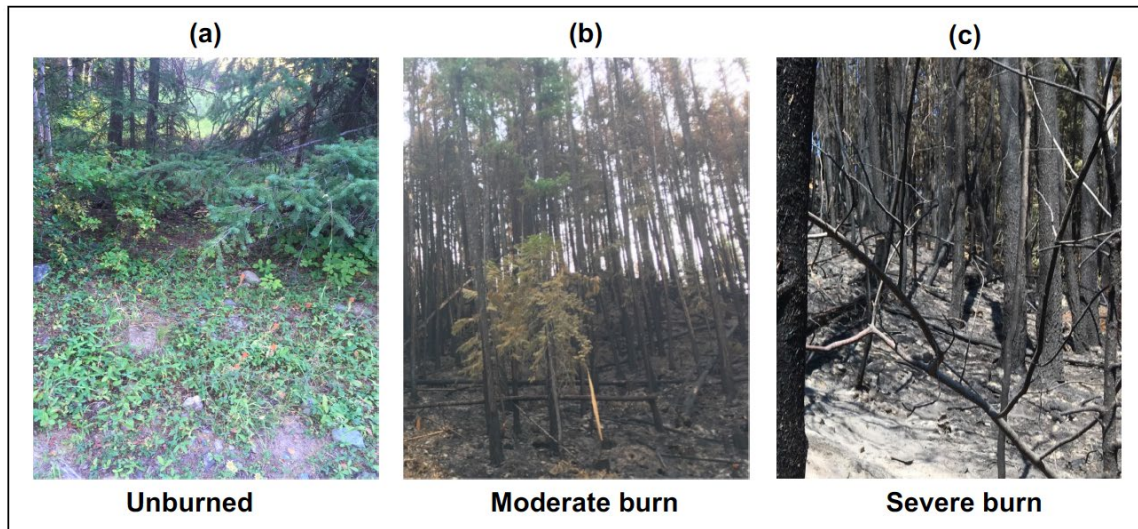
Figure 2.2: Landscapes with different levels of burn severity as indicated by visual assessment: (a) unburned, (b) moderate burn, and (c), and severe burn. The difference in burn severity conditions was indicated by level of vegetation consumed during the Thuya Lake Road wildfire in 2017, where both ground and canopy vegetation were assessed to determine burn severity.

2.5 Preparing wildfire ash-impacted water

2.5.1 Water quality targets representing wildfire impacts

In the United States and Canada, surface water must be treated by conventional treatment (i.e., coagulation, flocculation, clarification, granular media filtration, disinfection) or equivalent processes (USEPA 1975; 1989; 1996; 1998; 2002; 2006a;b; MECP 2019; Health Canada 2019b; Health Canada 2019; MECP, 2019); these approaches are common globally (Crittenden et al., 2012). The two main drivers of surface water treatment process selection and operation are turbidity and DOC concentration (Crittenden et al., 2012). DOC character (especially aromaticity, which is indicated by specific ultraviolet absorbance [SUVA]), alkalinity, and pH are also important because jointly with DOC concentration and turbidity, they govern coagulant dosing needs and coagulation process performance (Crittenden et al., 2012). If coagulation is ineffective, critical subsequent treatment processes such as granular media filtration and disinfection may be compromised; when this happens, service disruptions and even outages may occur (Emelko et al., 2011). Accordingly, while there are many potential impacts of wildfire on water quality, turbidity and DOC are the most relevant to evaluating drinking water treatability (Emelko et al., 2011). Wildfire often results in elevated turbidity and DOC concentrations in receiving waters (Clark, 2010; Dahm et al., 2015; Emelko et al., 2011; Emmerton et al., 2020; Gallaher & Koch, 2004; Hohner et al., 2016; Leak et al., 2003; Neary et al., 2005; Rhoades et al., 2011; White et al., 2006; Writer & Murphy, 2012). While any turbidity, DOC concentration, ultraviolet absorbance at 254 nm (UVA_{254}) (which can be readily measured online and relates

DOC concentration to aromaticity because SUVA is UVA_{254} normalized for DOC concentration [Weishaar et al., 2003]), or other aspects of water quality can be targeted, it is often difficult to concurrently target specified levels of multiple aspects of water quality when preparing wildfire ash-impacted source water for use in drinking water treatment evaluations.

A wide range of deteriorated water quality conditions have been reported following severe wildfire (Clark, 2010; Dahm et al., 2015; Emelko et al., 2011; Emmerton et al., 2020; Gallaher & Koch, 2004; Hohner et al., 2016; Leak et al., 2003; Neary et al., 2005; Rhoades et al., 2011; White et al., 2006; Writer & Murphy, 2012), peak values of turbidity and DOC concentration following severe wildfire where deteriorated water quality has been reported are summarized in Table 2.2. Turbidity levels greater than 500 NTU and DOC concentrations greater than 15 mg·L^{-1} are on the lower end of the range of these reported peak values, which may be considered representative of worst-case scenarios of deteriorated source water quality resulting from severe wildfire. Notably, although severely deteriorated water quality after wildfire can pose substantial challenges for drinking water treatment (Emelko et al., 2011), such water quality events are episodic and relatively short-lived, lasting anywhere from a day to a week after (Table 2.3). They are often associated with local high flow conditions (Emelko et al., 2011; Neary et al., 2005; Writer & Murphy, 2012). The short-lived and episodic nature of severely deteriorated source water quality events is critical to highlight, as associated treatment challenges may be relatively short in duration.

Table 2.2: Peak turbidity and dissolved organic carbon (DOC) following severe wildfire where deteriorated water quality has been reported.

Fire name	Location	Year	Turbidity (NTU)	DOC (mg L^{-1})	Reference
Cerro Grande	New Mexico, USA	2000	76000*	110**	Gallaher & Koch, 2004
Rodeo-Chediski	Arizona, USA	2002	51 000	N/A	Neary et al., 2005
Hayman	Colorado, USA	2002	>600	N/A	Rhoades et al., 2011
Missionary Ridge	Colorado, USA	2002	3640	18	Clark, 2010
Lost Creek	Alberta, Canada	2003	1311	20	Emelko et al., 2011
Australian Alps bushfire	Victoria, Australia	2003	>100000	51**	Leak et al., 2003
Cotter River	ACT/NSW, Australia	2003	3000	N/A	White et al., 2006
Fourmile Canyon	Colorado, USA	2010	50 000	>70	Writer & Murphy, 2012
Las Conchas	New Mexico, USA	2011	2500	N/A	Dahm et al., 2015
High Park	Colorado, USA	2012	4200	18	Hohner et al., 2016
Horse River	Alberta, Canada	2016	>1000	N/A	Emmerton et al., 2020

*Reported as total suspended solids (mg L^{-1})
**Reported as total organic carbon

Table 2.3: Duration (days) of severely deteriorated water quality following severe wildfire.

Wildfire Location	Deteriorated water quality duration	References
USA	~1-2 days	Oropeza, 2017
USA	2 days	Mast et al., 2016
Australia	2-6 days	Lyon & O'Connor, 2008
Australia	5 days	Leak et al., 2003
USA	~7 days	Dahm et al., 2015
USA	short period (days)	Murphy et al., 2015
USA	short period (days)	Writer & Murphy, 2012

2.5.2 Wildfire ash-impacted water source water preparation

Once ash has been collected, but prior to preparing wildfire ash-impacted source water, ash should be sieved to ensure that large debris is removed, and the sample is relatively homogeneous. The size of mesh used for sieving should be based on the specific sample and specific needs for an experiment, such as 1 mm mesh (Cawley et al., 2018; Harper et al., 2019) or 2 mm (Hageman et al., 2007; Ferrer et al., 2021; Majidzadeh et al., 2019; Plumlee et al., 2007). Although sieving ash is generally desired prior to preparing wildfire ash-impacted source water, there are instances where sieving may not be desirable, such as when investigating the impacts of larger debris on water quality.

The type of water used to prepare wildfire ash-impacted water source water is also important to consider. Differences in pH and alkalinity, for example, may impact ash dissolution and leaching, thereby ultimately impacting the treatability of the ash-impacted source water being tested. A range of waters may be used to prepare wildfire ash-impacted source water, including Milli-Q® or deionized water (Majidzadeh et al., 2019; Norwood et al., 2013; Plumlee et al., 2007; Tsai & Chow, 2016; Ubeda et al., 2009; Wang et al., 2015a), rain water (Chen et al., 2020; Uzun et al., 2020b), river water (Cawley et al., 2018), low carbon tap water (Hohner et al., 2019), and buffered water to replicate a specific water quality scenario (Harper et al., 2019; Revchuck & Suffet, 2014).

In addition to the water used to prepare a wildfire ash-impacted source water, the type of vessel used for mixing, the mixing method, and mixing time should also be considered. Various types of vessels have been used to prepare wildfire ash-impacted source water, including Pyrex beakers (Cawley et al., 2018), Erlenmeyer flasks (Wang et al., 2015a), and glass carboys (Hohner et al., 2017). Once ash is added to a vessel, different methods of mixing may be applied, such as magnetic stir bars (Ubeda et al., 2009), orbital

shaking (Harper et al., 2019; Tsai & Chow, 2016; Tsai et al., 2017), and paddles on a jar test apparatus (Chapter 3 and 5), or by manually shaking or with a glass stir rod (Cawley et al., 2018; Ferrer et al., 2021; Hageman et al., 2007). While various mixing methods are available, the most controlled mixing is achieved by using a jar test apparatus or orbital mixer, where mixing conditions (i.e., RPMs) can be set and maintained at a constant level. Whether samples are left open to atmosphere during mixing should also be considered; samples replicating surface water conditions ought to be open to atmosphere, however, samples may be mixed in sealed containers if subsurface conditions are being represented. The amount of time an ash-impacted source water sample should be mixed prior to being assessed for treatability will depend on the desired outcome of the source water. Various mixing times for wildfire ash in water have been reported, including 2 min (Cawley et al., 2018; Hohner et al., 2019), 5 min (Ferrer et al., 2021), 1 h (Majidzadeh et al., 2019), 2 h (Pereira et al., 2011b; Wang et al., 2015a), 4 h (Harper et al., 2019), 6 h (Wilkerson & Rosario-Ortiz, 2021), 24 h (Tsai & Chow, 2016), 48 h (Revchuck & Suffet, 2014), and 72 h (Tsai et al., 2017).

Further treatment after ash addition to water is an important consideration that is directly linked to the type of water (e.g., surface water, groundwater, partially treated water) or treatment scenario (e.g., direct runoff to surface water, surface water with raw water storage reservoir) being investigated. If the objective of an investigation is to represent water quality reflective of ash being mobilized from the landscape directly to receiving waters after a major runoff event without any time for settling and resulting in a "worst-case scenario", the water matrix should be well-mixed to preclude settling prior to analysis and/or treatment testing. The mixing time should be consistent with what might be experienced on the landscape; for example, it may reflect the time it takes runoff to reach a WTP intake ("surface runoff" scenario, Figure 2.1). If the study is designed to reflect storage of raw water in a reservoir, the water matrix should be well-mixed and settling should be permitted to reflect the residence time and extent of settling that would be expected at the intake location; in this case, only the supernatant would be used ("surface runoff + settling" scenario, Figure 2.1). In contrast, if passage through surficial forest floor and geologic materials is the focus of study (e.g., groundwater), the water matrix should be well mixed and then maximal leaching of materials to the aqueous phase should be considered and kinetics of those reaction may be required (Kasprzyk et al., 2019); leaching time should also be considered. Filtration can be used to reflect solids removal ("groundwater" scenario, Figure 2.1). While various filtration approaches have been used in leaching studies (e.g., Chen et al., 2020; Hohner et al., 2019; Cawley et al., 2018), they have not been validated with respect to the extent connectivity to drinking water treatment or contaminant transport in the subsurface.

The analysis of water quality will vary depending on the aspects of drinking water treatability which are to be assessed, and may include general water quality parameters such as turbidity, DOC, UVA_{254}, pH,

alkalinity, or conductivity. Additionally, the quantity of ash used to prepare a wildfire ash-impacted source water will be dependent on the specific targets for different water quality parameters of interest and the availability of ash. Conducting preliminary tests with different quantities of ash will aid in determining the optimal ash-to-water ratio, as is described in the subsequent section.

2.6 Case study: Preparation of severely deteriorated, wildfire ash-impacted surface water

The methods described above were used to prepare wildfire ash-impacted source water with quality representative of worst-case scenario, severely deteriorated water that occurs following wildfire. The specific post-fire scenario investigated was one in which ash remaining on the landscape is rapidly mobilized from hillslopes to receiving waters following a major storm event immediately after a severe wildfire, yielding severely deteriorated source water quality or "black water" conditions in which turbidity and DOC are elevated (i.e., >500 NTU and >15 mg·L^{-1}, respectively). A summary and justification of the various water quality set-points is provided in Table A1.

2.6.1 Ash collection

Fresh ash was collected from the Thuya Lake Road (TLR) wildfire (+51.4098 latitude, -120.2435 longitude; burn area 556 ha), which was part of the Little Fort Fire Complex that burned in July 2017, near Little Fort, British Columbia (BC), Canada (Figure 2.3). Ash was collected from this fire site due to it having been a severe wildfire, was easily accessible from major roadways, and permission was obtained to enter the site from wildfire authorities. The predominant tree species in the burn area were Douglas Fir (*Pseudotsuga menziesii* var. *glauca*), with a mixture of Spruce hybrids (genus *Picea*), Paper Birch (*Betula papyrifera*), and Lodgepole Pine (*Pinus contorta* var. *latifolia*). Ash was collected on August 2, 2017 prior to any precipitation events to ensure that water extractible organic matter had not been removed due to precipitation. Surface ash was randomly collected from an area of approximately 1.8 ha to ensure material was broadly representative of high severity wildfire across the landscape. All canopy vegetation and surface litter were consumed, and light-coloured ash deposition and layers of charred organic matter were several centimeters deep at the site, further indicating a severe wildfire (Keeley, 2009; Ryan & Noste 1985; Úbeda et al., 2009). The collected ash was generated by non-uniform heating conditions, as would be expected due to natural variability in fuel consumption (Parson et al., 2010) where high temperatures may exist in vegetation and litter and lower temperatures may exist below the soil surface (Alexis et al., 2007).

(a)

(b)

(c)

(d)
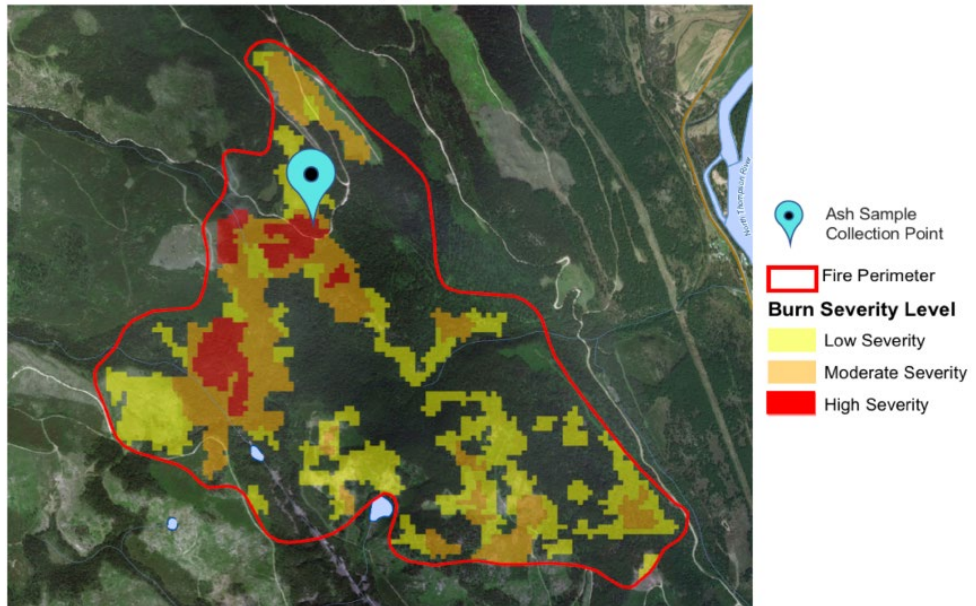
Figure 2.3: Ash collection at a severe wildfire burn site (Thuya Lake Road wildfire) in August 2017; (a) Burn severity map of the 2017 Thuya Lake Road (TLR) wildfire (image adapted from Government of British Columbia 2017); (b) Severe wildfire at the TLR ash collection site was indicated by crown burning where all canopy vegetation was consumed; (c) All surface vegetation was consumed by wildfire at the TLR ash collection site providing an indication of severe wildfire; (d) Ash was present on the landscape at a depth of approximately 2–5 cm across the burn site; ash deposits were not ubiquitous across the burn site and generally accumulated in surface depressions and under logs; (e) Soft-bristled brooms and snow shovels were used to collect ash samples; ash samples were collected in 19 L plastic pails.

The severe TLR wildfire resulted in substantial quantities of ash on the landscape, which was collected using soft-bristled brooms, dust pans, and shovels. The method employed for the ash collection was based on the need to collect large quantities of ash, where small implements, such as spoons or trowels, would have been inadequate. Care was taken to collect the top layer of the light, low-density ash and to minimize disturbance to the underlying soil so that the material collected was indicative of ash which is easily mobilized off the landscape following major runoff events. Samples consisted of burned material that ranged in depth from approximately 2–5 cm and was comprised of charred organic and mineral material components. Ash deposits were not ubiquitous across the sample site, since biophysical conditions, such as terrain topography, can impact ash accumulation (Bodí et al., 2014). Ash samples were generally collected from spaces where ash deposits had accumulated, such as below burned logs or in surface depressions. A total of 40 samples were collected in 19-L plastic pails, labelled, and stored in a cool, dry space.

2.6.2 Wildfire ash-impacted source water preparation

Wildfire ash-impacted source water was prepared (Figure 2.4) to reflect severely- deteriorated wildfire-impacted water by adding TLR ash to Elbow River water, collected from the Glenmore Reservoir in Calgary, Alberta, Canada. The Elbow River is a high-quality source water that provides the drinking water for approximately 50% of the city of Calgary. It is located in the montane and Rocky Mountain foothills region of southwest Alberta, Canada. The headwaters of the Elbow River originate in the mountains and flow through boreal foothills forests and then Aspen Parkland that has some anthropogenic impacts from agriculture and residential development. Wildfire is the predominant natural disturbance agent in region and influences vegetation type structure (Cumming, 2001; Rogeau et al., 2016). Elbow River water was used in the preparation of wildfire ash-impacted source water. It originates in the forested headwaters in the Montane Cordillera ecozone, where wildfire comprises the major disturbance regime. The Elbow River watershed has been impacted by wildfire historically and may potentially be impacted by it in the future. Elbow River was used (as opposed to distilled or Milli-Q® water) because it is a natural water matrix with quality (DOC concentration and character, turbidity, pH, alkalinity) that is linked to coagulation efficacy during drinking water treatment.
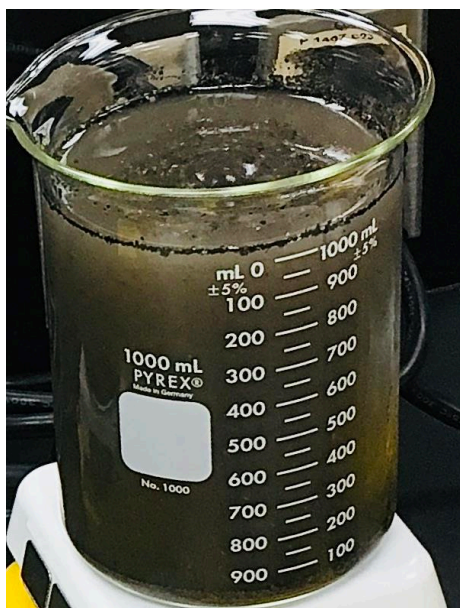
Figure 2.4: Severely-deteriorated wildfire ash-impacted source water prepared by adding TLR ash to high quality Elbow River water to yield high turbidity (>500 NTU), high DOC (>15 mg·L^{-1}) "black water" representing source water supplies impacted by wildfire ash transport directly from hillslopes to receiving waters after significant post-fire runoff events.

The preliminary preparation of wildfire ash-impacted source water was completed by mixing different quantities of ash with Elbow River water until the water appeared black and highly turbid, with a burnt odour. The purpose of the preliminary preparation of the ash-impacted source water was to determine the amount of TLR ash required to produce a severely-deteriorated ash-impacted source water with turbidity >500 NTU and DOC concentration >15 mg·L^{-1} (Table 2.2; Emelko et al., 2011; Hohner et al., 2016; Writer & Murphy, 2012). Although turbidity and DOC were concurrently investigated while preparing the wildfire ash-impacted source water, DOC concentration was major water quality target because it dictates coagulant dosing (Crittenden et al., 2012).

TLR ash samples of varying quantities (2.0g, 10.0g, and 20.0g) were sieved through a 1 mm screen to remove any large debris and conifer needles and to ensure homogeneity, as has been done in previous studies (Cawley et al., 2018; Harper et al., 2019). The TLR ash samples that were used in the preliminary tests were taken from five different pails to reflect variability in ash composition across the sample site. Ash from each pail was mixed with Elbow River water to achieve ash concentrations of 2.0, 10.0, and 20.0 g·L^{-1}. Ash samples were added to 1000 mL of Elbow River water in 2 L square beakers and mixed using a jar test apparatus (Phipps & Bird, PB-900 Series Programmable 6-Paddle Jar Tester) at 120 RPM for two minutes. The initial mixing speed was selected to ensure that a vortex was formed to promote effective mixing in the beakers. Samples were mixed for 2 minutes in the preliminary study to provide a rapid result to determine the general impacts of different quantities of ash on the wildfire-impacted source water. The turbidity, DOC concentration, and UVA$_{254}$ of the water samples were then evaluated. The preliminary studies indicated that an ash concentration of 5.0 g·L^{-1} obtained by adding TLR ash to Elbow River water was the minimum amount of ash that was required to meet the targeted turbidity and DOC concentrations. The method of preparation for the of 5.0 g·L^{-1} was slightly modified; here, 1-L Pyrex beakers were used to mix samples on the jar test apparatus for 30 min at 150 RPM prior to use in the drinking water treatability evaluations (Chapter 3). A longer mixing time (i.e., 2 vs. 30 min) and faster mixing speed (i.e., 120 vs. 150 RPM) were used to provide additional time for DOC leaching from the ash and promote efficient mixing.

2.6.3 Water quality measurement and analysis

Standard methods (APHA, 2012) were used for water quality analyses, including: turbidity (Method 2130B), UVA$_{254}$ (Method 5910B, pre-filtered through 0.45μm membrane), and DOC (Method 5310C, pre-filtered through 0.45μm membrane filter). Relative standard deviations (RSDs) were calculated to demonstrate water quality consistency in the wildfire ash-impacted source waters that were produced. Least squares

linear regression was used to find the line of best fit line to demonstrate the relationship between UVA_{254} and DOC in the wildfire ash-impacted source water.

2.7 Results and Discussion

While wildfire may affect several aspects of water quality (Emelko et al., 201; Smith et al., 2011); only turbidity, DOC concentration, and UVA_{254} were analyzed herein to demonstrate water quality consistency between the replicate wildfire ash-impacted source waters that were prepared, as these parameters are key drivers of coagulation during drinking water treatment.

The addition of the TLR wildfire ash to the Elbow River water increased DOC concentrations in all of the water samples, which is consistent with previous reports of wildfire ash-impacted source water prepared with fresh ash (Tsai et al., 2017; Wang et al., 2016). The DOC concentrations for the wildfire ash-impacted source waters prepared at 2.0, 10.0, and 20.0 $g \cdot L^{-1}$ were 8.0 ± 0.6, 27.4 ± 1.8, 52.5 ± 3.1 $mg \cdot L^{-1}$ (mean $\pm$ standard error [SE], n=5 in all cases), respectively (Figure 2.5). The resulting DOC concentrations were substantially higher than the Elbow River water, which had a DOC concentration of 1.9 ± 0.2 $mg \cdot L^{-1}$ (mean $\pm$ SE, n=8) prior to the addition of ash.
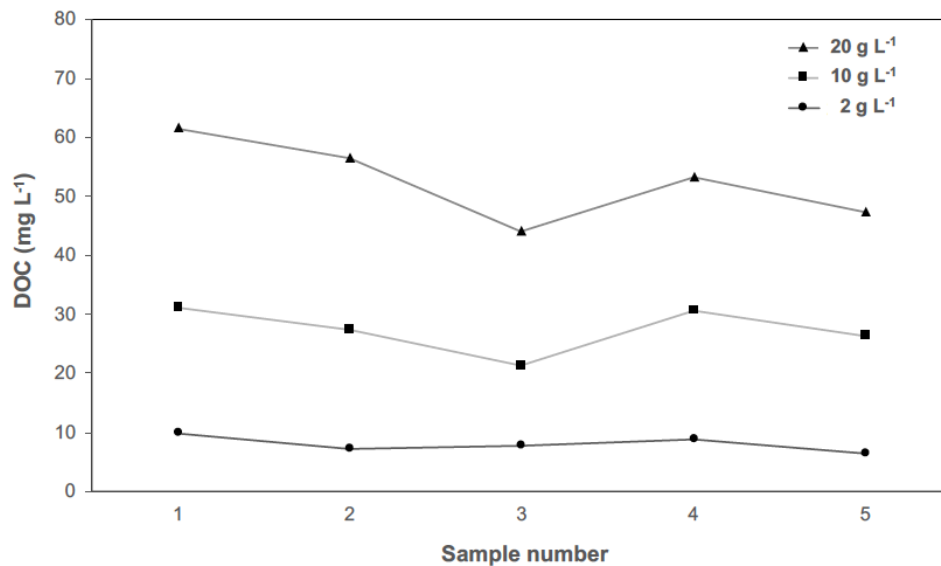
Figure 2.5: DOC variation between wildfire ash-impacted source waters prepared with ash collected at the Thuya Lake Road wildfire in 2017. Ash samples were mixed with Elbow River water to produce several (i.e., 2.0, 10.0, and 20.0 $g \cdot L^{-1}$) wildfire ash-impacted source water with varying concentrations. The sample number indicates the sample pail from where the ash was taken. Ash was collected in five different sample pails that had been collected across the same burn site. Data points are connected by lines in this figure only to improve visualization.

Although all five of the ash samples were collected from the same area at the TLR burn site, the resulting DOC concentrations varied, as would be expected given natural variability in vegetation cover and burn temperature during the fire. The RSDs of the DOC concentrations in the water samples to which 2.0, 10.0, and 20.0 g·L^{-1} of ash were added were 16.8%, 14.4%, and 13.3%, respectively. All of these RSDs were below the 20% target threshold, thereby demonstrating that wildfire ash-impacted source water with consistent DOC concentrations could be prepared using the approach described above. DOC concentration and UVA$_{254}$ were also demonstrated to be well-correlated (R^2=0.98, n=15) (Figure 2.6). This was expected, as good linear correlation between these parameters has been widely reported for surface waters in wildland and other non-urbanized watersheds (Chow et al., 2008), including those impacted by wildfire (Shams, 2018). Knowing that there was a good linear correlation between DOC and UVA$_{254}$ in the wildfire ash-impacted source water prepared with TLR ash, suggests that UVA$_{254}$ may be used as a surrogate parameter for DOC. This is beneficial when conducting drinking water treatability studies as UVA$_{254}$ can be analyzed relatively quickly and easily as compared to DOC concentration.
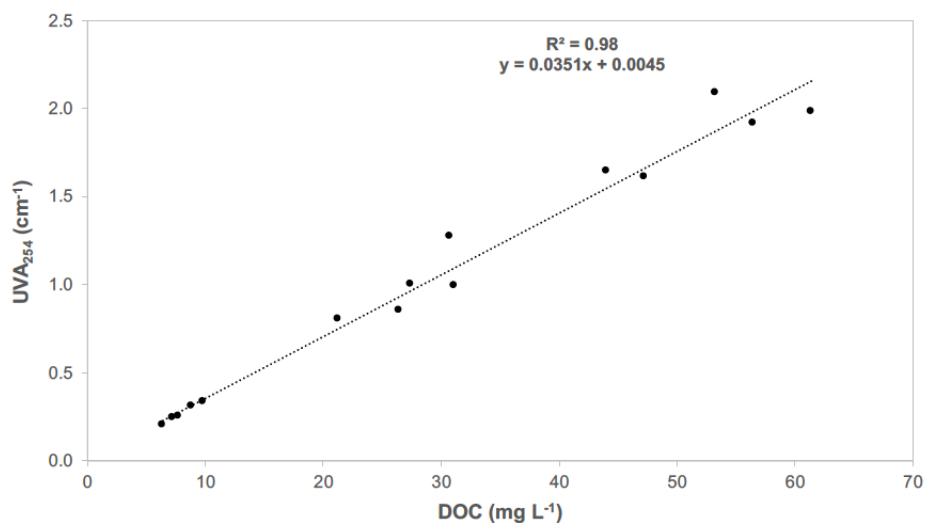
Figure 2.6: Linear correlation between DOC concentration and UVA$_{254}$ in the severely deteriorated ash-impacted source water prepared by adding TLR wildfire ash to Elbow River water. Data presented are from a range of concentrations of TLR ash mixed with Elbow River water (2.0–20.0 g·L^{-1}) during the preliminary assessment to determine the amount of TLR ash required to prepare the severely deteriorated ash-impacted source water to achieve the desired water quality targets (turbidity >500 NTU and DOC >15 mg·L^{-1}).

A 5.0 g·L^{-1} concentration of TLR ash in Elbow River water was used to prepare severely deteriorated, wildfire ash-impacted source water using the smallest quantity of ash possible (to conserve ash sample). Repeated preparations of the wildfire-impacted source water yielded turbidity values of 1,400 ± 60 NTU (mean ± SE, n=12), which was a substantial increase from the 1.11 ± 0.21 NTU (mean ± SE, n=10) baseline

turbidity of Elbow River water. The elevated turbidity levels measured in the wildfire ash-impacted source water were consistent with previous reports of severely deteriorated source water quality after wildfire (e.g., Emelko et al., 2011; Silins et al., 2009). While there was some variability in the turbidity, more consistent levels of DOC and UVA_{254} were achieved (Figure 2.7). The DOC concentrations were 16.0 ± 0.2 mg·L^{-1} (mean $\pm$ SE, n=11) and UVA_{254} values were 0.479 ± 0.009 cm^{-1} (mean $\pm$ SE, n=11). These values were substantially elevated relative to unamended Elbow River water, in which DOC concentrations and UVA_{254} levels were 1.9 ± 0.2 mg·L^{-1} (mean $\pm$ SE, n=8) and 0.049 ± 0.009 cm^{-1} (mean $\pm$ SE, n=9), respectively.
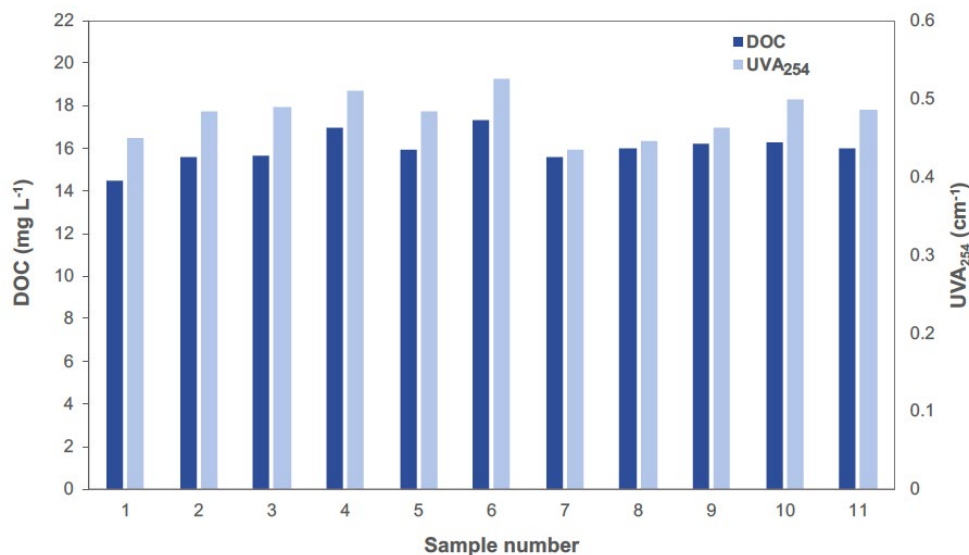
Figure 2.7: DOC and UVA_{254} for samples of severely deteriorated ash-impacted source water (n=11) that were prepared using 5.0 g of TLR ash and 1000 mL of Elbow River water. Consistent results were achieved when ash from the same sample pail was sieved through a 1.0 mm mesh to remove any large debris and homogenized prior to mixing with water.

Since all the source water samples were prepared at ash concentrations of 5.0 g·L^{-1} (with homogenized ash from the same sample pail), consistency in the observed DOC concentrations and UVA_{254} values was expected. An RSD value of 10% was set as a general threshold to indicate whether source water samples were similar or not. The RSD for DOC and UVA_{254} (n=11 in each case) in the wildfire ash-impacted source water demonstrated that a consistent preparation of source water was effectively achieved (i.e. <10%), in which the RSD values for DOC and UVA_{254} were 4.7% and 5.9%, respectively. In contrast, the RSD for turbidity was 13.9%. Notably, achieving consistent levels of DOC and UVA_{254}, is more useful from the perspective of conducting drinking water treatability studies following wildfire, as DOC has been noted to be the most problematic water quality parameter to manage after wildfire (Chen et al., 2020; Hohner et al., 2016) and is the key driver for coagulation (Crittenden et al., 2012).

The SUVA value for the wildfire ash-impacted source water was 2.99 ± 0.04 L·mg^{-1}·m^{-1} (mean $\pm$ SE, n=11), which was an increase from the SUVA of the Elbow River water used to mix ash, which had a SUVA of 2.66 ± 0.25 L·mg^{-1}·m^{-1} (mean $\pm$ SE, n=18). The increase in SUVA following ash addition indicates that the organic carbon was more aromatic in the ash-impacted source water, as SUVA is known to correlate well with the aromaticity and hydrophobicity of organic carbon and provides an indication of treatability through coagulation and DOC removal (Ghernaout et al., 2009). The SUVA results of this study are consistent with previous reports of post-fire water quality where SUVA increases were reported (e.g., Hohner et al., 2016) and are aligned with the anticipated results of the ash-impacted source water SUVA. Shifts toward more aromatic organic carbon after wildfire have been suggested to be a result of changes in functionality of organic carbon due to exposure to high levels of heating during wildfire (Knicker et al., 2007). Shifts in aromaticity, as indicated by SUVA, are important to consider from a drinking water treatment perspective as it provides an indication of expected removal of DOC following treatment (e.g., Edzwald & Tobiason, 1999) and is a valuable parameter for evaluating organic carbon character (i.e., aromaticity) in water before and after treatment.

2.8 Conclusions

The ability to prepare wildfire ash-impacted source waters representative of severely deteriorated water quality following major post-fire runoff events was investigated herein. Previously reported methods of wildfire ash-impacted water preparation were identified and synthesized. Thereafter, the available information was synthesized to propose guidance regarding (1) post-fire ash collection and (2) wildfire ash-impacted source water preparation for evaluating of wildfire effects on drinking water treatment. A case study approach was then used to demonstrate that a severely deteriorated wildfire ash-impacted source water with consistent quality representative of "black water" conditions after major runoff events following wildfire can be produced—this has not been previously demonstrated and advances the body of scientific and applied knowledge focused on evaluating wildfire impacts on drinking water treatability. The key conclusions from this study include:

- There is natural variability in ash samples that are collected from different locations at the same burn site. This leads to variable water quality (i.e., turbidity, DOC, and UVA$_{254}$) when preparing wildfire ash-impacted source waters, especially if ash is used from different sample containers;

- All water quality parameters (turbidity, DOC, and UVA$_{254}$) measured in the wildfire ash-impacted source waters were consistently increased as greater amounts of ash were added;

- DOC and UVA$_{254}$ were well-correlated, highlighting that UVA$_{254}$ may be used as an online surrogate for indicating DOC levels in the wildfire ash-impacted source water; and

- Wildfire ash-impacted source water with consistent quality was prepared at bench-scale (i.e., level of turbidity, DOC concentration, and UVA$_{254}$) when ash from the same sample was used; thereby demonstrating that post-fire, wildfire-impacted source water may be effectively prepared to assess drinking water treatability at bench-scale, and possibly pilot-scales.

Chapter 3:

Treatment of severely-deteriorated post-fire runoff:
Comparison of conventional and high-rate clarification
demonstrates key drinking water treatment capabilities and challenges

3.1 Summary

There is widespread concern that treatment of severely deteriorated water to potable standards may not be possible after severe wildfire. Although reports regarding wildfire impacts on drinking water treatment are increasingly available, they typically provide limited or no information about treatment technology capabilities. Here, the ability to treat worst-case scenario, ash runoff directly from hillslopes to source waters after severe wildfire was investigated—this has not been reported previously. The treatment responses of conventional chemical pre-treatment and high-rate clarification processes (sand-ballasted flocculation [SBF], SBF with enhanced coagulation, and SBF with powdered activated carbon [PAC]) were evaluated at bench-scale to (1) demonstrate key aspects of water quality change that can most challenge water treatment after severe wildfire, and (2) highlight that while technology is available to treat even the most severely deteriorated water, the highly uncertain and typically episodic nature of wildfire-associated shifts in source water quality require particular consideration in treatment infrastructure design and planning. This work showed that lower molecular weight (LMW) acids fraction of dissolved organic carbon (DOC) that is less readily removed by coagulation was substantially elevated after ash addition to high quality source water. While all investigated treatment approaches effectively reduced turbidity for subsequent treatment by filtration, reductions in DOC concentrations and aromaticity were often limited. Only SBF with PAC reasonably reduced DOC levels and demonstrated substantial reductions in disinfection by-product formation potential. While complete treatment was not investigated and would be system specific, the investigation provides reasonable evidence to suggest production of potable water after severe wildfire is possible given optimized treatment technology deployment and operation; however, the investment required to achieve this capability may be difficult to justify for some systems. Given that source water quality deterioration that can substantially challenge conventional drinking water treatment after wildfire is highly uncertain and typically episodic—but also potentially catastrophic in absence of resilient operational response capacity—investment in the advanced treatment technologies that would be required to treat significant amounts of wildfire ash runoff directly from hillslopes to source waters warrants system specific evaluation relative to other approaches that may offer greater co-benefits, including landscape management-based mitigation.

3.2 Introduction

Forested headwaters are integral to the provision of drinking water in many regions globally; in the United States alone, approximately 200 million people rely on forested regions for drinking water (Stein & Butler, 2004). These regions are under increasing stress from both natural and anthropogenic landscape disturbances, many of which are exacerbated by changing climate (e.g., wildfires, floods, hurricanes,

drought, insect infestation) (Dale et al., 2001). Very large wildfires are of particular concern in forested regions due to their increasing frequency and severity (Westerling et al., 2006).

Wildfires can degrade water supplies and substantially shift water quality, with the possibility of rapid deterioration during periods of high surface runoff, such as snowmelt or storm events (Moody & Martin, 2001). They can also affect watershed hydrology by changing the timing of snow melt and increasing net precipitation (Williams et al., 2019). Water quality can be deteriorated by the release of significant amounts of sediment, (Kunze & Stednick, 2006; Silins et al., 2009) nutrients, (Bladon et al., 2008; Ranalli, 2004; Rhoades et al., 2019; Silins et al., 2014), heavy metals, (Kelly et al., 2006; Wolf et al., 2008) and other contaminants (Crouch et al., 2006; Kalabokidis, 2000) to receiving waters. These impacts can propagate downstream and last for decades in some cases (Emelko et al., 2016; Stone et al., 2014), leading to more variable source water quality (Stone et al., 2011). This deterioration and increased variability in source water quality can substantially challenge water treatment operations (Emelko et al., 2011; Hohner et al., 2017) and increase treatment costs (Emelko et al., 2011; Price et al., 2017).

Several recent investigations provide insights to the increased potential to form disinfection by-products (DBPs) after wildfire if natural organic matter (NOM; including pyrogenic organic matter) is not adequately removed from source (untreated) water (Chen et al., 2020; Hohner et al., 2017; Uzun et al., 2020b). Notably, these studies were conducted with leachates of either wildfire-impacted river sediments, thermally-altered vegetation and forest floor materials, or post-fire ash, duff, and soil—in all cases, these leachates were filtered to remove most of the particulate matter to focus on evaluating water extractable organic matter (WEOM). Thus, while they inform WEOM reactivity after leaching, they are not representative of water quality resulting from either wildfire ash transport directly from hillslopes to source water supplies or "worst-case scenario," severely deteriorated water resulting from wildfire. Importantly, leachates from wildfire-impacted river sediments do not reflect water quality deterioration in wildfire-impacted rivers (Hohner et al., 2017). Similarly, thermally altered vegetation and forest floor materials should not be assumed indicative of post-wildfire ash because furnaces cannot adequately reflect wildfire burning conditions (Bodí et al., 2014). Thus, while such studies may inform factors that may contribute to potential formation of DBPs after wildfire, approaches in which solids and associated contaminants are removed prior to analysis are less informative for evaluating the drinking water treatment capabilities of various process configurations and the potential boil water advisories, service disruptions, or outages that can result from turbidity exceedances, filtration process overloads, inadequate disinfection, or inability to treat compounds of significant health concern, such as cyanotoxins.

While anecdotal and retrospective case studies about wildfire impacts on drinking water treatment are increasingly available, they typically provide limited information about treatment technology capabilities

because of factors such as inadequate time available to source materials (e.g., alternative coagulants or coagulant aids) or implement alternative treatment approaches (e.g., enhanced coagulation) or technologies (e.g., powdered activated carbon [PAC]). It is not surprising that there is widespread belief that treatment of severely deteriorated water may not be possible after wildfire because treatment technology response capabilities have not been thoroughly investigated.

The combination of highly erodible ash with accelerated runoff and erosion responses following wildfire threatens the provision of safe drinking water because it can rapidly transfer sediment and associated nutrients and contaminants of health and treatability significance to stream networks (Nunes et al., 2018). The objective of present investigation was to evaluate if "worst-case scenario," severely deteriorated "black water" resulting from wildfire ash transport directly from hillslopes to source water supplies can be adequately treated by conventional chemical pre-treatment and high-rate clarification technologies (i.e., sand-ballasted flocculation [SBF], SBF with enhanced coagulation through pH adjustment, and SBF with PAC pre-treatment) that are specifically designed to treat large fluctuations in influent water quality.

Although this study evaluates the efficacy of various treatment technologies on severely deteriorated water quality indicative of post-fire conditions, it also informs the ability to treat less severely deteriorated water post-fire. The approach utilized herein was proof-of-concept, as opposed to process optimization, which is necessarily system (e.g., water quality, process configuration, etc.) specific. The focus of the work was to (1) demonstrate how key aspects of water quality change after severe wildfire can most challenge drinking water treatment, and (2) highlight that, while technology is available to treat even the most severely deteriorated water after wildfire, the highly uncertain and typically episodic nature of wildfire-associated shifts in source water quality require particular consideration in treatment infrastructure design and planning.

While the wildfire ash-impacted source water tested in this study was prepared using ash from one wildfire, this investigation provides insight beyond a single case study because wildland fire ash delivery to receiving waters, if sufficient in quantity, is generally understood to result in elevated levels of DOC concentration, and turbidity (e.g., Chapter 2; Table 2.2), which are key drivers of drinking water treatment process selection and operation, and especially affect coagulation and therefore subsequent filtration (Critteneden et al., 2012; Ghernaout et al., 2009). While the extent to which these aspects of water quality are elevated after wildfire varies (Clark, 2010; Dahm et al., 2015; Emelko et al., 2011; Emmerton et al., 2020; Gallaher & Koch, 2004; Hohner et al., 2016; Leak et al., 2003; Neary et al., 2005; Rhoades et al., 2011; White et al., 2006; Writer & Murphy, 2012), the generally consistency in aspects of water quality that are impacted after wildland fire often enables operational and mechanistic insights to be drawn between investigations.

3.3 Materials and methods

The following information provides details of the various materials and methods used throughout this study. Table B1 provides a summary and justification for selecting the various set-points which were used to achieve the objective of this work.

3.3.1 Treatment performance evaluation

To inform capacity and potential risk, drinking water treatment performance evaluations require analysis of treatment response to concurrent shifts in water quality. Here, turbidity and DOC concentration—the major drivers of drinking water treatment process design (Crittenden et al., 2012)—were used to evaluate treatment efficacy. They represent significant potential water quality impacts of wildfire (Emelko et al., 2011; Hohner et al., 2017; Kunze & Stednick, 2006; Silins et al., 2009) that can (1) fluctuate more after wildfire than prior to it (Stone et al., 2011), (2) persist for decades or longer (Emelko et al., 2016; Stone et al., 2014), and (3) impact downstream water supplies over long distances from burned landscapes (Emelko et al., 2016; Stone et al., 2014).

Standard methods were used to evaluate turbidity (Method 2130B [APHA, 2012]; Hach 2100 N turbidimeter, Loveland, CO), pH (4500-H+B Electrometric method [APHA, 2012]; Orion 720A pH meter, Thermo Fisher Scientific, Waltham, MA), alkalinity (Method 2320 [APHA, 2012]; 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 [APHA, 2012]; Shimadzu TOC-V CPH analyzer, Kyoto, Japan), and ultraviolet absorbance ([UVA_{254}]; Method 5910B [APHA, 2012]; 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).

Disinfection by-product formation potentials (DBP-FPs) were evaluated using the uniform formation condition (UFC) approach of Summers et al., (1996), with a chlorine contact time of 24 hours. Chlorine demand was measured for each individual sample to ensure a chlorine residual yield of 1.0 ± 0.4 mg·L^{-1} remained after 24 h. Chlorine residuals were measured according to the colorimetric Method 4500-Cl G

(APHA, 2012) using N, N-diethyl-p-phenylene diamine (DPD) and were quenched after 24 h using ammonia chloride. Total trihalomethanes (TTHMs) were analyzed according to Method 501.1 (USEPA, 1979). THM analysis was conducted using an Atomax purge and trap instrument (Teledyne Tekmar; Mason, OH) connected to a gas chromatograph (Agilent, 6890 Series; Santa Clara, CA) equipped with an electron capture detector. Five haloacetic acids (HAA5) were analyzed using Method 552.3 (USEPA, 2003); a gas chromatograph was used for HAA5 analysis (as noted above).

3.3.2 Treatment technology selection

Conventional chemical pre-treatment comprised of coagulation, flocculation, and sedimentation processes is the first phase of conventional treatment that is used for treating surface waters with high turbidity (>20 NTU) or high DOC (>4 mg· L^{-1}) globally (Crittenden et al., 2012). Additionally, conventional chemical pre-treatment is widely practiced and is the most common surface water treatment approach in Canada and the United States (Crittenden et al., 2012; Statistics Canada, 2013); thus, it was investigated herein. Specific jar testing procedures are found in Section B1 (Appendix B). SBF was investigated because it is a high-rate, physico-chemical clarification process designed to rapidly respond to fluctuations in solids concentrations and has a substantially smaller footprint when compared to conventional chemical pre-treatment (Desjardins et al., 2002; Edzwald, 2011). SBF differs from conventional pre-treatment in that a ballasting-agent (microsand) is injected into the flocculation tank to increase floc weight, thereby substantially decreasing settling time (here, three minutes versus 15 minutes) (Desjardins et al., 2002; Edzwald, 2011; Ghanem et al., 2007). DOC removal in both conventional and SBF processes is typically reliant on metal salt (e.g., alum) coagulation for co-precipitation of DOC and metal hydroxide solids (Sillanpää et al., 2018). As coagulation can be effective in removing hydrophobic and high molecular weight organics, but less so in removing hydrophilic and lower molecular weight fractions (Nissinen et al., 2001), extensive DOC removal by conventional and SBF treatment processes was not expected. Thus, SBF with enhanced coagulation and SBF with PAC were also investigated. Enhanced coagulation involves the application of higher than typical doses of coagulant at acidic pH conditions so that relatively more positively-charged metal (e.g., aluminum) species are generated and react with DOC, which is predominantly comprised of organic compounds with negatively-charged functional groups—this enables more co-precipitation of DOC relative to conventional coagulation (Vepsäläinen et al., 2009; 2012). Additionally, lower pH conditions can reduce the charge density on organic carbon, thereby enhancing its removal (Pernitsky & Edzwald, 2006). Treatment with PAC was also investigated because DOC adsorbs in its large micropores and mesopores; thus, this material is especially effective in removing DOC when

delivered in a fine powdered form that maximizes available surface area for reactivity (Dunn & Knappe, 2013).

3.3.3 Severely deteriorated source water preparation

Fresh ash was collected from the Thuya Lake Road (TLR) wildfire (+51.4098 latitude, -120.2435 longitude; burn area 556 ha), which was part of the Little Fort Fire Complex that burned in July 2017, near Little Fort, British Columbia, Canada. Specific details regarding the methods used to collect ash are provided in Chapter 2, Section 2.4, Table 2.1. Ash was defined as the residual particulate matter remaining after the burning of wildland fuels that consists of charred organic and mineral materials remaining on the landscape after a wildfire (Bodí et al., 2014) and is easily mobilized and transported from hillslopes to receiving waters following major runoff events. Severely deteriorated source water quality following wildfire that can challenge treatment processes has been reported (Chapter 2) and the challenges that increased turbidity, DOC concentration, and aromaticity after wildfire in non-urbanized watersheds pose to drinking water treatability—when observed—are generally consistent between wildfires (Sham et al., 2013). Although ash composition may vary between wildfires, comparison of wildfire ash from various burn conditions or vegetation types was not an objective of this proof-of-concept treatment investigation.

The predominant tree species in the burn area are Douglas Fir (*Pseudotsuga menziesii* var. *glauca*), with a mixture of Spruce hybrids (genus *Picea*), Paper Birch (*Betula papyrifera*), and Lodgepole Pine (*Pinus contorta* var. *latifolia*). Ash was collected prior to any precipitation events to ensure that WEOM had not been leached from it prior to the evaluation. Surface ash was collected from an area of approximately 1.8 ha to ensure material was broadly representative of high severity wildfire. All canopy vegetation and surface litter were consumed, and white ash deposition and layers of charred organic matter were several centimeters deep at the site, further indicating high wildfire severity (Keeley, 2009; Úbeda et al., 2009). TLR ash was rich in calcium, magnesium, phosphorous, and potassium (Table B2, in Appendix B), consistent with other studies (e.g., Etiegni & Campbell, 1991; Thompson, 2008).

The severely deteriorated ash-impacted source water was prepared by adding TLR ash to high quality Elbow River water to reflect water quality resulting from ash mobilization off the landscape to receiving waters during a major post-fire runoff event. The water was collected from the Glenmore Reservoir in Calgary, Alberta, Canada. It originates in the Rocky Mountains and typically has low turbidity and DOC content, and high alkalinity (Table 3.1). The river water was used to prepare the wildfire ash-impacted source waters was shipped to the University of Waterloo in 19 L plastic pails and was stored in a dark refrigerator at 4°C until use.

Ash was sieved through a 1 mm screen to remove any large debris and conifer needles that typically would not be found in water treatment plant influent streams. Ash was mixed with Elbow River water at a concentration of 5.0 $g \cdot L^{-1}$ (i.e., 5.0 g in 1000 mL of river water) and was mixed in 1-L Pyrex beakers at 150 RPM for 30 minutes on a jar test apparatus (Phipps & Bird, PB-900 Series Programmable 6-Paddle Jar Tester, Richmond, VA) prior to treatment. Turbidity and DOC concentrations consistent with or slightly higher than the levels that have been reported following severe wildfire (i.e., >500 NTU and >15 $mg \cdot L^{-1}$, respectively) were targeted (Emelko et al., 2011; Hohner, et al., 2016; Sham et al., 2013; Silins et al., 2009; Writer & Murphy, 2012). Water quality before and after ash addition is detailed in Table 3.1.

Table 3.1: Elbow River water quality before and after 5.0 $g \cdot L^{-1}$ addition of TLR ash representing severely deteriorated water quality after a major post-fire runoff event.

Water quality parameter	Elbow River water	Elbow River water with TLR ash
	mean ± SE	mean ± SE
Turbidity (NTU)	1.11 ± 0.21 (n=10)	1400 ± 60 (n=12)
DOC (mg L^{-1})	1.9 ± 0.2 (n=8)	16.0 ± 0.2 (n=11)
UVA$_{254}$ (cm^{-1})	0.049 ± 0.009 (n=9)	0.479 ± 0.009 (n=11)
pH	8.07 ± 0.04 (n=11)	8.71 ± 0.05 (n=10)
Alkalinity (mg L^{-1} as CaCO$_3$)	179 ± 1 (n=3)	409 ± 4 (n=6)

3.3.4 Treatment performance evaluation

The wildfire ash-impacted source waters were mixed for 30 minutes at 150 RPM at controlled temperature (~21°C). Reagent grade liquid alum (Al$_2$[SO$_4$]$_3$•14H$_2$O, SG=1.33, 4.3% aluminum metal content, Veolia Water, Saint-Laurent, Canada) was used; doses were reported as commercial product dose (volume [$\mu L \cdot L^{-1}$] x specific gravity). Alum doses of 100, 200, 300, and 400 $mg \cdot L^{-1}$ were selected to not exceed the NSF maximum use level for alum in drinking water (NSF, 2017). While the coagulant doses are high compared to typical plant doses, these levels were tested to demonstrate that extreme/atypical treatment would be required after severe wildfire in absence of alternative water sources. Cationic polymer can decrease metal salt coagulant dose requirements, decrease alkalinity consumption, and increase flocculation efficiency (Crittenden et al., 2012); thus, it was also used (LT22S cationic polymer, Northland Chemical, Mississauga, Canada). Previously reported protocols (Section B1) were used to evaluate conventional and high-rate

clarification process performance (ASTM, 2013; AWWA, 2002; Desjardins et al., 2002). All jar-test experiments were evaluated in triplicate. DOC was analyzed within 24 hours of sample collection. All other analyses were conducted immediately following treatment.

3.3.5 Statistical analyses

Two-way ANOVA with post-hoc Tukey's tests were conducted to identify differences in mean treatment performance between treatment types and coagulant doses. One-way ANOVA with post-hoc Tukey's tests of multiple comparisons were used to compare chemical doses. SPSS® software (version 26, IBM®) was used for all analyses.

3.4 Results and discussion

3.4.1 Water quality

Repeated preparations of the 5.0 $g \cdot L^{-1}$ ash-impacted source water yielded consistent DOC concentrations of 16.0 ± 0.2 $mg \cdot L^{-1}$ (mean $\pm$ SE, n=11); UVA_{254} was 0.479 ± 0.009 cm^{-1} (mean $\pm$ SE, n=11), which resulted in a SUVA of 2.99 ± 0.04 $L \cdot mg^{-1} \cdot m^{-1}$ (mean $\pm$ SE, n=11). In contrast, ash-free Elbow River water DOC concentrations and UVA_{254} were 1.9 ± 0.2 $mg \cdot L^{-1}$ (mean $\pm$ SE, n=8) and 0.049 ± 0.009 cm^{-1} (mean $\pm$ SE, n=9), respectively. The pH of the wildfire ash-impacted source water increased from 8.07 ± 0.04 (mean $\pm$ SE; n=11) to 8.71 ± 0.05 (mean $\pm$ SE; n=10) after ash addition—this observation is consistent with other reports (Harper et al., 2019; Plumlee et al., 2007). This change is important because source water pH shifts can decrease the efficacy of coagulation and downstream treatment including filtration (Edzwald, 2011). Alkalinity also increased substantially after ash addition, from 179 ± 1 $mg \cdot L^{-1}$ (as $CaCO_3$) (mean $\pm$ SE; n=3) to 409 ± 4 $mg \cdot L^{-1}$ (as $CaCO_3$) (mean $\pm$ SE, n=16).   Finally, ash addition to the Elbow River water increased turbidity from 1.11 ± 0.21 NTU (mean $\pm$ SE; n=10) to $1,400 \pm 60$ NTU (mean $\pm$ SE; n=12), as would be expected and consistent with reports of severely deteriorated source water quality after wildfire (Sham et al., 2013).

LC–OCD analysis provided insight into the type of DOC present (Figure 3.1)—notably, this type of evaluation of wildfire ash impacts on water quality and treatability has not been previously reported. Elbow River water DOC (prior to ash addition) had a higher proportion of high molecular weight compounds, as indicated by the higher fractions of HS and BB present in the ash-impacted source water prior to ash addition. In contrast, the wildfire ash-impacted source water had an elevated proportion of LMW DOC fractions, especially LMW acids, which is consistent with previous hypotheses based on fluorescence index

(e.g., Hohner et al., 2016). The contrast between DOC fractions in impacted and unimpacted source waters is shown in Figure 3.2, which indicates that a relatively higher proportion of LMW compounds comprised DOC in the severely deteriorated, wildfire ash-impacted source waters. This observation is notable because LMW acids are biodegradable and may (1) lead to distribution system regrowth (Baghoth et al., 2009), (2) promote the dissolution of aluminum from alum oxides (Li et al., 2006), and (3) result in elevated aqueous aluminum concentrations after coagulation in absence of sufficient treatment.

Figure 3.1: BP, HS, BB, LMW neutrals, and LMW acids fractions (percentage) comprising DOC (mean ± SE; n=3 in all cases) in Elbow River water before and after addition of TLR wildfire ash.
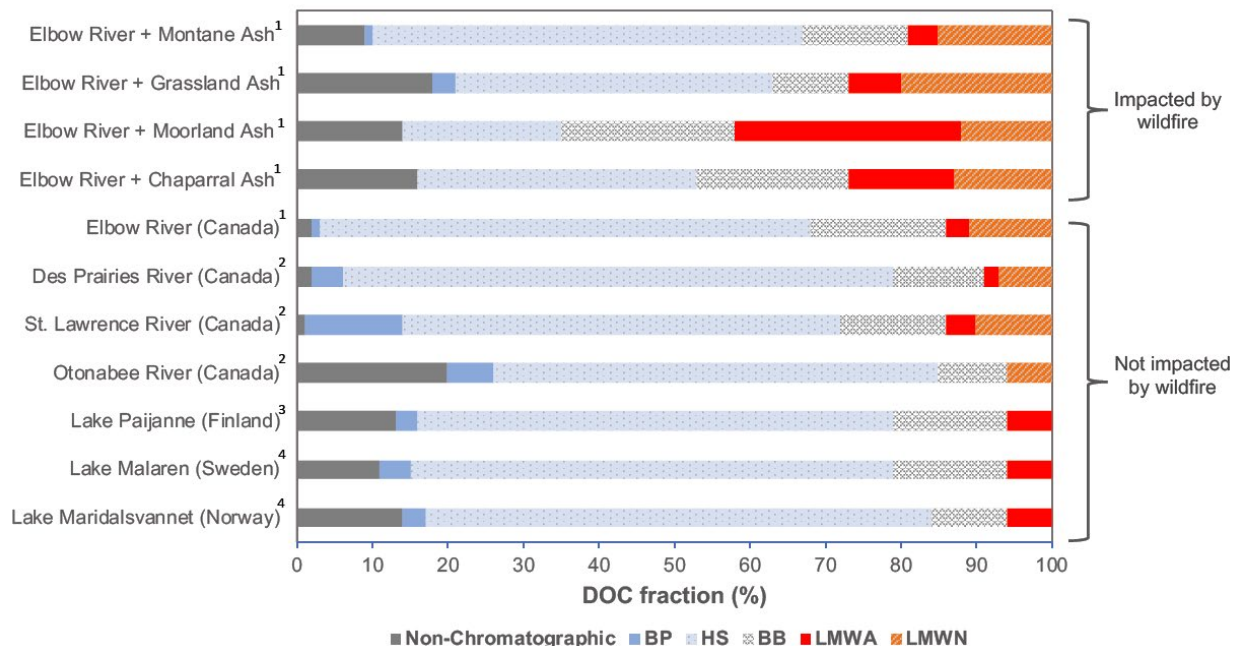
Figure 3.2: Comparison of DOC fractions (mean percentages) for BP, HS, BB, LMW neutrals, and LMW acids in source water samples impacted and not impacted by wildfire; non-chromatographic fraction indicates the portion of the organic carbon that remains on the column following analysis. Superscripts indicate referenced studies: (1) Chapter 5; (2) Lapointe et al., 2020; (3) Wassink et al., 2011; and (4) Krzeminski et al., 2019.

3.4.2 Treatment evaluation

3.4.2.1 Conventional, SBF, and SBF with enhanced coagulation

Average turbidities were reduced from ~1,400 NTU to less than ~2 NTU (>99% reduction) by conventional chemical pre-treatment, SBF, and SBF with enhanced coagulation at all alum doses investigated. The differences between untreated and treated water turbidity were significant (Figure 3.2[a]; $p< 8.1×10^{-11}$ in all cases; Table B7). Differences in treated water turbidities between the processes were statistically significant ($p≤0.011$ in all cases; Table B8). As might be expected, SBF resulted in the lowest clarified turbidity, followed by conventional treatment, and then SBF with enhanced coagulation. Notably, the lower pH required for enhanced coagulation was also challenging to stabilize and may have broken down some of the ash-laden floc, possibly leading to less optimal turbidity removal. Regardless, the differences observed between treatments at different coagulant doses were not practically relevant as the mean treated/clarified water turbidities ranged between 0.95 and 3.36 NTU (Table B3) and would thus have relatively negligible impacts on subsequent treatment by filtration. The importance of being able to achieve reductions in turbidity (such as those reported herein) during the first stages of drinking water treatment

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cannot be over-stated. The paramount objective of drinking water treatment is to protect public health from waterborne disease. Typically, the water from these pre-treatment/clarification processes is subsequently treated by granular media filtration for which a key objective is protozoan pathogen removal. Elevated turbidity can overload filtration processes; however, the values achieved herein following the treatment of severely deteriorated post-fire water quality (Figure 3.3[a]) are in the typical range of clarified water turbidities that are treated by subsequent physico-chemical filtration processes (Crittenden et al., 2012).

(a)

(b)

(c)
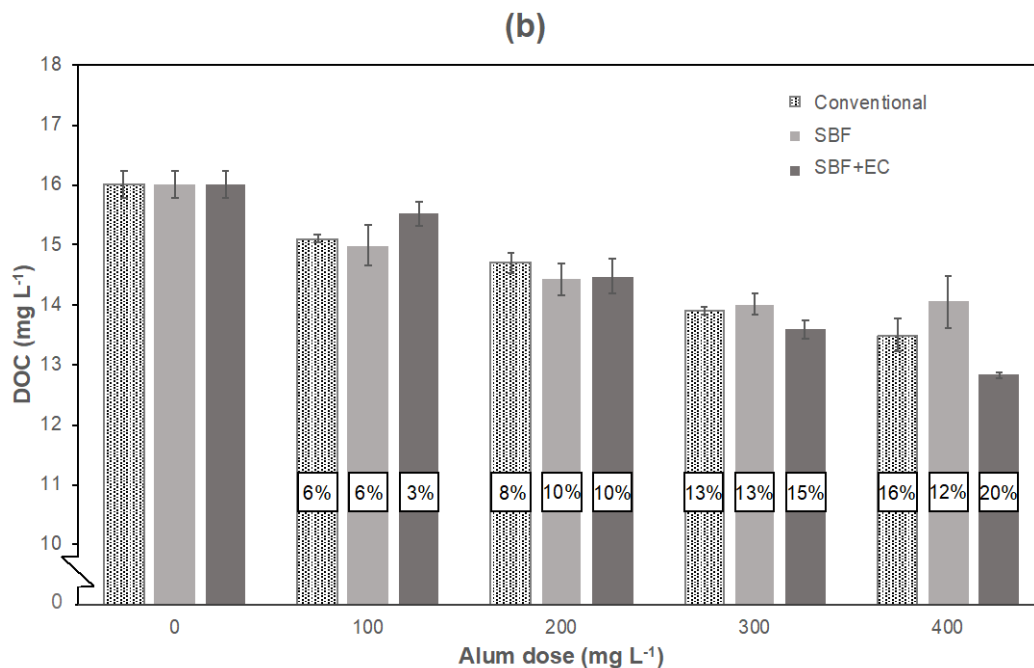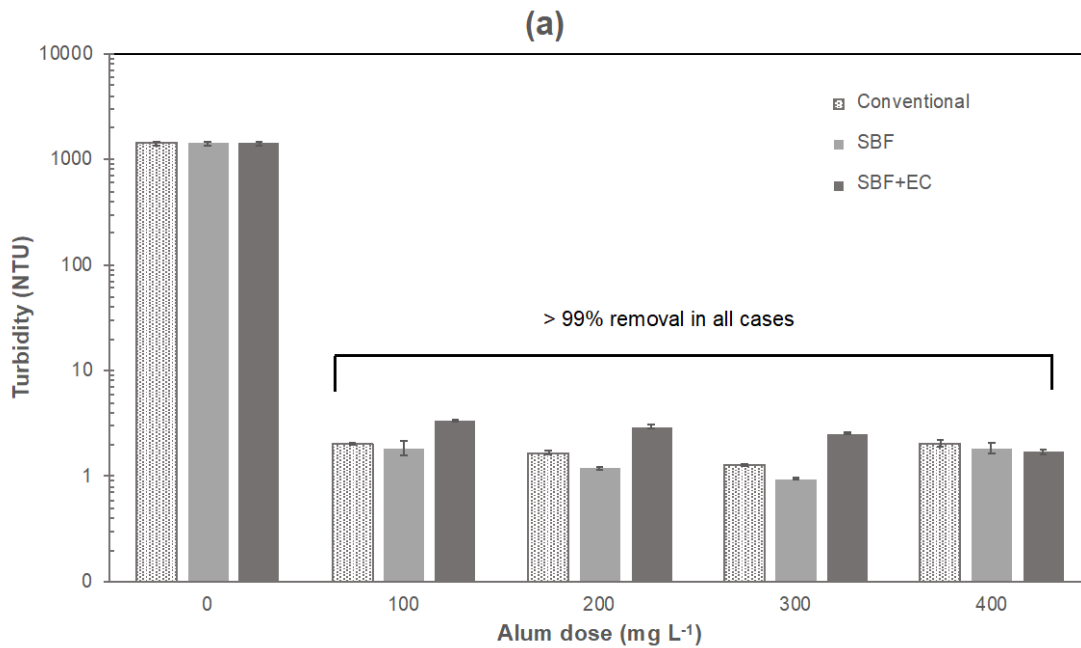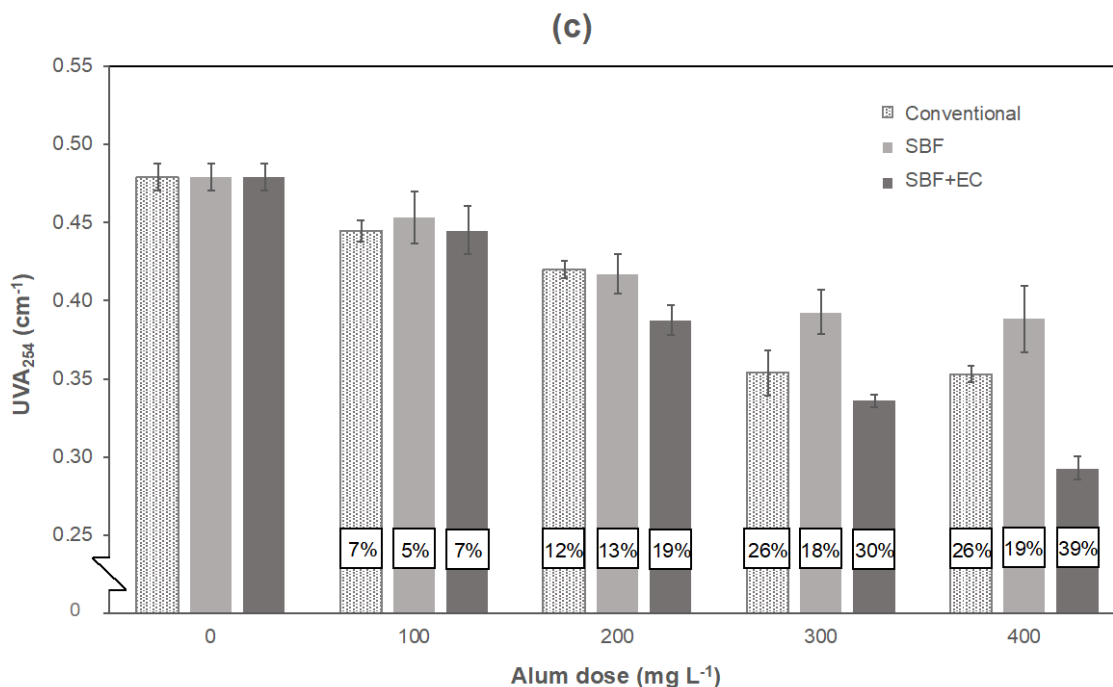
Figure 3.3: Treated water (a) turbidity, (b) DOC concentration, and (c) UVA_{254} after a range of treatment technologies, including: conventional chemical pre-treatment (conventional), sand-ballasted flocculation (SBF), and sand-ballasted flocculation with enhanced coagulation (SBF+EC) treatment of the severely deteriorated, high turbidity (>500 NTU), high DOC (>15 mg·L^{-1}) water representative of wildfire ash transport directly from hillslopes to source water supplies. Percent reductions from the pre-treatment condition (i.e., 0 mg·L^{-1} alum) are indicated. All parameters are reported as mean ± SE; n=3 in all cases. All p-values for the different operational conditions tested (i.e., coagulant doses) for the three treatment methods tested are provided in Table B7 (a, b, c) and p-values comparing the three treatment methods are provided in Table B8.

The DOC concentrations in the conventional, SBF, and SBF with enhanced coagulation processes also changed significantly from pre-treatment conditions after alum addition at 200 mg·L^{-1} and higher (Figure 3.3[b]; p<0.021 in all cases, details in Table B8). In general, differences in DOC concentrations in the water treated by the various processes were not significant (p>0.281 in all cases, Table B8). Significant changes in treated water DOC concentrations between applied alum doses for a specific process were sometimes observed (Table B7).

Consistent with the DOC data, the UVA_{254} of the water treated by conventional, SBF, and SBF with enhanced coagulation approaches also changed significantly after alum addition at 200 mg·L^{-1} and higher (Figure 3.3[c]; p<0.027 in all cases, details in Table B7). While the differences in UVA_{254} of water treated by conventional and SBF treatment were not significant (Figure 3.3[c]; p=0.085; Table B8), they were significant between each of these processes and SBF with enhanced coagulation (Figure 3.3[c]; p=0.015

and p=5.8×10^{-5}, respectively; Table B8). Collectively, these and the DOC results are not surprising given that alum coagulation preferentially removes aromatic DOC (Croué et al., 1993) and enhanced coagulation is designed to optimize co-precipitation of DOC during coagulation (Vepsäläinen et al., 2009; 2012). The importance of alum dose and pH is also evident in the significant differences in treated water UVA_{254} that were observed between lower (100 and 200 mg·L^{-1}) and higher (300 and 400 mg·L^{-1}) alum doses used during conventional treatment (Figure 3.3[c]; p≤0.028 in cases; Table B7). Specifically, alum addition between than 200 and 300 mg·L^{-1} improved UVA_{254} reduction; this was attributable in part to an associated decrease in pH (O'Melia et al., 1999). In contrast, while significant differences in treated water UVA_{254} were not observed between alum doses in the SBF process (Figure 3.3[c]; p≥0.078 in all cases; Table B7), treated water UVA_{254} after SBF with enhanced coagulation was significantly different between the highest dose at 400 mg·L^{-1} and the lowest doses of 100 and 200 mg·L^{-1} (p<0.0011, in both cases). The difference in UVA_{254} between doses of 300 and 400 mg·L^{-1} was not significant (Figure 3.3[c]; p=0.225). Although the linear correlation between DOC concentration and UVA_{254} in the severely deteriorated wildfire ash-impacted source waters was high (data not shown), UVA_{254} reduction by alum (on a percent basis) was consistently greater than the reduction in DOC concentration, which reflects preferential removal of aromatic and hydrophobic DOC by alum coagulation (Jarvis et al., 2006; Croué et al., 1993).

The presence of negatively charged natural organic matter (NOM) in water results in coagulant demand for positive charged metal species (e.g., aluminum) such that the stoichiometric relationship between coagulant (e.g., alum) dose and raw water DOC concentration is pH dependent (Edzwald & Tobiason, 1999). Enhanced coagulation is a recognized best available technology involves decreasing pH either by coagulant or acid addition to increase DOC removal by charge neutralization and precipitation mechanisms. Notably, the removal of DOC by enhanced coagulation might be expected, it is critical to recall that the efficacy of enhanced coagulation is influenced by the type/size fraction of NOM present, pH, alkalinity, presence of anions, characteristics of NOM-Al flocs, as well as coagulant type, dose and basicity and the composition and fractionation of NOM (Duan & Gregory, 2003; Edzwald & Van Benschoten, 1990; Ghernout et al., 2009). Accordingly, given that a relatively higher proportion of LMW compounds comprised DOC in the severely deteriorated, wildfire ash-impacted source water, the poor removal of DOC by enhanced coagulation was not surprising because, while higher molecular weight fractions of DOC including humic substances are the most easily removed by coagulation, LMW DOC fractions are not as easily removed, even by enhanced coagulation (Krzeminski et al., 2019; Galjaard et al., 2018). Overall, this evaluation highlights the critical importance of wildfire ash-derived DOC as a key consideration after wildfire. The observations regarding DOC and UVA_{254} are generally consistent with coagulation results for wildfire-impacted source waters (Emelko et al., 2011) and sediment leachates (Hohner et al., 2017). Notably,

although SBF with enhanced coagulation offered improved treated water quality over SBF and conventional chemical pre-treatment, the treated water DOC concentrations (and UVA_{254}) remained elevated. These data indicated that the 30% reduction of total organic carbon (TOC) that would be required by the U.S. Disinfectants and Disinfection Byproducts (D/DBP) Rule for managing DBP precursors in the high alkalinity source water would not have been met because TOC concentration would be equal to or higher than DOC concentration (USEPA, 1999).

Notably, it was challenging to control untreated water pH prior to coagulant addition during enhanced coagulation testing. This was likely due to high alkalinity imparted from the remnant combustion products that comprise the ash that were directly added to the source water. These mineralized materials contain alkaline materials rich in base cations and carbonates, which are released upon dissolution and can increase both the pH and alkalinity of receiving waters (Lydersen et al., 2014). High alkalinity levels like those reported herein are consistent with previous reports of wildfire-impacted waters (Cerrato et al., 2016; Earl & Blinn, 2003) and can adversely impact the efficacy of pH adjustment during treatment (Crittenden et al., 2012). Given that water quality can change rapidly after wildfire—especially during relatively short periods of deterioration typically associated with high energy/discharge events (Emelko et al., 2011; Emelko & Sham, 2014)—pH adjustment of severely deteriorated "black water" after wildfire would likely be operationally challenging and impractical. Thus, further attempts at enhanced coagulation treatment optimization were not pursued because the purpose of the present investigation was to identify treatment technologies capable of treating severely deteriorated post-fire water with reasonable operational effort.

3.4.2.2 SBF with PAC pre-treatment

 SBF with PAC pre-treatment resulted in high levels of turbidity removal (>99%) in all cases; post-treatment turbidity levels for the four PAC doses (100, 200, 400, and 1000 mg·L^{-1}) investigated were 2.33 ± 0.16 NTU, 1.50 ± 0.06 NTU, 0.98 ± 0.02 NTU, and 0.81 ± 0.01 NTU (mean ± SE, n=3), respectively. The differences between untreated and treated water turbidity were significant at all PAC doses ($p < 8.0 \times 10^{-11}$ in all cases, details in Table B9) DOC concentrations and UVA_{254} also changed significantly after treatment by SBF with PAC at all doses investigated (Figure 3.4; $p < 2.8 \times 10^{-8}$ and $p < 2.9 \times 10^{-11}$, respectively in all cases, Table B9). Specifically, the treated water DOC concentrations were 11.4 ± 0.2, 10.5 ± 0.5, 8.4 ± 0.1, 6.8 ± 0.3 mg·L^{-1} (mean ± SE; n=3) and the UVA_{254} values were 0.238 ± 0.006, 0.193 ± 0.005, 0.137 ± 0.000, and 0.089 ± 0.011 cm^{-1} (mean ± SE; n=3), after PAC pre-treatment at 100, 200, 400, and 1000 mg·L^{-1}, respectively, followed by SBF with a constant dose of 400 mg·L^{-1}. The treated water DOC concentrations after the use of higher PAC doses (400 and 1000 mg·L^{-1}) were significantly different from

those obtained with lower PAC doses (100 and 200 mg·L^{-1}) (Figure 3.4; p<0.009 in all cases, Table B9). While the treated water DOC concentrations obtained with the lower PAC doses were high relative to typical treated water targets, those obtained with the higher PAC doses were consistent with typical treated water quality (Crittenden et al., 2012). It is further important to note that clarified water typically undergoes additional treatment by granular media filtration, which has the further potential to reduce DOC concentrations when granular activated carbon filter adsorbers (Dvorak & Maher, 1999; Velten et al., 2011) or biological filtration processes are utilized (Hozalski et al., 1999; Kirisits et al., 2019). In some cases, advanced oxidation processes such as UV and/or ozone-based processes may provide further post-clarification treatment and potential for DOC removal, especially when integrated with other water technologies such as membrane filtration and adsorption, among others (Sillanpää et al., 2018).
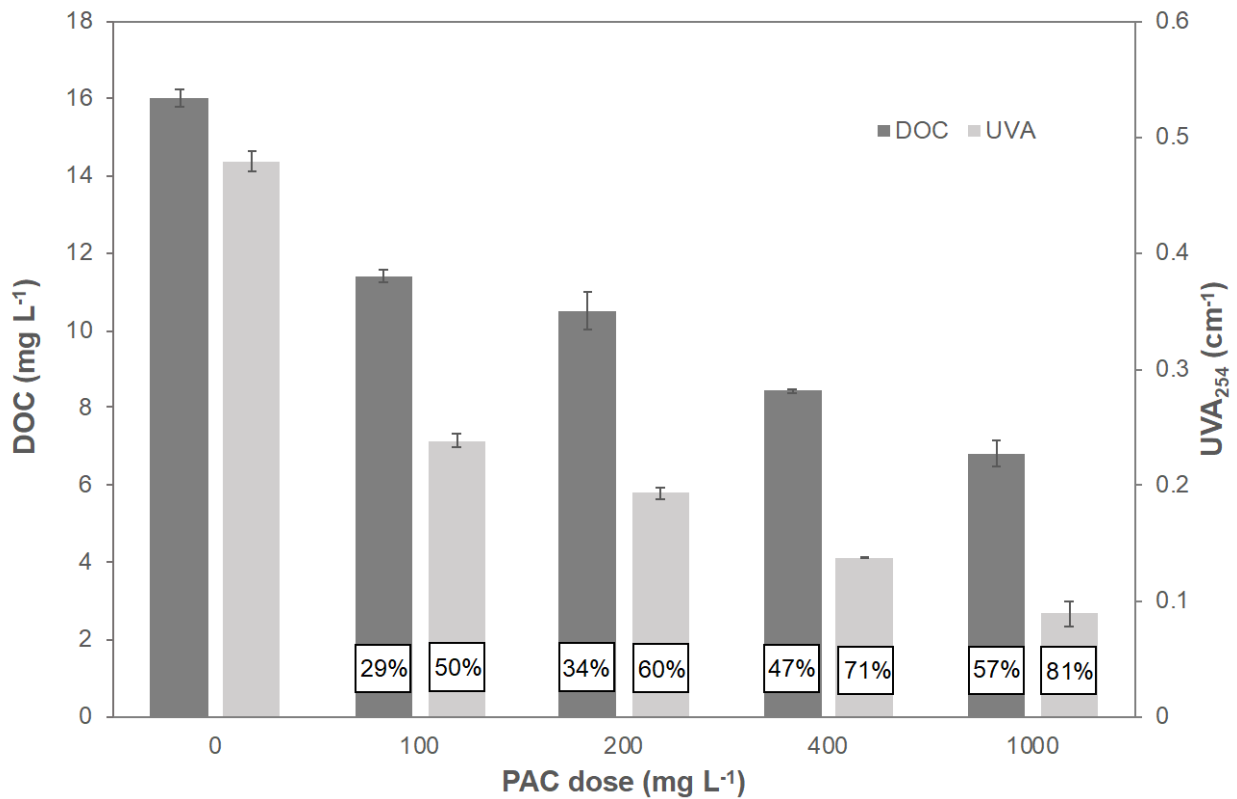
Figure 3.4: Treated water DOC concentration and UVA$_{254}$ after SBF with PAC pre-treatment of a wildfire ash-impacted source water representing "worst-case scenario," severely deteriorated, high turbidity (>500 NTU), high DOC (>15 mg·L^{-1}) water resulting from wildfire ash transport directly from hillslopes to source water supplies. Percent reductions from the pre-treatment condition are indicated. Parameters reported as mean ± SE; n=3 in all cases. All p-values comparing the different PAC doses on the different water quality parameters analyzed are provided in Table B9.

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Pre-treatment with PAC followed by SBF largely reduced the HS and BP fractions of DOC, with relatively little impact on the LMW acids (Figure 3.5). This observation is consistent with previous reports of DOC fraction removal by PAC (Shutova et al., 2020). Overall, these results align with previous reports of PAC (Uyak et al., 2007) including its combination with SBF (Plourde-Lescelleur et al., 2015) being effective for DOC removal. As DOC typically comprised approximately 90% of the TOC concentration in both the source and treated wildfire ash-impacted source water, the 30% reduction of TOC that would be required by the U.S. D/DBP Rule (and international equivalents) for managing DBP precursors in the high alkalinity source water would likely be met in all cases investigated except the 100 mg·L^{-1} PAC dose.
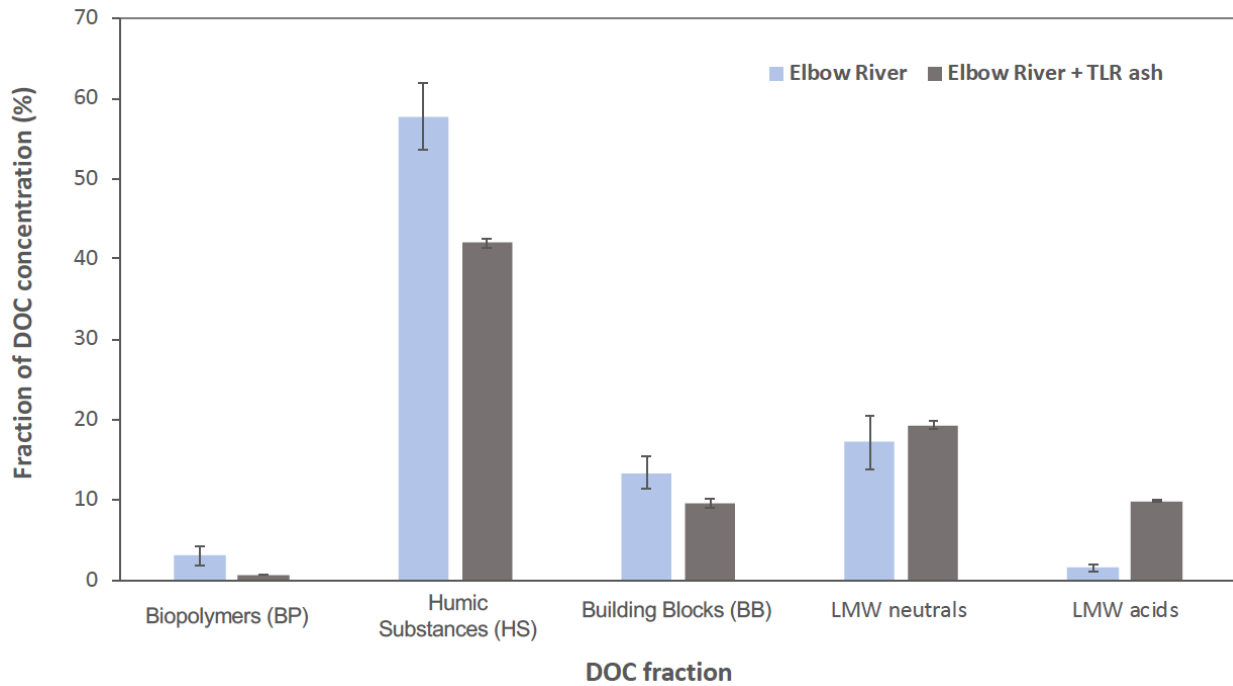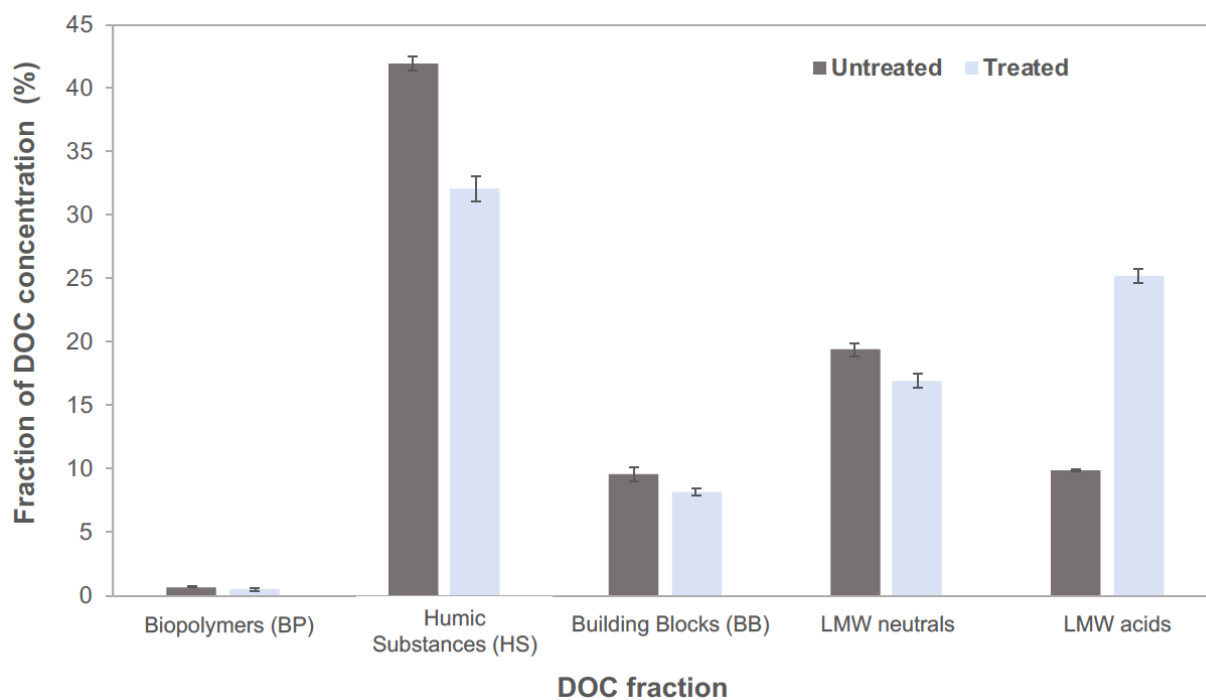
Figure 3.5: BP, HS, BB, LMW neutrals, and LMW acids fractions (percentage) comprising DOC (mean ± SE; n=3 in all cases) of Elbow River water with TLR ash at 5.0 g·L^{-1} before (untreated) and after treatment by SBF with PAC at 1000 mg·L^{-1} (treated).

The high efficacy of DOC removal demonstrated using PAC pre-treatment was an anticipated result of this study. Using PAC to reduce high levels of organic matter is a well-established method in drinking water treatment and has been utilized as means to reduce DOC responsible for the formation of DBPs (Edzwald, 2011). The mechanism by which PAC removes organic matter is through adsorption onto the surface of

PAC, where the high surface area on the PAC particles results in a high adsorptive capacity (Crittenden et al., 2012). Although PAC's efficacy is attributed to its high adsorption capacity, the mechanisms of adsorption are complicated and are attributed to range of factors, including electrostatic forces, pore volume distribution, and chemical interactions between organic matter and the surface functionalities on the surface of PACs (Bjelopavlic et al., 1999). In spite of these complexities, it has been noted that organic matter is primarily adsorbed into pores of activated carbon, namely mesopores and large micropores (Dunn & Knappe, 2013). The type of organic matter may also impact the performance of PAC, where high-molecular-weight compounds are excluded from internal adsorption sites in the PAC pores, and the most strongly adsorbed organic matter components are hydrophilic low- and medium- molecular weight compounds (Chowdhury et al., 2013). However, the results following pre-treatment with PAC followed by SBF indicated that there was an increase in the proportion of the LMW fraction of DOC after treatment, suggesting that PAC was not effective in removing the LMW compounds. In spite of there being a limited reduction in LMW compounds, pre-treatment with PAC demonstrated the highest overall efficacy for reducing DOC compared to the other treatment methods tested. Although pre-treatment with PAC did demonstrate the highest DOC reductions, it was not the intention of this study to provide a categorical ranking of drinking water treatment technologies through detailed optimization, but rather to provide a proof-of-concept demonstration of the potential efficacy of a range commonly available technologies for treating severely deteriorated source water quality post-fire.

Analysis of DBP formation potential at the highest dose of PAC (1000 $mg\cdot L^{-1}$) indicated substantial reductions of both TTHMs and HAA5, with reductions of $85.6 \pm 0.46\%$ and $92.1 \pm 0.25\%$ (mean $\pm$ SE, n=3), respectively (Figure 3.6). The post-treatment concentrations of TTHMs and HAA5 evaluated at uniform formation conditions were 79.0 ± 2.5 $\mu g\cdot L^{-1}$ and 177.3 ± 6.7 $\mu g\cdot L^{-1}$ (mean $\pm$ SE, n=3), respectively. Here, the mean TTHM concentration was essentially at the US EPA maximum contaminant level (MCL) of 80 $\mu g\cdot L^{-1}$ while the mean HAA5 concentration was above the US EPA MCL of 60 $\mu g\cdot L^{-1}$ (Federal Register, 2006).
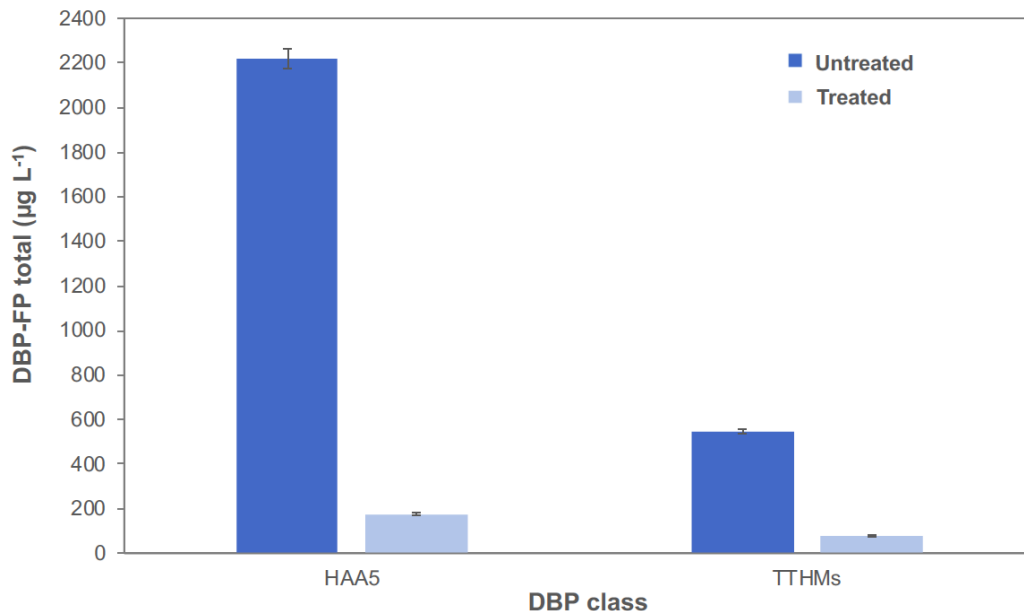
Figure 3.6: TTHM and HAA5 UFC formation potential at (mean ± SE; n=3 in all cases) of Elbow River water with TLR ash at 5.0 g·L⁻¹ before (Untreated) and after treatment by SBF with PAC at 1000 mg·L⁻¹ (Treated).

This work provides substantial evidence that even the most severely deteriorated water after wildfire can be treated to potable water standards with commercially available advanced treatment approaches. These results are not surprising because water can be treated to potable standards at a variety of challenging conditions (Ghernaout, 2018; Loo et al., 2012). While this investigation does not incontrovertibly prove that severely-deteriorated post-fire "black water" can be treated by current commercially available drinking water treatment technology approaches such as SBF with PAC, it does provide proof-of-concept evidence to suggest this. While this interpretation may seem unexpected, it is critical to be clear about how DBPs are regulated in the United States and Canada. In brief, Federal Register (2006) specifies that compliance with DBP regulations is at most based on one monthly TOC sample set (comprised of source water alkalinity, source water TOC, and treated TOC) and quarterly distribution system monitoring of DBPs for MCL compliance at 2 to 20 locations in the distribution system, based on population served; quarterly monitoring must include the month of highest DBP concentrations (Federal Register, 2006). Representative data are reported and MCL compliance is calculated using the locational running annual average (LRAA) for each monitoring location in the distribution system. Critically, the LRAA requirements for DBP MCL compliance reflect that THMs and HAAs are not regulated because of their toxicity, but rather because they serve as indicators of exposure to a diverse and complicated mixture of DBPs in chlorinated drinking water

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(Federal Register, 2006). Thus, the meeting the DBP MCLs on every sampling occasion is not required, though it is of course desirable.

In addition to the LRAA aspect of DBP MCL compliance, interpretation of the treatment performance observed herein also requires consideration of the severity of water quality deterioration investigated and how it connects to reported wildfire impacts on water quality. Although water quality deterioration as severe as that investigated herein (Figure 3.7; Emelko et al., 2011; Hohner, et al., 2016; Sham et al., 2013; Silins et al., 2009; Writer & Murphy, 2012) has been reported post-fire and can undoubtedly challenge conventional drinking water treatment, the extent and duration of that deterioration is highly uncertain and understood to be typically episodic. Available reports indicate that deteriorated water quality persists for periods of days—perhaps up to a week—following major runoff events; while relatively deteriorated water quality during these events may persist for years, peak turbidities and DOC concentrations are not sustained during those periods (Dahm et al., 2015; Lyon & O'Connor, 2008; Mast et al., 2016; Emelko et al., 2011; 2016; Murphy et al., 2015; Writer & Murphy, 2012). Of course, such fluctuations in source water utility may be inconsequential for some utilities and potentially catastrophic for others, especially in absence of resilient operational response capacity. The treatment performance demonstrated herein coupled with the short-lived, episodic nature of extreme water quality events after wildfire, the uncertainty (and lack of requirement) in capturing peak periods of water quality deterioration during compliance sampling, and the use of running annual averages for DBP MCL compliance, collectively suggest that even the most severely deteriorated water after wildfire can be treated to potable water standards with less common, but commercially available, advanced treatment approaches. Accordingly, it follows that less deteriorated water can also be treated using these approaches.
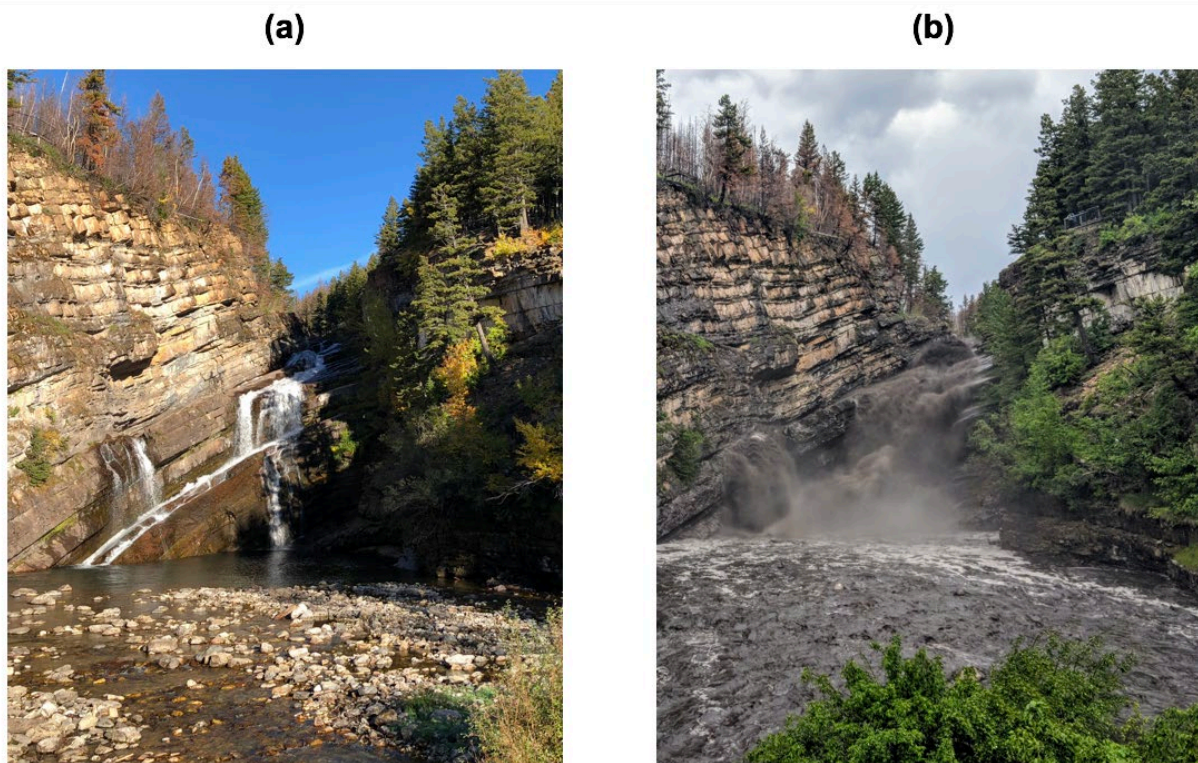
Figure 3.7: Episodic fluctuations in water quality at Cameron Falls observed during (a) base flow conditions (photo courtesy of Sheena Spencer/Southern Rockies Watershed Project), and (b) following a major runoff event after the severe 2017 Kenow wildfire in Waterton Lakes National Park, Alberta, Canada (photo courtesy of Kaleigh Watson/Parks Canada).

Importantly, in cases where water quality changes rapidly, the ability to produce potable water may not be limited by the capabilities of available treatment technologies, but rather by logistics, such as the timely availability of materials and/or implementation of alternative treatment approaches or technologies. For example, the PAC doses investigated here were much higher than the 5–25 mg·L^{-1} typically used in drinking water treatment (Crittenden et al., 2012). PAC dosing at the high concentrations required to meet potable water standards herein would not only require an adequate supply of PAC, but potentially additional infrastructure (e.g., chemical feed equipment) to ensure that required doses can be applied and produced sludge managed. Thus, even if specific technologies are available, deviations from typical practice may be required to respond to extreme deterioration of source water quality.

The capability, or potential capability, to treat severely deteriorated post-fire water with commercially available technology does not necessarily imply that utilities in wildfire prone regions should make longer-term investments in additional technologies to respond to such potential scenarios. The operational response capacity of a given water treatment system (i.e., capability to dose high concentrations of coagulant,

availability of coagulant/acid/PAC, etc.) must be considered and evaluated, in addition to the probability of "black water" event occurrence and longevity, which is relatively short-lived and episodic, or may not occur at all (Emelko & Sham, 2014; Lyon & O'Connor, 2008; Sham et al., 2013). Accordingly, drinking water system managers in fire-prone regions must weigh the probability of extreme, but episodic source water quality degradation against the costs of treatment infrastructure implementation and maintenance, or investment in watershed management-based mitigation of source water quality.

3.5 Conclusions and implications

The ability to treat worst-case scenario, "black water" representative of ash runoff directly from hillslopes to source waters after severe wildfire was investigated at bench-scale herein. While it is widely believed that severely deteriorated water quality after wildfire cannot be effectively treated (Emelko & Sham, 2014; Sham et al., 2013) the results from this bench-scale investigation have demonstrated that water quality indicative of a "worst-case scenario" post-fire can be reasonably treated, where major drinking water quality violations or system shutdowns would be avoided and where turbidity is sufficiently removed so that subsequent filtration can occur. This is the first reported study demonstrating a range of drinking water treatment technologies for treating severely deteriorated water quality post-fire. The key conclusions of this investigation are:

- The LMW acids fraction of dissolved organic carbon (DOC) was substantially elevated after ash addition to high quality source water;

- Sand-ballasted flocculation (SBF), SBF with enhanced coagulation, and SBF with powdered activated carbon (PAC) all effectively reduced turbidity for subsequent treatment by filtration, but reductions in DOC concentrations and aromaticity were often limited; and

- Only SBF with PAC reasonably reduced DOC levels and demonstrated substantial reductions in disinfection by-product formation potential.

Given these conclusions, key implications of this work are:

- Deteriorated source water quality after severe wildfire is uncertain and episodic, persisting for periods of days following major runoff events. While relatively deteriorated water quality during these events may persist for years, peak turbidities and DOC concentrations are not sustained during those periods, thereby calling into question the need to invest in the infrastructure capable of best treating such severely deteriorated water;

- The ability to produce potable water after severe wildland fire is likely not treatment technology-limited, but rather limited by the timely availability of materials and/or implementation of alternative treatment approaches or technologies; and

- Drinking water system owners must weigh the probability of extreme, but episodic source water quality degradation against the costs of treatment infrastructure implementation and maintenance, or investment in watershed management-based mitigation of source water quality.

Chapter 4:

Pilot-scale evaluation of the treatment of two different wildfire ash-impacted source waters

4.1 Summary

Severe wildfire is occurring with increased frequency globally and can have potentially catastrophic consequences for the provision of safe drinking water. Severely deteriorated source water quality following major post-fire runoff events is generally episodic and short-lived; nonetheless, it can challenge and even disrupt drinking water treatment because of large, sometimes rapid fluctuations in source water quality, especially dissolved organic carbon (DOC) concentration and character. While it is recognized that the drinking water treatment implications should almost always be evaluated at pilot-scale when substantial changes in either source water quality or treatment approach occurs, this is not always feasible; for example, such as in the evaluation of the treatment impacts of extreme events, including wildfires. While the treatment of wildfire ash- and other pyrogenic matter-impacted source water has been investigated at bench-scale, pilot-scale evaluation of wildfire ash-impacted water has not been reported to date. As such, the objective of this work was to conduct a proof-of-concept evaluation of the treatment of worst-case scenario where ash is mobilized from the landscape directly from hillslopes to source waters after severe wildfire at pilot-scale using commercially available treatment technologies to demonstrate the efficacy of drinking water treatment technologies beyond bench-scale. Here, the ability to treat severely deteriorated source waters after severe wildfire (turbidity >500 NTU; dissolved organic carbon (DOC) concentration >15 mg·L^{-1}) was investigated at pilot-scale. Sand-ballasted flocculation (SBF), SBF with enhanced coagulation through pH adjustment, SBF with powdered activated carbon (PAC) treatment, and dual-stage SBF approaches were evaluated in two fire-prone regions (i.e., Montane Cordillera and Boreal Plains) of Alberta, Canada with markedly different source water quality. The results demonstrated that turbidity was effectively reduced to the less than ~3 NTU needed for efficient subsequent filtration by all of the treatment configurations, as would be expected from high-rate clarification processes like SBF that are designed to respond to rapid changes in source water quality. DOC reduction, however, was limited; this was consistent with high THM and HAA disinfection by-product formational potentials after treatment, indicating the potential need to manage DBP formation if source water quality deterioration is sustained over longer periods of time (e.g., months)—this need is not likely given the episodic deterioration of source water quality after wildfire, which was described in Chapter 2. Thus, this investigation demonstrates that the treatment of some of the most severely, episodically deteriorated, wildfire ash-impacted water to potable water standards is likely if treatment technology is optimized and optimally operated. Notably, coordination of collection of >1 m^3 of wildfire ash prior to rainfall that was needed to conduct this investigation was challenging because it requires access to an area of active wildfire. Thus, while treatment performance optimization would have of course been desirable, the amount of ash that would be required to complete the associated investigations rendered it infeasible. Nonetheless, this investigation demonstrated that the treatment of severely deteriorated wildfire ash-impacted water to potable water standards is possible. By

implication, treatment of less severely deteriorated wildfire ash-impacted water to potable standards is also possible. Notably, the episodic, typically event/high-flow related nature of such deterioration may make it difficult to justify the investment required to achieve this capability. Accordingly, investment in the advanced treatment technologies that would be required to treat significant amounts of wildfire ash runoff directly from hillslopes to source waters warrants system specific evaluation relative to other approaches that may offer additional co-benefits more frequently, including landscape management-based mitigation.

4.2 Introduction

Landscape disturbances exacerbated by climate change are increasingly common where potentially catastrophic events, such as severe wildfire, are likely to increase by the end of the 21st century in wildfire-prone regions (Flannigan et al., 2013). Changes in the intensity and severity of wildfire have profound impacts on landscapes where highly erodible material may be rapidly mobilized and transported to receiving waters (Santín et al. 2015; Santín & Doerr, 2016). This can lead to substantial shifts in water quality, with the possibility of rapid water quality deterioration in association with high surface runoff events, including snowmelt or storms (Moody & Martin, 2001). These impacts can be amplified following wildfire due to changes in the timing of snowmelt and increases in net precipitation (Williams et al., 2019). Thus, wildfire has many implications for aquatic ecosystems, which include increased delivery of sediment (Kunze & Stednick, 2006; Santín et al., 2015; Silins et al., 2009), nutrients (Bladon et al., 2008; Emelko & Sham, 2014; Ranalli, 2004; Rhoades et al., 2019) heavy metals (Kelly et al., 2006; Wolf et al., 2008), and other contaminants (Crouch et al., 2006; Kalabokidis, 2000). Source water quality deterioration following wildfire can also significantly challenge drinking water treatment operations (Emelko et al., 2011; Emelko & Sham, 2014; Writer et al., 2014) and lead to increased costs of treatment (Emelko et al., 2011; Price et al., 2017). In some cases, the impacts of wildfire on water quality can last for years or decades (Emelko et al., 2016; Stone et al., 2014). In contrast, relatively short-lived, episodic degradation of water quality may occur following major runoff events after wildfire that can lead to severely deteriorated water quality, which persists for periods ranging from one day to one week (Dahm et al., 2015; Leak et al., 2003; Lyon & O'Connor, 2008; Mast et al., 2016; Murphy et al., 2015; Writer & Murphy, 2012). Episodic severely deteriorated source water quality would be very challenging for drinking water treatment operations and would require deviation from typical operating procedures, such as the need for higher than typical coagulant dosing. When source water quality is severely deteriorated, source water intakes ideally would be closed or alternative source water supplies would be used; however, these options are not always available, and severely deteriorated source water may require treatment to prevent service disruptions.

Although there are an increasing number of case studies that provide anecdotal and retrospective insight into the impacts of wildfire on drinking water treatment, these studies typically provide limited or no

information about actual treatment technologies or the implications for operational capacity required to respond to severely deteriorated water quality. Correspondingly, there is a widespread belief that drinking water treatment infrastructure may be inadequate to treat the severely deteriorated water quality that may occur following wildfire. Previous bench-scale work has suggested that severely deteriorated water can be treated given appropriate technology and operational response capacity (Chapter 3).

While bench-scale testing may represent the chemical aspects of a treatment process fairly well and aid in identifying potential treatment chemicals and dose requirements, pilot-scale testing provides a better indication of the physical attributes of a full-scale WTP (Edzwald, 2011; Government of Ontario, 2014). For example, during jar-testing, complete mixing occurs in a beaker; however, residence time distributions in mixing tanks during pilot-scale treatment may result in non-ideal mixing conditions, which are more representative of reality at a full-scale WTP (Crittenden et al., 2012; Edzwald, 2011). Furthermore, the mixing conditions during pilot-scale treatment are more indicative of full-scale systems due to the potential for short-circuiting or dead zones in mixing tanks which may result in sub-optimal mixing (Crittenden et al., 2012; Edzwald, 2011).

Pilot-scale testing also provides a means to investigate settling conditions which are more representative of full-scale systems, where differences in settling tank depth (versus a beaker) can provide a more accurate indication of settling conditions of a full-scale WTP (Edzwald, 2011). In addition to the physical aspects of treatment being more representative of reality at pilot-scale, pilot studies can provide a means to illustrate the importance of operational aspects of treatment which are not accounted for during bench-scale assessments. For instance, the need to rapidly adjust chemical doses (e.g., coagulant, polymer, acid) to operationally respond to shifting water quality, such those tested in this research, cannot be effectively tested at bench-scale.

Pilot studies also offer a means to test innovative treatment technologies without interrupting existing treatment process and eliminate potential consumer risks associated with conducting investigations at full-scale (Haas & Fox, 1991). While pilot testing provides a basis for comparing the efficacy of alternative systems or new technologies, it should be conducted over an extended time period, ranging from several months to a year (Crittenden et al., 2012). However, due to the limited amount of test water available for the pilot studies conducted in this research (i.e., wildfire ash-impacted source water; Chapter 2), pilot testing on water quality representative of severely deteriorated post-fire scenarios was only able to be conducted for limited periods (i.e., hours). Accordingly, the objective of this work was to conduct a proof-of-concept evaluation of the treatment of worst-case scenario, ash runoff directly from hillslopes to source waters after severe wildfire (turbidity >500 NTU; DOC concentration >15 mg·L^{-1}) at pilot-scale using commercially available treatment technologies. The different treatment technologies tested in this research aimed to

demonstrate that water can be reasonably treated, where major water quality violations and potential plant shutdowns would be avoided and where solids could be removed through coagulation to provide clarified water which could then be effectively filtered without overloading filters. This research also highlights that if episodic, short-lived severely deteriorated water quality occurs, commonly employed drinking water treatment technologies will be adequate to ensure water can continue to be treated, albeit potentially to a lesser than potable standard, to ensure water is available to for basic sanitation and fire response until source water quality conditions improve. Additionally, although high levels of DOC may be present following treatment in some cases post-fire and may lead to questions about the potential formation of DBPs, reports of such source water quality deterioration indicate that these conditions are episodic and relatively short-lived; thus, they would not be expected to pose significant threats to the provision of safe drinking water.

Although the availability of fresh post-fire ash limited the extent of pilot-scale investigation that could be conducted, it is critical to underscore that a proof-of-concept demonstration of treatment of severely deteriorated, wildfire fire-ash impacted water at pilot-scale provides insight beyond a single case study. As shown in Table 2.1 of Chapter 2, source water quality deterioration after wildland fire challenges drinking water treatability in the immediate and longer terms because of potential increases in DOC concentration and turbidity, as well as changes in DOC character—these changes in source water quality are commonly reported when wildfires have impacts on source water quality. While the magnitude of these changes in source water quality aspects that drive treatability varies, the impacts themselves do not vary; thus, the implications to treatment, especially the need for effective coagulation so that demands can be met without compromising downstream treatment (i.e., filtration, disinfection). A critical implication of a demonstration that drinking water treatment can proceed and continue to provide sufficient treatment despite severely deteriorated source water quality is critical to informing operational response strategies focused on ensuring operator and utility preparedness when such events occur. Moreover, by implication, such a demonstration indicates that treatment of less severely deteriorated wildfire ash-impacted water to potable standards is also possible. Accordingly, a proof-of-concept demonstration of treatment of severely deteriorated, wildfire fire-ash impacted water at pilot-scale can inform decision-making regarding investment in treatment technologies and/or operational response capacities (e.g., near real-time laboratory analyses, online sensors) that increase the potential for achieving desired treatment performance.

It was anticipated that pilot-scale SBF would effectively reduce turbidity because it is designed to do this and contributed to continued provision of safe water at full-scale WTP after the 2016 Horse River wildfire in Fort McMurray, Canada (Emelko et al., 2020). In contrast, high levels of DOC removal by SBF were not expected—the process is not designed for DOC removal and limited DOC removal has been reported by SBF has been previously reported (e.g., Desjardins et al., 2002; Plum et al., 1998). Given the bench-

scale results reported in Chapter 3, it was important to re-examine SBF treatment in combination with either enhanced coagulation through pH adjustment or pre-treatment with PAC because they are recognized as the best available technologies for reducing DOC levels in water (e.g., Crittenden et al., 2012; Edzwald, 2011; USEPA, 1999). Notably, however, the impacts of wildfire ash on source water pH and alkalinity that were reported in Chapter 3 and by others (Cerrato et al., 2016; Earl & Blinn, 2003; Harper et al., 2019; Murphy et al., 2018) also must be considered because they impact the efficiency of DOC removal, especially by enhanced coagulation (e.g., Crittenden et al., 2012; USEPA, 1999).

4.3 Methods

To conduct this research, severely deteriorated source water representative of a "worst-case" scenario in which "black water" results from wildfire ash transport directly from hillslopes to source water supplies. In total, three pilot studies were conducted where several technologies were evaluated using a range of chemical coagulant doses. SBF (Actiflo®, Veolia Water), SBF with enhanced coagulation through pH adjustment, and dual-stage SBF with PAC treatment (Actiflo® Twin Carb, Veolia Water) were evaluated in two wildfire-prone regions (i.e., Montane Cordillera and Boreal Plains) of Alberta, Canada with markedly different source water quality. Several indicators of treatment performance were evaluated, including turbidity, DOC concentration, and ultraviolet absorbance at 254 nm (UVA$_{254}$). Table C1 provides a summary and justification for the various set-points which were selected throughout this study. Additional analyses of THM- and HAA- DBP formation potential was also investigated before and after treatment with dual-stage SBF were also conducted. Detailed methods are presented below.

4.3.1 Treatment technology selection

SBF treatment was investigated because it is a high-rate clarification technology that differs from conventional chemical pre-treatment in that a ballasting-agent (microsand) is injected into the flocculation tank, which increases the floc weight, resulting in a decreased settling time (Desjardins et al., 2002; Ghanem et al., 2007). SBF is a robust treatment technology that is not easily upset by shifts in raw water quality and is able to respond rapidly to changing source water conditions (Crittenden, 2012). This technology was developed to respond to rapid shifts in source water quality. For instance, SBF has been demonstrated to effectively treat severely deteriorated water following flood, in which high turbidity (>4000 NTU) and DOC (>20 mg·L^{-1}) were present (Jagorinec, 2015). The removal of DOC through SBF treatment is typically reliant on metal salt (e.g., alum) coagulation for co-precipitation of DOC and metal hydroxide solids (Sillanpää et al., 2018). As coagulation can be effective in removing hydrophobic and high molecular

weight organics, but less so in removing hydrophilic and lower molecular weight fractions (Nissinen et al., 2001), extensive DOC removal by SBF treatment processes alone was not expected. Thus, SBF with enhanced coagulation and SBF with PAC were also investigated.

Lowered pH during coagulation typically results in increased DOC, which occurs optimally at a pH 5–6 with alum coagulation (Anderson et al., 1995; Edzwald & Van Benschoten, 1990). Enhanced coagulation involves the application of higher than typical doses of coagulant at acidic pH conditions so that relatively more positively-charged metal (e.g., aluminum) species are generated and react with DOC, which is predominantly comprised of organic compounds with negatively-charged functional groups—this enables more co-precipitation of DOC relative to conventional coagulation (Vepsäläinen et al., 2009; Vepsäläinen et al., 2012). Although elevated levels of dissolved residual aluminum may occur at lower pH when high doses of aluminum-based coagulants are used (Pernitsky & Edzwald, 2003).

Pre-treatment with PAC was selected as it is an effective in removing DOC because it has high adsorptive surface area due to DOC adsorbing in PAC's mesopores and large micropores (Dunn & Knappe, 2013). The efficacy of PAC in removing DOC from severely deteriorated post-fire source water has been previously reported at bench-scale (Chapter 3). Dual-stage SBF with PAC pre-treatment, where PAC is recirculated to maximize the adsorption capacity of PAC, was also tested as means to achieve a very high dose of PAC without requiring a constant dose of fresh PAC. Dual-stage SBF is beneficial as it ultimately minimizes the chemical costs associated with high PAC dosing that may be necessary to remove high levels of DOC, such as during severely deteriorated water quality post-fire following major runoff events.

4.3.2 Ash collection following severe wildfire

Fresh ash samples were collected from two severe wildfire sites, prior to any precipitation events to ensure water extractable organic matter was not removed. Ash collection prior to any precipitation events is especially challenging as limited time is available for collection to occur after a wildfire is extinguished. This investigation required nearly 1 ton (approximately 1.5 m^3) of recently burned, post-fire ash. While ash may be defined in numerous ways, it is defined herein as the residual particulate material remaining on the landscape following the burning of wildland fuels that consists of charred mineral and organic materials (Bodí et al., 2014). Severe wildfire had occurred at both ash collection sites, which was indicated by all canopy vegetation and surface litter being consumed and where light-coloured ash and charred organic matter were several centimeters deep (Keeley, 2009; Úbeda et al., 2009).

Figure 4.1: Ash collection following the Thuya Lake Road (TLR) wildfire near Little Fort B.C. **(a)**; pails of post-wildfire ash samples used for preparing the severely deteriorated source water used during pilot-scale testing **(b)**.

The first round of ash collection from the Thuya Lake Road (TLR) wildfire occurred on August 02, 2017 (Chapter 2; Figure 4.1[a]), where 40, 19-L pails of ash were collected. The second round of ash collection was after the Elephant Hill Fire Complex, which burned nearly 200,000 ha from Ashcroft to Cache Creek, BC, Canada. Ash was collected near Scottie Creek Road (SCR) from an area of approximately 2.5 ha that experienced high severity burning (+50.9834, -121.4009). The predominant tree species in the collection area were Douglas Fir (*Pseudotsuga menziesii* var. glauca), with a variety of other species, including Spruce hybrids (genus *Picea*), Yellow Pine (*Pinus ponderosa*), and Trembling Aspen (*Populus tremuloides*). A total of 61, 19-L pails was collected at this site and stored in a cool dry place.

The ash samples which were collected were generated by non-uniform heating conditions due to natural variability in fuel consumption (Parson et al., 2010), and where higher temperatures occur above the surface and lower temperatures occur below the soil surface (Alexis et al., 2007). The natural variability in the collected ash is reflective of the post-fire material that may be transported directly from hillslopes to source water supplies following major runoff events. The composition of the TLR and SCR ash is consistent with previous descriptions of ash (e.g., Etiegni & Campbell, 1991; Thompson, 2008) in which high levels of calcium, magnesium, phosphorous, and potassium are present (Table C2; Appendix C).

4.3.3 Wildfire ash-impacted source water preparation

The severely-deteriorated source water used throughout this investigation was prepared by adding ash to the raw water from either (1) the Elbow River in Calgary (i.e., Montane Cordillera region), or (2) the Athabasca River in Fort McMurray (i.e., Boreal Plains region) of Alberta, Canada. The Elbow River is a high-quality source with typically low turbidity (typically less than 3 NTU) and DOC concentration (typically less than 2 mg·L^{-1}), and high alkalinity (typically higher than 150 mg·L^{-1} as CaCO$_3$) (Beers & Sosiak, 1993). In contrast, the Athabasca River is typically high in turbidity (typically higher than 10 NTU), DOC concentration (typically higher than 10 mg·L^{-1}) (Glozier et al., 2018), and high alkalinity (typically higher than 120 mg·L^{-1} as CaCO$_3$) (see Table 4.1).

Ash samples were first sieved through a 1 mm screen to remove any conifer needles and large debris that would not typically be found in drinking water treatment plant influent streams. It was then added to the untreated river water to achieve black-coloured water with turbidity and DOC concentrations at levels (i.e., >500 NTU and >15 mg·L^{-1}, respectively) consistent with those that have been previously reported after severe wildfire (Emelko et al., 2011; Hohner et al., 2016; Leak et al., 2003; Lyon & O'Connor 2008; Sham et al., 2013; Silins et al., 2009; Writer et al., 2012). The severely deteriorated, wildfire ash-impacted source water was prepared in round 5000 L polyethylene tanks. Determined *a priori* at bench-scale (as described in Chapter 3), respective ash concentrations of 5.0 g·L^{-1} and 10.0 g·L^{-1} were required to reach water quality targets when using the TLR and SCR ash, respectively. The wildfire ash-impacted source was mixed using submersible pumps placed at the bottom of each tank. Two tanks were used during each investigation to enable continuous flow to pilot plant. The tanks were situated approximately 2 m above the intake of the pilot plant to ensure sufficient pressure head for gravity flow through 1.5" flexible PVC hose and the pilot plant.

As noted in Table C1, there was variable mixing time in the tanks prior to being treated a pilot scale, although all tanks were allowed to mix for a minimum of 1 h. While under ideal conditions all ash-impacted source waters would have been mixed for identical times, which was achieved in previous bench-scale studies (e.g., Chapter 3), this was not logistically possible for reasons noted in Table C1. In spite of this, the variability in mixing times were indicative of different mixing conditions where ash would be mobilized into a receiving water body, remain in the water where mixing and leaching of DOC occurred, and then be mobilized directly to the intake of a WTP for subsequent treatment. Although there was variability in mixing times, the general implication for water quality were the same, where elevated turbidity and DOC resulted; however, additional mixing time may have resulted in marginal increases in DOC leaching from ash.

4.3.4 Pilot Plant description

Three pilot studies were conducted. The first and third studies (referred to as GMWTP1 and GMWTP2) were conducted in Calgary, Alberta, Canada at the Glenmore WTP on October 22 to 27, 2018 and October 17 to 20, 2020, respectively. The second study (referred to as FMWTP) was completed in Fort McMurray, Alberta, Canada at the Fort McMurray WTP on May 21 to 26, 2019. The available quantities of wildfire ash limited the duration of the experiments and precluded the opportunity for subsequent process performance optimization.

The first two studies were conducted using a portable trailer-mounted SBF water treatment plant (Actiflo® mini, Veolia Water). The third pilot study was conducted using a permanent SBF pilot-scale treatment plant (Actiflo®, sand-ballasted flocculation technology) located at Calgary's Glenmore WTP. The pilot plants were configured with a coagulation tank (to which coagulant and polymer were added), an injection tank for microsand and polymer addition, a maturation tank, and a settling/clarification tank (Figure 4.2). After settling, clarified water passes up through inclined tube settlers to enhance settling and is then discharged from the system. The water passing through the treatment process had a total residence time of approximately 15 minutes. Sludge consisting of settled floc particles and microsand is recircuited to a hydrocyclone that separates and recycles microsand to the injection tank while discharging solids to waste. Constant flow rates through the pilot plants were maintained using an automated flow control valve on the pilot influent line. Following any changes in coagulant or polymer dose conditions, the pilot plants stabilized by operation over three full cycles of water through the pilot plant (total of approximately 45 minutes). Aluminum-based coagulants were used for all pilot studies (either aluminum sulfate [alum] or polyhydroxy aluminum chloride [PACl]). Details of each pilot plant study, including treatment chemical specifics, are provided in Table C3.
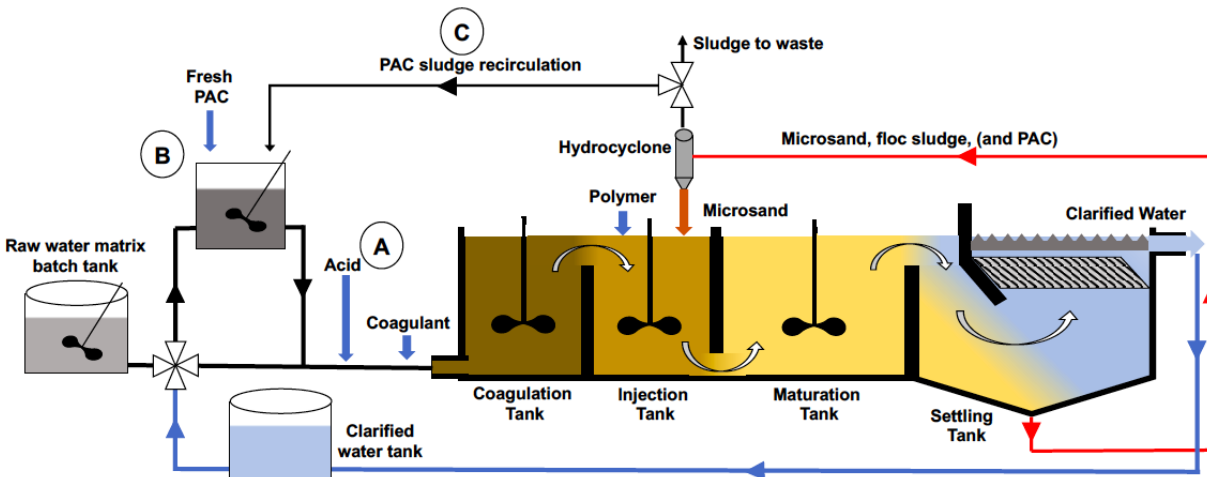
Figure 4.2: Schematic of sand-ballasted flocculation (SBF) pilot plant system. Point (A) is the point of acid addition for enhanced coagulation through pH adjustment; (B) indicates pre-treatment with powdered activated carbon (PAC) in a continuous flow stirred tank reactor (CFSTR); and (C) shows the path of PAC sludge recirculation from the SBF system to the CFSTR after being separated from the microsand in the hydrocyclone as part of the dual-stage clarification process. Water entering the CFSTR during the dual-stage SBF process had been previously clarified through a first round of SBF treatment to remove the majority of suspended solids.

Water samples were collected in sterilized amber glass or high-density polyethylene plastic bottles which were rinsed with sample before filling from either an influent (pre-treatment) or effluent (post-treatment) sample port. Water quality analyses were conducted either by field staff at the pilot location, shipped to the University of Waterloo for analysis, or submitted to a third-party lab for analysis. Samples that required shipment were packaged with ice packs in coolers and couriered at the end of each day of pilot testing. Throughout the course of all three pilot studies a total of 202 samples were collected. In addition to grab samples, online turbidity and pH were monitored (Table C3) to indicate performance stabilization after any operational adjustments (e.g., changes in chemical dosing). Plant flow rate and chemical dosing levels were also monitored online.

4.3.5 Treatment methods

Conventional SBF, SBF with enhanced coagulation through pH adjustment, SBF with PAC pre-treatment, and a dual-stage SBF treatment approaches were investigated. Treatment configuration details are provided below.

4.3.5.1 Sand-ballasted flocculation

During the GMWTP1 study, SBF treatment was evaluated. All coagulant doses herein are reported as commercial product (volume [$\mu L \cdot L^{-1}$] × specific gravity). The influent water temperature for the GMWTP1 study was ~10°C throughout the pilot study. Coagulant (aluminum sulfate [alum]) doses ranged from 102 to 407 mg·L^{-1} and cationic polymer doses ranged from 0.76 to 0.78 mg·L^{-1}. The upper concentration limit for alum dosing (~400 mg·L^{-1}) was based on the upper limit indicated by the NSF guidelines for commercial product dose (NSF, 2017).

Conventional SBF treatment was also evaluated during the FMWTP pilot study. There, polyhydroxy aluminum chloride (PACl) doses ranging from 122 to 407 mg·L^{-1} and 1.01 mg·L^{-1} of cationic polymer were applied. Although the NSF guideline for PACl dose is 200 mg·L^{-1}, higher doses were used because of the high coagulant demand of the Athabasca River (which is naturally very high, regular necessitating coagulant doses of more than 100 mg·L^{-1}), which increased as a result of ash addition. The influent water temperature throughout the pilot study at FMWTP was ~14°C.

4.3.5.2 SBF with enhanced coagulation

Enhanced coagulation through pH adjustment was evaluated during the GMWTP1 by maintaining a constant, lower pH level in the coagulation tank via muriatic acid (i.e., hydrochloric acid [HCl]) addition immediately prior to coagulant addition (Figure 4.2). Alum doses ranging from 110 to 411 mg·L^{-1} were investigated; cationic polymer dose was maintained at 0.76 to 0.79 mg·L^{-1}. Commercial grade HCl (31.45%, by weight) was diluted to 10% by weight (3.2 mol·L^{-1}) prior to dosing. HCl dose conditions were inversely associated with alum dose due to pH suppression by the alum. The pH in the coagulation tank was monitored with an online probe to ensure it remained between 5.0 and 6.0.

During the FMWTP pilot study, enhanced coagulation through pH adjustment was evaluated by varying the pH (4.97–6.43) during coagulation while maintaining an approximate constant doses of coagulant (PACl) and cationic polymer, 398–406 mg·L^{-1} and 0.96–1.05 mg·L^{-1}, respectively. Commercial grade HCl was added to control pH, as described above.

4.3.5.3 SBF with PAC pre-treatment

Pre-treatment with PAC followed by SBF treatment was evaluated during both the GMWTP1 and FMWTP studies. A 1000 L CFSTR with a retention time of approximately 45 minutes was used to mix a continuous dose of PAC slurry with the severely deteriorated ash-impacted source water, where coal-based PAC (Table C3) was used. It was prepared as a slurry by mixing dry PAC with potable service water for a minimum of

24 h to ensure it was fully hydrated. PAC slurries were batched at concentrations of either 200 $g \cdot L^{-1}$ (GMWTP1) or 25 $g \cdot L^{-1}$ (FMWTP); this concentration was dependent on doing pump capacity.

PAC doses of 50 to 250 $mg \cdot L^{-1}$ were applied during the GMWTP1 pilot study, while alum and cationic polymer doses were maintained at 397 $mg \cdot L^{-1}$ and 0.79 to 0.99 $mg \cdot L^{-1}$, respectively. To enable adequate flocculation, additional cationic polymer was added as PAC dose increased. Higher PAC doses of 100 to 1000 $mg \cdot L^{-1}$ were tested during the FMWTP study; PACl was maintained at an approximate constant level (405 to 411 $mg \cdot L^{-1}$) and cationic polymer doses varied between 1.05 to 2.09 $mg \cdot L^{-1}$; additional polymer was required to ensure adequate floc formation as PAC dose increased.

4.3.5.4 Dual-stage SBF clarification with PAC recirculation

Dual-stage clarification in which SBF was used two times in series (Actiflo® Twin Carb™) was investigated during the GMWTP2 study. The first stage of SBF treatment removed suspended solids; the second stage of SBF was a polishing process focused on DOC removal through the application of coconut-based PAC (Table C3). Since only one SBF pilot unit was available, the clarified effluent from the first stage of SBF was collected in a 5000 L polyethylene tank and passed through the SBF system a second time after first being pre-treated with PAC in a CFSTR with a retention time of approximately 15 minutes. The PAC slurry was prepared at 20 $g \cdot L^{-1}$ (hydrated for a minimum of 24 h) and added to the CFSTR at a constant dose of ~140 $mg \cdot L^{-1}$. The sludge from the second SBF stage was recirculated to the CFSTR after the microsand had been recycled back the system via the hydrocyclone (Figure 4.2); the recirculated sludge consisted almost entirely of PAC. PAC sludge recirculation enabled achievement of an extremely high dose of PAC (>2000 $mg \cdot L^{-1}$) and precluded wasting PAC whose adsorptive capacity had not been fully utilized. To balance the fresh PAC being dosed at ~140 $mg \cdot L^{-1}$, a small portion of the recirculated sludge was periodically wasted to ensure a consistent dose of PAC was achieved in the CFSTR through the addition of both recirculated sludge containing PAC and fresh PAC slurry.

Two trials were conducted during the GMWTP2 pilot study. In the first trial, TLR ash (5.0 $g \cdot L^{-1}$) was used. The same dual-stage SBF conditions were investigated during the second trial, however, SCR ash (10.0 $g \cdot L^{-1}$) was used. The process influent water temperature ranged between 5 and 11°C during the trials due to cold outdoor temperature and the requisite outdoor storage of the 5000 L tanks.

4.3.6 Water quality analyses

Standard methods (APHA, 2012) were used for water quality analyses: turbidity (Method 2130B), pH (Method 4500-H+B), UVA_{254} (Method 5910B, pre-filtered through 0.45μm membrane); DOC (Method

5310C, pre-filtered through 0.45µm membrane), alkalinity (Method 2320), and conductivity (Method 2510) were analyzed. Details of specific laboratory instrumentation and additional information are provided in Table C4. Online instrumentation was used to monitor pH in the coagulation tank and on the clarified water; clarified water turbidity was also evaluated. The specific ultraviolet absorbance at 254 nm (SUVA) was calculated by dividing UVA_{254} by the concentration of DOC (Weishaar et al., 2003).

The DBP total formation potential for trihalomethanes (THMs) and haloacetic acids (HAAs) was determined according to Methods 5710 B and 5710 D, respectively, with a chlorine reaction time of seven days (i.e., true formation potential). Samples were buffered at a pH of 7.0 ± 0.2 and a chlorine residual of $3.0–5.0 \ mg \cdot L^{-1}$. Chlorine residuals were measured using the colorimetric Method 4500-Cl G (APHA, 2012) using N, N-diethyl-p-phenylene diamine (DPD) and were quenched after 7 days with ammonium chloride. Total trihalomethanes (TTHMs) were analyzed following Method 501.1 (USEPA, 1979) where four different THMs were analyzed. Five haloacetic acids (HAA5) were analyzed according to Method 552.3 (USEPA, 2003). Additional details of the specific DBPs analyzed and methodology are available in Table C4.

4.3.7 Statistical analyses

One-way ANOVA tests with a post-hoc Tukey's test of multiple comparisons were conducted to evaluate the efficacy of different chemical doses (i.e., coagulant or PAC) or compare the performance of different treatment technologies where three or more independent variables were present. Independent samples t-tests were used to evaluate differences in treatment efficacy where two independent variables were being assessed. All statistical tests were conducted using SPSS® software (version 26, IBM®).

4.4 Results and discussion

4.4.1 Wildfire ash-impacted water

To conduct the pilot-scale treatment studies it was necessary to first prepare severely deteriorated water which could be subsequently treated. However, maintaining consistent severely deteriorated, wildfire ash-impacted source water quality was challenging, likely due to imperfect mixing in the 5000 L storage tanks and differences in wildfire ash composition. Nominal source and wildfire ash-impacted water quality during the GMWTP1 and FMWTP studies are summarized in Table 4.1. The data provided in this table underscores that the addition of wildfire ash to the river water resulted in substantial increases in turbidity,

DOC, UVA$_{254}$, pH, alkalinity, and conductivity that were consistent with previous reports of elevated turbidity, DOC concentrations, and UVA$_{254}$ after wildfire (Emelko et al., 2011; Sham et al., 2013).

Table 4.1: Water quality data for pilot-scale studies. Data is provided for Elbow and Athabasca Rivers (nominal quality over 8 years and specific quality during pilot testing) and the severely deteriorated wildfire ash-impacted source waters prepared for pilot-scale testing at Glenmore WTP (GMWTP1) and Fort McMurray WTP (FMWTP). Nominal water quality data for Elbow and Athabasca River is presented as mean ± standard deviation (SD) and all other data is presented as mean ± standard error (SE). The wildfire ash-impacted source water were prepared using Thuya Lake Road (TLR) ash (5.0 g·L^{-1}) or Scottie Creek Road (SCR) ash (10.0 g·L^{-1}). Parameters presented include turbidity, dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UVA$_{254}$), pH, alkalinity, and conductivity.

Water category	Turbidity (NTU)	DOC (mg L^{-1})	UVA$_{254}$ (cm^{-1})	pH	Alkalinity (mg L^{-1} as CaCO$_3$)	Conductivity (μS cm^{-1})
Nominal Elbow River quality at Glenmore WTP* (mean ± SD)	1.1 ± 0.7	1.2 ± 0.4	0.03 ± 0.01	8.2 ± 0.1	151 ± 12	409 ± 41
Elbow River water during GMWTP1 pilot study (mean ± SE)	0.5 ± 0.02 (n=6)	1.0 ± 0.0 (n=2)	0.02 ± 0.01(n=2)	8.4 ± 0.02 (n=6)	151 ± 3 (n=2)	424 ± 4 (n=2)
Elbow River water + TLR ash during GMWTP1 pilot study (mean ± SE)	602 ± 106 (n=19)	13.4 ± 0.5 (n=19)	0.51 ± 0.02 (n=19)	8.9 ± 0.02 (n=9)**	378 ± 17 (n=19)	504 ± 3 (n=19)
Nominal Athabasca River quality at Fort McMurray WTP* (mean ± SD)	3.1 ± 1.9	7.4 ± 2.3	0.20 ± 0.06	7.8 ± 0.1	125 ± 28	301 ± 69
Athabasca River water during FMWTP pilot study (mean ± SE)	12.3 ± 1.1 (n=5)	10.3 ± 0.3 (n=3)	0.33 ± 0.01 (n=3)	8.2 ± 0.1 (n=3)	121 ± 1 (n=3)	294 ± 2 (n=3)
Athabasca River water + SCR ash during FMWTP pilot study (mean ± SE)	396 ± 8 (n=9)***	20.1 ± 0.6 (n=36)	1.16 ± 0.05 (n=36)	9.5 ± 0.03 (n=36)	488 ± 25 (n=36)	619 ± 11 (n=36)

* Nominal water quality data for Elbow River and Athabasca River (entering WTP) using monthly mean data for 8 year period (Janurary 2010- December 2017); monthly means within the 85th percentile were used to calculate the overall mean and standard deviation; total organic carbon is reported due to availability of data.
** Data taken from GMWTP2 pilot-study using Elbow River water and TLR ash (5 g L^{-1}), ***data taken from GMWTP2 using Elbow River and SCR ash (10 g L^{-1}).

During the GMWTP2 study, turbidity levels (not provided in Table 4.1) were comparable levels during the GMWTP1 study, where turbidity levels were 691 ± 18 NTU (mean ± SE, n=9) after addition of 5.0 g·L^{-1} of TLR ash to Elbow River water. The elevated turbidity levels in the severely deteriorated wildfire ash-impacted source water during all the pilot studies would lead to drinking water treatment challenges, such as requiring higher coagulant doses and managing high levels of sludge. WTPs in regions where deteriorated conditions are typically experienced following major runoff events may be more aptly prepared (compared to WTPs which rely on a high-quality water source) to manage severely deteriorated conditions post-fire due to having the infrastructure and operational capacity available.

DOC and UVA$_{254}$ were substantially higher than baseline river water conditions (Table 4.1). For instance, the quality of the wildfire ash-impacted source water starkly contrasted the Elbow River which had low levels of turbidity, DOC, and UVA$_{254}$ (Table 4.1), which are characteristic of high-quality source waters in the Montane Cordillera region. The severely deteriorated ash-impacted source water prepared for pilot testing at FMWTP also resulted in high levels of DOC and UVA$_{254}$, which were elevated from the baseline Athabasca River water quality. However, the baseline water quality of the Athabasca River had

substantially higher turbidity, DOC, and UVA_{254} than that of the Elbow River, which is characteristic of many source waters the Boreal Plains region.

The SUVA values for the severely deteriorated wildfire ash-impacted source water used for the GMWTP1 and FMWTP pilot studies were 3.79 ± 0.09 L·mg^{-1}·m^{-1} (mean ± SE, n=19) and 5.80 ± 0.19 (mean ± SE, n=36) respectively. DOC removal using alum coagulation is expected to be 25–50% when the SUVA is 2–4 L·mg^{-1}·m^{-1} and >50% removal when the SUVA is >4 L·mg^{-1}·m^{-1} (Edzwald & Tobiason, 1999); however, this expected DOC removal is based on source water quality which has not been impacted by wildfire.

Consistent with previous reports, the pH levels of the severely deteriorated ash-impacted source water were higher when compared to the pH of the baseline river water (Harper et al., 2019; Plumlee et al., 2007; Revchuk & Suffet, 2014). The pH of the wildfire ash-impacted source water used in the GMWTP1 study increased from the Elbow River baseline of 8.4 ± 0.02 (mean ± SE, n=6) to 8.9 ± 0.02 (mean ± SE, n=9). Similarly, the wildfire ash-impacted source water prepared for the FMWTP pilot study increased from a baseline of 8.2 ± 0.1 (mean ± SE, n=3) for the Athabasca River water to 9.5 ± 0.03 (mean ± SE, n=36). Similar increases in pH were demonstrated during the GMWTP2 pilot study. The upward shift in pH following wildfire may decrease coagulation efficacy and impact subsequent physico-chemical treatment processes such as filtration (Pernitsky & Edzwald 2006).

Alkalinity also increased substantially in all cases following the addition of ash to the river water, where final values for the source water demonstrated a stark contrast from the baseline river water alkalinity levels for the Elbow and Athabasca Rivers (Table 4.1). The increase in both alkalinity and pH may be attributed to the mineralized materials in the alkaline ash products that contain high levels of carbonates and base cations that are released upon dissolution (Lydersen et al., 2014). The elevated alkalinity levels in the severely deteriorated wildfire ash-impacted source water are consistent with other reports of increased alkalinity in waters impacted by wildfire (Cerrato et al., 2016; Earl & Blinn, 2003; Murphy et al., 2018) which may be problematic for effective pH adjustment during treatment due to high alkalinity waters being resistant to changes in pH (Crittenden et al., 2012). High levels of alkalinity and pH may lead to operational challenges, as higher coagulant doses or the addition of acid to reduce the pH will be needed to promote effective coagulation. In general, the water quality results for the ash-impacted source waters prepared for the pilot-scale were aligned with the expected result that substantial increases in parameters that will impact the efficacy of treatment (i.e., turbidity, DOC, alkalinity, and pH) regardless of the baseline river water quality that was used to prepare the severely deteriorated wildfire ash-impacted source water, which has been previously demonstrated (e.g., Chapter 2 and 3), and is a result of the quantity of ash which was added to the baseline river waters. The water quality results from the ash-impacted source waters prepared for pilot-scale studies were aligned with the target values for DOC and turbidity (as described in Chapter 2) to

be representative of severely deteriorated post-fire water quality which could then be tested for treatment efficacy at pilot-scale.

4.4.2 Pilot-scale drinking water treatment

4.4.2.1 Sand-ballasted flocculation

Turbidity was effectively reduced by SBF from >500 NTU to ≤3.3 NTU (>99% reduction) at all of the coagulant dosing conditions investigated during the GMWTP1 pilot study (Figure 4.3). Although there were differences observed between turbidity values at different dosing conditions (102–407 mg·L^{-1}), these differences were likely not of practical relevance as the turbidity in treated/clarified water was reduced to 1.6–3.3 NTU following SBF. It should be emphasised that these turbidity values are for clarified water and that subsequent filtration would generally be applied at a full-scale WTP, resulting in further reduction of turbidity. Although turbidity was effectively reduced at the lowest alum dose (~100 mg·L^{-1}), higher coagulant doses were investigated because of the need for concurrent removal of DOC, which is a precursor of regulated DBPs (i.e., THMs and HAAs) and can contribute to bacterial growth in distribution systems.
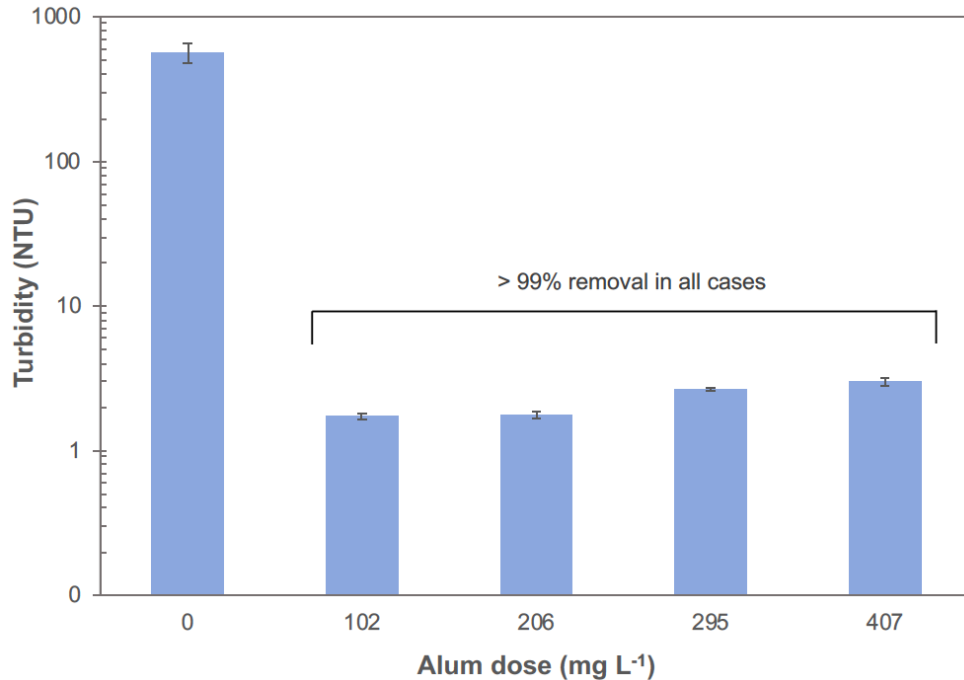
Figure 4.3: Treated water turbidity after GMWTP1 pilot-scale treatment using SBF at different coagulant doses (alum) to treat a severely-deteriorated wildfire ash-impacted source water representing a "worst-case scenario" with high turbidity (>500 NTU), and where "black water" conditions result from wildfire ash being transported directly from hillslopes to source water supplies. Treated effluent samples were collected in triplicate for each alum dose; error bars indicate standard error. Percent reduction from the pre-treatment condition is indicated.

During the FMWTP study, clarified water turbidity ranged from 3.4 to 17.4 NTU after SBF testing a range of coagulant doses. These results were not surprising because the Athabasca River water already exerts substantial coagulant demand in absence of wildfire ash addition. Although similar reductions of turbidity were observed during the GMWTP1 study regardless of the coagulant dose during SBF treatment, this was not demonstrated during the FMWTP1 pilot study, where low turbidity levels were only achieved at the highest PACl doses of 314 and 407 mg·L^{-1}, which yielded clarified water turbidities of 3.4 and 3.9 NTU, respectively.

The GMWTP1 and FMWTP clarified water turbidities were consistent with observations from previous bench-scale evaluations of turbidity removal by SBF of severely deteriorated wildfire ash-impacted water (Chapter 3). The importance of achieving turbidity reductions during the first stages of drinking water treatment, cannot be over-stated. The principal objective of drinking water treatment is the protection of public health from waterborne disease and effectively reducing elevated turbidity is an essential first step. While the turbidity was greatly reduced following SBF, clarified water would typically go on to subsequent

granular media filtration treatment with the essential objective of removing protozoan pathogens and ultimately safeguarding public health (Crittenden et al., 2012; Federal Register, 1989). The turbidity values achieved throughout the SBF treatment pilot studies are in the typical range of clarified water turbidity that would be treated by subsequent physico-chemical filtration processes, which are crucial for the removal of protozoan pathogens (Emelko et al., 2005). The SBF pilot studies demonstrated that effective reduction of high turbidity in treated/clarified/pre-filter can be achieved following major runoff events, avoiding plant shutdowns due to elevated turbidity overloading filtration processes.

It has been previously noted that burned particulate material following wildfire settles at a lower velocity due to its low density (Clark, 2010) and higher porosity compared to unburned material (Stone et al., 2011); however, the results from this study demonstrate that the high turbidity associated with burned particulate matter may be effectively reduced. During the studies it was observed that some low-density material remained on the water surface in the treatment tanks of the pilot system. This low-density material also collected on the inner sides of the tanks near the surface and was not effectively settled out through the SBF process.

DOC and UVA_{254} were not removed to the same extent as turbidity during the GMWTP1 and FMWTP pilot studies. DOC and UVA_{254} removal following SBF during the GMWTP1 pilot study conducted with alum doses 102 to 407 $mg \cdot L^{-1}$ are presented in Figure 4.4. There was a significant difference in DOC removal between the 407 $mg \cdot L^{-1}$ dose and all lower doses ($p \leqslant 3.0 \times 10^{-6}$), where a $22.3 \pm 0.3\%$ (mean $\pm$ SE, n=3) reduction in DOC was achieved, yielding a DOC of 9.6 ± 0.03 $mg \cdot L^{-1}$ (mean $\pm$ SE, n=3) in the clarified water (Table C5). The reduction of UVA_{254} was significantly different between alum doses ($p \leqslant 0.001$), where the highest reduction of $34.6 \pm 0.3\%$ (mean $\pm$ SE, n=3) was achieved at an alum dose of 407 $mg \cdot L^{-1}$ with clarified water yielding 0.291 ± 0.001 cm^{-1} (mean $\pm$ SE, n=3), as reported in Table C5. The reduction of UVA_{254} by alum (on a percent basis) following SBF during the GMWTP1 was consistently greater than the reduction in DOC, which is reflective of the preferential removal of aromatic DOC with alum (Croué et al., 1993; Reckhow & Singer, 1990).

Although DOC reduction is typically lower than UVA_{254} reduction during coagulation, the best treatment performance with SBF treatment during the FMWTP pilot study (coagulant dose 311 $mg \cdot L^{-1}$ of PACl) resulted in DOC and UVA_{254} reductions of $45.0 \pm 2.9\%$ and $41.4 \pm 2.2\%$ (mean $\pm$ SE, n=3 in both cases), respectively. While the DOC reduction was atypically higher than UVA_{254} in this case, this relationship was not observed at any other time during the FMWTP pilot study. The best clarified water quality results for SBF during the FMWTP pilot study (311 $mg \cdot L^{-1}$ PACl) for DOC and UVA_{254} were 11.0 ± 0.6 $mg \cdot L^{-1}$ (mean $\pm$ SE, n=3) and 0.463 ± 0.02 cm^{-1} (mean $\pm$ SE, n=3), respectively. It is worth noting that previous

bench-scale work has suggested that SBF treatment would yield similar reductions of DOC as conventional chemical pre-treatment (e.g., coagulation-flocculation-sedimentation) for treating severely deteriorated source water (Chapter 3). Therefore, it is expected that conventional chemical pre-treatment may provide similar results, albeit without the benefit of being a high-rate clarification process.
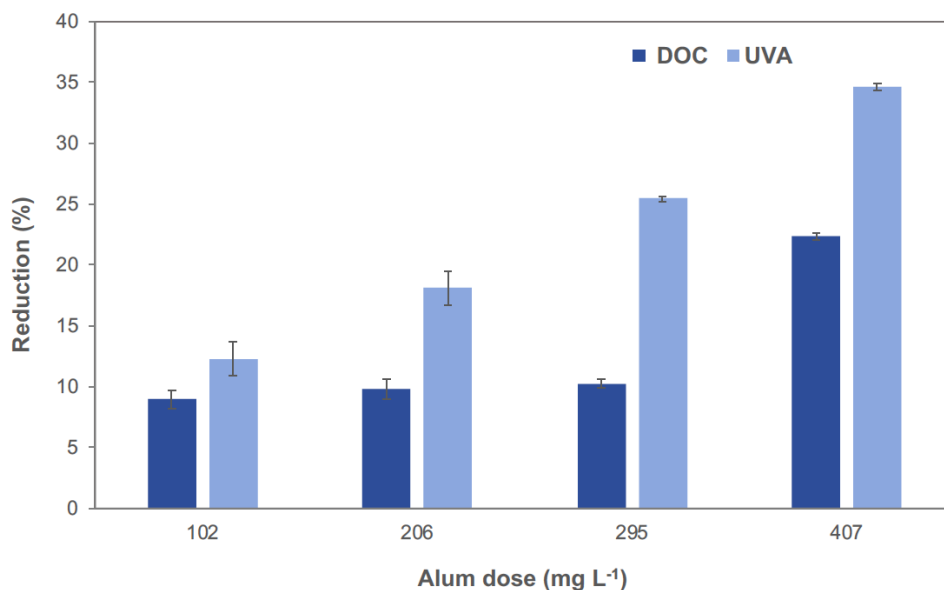
Figure 4.4: Percent reductions of DOC and UVA_{254} in treated water after GMWTP1 pilot-scale treatment using sand-ballasted flocculation (SBF) at different coagulant doses (alum) to treat severely deteriorated source water quality representing a "worst-case scenario" following wildfire. Treated effluent samples were collected in triplicate; error bars indicate standard error. All parameters reported as mean ± SE, n=3 in all cases. All p-values comparing different coagulant doses on DOC and UVA_{254} reductions are provided in Table C5.

The limited organic carbon removal using SBF treatment was in agreement with the anticipated results, as SBF is only expected to be minimally effective for DOC removal (e.g., Desjardins et al., 2002; Plum et al., 1998). This result was supported by previous bench-scale testing (Chapter 3) where limited DOC removal was demonstrated using SBF treatment on severely deteriorated post-fire water quality. As such, it is expected that augmenting SBF treatment with either enhanced coagulation measures or the use of PAC will result in achieving a higher reduction of DOC due to the direct precipitation through enhanced coagulation (Ghernaout et al., 2009) or adsorption of PAC onto activated carbon particles (Dunn & Knappe, 2013).

4.4.2.2 Sand-ballasted flocculation with enhanced coagulation

SBF with enhanced coagulation (SBF+EC) with acid addition was also investigated during the GMWTP1 and FMWTP studies—the results from those studies are presented in Figure 4.5. Although pH may be lowered by adding high levels of coagulant, additional acid was required to sufficiently lower the pH into

optimal ranges for DOC removal by coagulation. During the GMWTP1 pilot study the pH levels were decreased to 5.8 ± 0.1 (mean $\pm$ SE, n=4) by adding HCl prior to coagulant addition throughout the SBE+EC study across different coagulant doses. There was a substantial reduction in turbidity, where the turbidity of the clarified water was 1.7 to 3.8 NTU. Though still low (i.e., <30 % [USEPA, 1999]), DOC removals were $24.2 \pm 0.4\%$ (mean $\pm$ SE, n=3) for SBF+EC; a statistically significantly difference in the removal for DOC was observed when compared to SBF without pH adjustment at the same dose ($\sim$400 mg·L^{-1}) (p=0.019). UVA$_{254}$ was reduced by $46.2 \pm 0.3\%$ (mean $\pm$ SE, n=3) following SBF+EC (see Figure C1); thus, the difference in UVA$_{254}$ removal between SBF and SBF + EC (at $\sim$400 mg·L^{-1}) was also significant (p=1.1×10^{-5}).
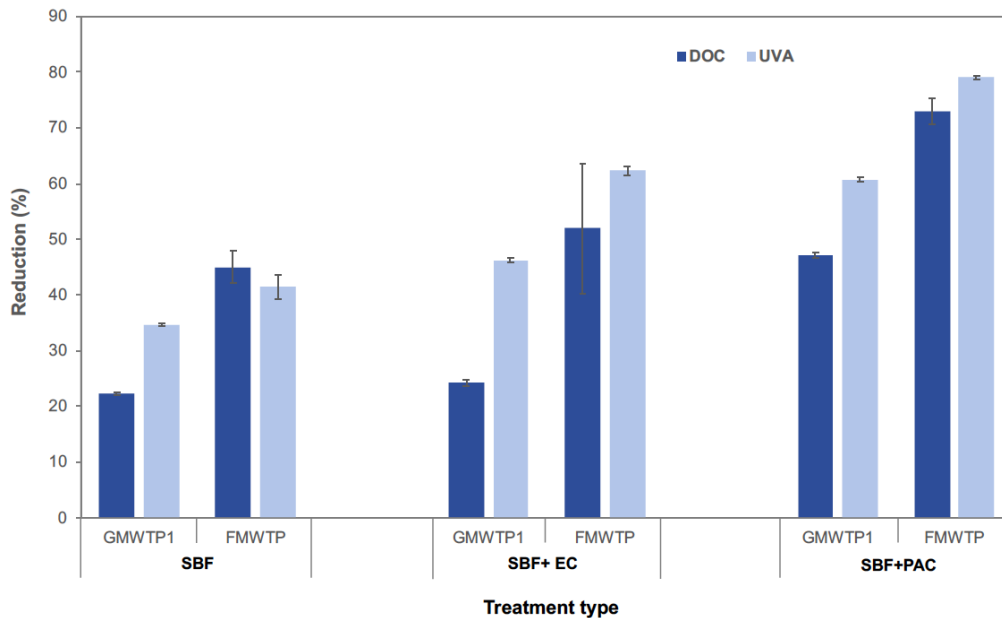
Figure 4.5: Percentage reduction of dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UVA$_{254}$) in treated water for three different treatment scenarios, including: sand-ballasted flocculation ('SBF'); SBF with enhanced coagulation through pH adjustment ('SBF+EC'); and, SBF with powdered activated carbon pre-treatment ('SBF+PAC'). The results provided are from the best treatment outcomes achieved under each of the three treatment scenarios for pilot studies at Glenmore water treatment plant (GMWTP1) and the Fort McMurray water treatment plant (FMWTP). Error bars indicate standard error. All parameters reported as mean $\pm$ SE, n=3 in all cases. All p-values for comparisons of different operational conditions for DOC and UVA$_{254}$ reductions are provided in Table C7 and Table C8 for GMWTP1 and FMWTP, respectively.

During the FMWTP pilot study SBF+EC through pH adjustment was conducted using a constant coagulant (PACl) dose ($\sim$400 mg·L^{-1}) and pH was varied from 4.97–6.43. The lowest turbidity values were found at pH values of 5.86 and 5.51, where turbidity levels were 2.7 NTU and 2.5 NTU, respectively, in the clarified

water. In contrast to these results, turbidity at the lowest pH (4.97) resulted in sub-optimal removal, with turbidity of 51.0 NTU remaining in clarified water.

The best performance for DOC and UVA$_{254}$ reductions through coagulation-flocculation were demonstrated for SBF+EC during the FMWTP study were at a 51.9 ± 11.7% (mean ± SE, n=3) and 62.3 ± 0.8% (mean ± SE, n=3) at a dose of 406 mg·L^{-1} PACl when the pH was 4.97. The optimal DOC removal using PACl at a pH ~5 during the FMWTP study was lower than previous studies where PACl was reported to most effectively reduce DOC at a pH of ~6 (Li et al., 2014); however, these tests were not indicative of water quality conditions after wildfire. An independent samples t-test indicated that the removal of UVA$_{254}$ using SBF+EC was significantly higher (p=1.3×10^{-4}) under the best treatment performance conditions compared to SBF treatment. The results of UVA$_{254}$ reductions under different pH conditions is provided in Figure C2. Although the maximum efficacy for DOC removal was achieved at a pH of ~5, there was poor settling of floc resulting in sub-optimal turbidity removal, as previously noted. In spite of this, the results from the enhanced coagulation pilot test were aligned with the anticipated result, where enhanced coagulation would result in a substantially higher DOC removal when compared to SBF treatment in the absence of pH adjustment. The increased reduction of DOC through enhanced coagulation at a lower pH is a result of the overall charge on the molecules becoming less negative or neutral which can improve the efficacy of organic carbon removal by coagulation (Croue et al., 2000). The dominant mechanism responsible for the removal of DOC under enhanced coagulation conditions are the direct precipitation through complexation with metal species, where there is less direct adsorption of DOC directly onto precipitated metal hydroxide solids (Ghernaout et al., 2009).

While enhancing coagulation conditions through pH adjustment did demonstrate superior performance, attempting to control the pH of the severely deteriorated wildfire ash-impacted source water during coagulation was very challenging, likely due to high alkalinity in the water. Given that water quality can shift rapidly after wildfire—particularly during relatively short periods of severely deteriorated source water quality following high runoff events (Emelko et al., 2011; Emelko & Sham, 2014)—attempting to adjust the pH of severely-deteriorated water after wildfire would likely be impractical and operationally difficult.

4.4.2.3 Sand-ballasted flocculation with PAC pre-treatment

Substantial removal of organic carbon, as indicated by DOC concentration and UVA$_{254}$, by PAC pre-treatment followed by SBF was observed, as compared to SBF and SBF+EC (see Figure 4.5). The best performance during the GMWTP1 pilot study using PAC pre-treatment (PAC dose of 250 mg·L^{-1}) resulted in a DOC reduction of 47.2 ± 0.5 % and a UVA$_{254}$ reduction of 60.8 ± 0.4% (mean ± SE, n=3 in each case)

(Figure C3). While PAC pre-treatment did demonstrate the highest efficacy, differences between PAC pre-treatment at the lowest dose of PAC (50 mg·L^{-1}) and SBF or SBF+EC were not statistically significant for DOC reductions (p=0.636). However, there were significant differences in treatment when PAC was dosed at concentrations greater than 100 mg·L^{-1}, where p$\leqslant$ 1.3.×10^{-9} for DOC and p$\leqslant$ 1.9×10^{-10} for UVA when compared to either SBF or SBF+EC (Table C7). The best overall water quality after pre-treatment with PAC (250 mg·L^{-1}) was a DOC concentration of 6.5 ± 0.1 mg·L^{-1}, a UVA$_{254}$ of 0.153 ± 0.002 cm^{-1}, and turbidity of 1.4 ± 0.03 NTU (mean ± SE, n=3 in all cases).

PAC pre-treatment (up to a maximum dose of dose of 1000 mg·L^{-1}) with subsequent SBF was evaluated during the FMWTP (Figure C4) and yielded comparable results to those during the GMWTP pilot study, where the best overall water quality results were achieved using PAC, compared to SBF or SBF+EC. The highest decreases for both DOC and UVA$_{254}$ were found at the highest PAC dose (1000 mg·L^{-1}), with reductions of 73.0 ± 2.3% and 79.0 ± 0.32% (mean ± SE, n=3 in both cases), respectively. Figure C4 provides the performance results of PAC doses ranging 100–1000 mg·L^{-1} on UVA$_{254}$ reduction. The clarified water following PAC treatment had a DOC of 5.7 ± 0.3 mg·L^{-1}, a UVA of 0.217 ±0.003 cm^{-1} (mean ± SE, n=3 in all cases) and turbidity of 1.3 NTU (as indicated by online measurement). Significant differences were found between PAC pre-treatment at 1000 mg·L^{-1} and SBF or SBF+EC for UVA$_{254}$ reduction, where p$\leqslant$2.3×10^{-8} in both cases (Table C8).

Pre-treatment with PAC prior to SBF demonstrated the greatest efficacy for reducing DOC and UVA$_{254}$ relative to SBF and SBF+EC, thus highlighting that the use of PAC was the most effective treatment option for removing elevated levels of organic carbon in severely deteriorated conditions post-wildfire. Of course, DOC removal by PAC is not surprising (Najm et al., 1991; Kristiana et al., 2011). It is notable that this is the first pilot-scale study to demonstrate that PAC is effective in reducing DOC in severely deteriorated, wildfire ash-impacted water. It is further notable that the PAC dose (1000 mg·L^{-1}) was substantially higher than the typical range of 5 to 25 mg·L^{-1} (Crittenden et al., 2012). A PAC dose as high as that tested herein would be very costly for drinking water treatment utilities, though the need for PAC may be limited by the relatively short-lived, episodic nature of severe water quality deterioration following wildfire and system specific performance optimization options such as multi-source blending. Finally, it is worth noting that although pre-treatment with PAC prior to SBF removed DOC reasonably well, conventional chemical pre-treatment (coagulation-flocculation-sedimentation), which was not investigated herein, may have similar success in reducing both turbidity and DOC when used in combination with PAC.

The high effectiveness of DOC removal demonstrated during the pilot studies using PAC pre-treatment agreed with the expected results, previously noted. The use of PAC is a well-established method for

removing DOC in drinking water treatment (Edzwald, 2011), where the high surface area and the high adsorptive capacity of PAC make it an ideal chemical for removing high levels of organic carbon (Crittenden et al., 2012). While specific adsorption mechanisms of DOC on PAC are complex (Bjelopavlic et al., 1999), it has been noted that organic matter is primarily adsorbed into large micropores and mesopores which are present in activated carbon particles (Dunn & Knappe, 2013), which is likely the mechanism responsible for the high efficacy demonstrated during the pilot-scale studies conducted herein.

4.4.2.4 Dual-stage SBF

Dual-stage SBF was investigated during two trials of the GMWTP2 pilot study. The results are presented in Figure 4.6 and demonstrate DOC removal similar to that observed by pre-treatment with PAC during the GMWTP1 and FMWTP pilot studies. The principal difference between the dual-stage SBF treatment and PAC pre-treatment with SBF was that extremely high PAC doses (>2000 mg·L^{-1}) were achieved due to PAC recirculation. Specific chemical dose conditions were variable throughout the study and are provided in Table C9. Two trials were conducted for dual-stage SBF during the GMWTP2 pilot study; the results are provided in Figure 4.6, in which performance following the first pass (SBF) and second pass (dual-stage SBF) are specified.
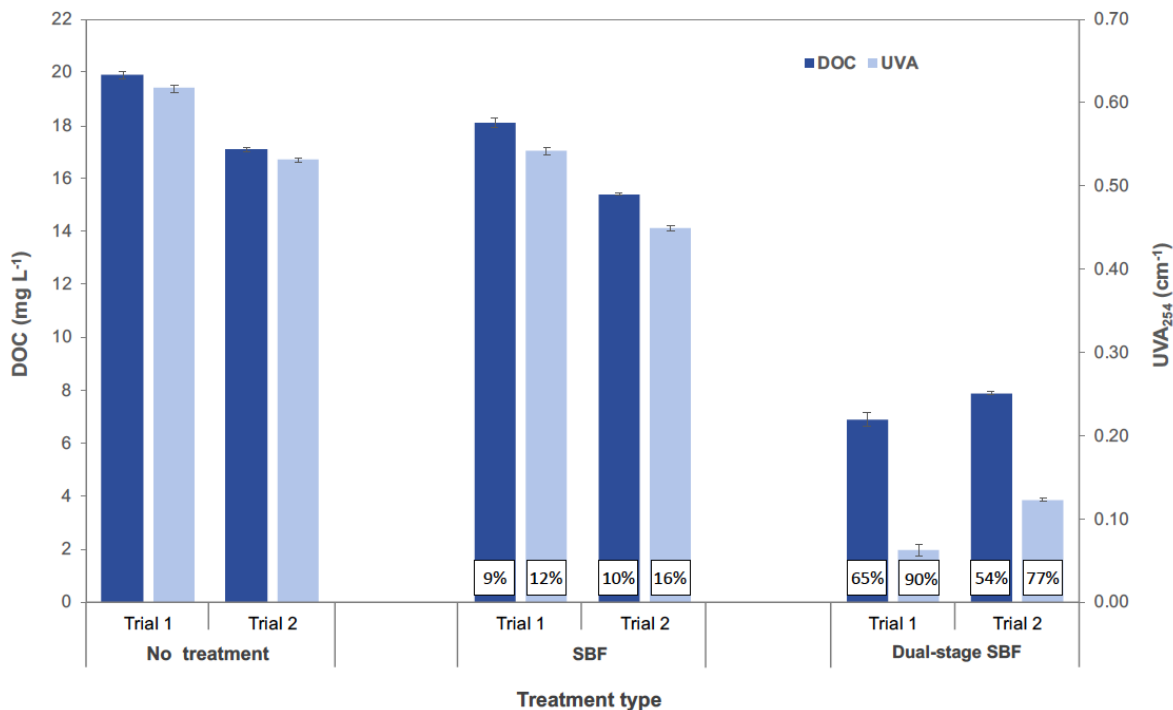
Figure 4.6: DOC and UVA$_{254}$ for dual-stage SBF treatment comparing untreated water ('No treatment') with sand-ballasted flocculation ('SBF') and dual-stage clarification-sand ballasted flocculation with powdered activated carbon treatment ('Dual-stage clarification'). Percent reduction values are provided in the boxes. Error bars indicate standard error. All parameters reported as mean ± SE, n=9 in all cases.

In trial 1, a total PAC dose of approximately 2200 mg·L^{-1} was achieved using a fresh PAC dose of 140 mg·L and the recirculation of PAC sludge. DOC and UVA$_{254}$ reductions were 65.4 ± 1.3 % and 89.8 ± 1.2% (mean ± SE, n=9 in both cases), respectively. Final clarified water following the dual-stage SBF had a DOC concentration of 6.9 ± 0.3 mg·L^{-1}, a UVA$_{254}$ of 0.063 ± 0.007 cm^{-1}, and a final turbidity of 1.8 ± 0.1 NTU (mean ± SE, n=9 for all three parameters). Additional details of the water quality during the dual-stage SBF process are available in Table C10.

In trial 2, a PAC dose of approximately 2600 mg·L^{-1} was achieved using a fresh PAC dose of 135 mg·L^{-1} and the recirculation of PAC sludge. DOC removal was 54.2 ± 0.2% (mean ± SE, n=9) and UVA$_{254}$ reduction was 76.8 ± 0.6% (mean ± SE, n=9). The final clarified water had a DOC concentration of 7.9 ± 0.04 mg·L^{-1} (mean ± SE, n=9), a UVA$_{254}$ 0.123 ± 0.003 cm^{-1} (mean ± SE, n=9), and a turbidity of 0.6 ± 0.02 NTU (mean ± SE, n=9). The difference in performance between the trials may represent natural variability in the ash used to prepare the wildfire ash-impacted source waters leading to differences in the ash-impacted source water quality (e.g., pH, alkalinity, DOC, and turbidity levels), or it may be attributable to reduced

adsorption capacity of the recirculated PAC sludge due its use during trial 1. It is important to note that although the dual-stage SBF pilot study was successfully executed, there were substantial challenges faced in configuring the pilot plant and attempting to achieve hydraulic stability to promote adequate flow through the system. Additionally, the conducting pilot-scale experiments using the dual-stage clarification system was difficult due to the limited amount of ash available to prepare the severely deteriorated wildfire ash-impacted source water needed to conduct treatment evaluations.

DBP formation potential (DBP-FP) was also investigated during the GMWTP2 pilot study; these data are presented in Figure 4.7. This is the first study to present DBP-FP data for any post-wildfire drinking water treatment at pilot-scale and provides valuable insight into DBP removal during drinking water treatment. Analysis of DBP-FP following dual-stage SBF for trial 1 indicated a substantial reduction in both TTHMs and HAA5 from the untreated severely deteriorated ash-impacted source water, with reductions of 93.9 ± 0.3 % and 93.7 ± 0.2% (mean $\pm$ SE, n=3 in both cases), respectively. TTHMs values were 85.8 ± 1.7 $\mu g \cdot L^{-1}$ (mean $\pm$ SE, n=3) and HAA5 values were 224.9 ± 5.6 $\mu g \cdot L^{-1}$ (mean $\pm$ SE, n=3) in the final clarified water for trial 1. The results of the TTHMs and HAA5 reductions for trial 2 were 80.0 ± 1.5% and 82.7 ± 1.1% (mean $\pm$ SE, n=3 in both cases), respectively, where final values for TTHMs and HAA5 were 137.1 ± 10.0 $\mu g \cdot L^{-1}$ (mean $\pm$ SE, n=3) and 270.4 ± 16.5 $\mu g \cdot L^{-1}$ (mean $\pm$ SE, n=3), respectively.

The values for both TTHMs and HAA5, analyzed using DBP-FP, in the clarified water following trial 1 and trial 2 of the dual-stage SBF were above the US EPA maximum contaminant level of (MCL) of 80 $\mu g \cdot L^{-1}$ for TTHMs and 60 $\mu g \cdot L^{-1}$ for HAA5. Of course, it should be emphasized that the hyper-chlorination conditions used in the DBP-FP analysis are not of typical chlorine application for disinfection; therefore, lower DBP concentrations would be expected in practice at a full-scale WTP. Additionally, while the levels of DBP-FPs reported are above the US EPA MCL, it must be highlighted that DBP compliance in Canada and United States, as specified in the Federal Register (2006), is based on one monthly TOC sample set and a quarterly monitoring for DBPs in the distribution system. As such, meeting of DBP MCL, although desirable of course, is not required on every sampling occasion, where a single episodic event where high organic carbon would not place a utility outside of compliance (see Chapter 3 for further details).
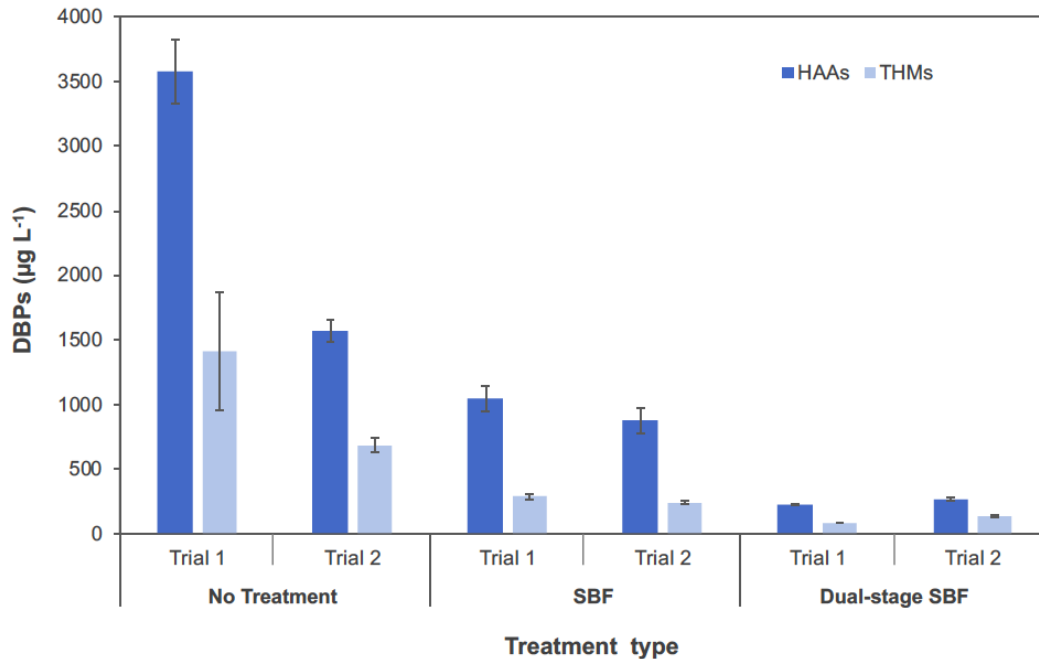
Figure 4.7: Disinfection by-product (DBP) formation potential for total trihalomethanes (TTHMs) and total haloacetic acids (HAA5) for GMWTP2 pilot study. Data from two trials is presented, where severely deteriorated source water was prepared using Elbow River water and TLR ash (Trial 1) or SCR ash (Trial 2) and was treated using dual-stage sand-ballasted flocculation (SBF). The clarified water from the first stage of SBF treatment (indicated by 'SBF' in the figure) was subsequently treated by a second-stage of pre-treatment with powdered activated carbon followed by SBF ('Dual-stage SBF'). The mean is presented for each outcome, where n=3 in all cases; error bars indicate standard error.

The key benefit of using dual-stage SBF was the ability to achieve a high dose of PAC without necessitating a constant high dose of fresh PAC. The results of the pilot-scale testing using dual-stage SBF were aligned with expected results, where high solids removal (through SBF) and high DOC reductions (through PAC treatment) were anticipated, based on bench-scale assessment (Chapter 3) and preceding pilot-scale testing results. The dual-stage SBF treatment was successful in reducing DOC due to the adsorption capacity of the PAC (e.g., Chowdhury et al., 2013; Dunn & Knappe, 2013) being maximized through the recirculation of sludge (Figure 4.8). The recirculation of PAC ultimately results in substantial cost reduction for treatment with PAC; this is highlighted by the fact that similar results were demonstrated for DOC and UVA$_{254}$ reductions in the GMWTP2, where only ~130 mg·L^{-1} of fresh PAC was added, compared to the FMWTP study where 1000 mg·L^{-1} of fresh PAC was added. Although dual-stage SBF clarification is not a commonly employed treatment technology, it does show promise for treating severely deteriorated water quality post-fire as it permits extremely high levels of PAC dose without the need for a constant high dose of fresh PAC. Despite the efficacy of the dual-stage SBF, this process requires a WTP to be configured appropriately and

may pose challenges for retrofitting an existing system. The installation of this system would also result in substantial costs and may not be economically feasible for regions with typically low levels of DOC, where the system would not be regularly operated.
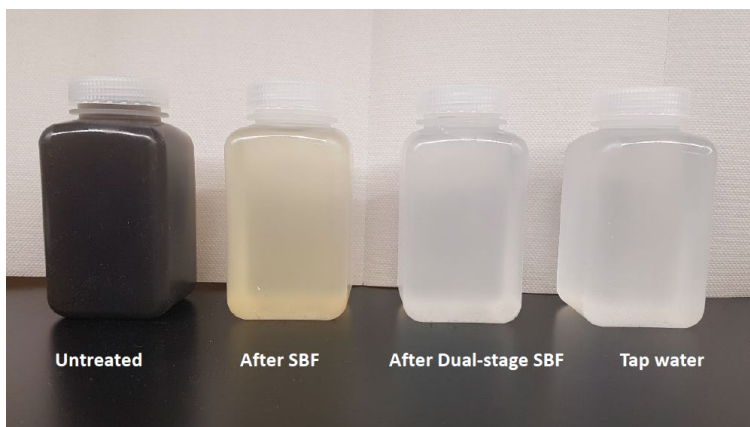
Figure 4.8: Water samples from the dual-stage SBF pilot study at Glenmore WTP (GMWTP2). Water quality is demonstrated at different stages of the treatment process, including: the severely deteriorated wildfire ash-impacted source water prepared by adding wildfire ash to Elbow River water ('Untreated'); water quality following the first stage of sand-ballasted flocculation (SBF) ('After SBF'); and water quality after dual-stage SBF, where water from the first stage of SBF was passed through a subsequent stage of SBF following pre-treatment with re-circulated powdered activated carbon ('After Dual-stage SBF'). A sample of high-quality tap water from Glenmore WTP is presented for comparison ('Tap water').

4.5 Conclusions and implications

This work showed that:

- Similar extent of treatment of severely deteriorated, wildfire ash-impacted water originating in two ecozones (Montane Cordillera and Boral Plains) with markedly different source water quality.

- SBF, SBF with enhanced coagulation through pH adjustment, SBF with PAC pre-treatment, and dual-stage SBF all reduced turbidity to the less than ~3 NTU needed for efficient subsequent filtration, as would be expected from high-rate clarification processes like SBF that are designed to respond to rapid changes in source water quality;

- Only PAC pre-treatment followed by SBF, and dual-stage SBF reasonably removed DOC and reduced THM- and HAA- DBP formation. The DOC reduction, while substantial, was not ideal and THM and HAA disinfection by-product formational potentials remained sub-optimally elevated. Despite this result, this investigation demonstrates that the treatment of some of the most

severely, episodically deteriorated, wildfire ash-impacted to potable water standards is likely if treatment technology is optimized and optimally operated, which is consistent with previous bench-scale assessments (Chapter 3);

- Shifts in post-fire pH, alkalinity, and dissolved organic carbon (DOC) concentration and character may collectively contribute to challenges associated with DOC removal/carbonaceous DBP precursor removal during SBF, SBF with enhanced coagulation through pH adjustment, SBF with PAC pre-treatment, and dual stage SBF;

- Treatment of wildfire ash-impacted, severely deteriorated source water by SBF technology was generally comparable in two very diverse forested ecozones (i.e., Montane Cordillera and Boreal Plain) with very different source water quality (i.e., typically high quality with low turbidity and low DOC, and degraded quality with high turbidity and high DOC, respectively). This underscored that while wildfire on that natural landscape has the potential to (i) impact all of the key drivers of physico-chemical drinking water treatment (i.e., turbidity, organic carbon, pH, and alkalinity) and (ii) result in extremely deteriorated source water quality that is challenging to treat using conventional approaches, it does not lead to unusual water quality deterioration that would necessitate a paradigm shift in water treatment process design and optimization.

Chapter 5:

Treatment of wildfire ash-impacted water: Insights to the impacts of burn severity and physiographic setting

5.1 Summary

Wildfire is expected to increase in both frequency and severity over the 21st century, which will likely lead to increased degradation of source water quality following wildfire where extreme levels of turbidity and dissolved organic carbon (DOC) may be expected. Degraded source water conditions post-fire will ultimately lead to drinking water treatment challenges and require deviation from typical operating procedures. While several studies have investigated the treatability in post-fire conditions, investigations are scant into the treatment of source waters representative of different burn severity conditions or different physiographic regions in which there are different predominant vegetation types. As such, this study explores drinking water treatment performance on the concurrent reduction of both turbidity and DOC from ash-impacted source waters prepared using natural post-fire material representative of a range of burn conditions (unburned, moderate burn, and severe burn) and a range of physiographic regions where different predominant vegetation types are present (chaparral, moorland, grassland, and montane) where severe wildfire had occurred. Comparisons of different burn severities demonstrated that substantially elevated levels of turbidity were effectively reduced, where ≥99% of turbidity was removed under all treatment scenarios. The reduction of DOC varied considerably between burn severity conditions, where the lowest reductions in DOC were found in the source water samples indicative of severe burn conditions. Liquid chromatography–organic carbon detection (LC–OCD) analysis also revealed that there was a shift toward lower molecular weight (LMW) compounds in severely burnt material which were less amenable to removal with conventional chemical pre-treatment.

Treatability comparisons between ash-impacted source waters prepared with ash from severe wildfires in different physiographic regions with different predominant vegetation types showed that turbidity was effectively reduced (>99%) under all treatment scenarios; however, DOC reductions were minimal with ≤ 22% reductions across all physiographic regions investigated. LC‐OCD analysis indicated that there were higher proportions of LMW DOC species in all ash-impacted source waters prepared with ash from severe wildfires in different physiographic regions with different predominant vegetation types compared to DOC in river water not impacted by wildfire. Additionally, all physiographic regions evaluated for disinfection by-product (DBP) formation potential demonstrated similar results for reductions in DBPs following conventional chemical pre-treatment, as indicated by normalized DBP yields on a per mg carbon basis. Overall this research provides insight into how wildfires of different severities and in different physiographic regions with different predominant types of vegetation may impact water quality and drinking water treatment performance in fire-prone regions and may aid in the development of effective treatment strategies.

5.2 Introduction

The frequency and severity of wildfires are expected to increase by the end of the 21st century (Flannigan et al., 2013) which will likely have adverse impacts on source waters which are relied upon for drinking water (Emelko et al., 2011; Robinne et al., 2021). Following severe wildfire, material remaining on the landscape may be rapidly mobilized following major runoff events, such as snow melt and major storms, which then enters receiving water bodies and degrades water quality (Moody & Martin, 2001; Shakeby & Doerr, 2006). Specific deleterious impacts to drinking water sources following severe wildfire include: extreme levels of suspended solids (Silins et al., 2009; Stone et al., 2014), elevated concentrations of dissolved organic carbon (DOC) (Emelko et al., 2011; Emelko & Sham, 2014; Writer et al., 2014), excessive levels of nutrients, such as phosphorous and nitrogen (Bladon et al., 2008; Emelko et al., 2011; Silins et al., 2014), and high levels of heavy metals (Kelly et al., 2006; Wolf et al., 2008). The deterioration of water quality after wildfire can have serious implications for drinking water treatment, where treatment capacity and operational response may be challenged to adequately meet drinking water targets (Emelko et al., 2011). There has been, however, limited work focused on the treatability of deteriorated water quality post-fire which concurrently investigates the removal of substantially elevated levels of solids and DOC. Additionally, there is limited information comparing treatability of source waters impacted by wildfire across different burn severities or across different physiographic regions with different predominant vegetation types where severe wildfire had occurred. As such, the objective of this work is to evaluate the impacts of different wildland (i.e., non-urban) fire conditions on drinking water treatment using conventional chemical pre-treatment, namely between different burn severities and different physiographic wildland regions with diverse predominant vegetation types where severe wildfire had occurred. To compare the impacts of different wildfire burn severities on drinking water treatment, material was collected from a single burn site representative of unburned, moderate burned, and severe burned wildland fire conditions. Comparisons of the impacts of different physiographic regions with different predominant vegetation types on drinking water treatment were conducted using ash that was collected in four different regions with considerably different predominant vegetation types, including grasses, heather, softwoods, and hardwoods (Table 5.1).

It was anticipated that wildfire ash-impacted source waters prepared with material from different burn severities would have different impacts on the efficacy of treatment (e.g., turbidity and DOC removal), where severe wildfire conditions would challenge drinking water treatment more so than lower severity burn conditions. Previous studies have characterized ash from wildfires with different burn severities and have indicated that ash composition and character changes with burn severity; for example, organic carbon levels increase with increased burn severity (e.g., Almendros et al., 1992; Fernandez et al., 1997; Norwood

et al., 2013; Ulery et al., 1993), where higher organic carbon levels will adversely impact drinking water treatment due to impacting the efficacy of coagulation and require higher coagulant dosing (Crittenden et al., 2012; Edzwald, 2011). In addition to the quantity of organic carbon increasing due to wildfire, the character of carbon may also change, ultimately impacting treatment efficacy, namely coagulation. For instance organic matter which is not burned, is generally amenable to conventional water treatment due to the hydrophobic character and high molecular weight of these compounds (Crittenden et al., 2012); however, after severe wildfire impacted source water appears less amenable to treatment by coagulation (Chapter 3 and 4; Hohner et al., 2017; Hohner et al., 2018), possibly due to shifts toward lower-molecular weight (LMW) DOC (Hohner et al., 2018; Hohner et al., 2019b), which are less amenable to removal through conventional chemical pre-treatment (Edzwald, 1993; Quang et al., 2015; Zhao et al., 2009).

It was also expected that wildfire-impacted source waters prepared with ash from severe wildfires in different physiographic regions with different predominant vegetation types will exhibit similar changes in water quality (e.g., increases in both turbidity and DOC concentration), but not necessarily the magnitude of those impacts. Although ash from physiographic regions with different predominant vegetation types varies considerably in its characteristics, including the quality and quantity of carbon, pH, and alkalinity (eg. Bodi et al., 2011; Certini 2005; Harper et al., 2019; Plumlee et al., 2007), the implications to water treatability resulting from different types of burned materials predominantly comprised of vegetation are expected to be more similar to each other in composition (Chapter 3 and 4), especially in contrast to other anthropogenic contributors to source water quality (e.g., urban stormwater) that typical drinking water treatment is designed to manage. The impacts on water quality following wildfire have been widely reported, namely where DOC and turbidity levels increase substantially following severe wildfire (e.g., Clark, 2010; Dahm et al., 2015; Emelko et al., 2011; Emmerton et al., 2020; Gallaher & Koch, 2004; Hohner et al., 2016; Leak et al., 2003; Neary et al., 2005; Rhoades et al., 2011; White et al., 2006; Writer & Murphy, 2012), which are key drivers of drinking water treatment process selection and operation (Crittenden et al., 2012; Edzwald, 2011). Increases in turbidity and DOC are expected in post-fire scenarios regardless of the physiographic region in which a wildfire occurs, demonstrating that the impacts to drinking water treatment will be similar in different fire-prone regions globally. While drinking water treatment is driven by water quality, and the type of predominant vegetation burned in a wildfire will potentially impact the quality of water, it must be highlighted that there are a multitude of other factors which will impact water quality following wildfire, including topography, catchment hydrology, geology/soil type, and climate (Lintern et al., 2018). As such, attempting to predict water quality post-fire (and hence the impacts to drinking water treatment) is extremely difficult due to the wide range of factors which may contribute to the degradation of source waters.

While a range of treatment conditions (i.e., coagulant doses) were tested throughout this study, this work was not intended as a detailed optimization study for each water quality scenario investigated (due to limited quantities of test water available as a result of small quantities of ash samples available) and was designed as a proof-of-concept demonstration across different wildfire conditions. Throughout the course of this work several water quality parameters were used as metrics to gauge the efficacy of conventional chemical pre-treatment, including turbidity, DOC, ultraviolet absorbance at 254 nm (UVA_{254}), liquid chromatography–organic carbon detection (LC-OCD), and disinfection by-product formation potential (DBP-FP).

Here, conventional chemical pre-treatment (i.e., coagulation) of forest floor materials from diverse physiographic regions was investigated. Forest floor materials collected before (i.e., unburned conditions) and after wildfire (i.e., fresh ash that had not been exposed to precipitation) were used because these are the materials that can be mobilized directly from the landscape to receiving waters, resulting in water quality change, including elevated levels of turbidity and DOC concentration. Although thermally-altered vegetation and forest floor materials prepared in laboratory furnaces may be beneficial to compare controlled variables (e.g., temperature), these materials should not be assumed to be representative of post-wildfire ash as the conditions under which they are prepared cannot adequately reflect the burning conditions of wildfire (Bodí et al., 2014; Santín et al., 2013). Additionally, attempting to replicate burn conditions which sufficiently replicate oxygen availability during wildfire burning can be challenging to achieve (Bryant et al., 2005; Wang et al., 2015a). As such, this study used ash samples from actual wildfires to reflect burn conditions of natural wildfire.

Although the impacts of wildfire may be evident for years or decades (Emelko et al., 2016; Stone et al., 2014), the source waters investigated in this study aim to represent post-fire conditions where water quality is rapidly deteriorated following episodic, short-lived events after major runoff, that typically persist for a day to a week (Chapter 2; Dahm et al., 2015; Leak et al., 2003; Lyon & O'Connor, 2008; Mast et al., 2016; Murphy et al., 2015; Writer & Murphy, 2012). Such deteriorated water quality will require extreme levels of treatment which deviate from typical operating procedures, albeit for brief periods of time.

5.2.1 Burn severity impacts to water quality

Burn severity, which is largely based on the loss of organic matter from soil and aboveground that is converted to ash (Keeley, 2009), has been highlighted as a key parameter impacting water quality after wildfire. Wildfire burn severity has been noted as a factor which may have variable impacts on water quality (Chen et al., 2020; Santín et al., 2015). Loss of vegetation after severe wildfire can lead to increased erosion

and result in greater quantities of water moving off the landscape (Silins et al., 2016; Tecle & Neary, 2015; Williams et al., 2019). Additionally, hydrophobic soil conditions following severe wildfire can reduce soil permeability and ultimately increase overland flow (Certini, 2005; Doerr et al., 2000; Neary et al., 2005), mobilizing substantial quantities of post-fire material into receiving water bodies, potentially resulting in extreme turbidity levels (Emelko et al., 2011; Emmerton et al., 2020; Neary et al., 2005). In addition to elevated turbidity, there have also been post-fire reports of high alkalinity concentrations (Cerrato et al., 2016; Earl & Blinn, 2003; Murphy et al., 2018) and high pH levels (Dahm et al., 2015; Pereira et al., 2012), which can have adverse impacts on the efficacy of drinking water treatment using conventional chemical pre-treatment (Crittenden et al., 2012). Severe wildfire has also been reported to substantially elevate levels of DOC in water bodies (Emelko et al., 2011; Writer & Murphy, 2014), where shifts toward LMW species in DOC have also been reported following severe wildfire (Cawley et al., 2017; Hohner et al, 2016), as well as changes in carbon functionality (Gonzalez-Perez et al., 2004; Knicker et al., 2007). These shifts in DOC characteristics following severe fire have been noted to adversely impact the efficacy of drinking water treatment using conventional treatment (Hohner et al., 2016; Hohner et al., 2019b). While these studies provide valuable insight into the potential implications of severe wildfire on treatability, the current study aims to build on existing knowledge by investigating the treatability of source waters representative of different burn severity scenarios (i.e., unburned, moderate burn, severe burn) using material from natural conditions indicative of deteriorated water quality following major runoff events. Comparing the treatability of source waters impacted by wildfires of different burn severities will aid drinking water providers in making decisions regarding potential water treatment strategies under different wildfire scenarios where the impacts to source waters may vary with burn severity. In addition to studying the impacts of burn severity on drinking water treatment, further examination of treatability following severe wildfire in different physiographic regions where there are different predominant vegetation types is also investigated in this work.

5.2.2 Vegetation type impacting water quality post-fire

To date, there is limited information comparing treatment performance on deteriorated water quality after severe wildfire representative of different physiographic regions (e.g., Hohner et al., 2019b). This is the first study to compare treatment efficacy using ash-impacted source waters prepared with material from natural wildfires from a range of physiographic regions with different predominant vegetation types globally. As such, this study provides an assessment of treatment performance on post-fire source water conditions representative of different physiographic regions, including chaparral (USA), moorland (UK), grassland (Canada), and montane (Canada). Although every wildfire ash is unique to a specific ecosystem and can vary considerably between physiographic regions with different predominant vegetation types,

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there are certain aspects of ash from severe wildfire which are similar. For instance, it has been previously reported that the ash from six wildfires in different physiographic regions demonstrated an overall similar composition of elements, albeit in different concentrations (Harper et al., 2019). Similarly, it has been reported that, in spite of the high variability between ash types, there are characteristics which demonstrate narrow ranges between ashes of different biomass types, where the orders of chemical elements present in ash samples (in decreasing order of abundance) are commonly O > Ca > K > Mg > Al > Fe > P > Na (Vassilev et al., 2013). Beyond the specific composition of ash, the impact of ash on water quality following severe wildfire has been reported to be similar following major runoff events, where extreme levels of total suspended solids/turbidity and DOC have been reported in different regions globally, such as chaparral (Stein & Brown 2009), montane (Emelko et al, 2011), grasslands (Neary & Leonard, 2020), and moorland (Kettridge et al., 2019). Elevated turbidity levels and DOC concentrations after wildfire are problematic from a water treatment perspective and attempting to adequately treat such conditions, regardless of geographic region, may pose considerable challenges for drinking water providers. While a wide-range of previous studies have been conducted related to different aspects of drinking water treatment following wildfire (see Table D2) this is the first study to comparatively study treatment performance on source waters prepared with natural severe wildfire ash from a range of physiographic regions with different predominant vegetation types, where the reduction of turbidity and DOC are concurrently investigated. Furthermore, this work is first to investigate treatment performance on post-fire source water conditions representative of non-forested regions, namely grassland and moorland. The information provided herein will be useful for drinking water providers in fire-prone regions as it demonstrates the similarities and differences between drinking water treatability in different geographic locations.

5.3 Methods

The following information provides details of the various materials and methods used throughout this study. Table D1 provides a summary and justification for the various set-points which were selected to achieve the objective of this work.

5.3.1 Ash samples

Samples used for comparing burn severity were collected from the Thuya Lake Road fire in 2017, which was part of the Little Fort Fire Complex. Three samples were collected which were representative of three burn conditions, including: severe burn, moderate burn, and unburned conditions (Figure 5.1). The material representative of unburned conditions was collected adjacent to the area where the high severity wildfire

had occurred by extracting a section of the forest floor approximately 50×50 cm and 5 cm in depth inclusive of the detritus, duff and O-horizon, using a metal spade; all unburned material within the extracted section was collected in a 19 L plastic pail and stored in a cool, dry space. Unburned samples were collected to provide a control by which to compare ash samples from moderate and severe burn conditions. Ash samples were collected from moderate and severe burn sites, where ash is defined herein as the residual particulate material remaining on the landscape following the burning of wildland fuels consisting of charred organic and mineral materials (Bodí et al., 2014). Ash collected from the moderate and severe burn sites consisted of the light material residing on the surface which may be easily mobilized following major runoff events, such as during snow melt or storm events. Specific details of the methods employed for ash collection are provided in Chapter 2, Section 2.4, Table 2.1.
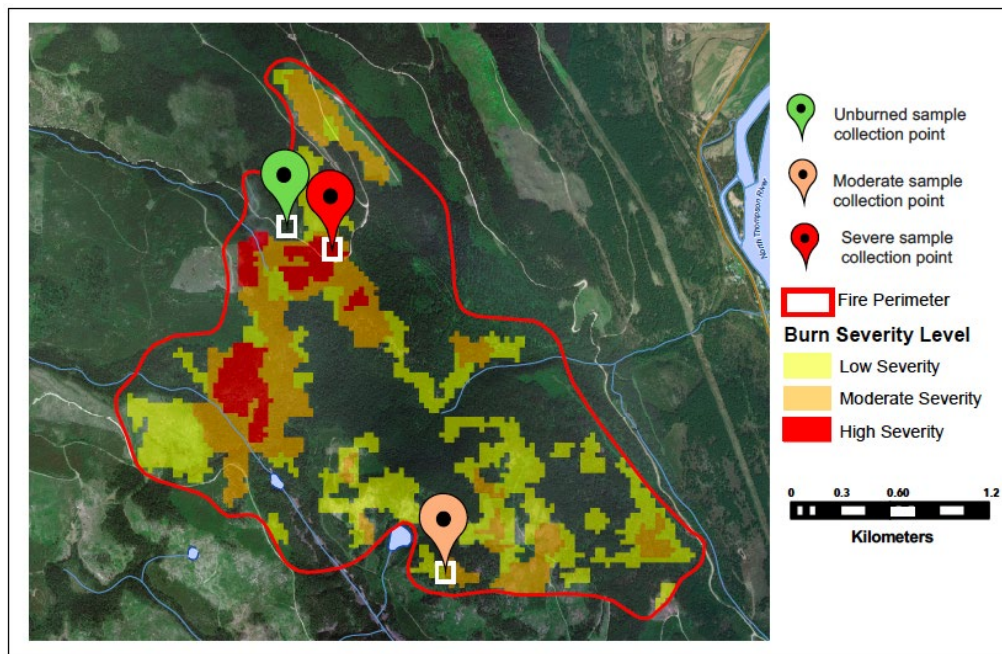
Figure 5.1: Sample collection sites for unburned, moderate burn, and severe burn material which was used to prepare ash-impacted source waters for comparing treatability under different burn severity conditions. All sample collection sites were in the area of the Thuya Lake Road wildfire which was part of the Little Fort Complex, near Little Fort, B.C., Canada. Samples were collected in August, 2017. The image is adapted from Government of British Columbia TLR burn severity map (Government of British Columbia, 2017).

The moderate and severe burn ash samples were collected immediately after the fire and prior to any precipitation events. The severe burn condition was identified in the field by the visual assessment of the

landscape, where crown burning had occurred; litter, duff, twigs and small branches were completely consumed; and, where remaining large branches were deeply charred (Ryan & Noste 1985; Stockdale et al., 2016). The moderate burn (i.e., moderate-severity) condition was identified by there being no crown burning; the duff layer was deeply charred or consumed; and, some branch wood is present, but fine twigs and branches of shrubs were mostly consumed (Ryan & Noste 1985; Ryan, 2002). Although the classification of burn severity used in this study is consistent with descriptions elsewhere based on the loss of organic matter following wildfire, a single system to quantify burn severity does not exist due to variance between ecosystems and the specific metrics which may be assessed (DeBano et al., 1998; Keeley, 2009). In spite of this, the field-level burn severity assessment (see Figure D1) was affirmed by burn severity mapping using satellite imagery following the TLR wildfire (Figure 5.1; Government of British Columbia, 2017).

Four ash samples were also obtained from different physiographic regions with different predominant vegetation types where severe wildland fire had occurred, including chaparral, moorland, grassland and montane regions, which are summarized in Table 5.1. The aim of this analysis was to compare ash-impacted source waters prepared with ash samples from severe wildfires; however, due to the different physiographic regions varying considerably, there does not exist a single fire-severity index which may be applied commonly to all physiographic regions from where the ash samples were collected. As such, all samples collected are indicative of severe wildfire based on the fact that all ground vegetation was consumed. All ash samples were collected prior to any precipitation events. As ash samples from wildland fires are often extremely difficult to acquire, a very limited amount of sample was available upon which to conduct treatability assessments.

Table 5.1: Ash sample information for the four ash samples which were used to compare the treatability of deteriorated water quality from severe wildfires in different physiographic regions with different predominant vegetation types; severe wildfire ash samples include chaparral (USA), moorland (UK), grassland (Canada), and montane (Canada).

Ash sample name	Name of fire (date)	Vegetation cover	Location	Wildfire information
Chaparral (USA)	Thomas fire (2017/2018)	Mixed chaparral with dominant species including coast live oak, toyon, coyote brush, holly-leaf cherry	Santa Barbara and Ventura counties, California (USA); (+34.420556 latitude, -119.510833 longitude)	Oakley et al., 2018
Moorland (UK)	Saddleworth fire (2018)	Heather dominated with underlying peat.	Saddleworth moor, near Manchester (UK); (+53.5153979 latitude,-2.004863 longitude)	Longhands & Hunter, 2018; Marrs et al., 2019; Graham et al., 2020
Grassland (CAN)	Milk River fire (2012)	Mixed grasses	Milk River, Alberta (CAN); (+49.086144 latitude,-112.430764 longitude)	Alexander et al., 2013
Montane (CAN)	Thuya Lake Road fire (2017)	Dominant Douglas Fir, with a mixture of Spruce Hybrids, Paper Birch, and Lodgepole Pine	Little Fort, BC, (CAN); (+51.4098 latitude, -120.2435 longitude	Government of BC, 2017

5.3.2 Deteriorated source water preparation

Deteriorated ash-impacted source waters were prepared by adding ash to river water to create degraded water quality representative of deteriorated conditions, which may occur after wildfire where ash is mobilized from the landscape to source waters during major runoff events. High quality water from the Elbow River (collected from the Glenmore Reservoir in Calgary, Alberta, Canada) was used to mix with ash samples for all experiments described herein. The Elbow River originates in the Rocky Mountains and has typically has low levels of turbidity and DOC, and high alkalinity (Beers & Sosiak, 1993); this river water was used throughout this study as it is representative of a source water which may potentially be impacted by wildfire due to its origin in a forested region. Prior to mixing with river water, all samples were sieved through a 1 mm mesh to remove any conifer needles and large debris that would typically not be present in water treatment plant influent streams.

To compare the impacts of burn severity on treatability, equal amounts of TLR samples (5.0 g) representative of different burn severities (i.e., unburned, moderate burned, and severe burned) were added to 1000 mL of Elbow River water in a 1 L Pyrex beaker. A concentration of 5.0 g·L^{-1} was selected as it had yielded severely deteriorated water quality (turbidity >500 NTU and DOC >15 mg·L^{-1}) in previous work where severely burned material from the TLR wildfire was added to Elbow River water (see Chapter 2).

This concentration was kept constant (e.g., 5.0 g·L^{-1}) for all burn conditions to provide a means to compare scenarios following major runoff events when the same amount of material would be mobilized into a water source, regardless of its burn severity. After ash was added to the river water, samples were mixed on a jar test apparatus (Phipps & Bird, PB-900 Series Programmable 6-Paddle Jar Tester, Richmond, VA) for 30 min at 150 RPM, which was followed by subsequent bench-scale drinking water treatment testing.

Following the first phase of this study where different burn severities were compared, the second phase investigated treatment performance comparing source waters prepared with ash from severe wildfires in different physiographic regions with different predominant vegetation types. To assess the treatment performance, it was necessary to establish a common baseline upon which to compare the efficacy of treatment. It was determined that UVA$_{254}$ would be used as a baseline metric to prepare the ash-impacted source waters which could be then compared following treatment; UVA$_{254}$ was selected as the comparative metric as it is a good surrogate for DOC in water (Chow et al., 2008), requires a small amount of analyte compared to DOC analysis, and could be measured rapidly. Preliminary tests determined that a value of 0.240 cm^{-1} would be used as the approximate target for the ash-impacted source waters prepared with ash from different physiographic regions; this target value was based on the limited quantity of ash available for the study. To achieve the UVA$_{254}$ target with the ash types from different physiographic regions with different predominant vegetation types, different quantities of ash type were required to prepare each ash-impacted source water due to the variability in DOC between the samples. After the amount of ash was determined for each sample type, it was added to Elbow River water and mixed on a jar test apparatus for 12 h at 150 rpm to maximize DOC leaching from each sample and was then evaluated for drinking water treatment performance at bench-scale.

5.3.3 Treatment performance evaluation

All jar tests were conducted at a controlled temperature of ~21°C using the jar tester described above, where the deteriorated ash-impacted source water samples were prepared in 1-L glass beakers by mixing sieved ash with 1000 mL of Elbow River water. Conventional chemical pre-treatment (i.e., coagulation, flocculation, and sedimentation) with alum was used for all treatment performance evaluations throughout this study. Reagent grade liquid aluminum sulfate (alum) was used (Al$_2$[SO$_4$]$_3$•14H$_2$O, SG=1.33, 4.3% aluminum metal content; Veolia Water, Saint-Laurent, Canada) with alum doses reported as commercial product dose (volume [μL·L^{-1}] × specific gravity). For jar tests comparing burn severity, alum was dosed at 50, 100, 200, and 400 mg·L^{-1}and for tests comparing ash from different physiographic regions alum was tested at doses of 50, 200, and 400 mg·L^{-1}. The maximum alum dose of 400 mg·L^{-1} was selected as this is

the NSF maximum use level for alum in drinking water (NSF, 2017). Although the doses of alum tested were comparatively high to what may typically be dosed at a WTP, the purpose of this study was to demonstrate that extreme treatment measures may need to be implemented if alternate water sources are not available following a wildfire where severely deteriorated conditions may occur. A cationic polymer (LT22S cationic polymer; Northland Chemical, Mississauga, Canada) was used in combination with alum during treatment (dosed at 0.5 mg·L^{-1} in all cases). Cationic polymer, when used as a coagulant aid, can decrease coagulant dose requirements, decrease alkalinity consumption, and increase flocculation efficiency (Crittenden et al., 2012) and has been demonstrated to be effective for treating deteriorated post-fire water conditions when used in combination with coagulant (see Chapters 3 and 4). All jar tests were conducted in triplicate according to ASTM method D2035-13 (ASTM, 2013). Water quality analysis was conducted immediately following treatment, with the exception of DOC which was analyzed within 24 hours.

5.3.4 Analytical methods

Water quality was analyzed according to Standard Methods (APHA, 2012), where the following methods were used: alkalinity (Method 2320), conductivity (Method 2510), DOC (Method 5310C, pre-filtered through 0.45 µm membrane), pH (Method 4500-H+B), turbidity (Method 2130B), and UVA$_{254}$ (Method 5910B, pre-filtered through 0.45µm membrane). Specific details of the laboratory instrumentation used for analysis and additional particulars for analytic methodology are provided in Table D3. Calculations for the specific ultraviolet absorbance at 254 nm (SUVA) were completed by dividing UVA$_{254}$ by the DOC concentration and multiplying by 100 (Weishaar et al., 2003).

The DBP-FP was determined following Methods 5710 B and 5710 D (APHA, 2012) for trihalomethanes (THMs) haloacetic acids (HAAs), respectively. A chlorine reaction time of 7 days was applied where samples were buffered at a pH of 7.0 ± 0.2 and a chlorine residual was maintained at 3.0–5.0 mg·L^{-1}. Chlorine residuals were measured using N, N-diethyl-p-phenylene diamine (DPD) by the colorimetric Method 4500-Cl G (APHA, 2012) and were quenched after 7 days with ammonia chloride. Four different THMs were analyzed following Method 501.1 (USEPA, 1979) and are discussed as individual THMs or as total THMs (TTHMs) herein. Five haloacetic HAAs were analyzed according to Method 552.3 (USEPA, 2003); reference to five HAAs collectively will be noted as total HAAs (HAA5) herein. Additional details of the DBP analysis methodology and specific DBPs analyzed are available in Table D3.

LC-OCD analysis was conducted following the method described in previous work (Huber et al., 2011), where samples were passed through a pre-rinsed 0.45 µm membrane filter prior to analysis.

Chromatographic separation was accomplished using a weak cationic exchange column (Toyopearl, TSK HW 50S, Tosoh, Japan) and chromatographs were processed using a customized software (ChromCALC, DOC-LABOR, Karlsruhe, Germany), where the chromatography subdivides DOC into five fractions based on size including (in descending size fraction) biopolymers, humic substances, building blocks, LMW acids, and LMW neutrals.

5.3.5 Statistical analyses

One-way ANOVA tests with post-hoc Tukey's tests of multiple comparisons were used to evaluate the efficacy of different coagulant doses on treatment efficacy and to compare treatment performance between different burn severity conditions or ash from different physiographic regions with different predominant vegetation types. The least squares linear regression method was used to demonstrate the relationship between water quality parameters, such as DOC and DBPs. All statistical tests were completed using SPSS® statistics software (version 26, IBM®).

5.4 Results and discussion

5.4.1 Comparison of burn severity impacts on drinking water treatability

To comparatively assess the impacts of different burn severities on drinking water treatability, three source waters were prepared using material representative of unburned, moderate burned, and severe burned conditions collected from the TLR wildfire. The source waters were subsequently subjected to treatment performance evaluation at bench-scale using convention chemical pre-treatment.

5.4.1.1 Comparison of source waters impacted by wildfire of different burn severities

The wildfire ash-impacted source waters prepared with material from different burn severities and Elbow River water varied substantially from the high-quality baseline conditions of the Elbow River water following the addition of unburned or burned material, where increases were observed in turbidity, DOC, and UVA_{254} in all cases. Water quality details of the of the deteriorated source waters prepared with material from different burn severities is available in Table D4. The source water prepared with the ash from the severe burn condition had substantially higher turbidity when compared to the unburned and moderate burned material prepared at the same concentration (5.0 g·L^{-1}), resulting in turbidity values of 149 ± 8 NTU, 487 ± 62 NTU, and 771 ± 49 NTU (mean $\pm$ standard error [SE], n=3 in all cases), for unburned, moderate burned, and severe burned, respectively. The elevated turbidity in the severe burn case is likely due to post-

fire particulate matter being of lower density and remaining suspended in the water column for longer periods compared to unburned material (Stone et al., 2011; Silins et al., 2016). This may be particularly problematic from a drinking water perspective as the low-density material persisting in the water column for extended periods may be transported great distances in a stream or river system, posing challenged for drinking water providers far from the location of a severe wildfire. The high level of turbidity would especially pose treatment difficulties for utilities which are accustomed to treating high quality water sources and may not be adequately prepared to treat extreme levels of turbidities. In addition to turbidity, the source water representative of the severe burn condition also had comparatively higher DOC and UVA_{254}, as indicated in Figure 5.2. This result suggests that levels of carbon may be higher in source waters after severe wildfire, compared to unburned or moderate burned conditions following major runoff events where similar amounts of material would be mobilized from the landscape into receiving waters.

Following the addition of ash from the severe burn condition, there was a substantial increase in alkalinity, which increased to 409 ± 4 mg·L^{-1} $CaCO_3$ (mean $\pm$ SE, n=6) from the baseline Elbow River water alkalinity of 179 ± 1 mg·L^{-1} as $CaCO_3$ (mean $\pm$ SE, n=3). The elevated alkalinity in the severe burn condition is consistent with previous reports of increased alkalinity in waters post-fire (Cerrato et al., 2016; Earl & Blinn, 2003; Murphy et al., 2018). Elevated levels of alkalinity may adversely impact the ability to effectively adjust pH during treatment which can lead to sub-optimal coagulation (Crittenden et al., 2012). There was also a notable increase in pH in the severity burn scenario, where the pH increased to 9.1 ± 0.03 (mean $\pm$ SE, n=3) from the baseline Elbow River water pH of 8.1 ± 0.0 (mean $\pm$ SE, n=3). The increase in both pH and alkalinity in the severe burn conditions may be attributed to the mineralized materials in the alkaline ash products that contain elevated levels of base cations and carbonates released upon dissolution (Lydersen et al., 2014). Increased levels in both alkalinity and pH after wildfire may lead to operational challenges due to necessitating higher coagulant dose or the addition of acid to lower the pH to promote effective coagulation.

While the results of the source waters across different burn severities are indicative of conditions on the landscape where equal amounts of material are being mobilized into source water, it is must be acknowledged that runoff conditions following wildfire, especially severe conditions, are often starkly different than unburned conditions. For instance, loss of vegetation and hydrophobic soil conditions following wildfire can result increased erosion due to amplified overland runoff and the rapid mobilization of material into receiving streams (Doerr et al., 2000; Neary et al., 2005; Santín et al., 2015a; Silins et al., 2016). As such, it can be expected that following severe burn conditions greater amounts of ash will be transported off the landscape after major runoff events, further exacerbating the degradation of water quality when compared to unburned or moderate burned scenarios.
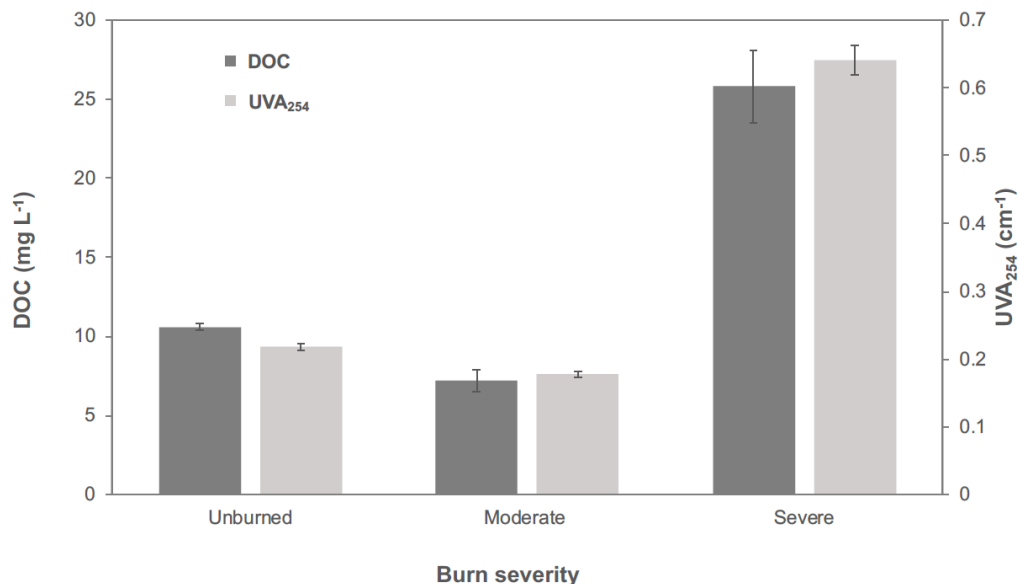
Figure 5.2: Dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UVA$_{254}$) for source waters prepared using Elbow River water and material from different burn severities (unburned, moderate burned, and severe burn) at a concentration of 5.0 g·L^{-1}, error bars indicate standard error; all parameters reported as mean ± SE, n=6 in all cases.

In addition to differences in the amount of DOC in the source waters, the character of the DOC present in the samples also varied considerably. LC-OCD analysis indicated that there were considerable differences in the proportions of DOC fractions between the source waters indicative of different burn conditions (Figure 5.3). LC-OCD results demonstrated that the severe burn conditions produced a higher proportion of LMW organic carbon species when compared to unburned or moderate burned conditions. This finding is consistent with previous work demonstrating that higher burning temperature resulted in a shift toward LWM carbon species (Cawley et al., 2017; Hohner et al., 2016; McKay et al., 2020). Elevated levels of LMW carbon compounds following severe fire will likely pose drinking water treatment challenges as these compounds are less amenable to removal using common treatment methods (Nissinen et al., 2001). This is the first time that LC-OCD was employed to compare the impacts of different burn severities on carbon speciation and provides valuable insight into the potential difficulties which may be faced when managing elevated levels of DOC.
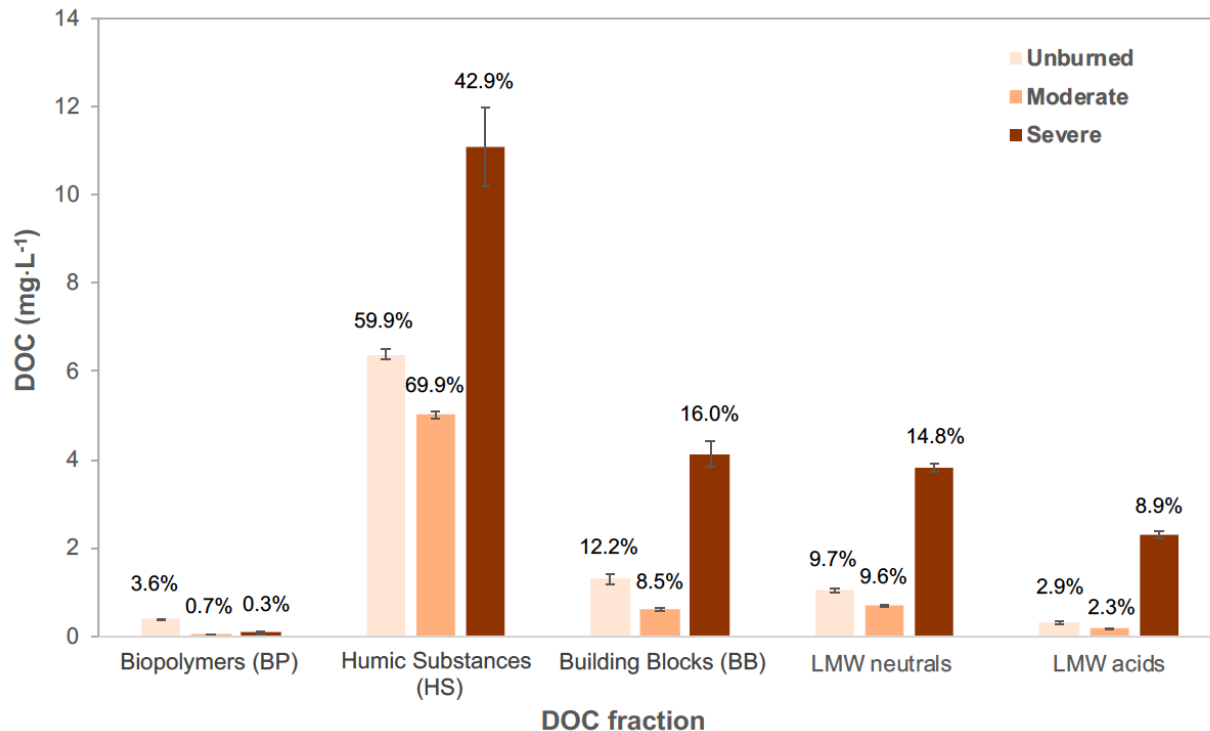
Figure 5.3: Liquid chromatography organic carbon detection (LC-OCD) for different organic fractions in deteriorated source waters prepared with Elbow River water and material from a range of burn severities (unburned, moderate burn, and severe burn) where: LC-OCD fractions are presented as total dissolved organic carbon (DOC) concentration (mean ± SE, n=3 in each case) and the percent of LC-OCD fractions of the total DOC are indicated for each condition. DOC fractions reported include BP, HS, BB, low-molecular-weight [LMW] neutrals, and LMW acids.

5.4.1.2 Drinking water treatability of waters impacted by wildfires of different burn severities

Jar testing results comparing treatment efficacy using conventional chemical pre-treatment on source waters representative of water quality impacted by wildfires of different burn severities demonstrated an effective reduction in turbidity under all scenarios tested, where turbidity was reduced to $\leqslant$ 2.7 NTU ($\geqslant$ 99% reduction) when the highest coagulant dose was applied (400 mg·L^{-1} alum) (Figure 5.4). Although there were differences observed between alum doses (50-400 mg·L^{-1}) on turbidity reduction in the moderate and severe burn conditions, these results were not of practical relevance as the final turbidity values were 1.0–4.2 NTU, which are within a desirable level of <5 NTU for pre-filtration water (Government of Ontario, 2014). The effective turbidity removal from the deteriorated source waters indicative of post-fire conditions is aligned with previous reports of effective turbidity reduction at bench- and pilot-scales (Chapters 3 and 4). The turbidity reduction from the unburned condition demonstrated a wider range across alum doses, where turbidity ranged 1.6–13.2 NTU; full results can be seen in in Figure D2. These results suggest that

the material causing high turbidity in the burn conditions (moderate or severe) may be more amenable to removal compared with unburned conditions. It should also be emphasised that the turbidity values presented herein are for clarified water and that at a full-scale WTP subsequent filtration would typically be applied, resulting in additional turbidity reduction. Although the turbidity was effectively reduced even under the lowest alum dose conditions, higher doses of alum were applied to investigate the concurrent removal of turbidity and DOC.
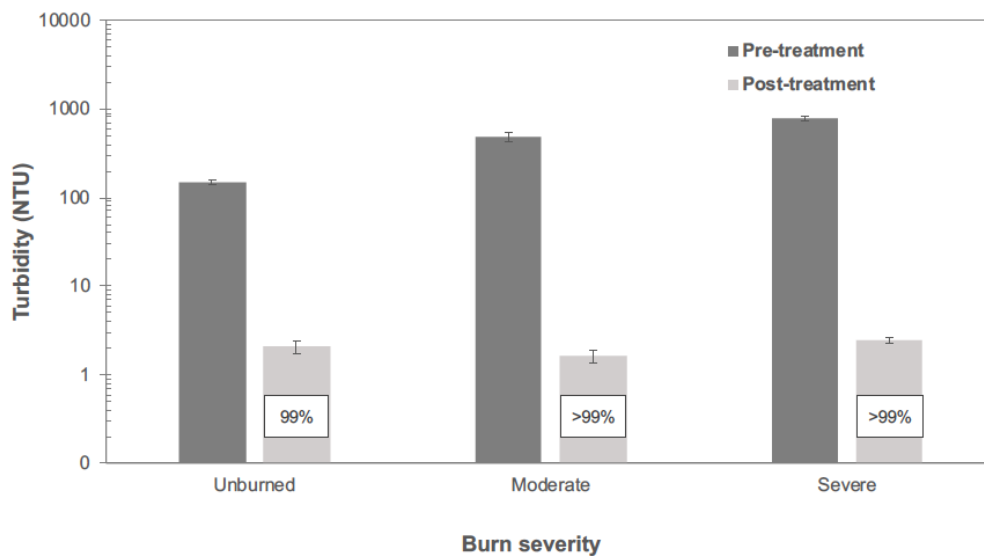
Figure 5.4: Turbidity levels before and after treatment of source waters prepared with Elbow River water and material from unburned, moderate burned, and severely burned conditions (5.0 g·L^{-1} in all cases). Post-treatment samples were collected following conventional chemical pre-treatment with alum at 400 mg·L^{-1}. Percent reduction of turbidity following treatment is indicated for each burn condition. Turbidity reported as mean ± SE, n=3 in all cases.

Although it was expected that burn severity would impact the efficacy of turbidity removal, the results demonstrated an effective reduction in turbidity under all burn conditions. The high level of turbidity removal using conventional chemical pre-treatment is assumed to be a result sweep coagulation, which is the key mechanism responsible for the high efficacy of turbidity removal at high coagulant doses, where colloids are entrapped within precipitating aluminum hydroxide species (Amirtharajah & Mills, 1982). These results of the high efficacy of turbidity removal from water impacted by severe burn conditions are aligned with previous reports of effective turbidity removal in post-fire waters indicative of severely deteriorated water quality (Chapter 3 and 4). The results highlight that, regardless of the severity of a wildfire burn in a watershed, the ability to effectively remove extreme levels of turbidity will be similar using conventional chemical pre-treatment.

In contrast to the effective reduction of turbidity across all the burn conditions tested, the same extent of reduction was not demonstrated for DOC in the source waters representative of different burn severities. SUVA values were calculated to provide an indication of what DOC reductions may be expected using alum coagulation based on the DOC and UVA_{254} levels of the pre-treated source waters. The SUVA values for the moderate and severe burn conditions were both higher than the values for the unburned condition; however, there was no clear demonstration of an increase in SUVA from moderate to severe burn conditions. The increase in SUVA (due to increased aromaticity) following heating in the moderate and severe burn conditions may be attributed to fire-induced transformation of organic leading to greater aromaticity (Knicker et al., 2006). Since the SUVA values were between 2–4 $L \cdot mg^{-1} \cdot m^{-1}$ for the different burn conditions (Figure 5.5), it could generally be anticipated that DOC should be reduced by 25–50% (Edzwald & Tobiason, 1999); however, these anticipated reductions are based on DOC which has not been impacted by wildfire. The greatest shift in the SUVA between the different burn severities from pre- and post-treatment conditions was demonstrated in the unburned source water scenario, which is reflective of the high reduction of UVA_{254} due to the removal of the aromatic portion of the DOC.
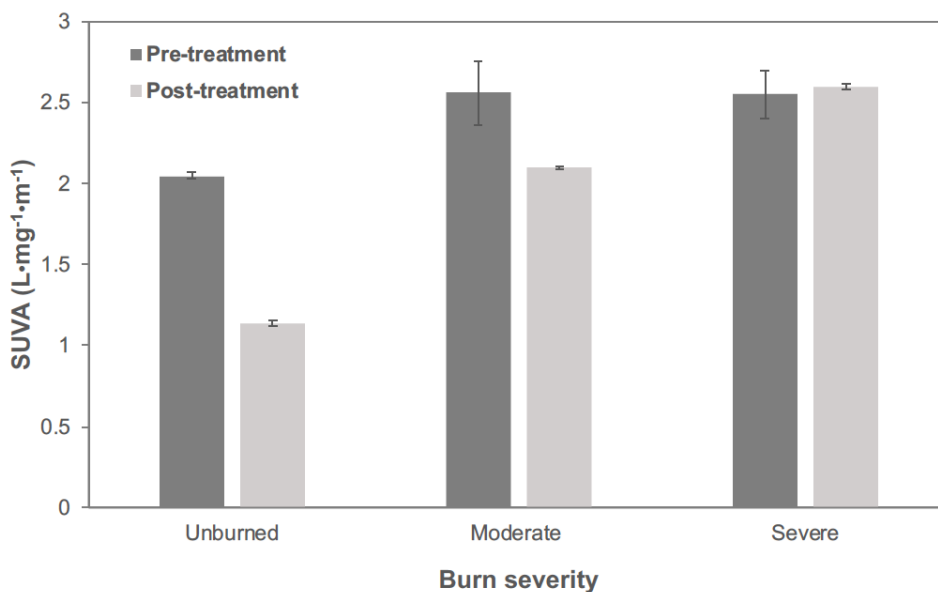
Figure 5.5: Comparison of specific ultraviolet absorbance at 254 nm (SUVA) for source waters prepared using material from different burn severities (unburned, moderate burned, and severe burned) and Elbow River water at 5.0 $mg \cdot L^{-1}$ before and after conventional chemical pre-treatment with alum (400 $mg \cdot L^{-1}$). SUVA is reported as mean ± SE, n=3 in all cases.

The best overall reductions of DOC and UVA_{254} following conventional chemical pre-treatment (at 400 $mg \cdot L^{-1}$ alum dose) for the three different burn severities is presented Figure 5.6. An ANOVA test indicated

that there was a significant difference between the burn severities for the reductions of DOC and UVA$_{254}$ following treatment; post-hoc Tukey tests revealed that $p \leqslant 7.1 \times 10^{-5}$ and $p \leqslant 2.0 \times 10^{-4}$ for DOC and UVA$_{254}$, respectively, when the different burn severities were compared (see Table D5). The lowest DOC levels achieved in the clarified water for unburned, moderate burn, and severe burn conditions were 5.6 ± 0.1 mg·L^{-1}, 3.2 ± 1.0 mg·L^{-1}, 17.8 ± 0.2 mg·L^{-1} (mean $\pm$ SE, n=3 in all cases), respectively. The lowest UVA$_{254}$ levels achieved for the unburned, moderate, and severe conditions were 0.064 ± 0.001 cm^{-1}, 0.064 ± 0.001 cm^{-1}, and 0.462 ± 0.004 cm^{-1} (mean $\pm$ SE, n=3 in all cases), respectively. Although these results only depict the treatment conditions at the highest dose of alum (400 mg·L^{-1}), additional details for DOC and UVA$_{254}$ reductions under a range of alum dose conditions are provided in Figure D3.

While the DOC reductions were within the expected removal (i.e., 25–50%), based on SUVA values, under all burn conditions, the lowest reductions were observed under the severe burn conditions, where only 31% reduction was achieved under the best treatment condition using 400 mg·L^{-1} of alum. The lower removal of DOC and UVA$_{254}$ in the severe burn conditions compared to the unburned and moderate burned conditions may be due to the altered character DOC following severe fire, such as having a higher proportion of LWM compounds and shifts in functionality (Chen et al., 2020; Hohner et al., 2019; Knicker et al., 2007; Uzun et al., 2020b). The results from the LC-OCD analysis (Figure 5.3) indicate that there was a larger proportion of LMW compounds in the deteriorated source water representing the severe burn scenario when compared to the unburned and moderate burned conditions, which likely impacted the treatment performance. Beyond the post-fire character of DOC potentially impacting the efficacy of treatment for the severe burn condition, the excessive alkalinity may have also adversely impacted treatment performance by hindering the ability of pH to be adjusted for optimal coagulation (Crittenden et al., 2012).

The results of the treated source waters representing the severe burn condition demonstrated that a higher proportion of DOC was removed compared to UVA$_{254}$. This is contrary to the results from the unburned and moderate burned treatment tests, where reductions for DOC and UVA$_{254}$ in the severe burn condition were $31.0 \pm 0.7\%$ and $28.0 \pm 0.7\%$ (mean $\pm$ SE, n=3 in both cases), respectively, were achieved under the highest alum dose condition (see Figure 5.6). It is generally expected in that a higher percentage of UVA$_{254}$ is removed compared to DOC when alum is used as it preferentially removes aromatic DOC (Croué et al., 1993; Reckhow & Singer, 1990).
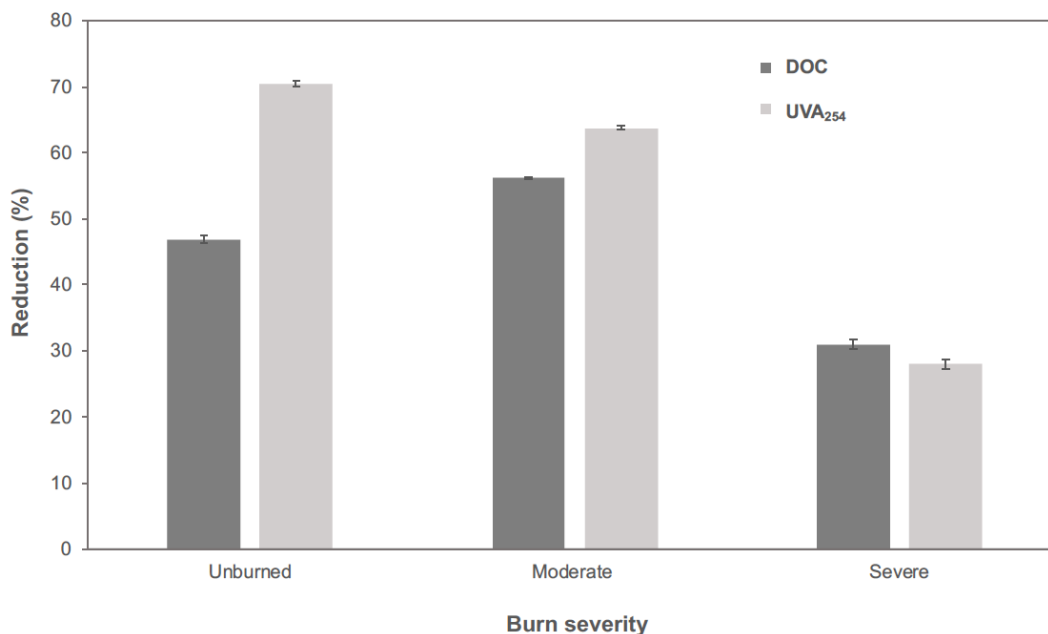
Figure 5.6: Percent reduction of DOC and UVA$_{254}$ after treatment of source water with conventional chemical pre-treatment with alum (400 mg·L^{-1}). The source waters were representative of deteriorated conditions and were prepared with material from different burn severities (unburned, moderate burned, and severe burned) and Elbow River water at 5.0 g·L^{-1}. Parameters reported as mean ± SE, n=3 in all cases. All p-values comparing the different burn severity conditions for DOC and UVA$_{254}$ reduction after treatment are provided in Table D5.

The results demonstrating that there was a notable difference in DOC and UVA$_{254}$ reduction across the different burn severities tested, were aligned with the expected results of this study. Previous studies have demonstrated limited success in removing DOC from post-fire waters (e.g., Chapter 3; Hohner et al, 2017) which may be due to shifts in carbon character after severe wildfire, such as changes in aromaticity and functionality (Gonzalez-Perez et al., 2004; Knicker et al., 2006; Knicker et al., 2007). Similar results were anticipated due to the ash-impacted source water prepared for this study having demonstrated shifts in water quality, such as an increase in SUVA, as an indicator increased aromaticity. Beyond this, the higher proportion of LMW carbon species in the water samples representative of severe burn conditions may have also limited the efficacy of DOC reduction, where it has been found in previous studies that LWM carbon compounds are less amenable to removal through conventional coagulation (Edzwald, 1993; Quang et al., 2015; Zhao et al., 2009). Additionally, the high alkalinity in the severely deteriorated source water may complicate coagulation using conventional chemical pre-treatment, as elevated alkalinity can inhibit shifts toward lower pH levels after coagulant addition, which promote effective removal of DOC through direct precipitation or adsorption on metal hydroxide solids (Crittenden et al., 2012; Ghernaout et al., 2009).

5.4.2 Comparison of impacts of wildfires from different physiographic regions on drinking water treatability

To assess the impacts of ash from different physiographic regions with different predominant vegetation types on drinking water treatability, four deteriorated ash-impacted source waters were prepared using ash from severe wildfires in different physiographic regions globally, including chaparral (USA), moorland (UK), grassland (Canada), and montane (Canada) (Figure 5.7). The ash-impacted source waters were subsequently used in treatment performance evaluation at bench-scale with conventional chemical pre-treatment.
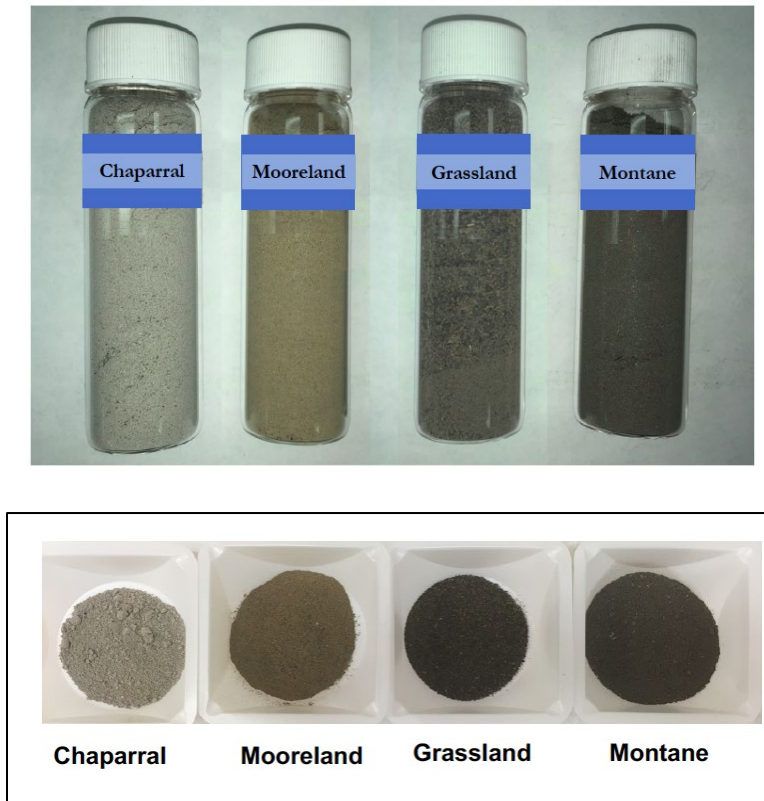
Figure 5.7: Ash samples from severe wildfires in different physiographic regions, including chaparral (USA), moorland (UK), grassland (Canada), and montane (Canada). Samples were used to prepare ash-impacted source waters which were then subsequently treated using conventional chemical pre-treatment.

5.4.2.1 Comparison of source waters impacted by wildfire from different physiographic regions

The deteriorated ash-impacted source waters representing post-fire water quality in different physiographic regions were prepared using Elbow River water and ash from four different physiographic regions with different predominant vegetation types where severe wildfire had occurred. Under all conditions, turbidity,

DOC and UVA_{254}, increased from the baseline Elbow River quality following the addition of ash (see Table D6). There was also a considerable difference between the turbidity values of the source waters prepared with ash from different physiographic regions with different predominant vegetation types, where mean values ranged 193–2643 NTU. Despite this wide range in turbidities, the objective of the treatability testing was to investigate the concurrent treatment of both turbidity and DOC, where the later took precedence as it was previously demonstrated to be the most challenging parameter in remove from deteriorated source waters indicative of post-fire scenarios (e.g., Chapters 3 and 4).

UVA_{254} was used a baseline water quality parameter upon which treatment performance between different ash types was comparatively evaluated, as UVA_{254} has been demonstrated to correlated with DOC (Chapter 2) and can be measured easily and quickly, compared to DOC. By achieving a similar UVA_{254} value for each of four the ash-impacted source waters prior to treatment, the treatment efficacy could be comparatively evaluated as indicated by reductions in UVA_{254}. In order to achieve a similar baseline UVA_{254} level, different amounts of ash were required to be added to prepare source waters for each of the different vegetation types. As such, varying amounts of ash from the four wildfire sites were mixed with Elbow River water to achieve similar UVA_{254} values, where for chaparral (7.0 $g \cdot L^{-1}$), moorland (6.5 $g \cdot L^{-1}$), grassland (2.5 $g \cdot L^{-1}$), and Montane (1.5 $g \cdot L^{-1}$) the UVA_{254} values achieved were 0.240 ± 0.002 cm^{-1}, 0.303 ± 0.021 cm^{-1}, 0.273 ± 0.08 cm^{-1}, 0.243 ± 0.003 cm^{-1} (mean ± SE, n=3 in all cases), respectively. Under ideal circumstances, the exact same UVA_{254} values would have been achieved for all ash-impacted source waters; however, this was extremely challenging to achieve due to natural variability in the ash samples collected. An ANOVA test indicated that there was a significant difference between the UVA_{254} values for the four ash-impacted source waters prepared with ash from different vegetation regions, where p=0.014. Although an ANOVA test revealed an overall significant difference in UVA_{254}, a post-hoc Tukey test indicated that there were not significant differences in all cases, such as when the grassland source water was compared to the other three ash-impacted source waters, where p≥0.24 (see Table D7). Although the UVA_{254} was maintained approximately constant in all the source waters prepared with different ash from different physiographic regions with different predominant vegetation types, there were clear differences in the DOC concentrations (see Figure 5.8). Since different amounts of ash were used to achieve the UVA_{254} baseline condition prior to treatment, this indicates that the DOC yield per gram of ash varied between different vegetation types. For instance, for chaparral, moorland, grassland, and montane the respective mean values of DOC per gram of ash were 1.0 mg L^{-1} g^{-1}, 1.8 mg L^{-1} g^{-1}, 5.5 mg L^{-1} g^{-1}, and 5.3 mg L^{-1} g^{-1} (n=3 in all cases); demonstrating that different ash types will yield different levels of DOC given the same amount enters water. This highlights that the mobilization of the same amount of ash from the landscape into a water body may have substantially different impacts on water quality from one region to another. The

differences in DOC resulted in variability in the SUVA values for the ash-impacted source waters prior to treatment (Figure 5.9). Since the SUVA values were all between 2–4 $L \cdot mg^{-1} \cdot m^{-1}$, it may be expected that the removal of DOC would be 25–50% when treating water with alum (Edzwald & Tobiason, 1999); however, this expectation of DOC removal is based on conditions where the organic matter in water has not been subjected to wildfire.
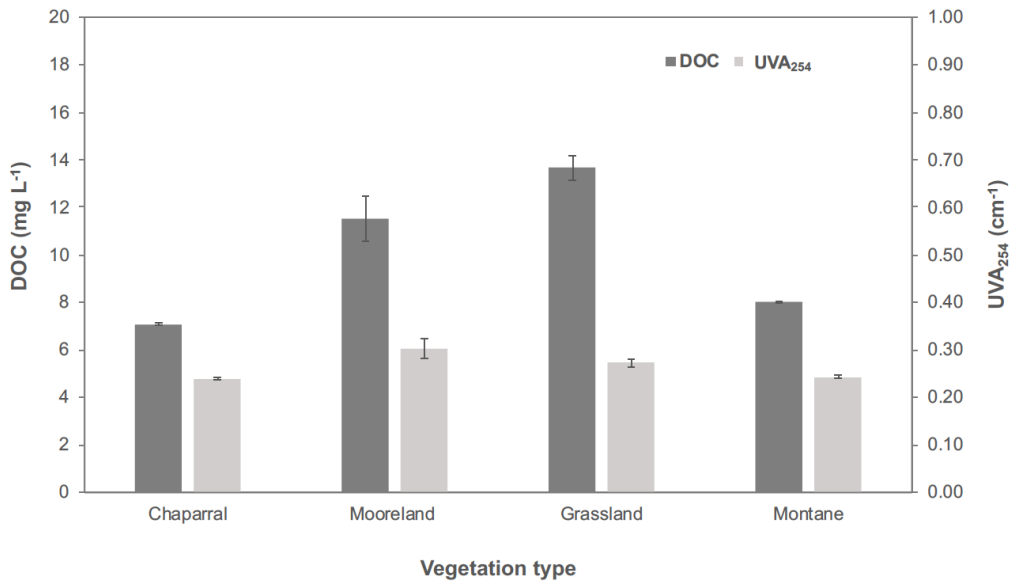
Figure 5.8: Dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UVA$_{254}$) for deteriorated ash-impacted source waters prepared using Elbow River water and ash from severe wildfires in different vegetation regions (chaparral, moorland, grassland, and montane). Varying amounts of each ash type were mixed with Elbow River water to prepare deteriorated wildfire ash-impacted source waters which had similar UVA$_{254}$ values to provide a baseline for subsequent treatability testing. Error bars indicate standard error; parameters reported as mean ± SE, n=3 in all cases.
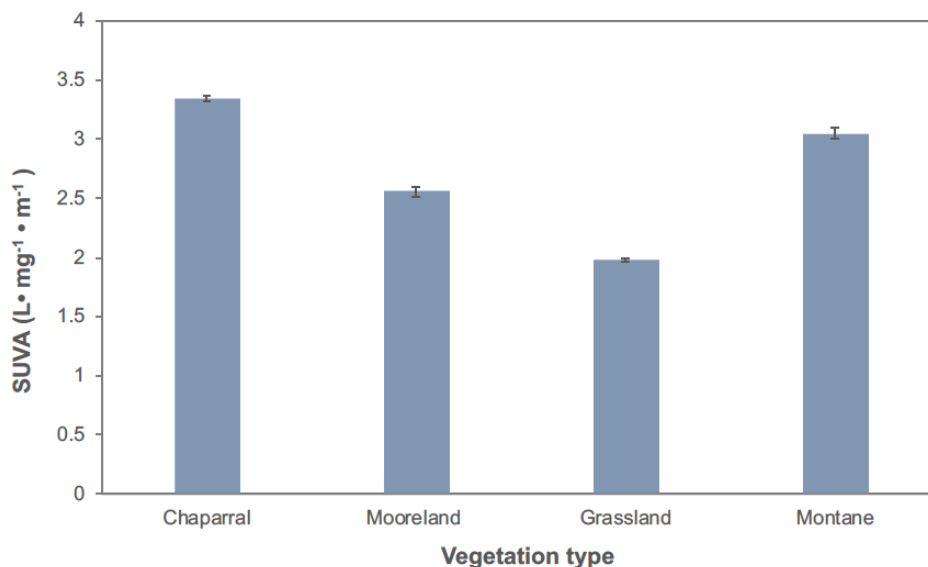
Figure 5.9: Specific ultraviolet absorbance at 254 nm (SUVA) comparing source waters prepared with ash from severe wildfires in different vegetation regions. Error bars indicate standard error; SUVA reported as mean ± SE, n=3 in all cases.

The results from the LC-OCD analysis indicated that there were substantial differences between the proportions of DOC fractions in the different source waters prepared with different ashes (Figure 5.10). However, under all ash-impacted source water conditions there was a lower percent fraction for the humic component compared to the Elbow River water, where the fraction of humic substances for the Elbow River water was 64.5 ± 3.6% (mean ± SE, n=3), compared to all the vegetation type source waters which had mean proportions of humic substances ranging 20.6–57.3%. Additionally, all of the wildfire ash-impacted source waters demonstrated a higher fraction of LMW compounds compared to the baseline Elbow River water, which had 11.0 ± 0.8% and 2.5 ± 0.1% (mean ± SE, n=3) for LMW neutrals and LMW acids, respectively. The levels for LMW neutrals and LMW acids in the source waters prepared with ashes from different physiographic regions ranged between 12.3–20.2% and 4.1–30.4%, respectively. The higher proportion of LMW compounds in water samples is aligned with the results from the study of burn severity impacts on water quality described earlier in this work and other studies which have noted increases in LMW carbon species post-fire (e.g., Cawley et al., 2017; Hohner et al., 2016).
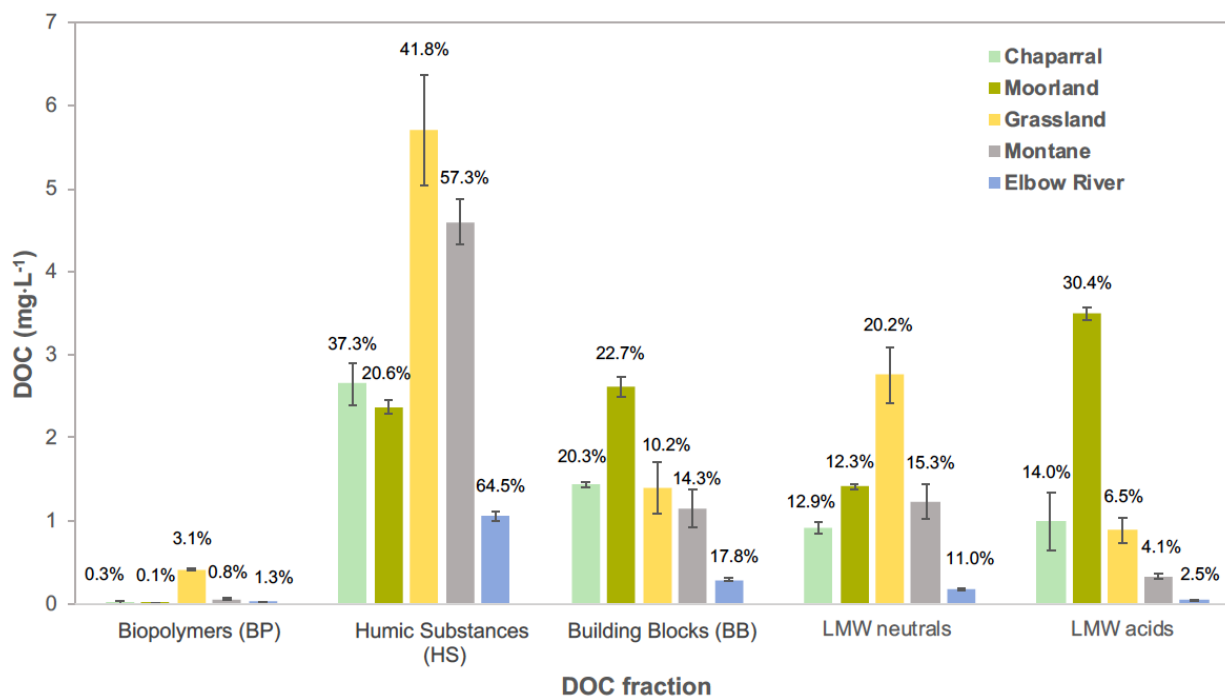
Figure 5.10: Liquid chromatography organic carbon detection (LC-OCD) for comparing Elbow River water (as a control) and deteriorated ash-impacted source waters prepared with Elbow River water and ash from severe wildfires in different physiographic regions with different predominant vegetation types (chaparral, moorland, grassland, and montane), where: LC-OCD fractions are presented as total dissolved organic carbon (DOC) concentration (mean ± SE, n=3 in each case) and the percent of LC-OCD fractions of the total DOC are indicated for each condition. Different organic fractions include: BP, HS, BB, low-molecular-weight (LMW) neutrals, and LMW acids.

The results for pH and alkalinity varied between the deteriorated source waters prepared with ash from severe wildfires in different physiographic regions with different predominant vegetation types. Under all conditions representative of different physiographic regions, the ash-impacted source waters demonstrated increases in pH from the Elbow River water baseline level of 8.2 ± 0.1 (mean ± SE, n=6) prior to adding to ash. The highest pH resulted following the addition of the chaparral ash, where the pH was 10.2 ± 0.03 (mean ± SE, n=3). The source water indicative of the chaparral region also demonstrated an increase in alkalinity to 207 ± 1 mg·L^{-1} as CaCO$_3$ (mean ± SE, n=3) from the Elbow River water baseline condition with an alkalinity 166 ± 1 mg·L^{-1} CaCO$_3$ (mean ± SE, n=6). Although increases in alkalinity have been previously reported for post-fire conditions in forested regions (e.g., Cerrato et al., 2016; Earl & Blinn,

2003; Murphy et al., 2018), this study showed that alkalinity did not increase for all the ash-impacted source waters prepared with ash from different regions. For instance, decreases in alkalinity were demonstrated after ash from the moorland and grassland wildfires were added to the Elbow River water, where alkalinity levels were 115 ± 5 mg·L^{-1} as $CaCO_3$ (mean $\pm$ SE, n=3) and 164 ± 3 mg·L^{-1} as $CaCO_3$ (mean $\pm$ SE, n=3), respectively. While increases in alkalinity in source water are generally expected following severe wildfire, reduced alkalinity levels in post-fire lakes have been reported (McEachern et al., 2000). Regardless of whether alkalinity levels increase or decrease following severe wildfire, abrupt changes in alkalinity following major runoff events post-fire will likely present challenges for drinking water treatment, specifically coagulation, where coagulant dosing strategies may need to be adjusted due to shifts in alkalinity.

5.4.2.2 Drinking water treatability of waters impacted by wildfires in different physiographic regions

The treatment evaluation comparing ash-impacted source waters prepared with ash from wildfires in different physiographic regions demonstrated that turbidity was effectively reduced in all scenarios. Although there was a range of turbidity values across the different ash-impacted source waters being tested, turbidity was effectively reduced to $\leqslant 2.3$ NTU (>99% reduction) under the highest alum dose condition (Figure 5.11). Substantial reductions in turbidity were demonstrated under all alum dose conditions for each of the four wildfire ash-impacted source waters prepared (see Figure D4). Turbidity results were <5.0 NTU in clarified water for all scenarios, with the exception of the chaparral condition at the lowest alum dose (50 mg·L^{-1}). These results are a promising indication that conventional treatment is effective in reducing high levels of turbidity in post-fire scenarios, as the post-treatment results were within a desirable level of <5 NTU for pre-filtration water (Government of Ontario, 2014). Again, the clarified water following treatment with conventional chemical pre-treatment would typically undergo subsequent filtration, thereby further reducing the level of turbidity. However, there are WTP facilities which are not fitted with infrastructure for filtration due to reliance on high quality source waters. As such, it may be beneficial to consider how source water reservoirs may potentially be used as coagulation basins to reduce turbidity prior to water reaching a WTP in emergency post-fire situations, such as the case of the Kensico Reservoir in New York State, where alum is added directly to the reservoir during episodes of high turbidity following storm events (National Academies of Sciences, 2020).
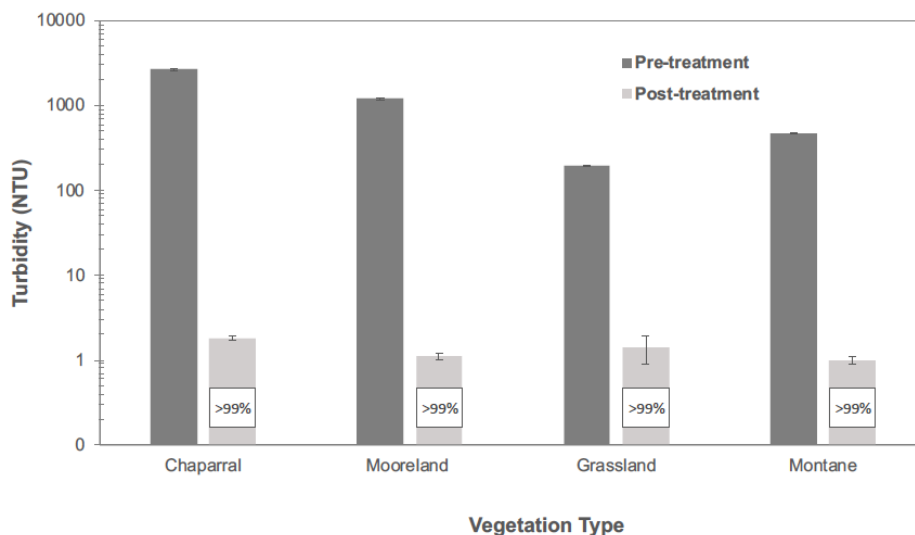
Figure 5.11: Turbidity comparing pre-treatment and post-treatment of wildfire-impacted source waters prepared using Elbow River water and ash from severe wildfires in different physiographic regions (chaparral, moorland, grassland, and montane). Conventional chemical pre-treatment was used to for all treatment tests using 400 mg·L^{-1} of alum. Turbidity reported as mean ± SE, n=3 in all cases; error bars indicate standard error.

Although substantial turbidity reduction was demonstrated under all treatment scenarios representative of ash from severe wildfires in different physiographic regions, similar reductions in DOC were not demonstrated. Since the SUVA values for the different source waters prepared with ash from different physiographic regions ranged between 2.0–3.4 L·mg^{-1}·m^{-1}, it would be expected that DOC reductions using alum coagulation would be 25–50% (Edzwald & Tobiason, 1999). However, regardless of the type of wildfire ash (i.e., which physiographic region) used to prepare the wildfire-impacted source water, the maximum DOC removal achieved with alum coagulation was 22% for the source water representative the montane region (Figure 5.12). The low efficacy of DOC removal may be a result of shifts in DOC character due to heating during wildfire (Hohner et al., 2019), such as DOC being composed of a higher proportion of LMW species or shifts in functionality.
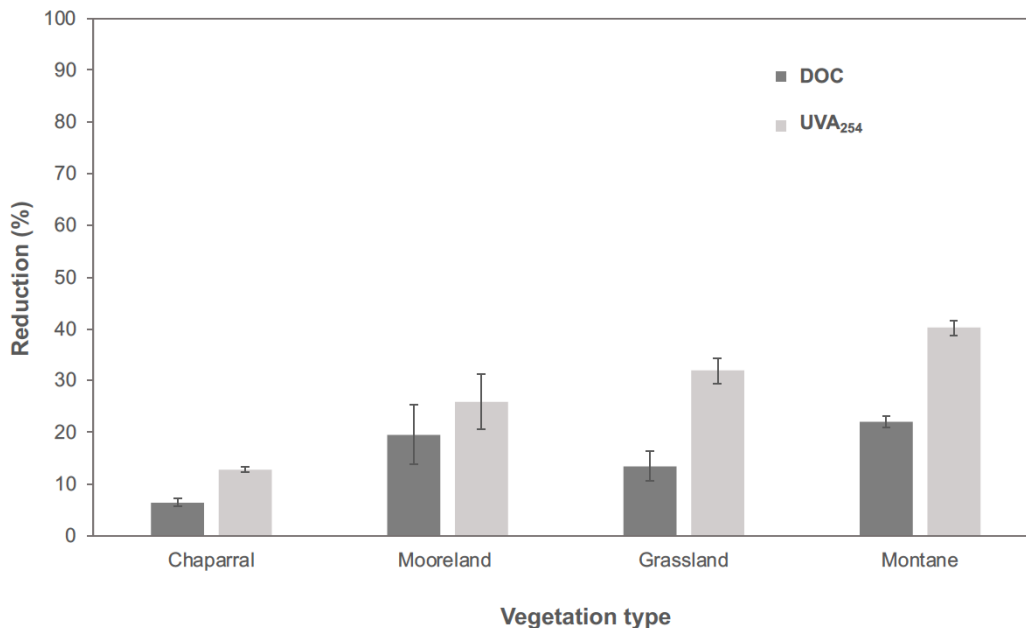
Figure 5.12: Percent reduction of DOC and UVA$_{254}$ in treated water following conventional chemical pre-treatment with alum (400 mg·L^{-1}) of source waters representing deteriorated conditions which were prepared with wildfire ash from different physiographic regions (chaparral, moorland, grassland, and montane) and Elbow River water. Parameters reported as mean ± SE, n=3 in all cases; error bars indicate standard error. All p-values comparing the four different physiographic conditions for DOC and UVA$_{254}$ reductions are provided in Table D8.

In addition to turbidity and DOC being key drivers for coagulation during drinking water treatment, pH and alkalinity are also integral parameters in coagulation, where high levels of pH and/or alkalinity may adversely impact treatment efficacy. As an example, the lowest treatment efficacy was demonstrated for the chaparral condition (Figure 5.12), which may have been impacted by the comparatively high pH and alkalinity in the ash-impacted source water prior to treatment (see Table D6).

The lowest DOC values for each of the source waters prepared with ash from different physiographic regions with different predominant vegetation types (chaparral, moorland, grassland, and montane) following conventional chemical pre-treatment with an alum dose of 400 mg·L^{-1} were 6.6 ± 0.1 mg·L^{-1}, 9.3 ± 0.7 mg·L^{-1}, 11.8 ± 0.4 mg·L^{-1}, and 6.3 ± 0.1 mg·L^{-1}, respectively for each vegetation type. Additional details for DOC and UVA$_{254}$ reductions over a range of alum doses is provided in Figure 5.13. The DOC values in the clarified water following the high alum dose condition would still be considered elevated from a drinking water treatment perspective and would likely require alternative treatment methods to further reduce DOC. Such methods could include enhanced coagulation through pH adjustment or the use of powdered activated carbon, as had been previously tested on severely deteriorated source water

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representative of conditions following wildfire (i.e., Chapters 3 and 4). Although DOC reductions were low for each vegetation condition, there was a statistically significant difference between the percent reductions for each source water condition (ANOVA, $p=0.04$). However, a post-hoc Tukey test indicated that there were not significant differences between all vegetation types compared for DOC reduction; for instance, both the moorland and grassland conditions had $p \geq 0.08$ when compared to all other vegetation types for DOC reduction based on percent removal (see Table D8).
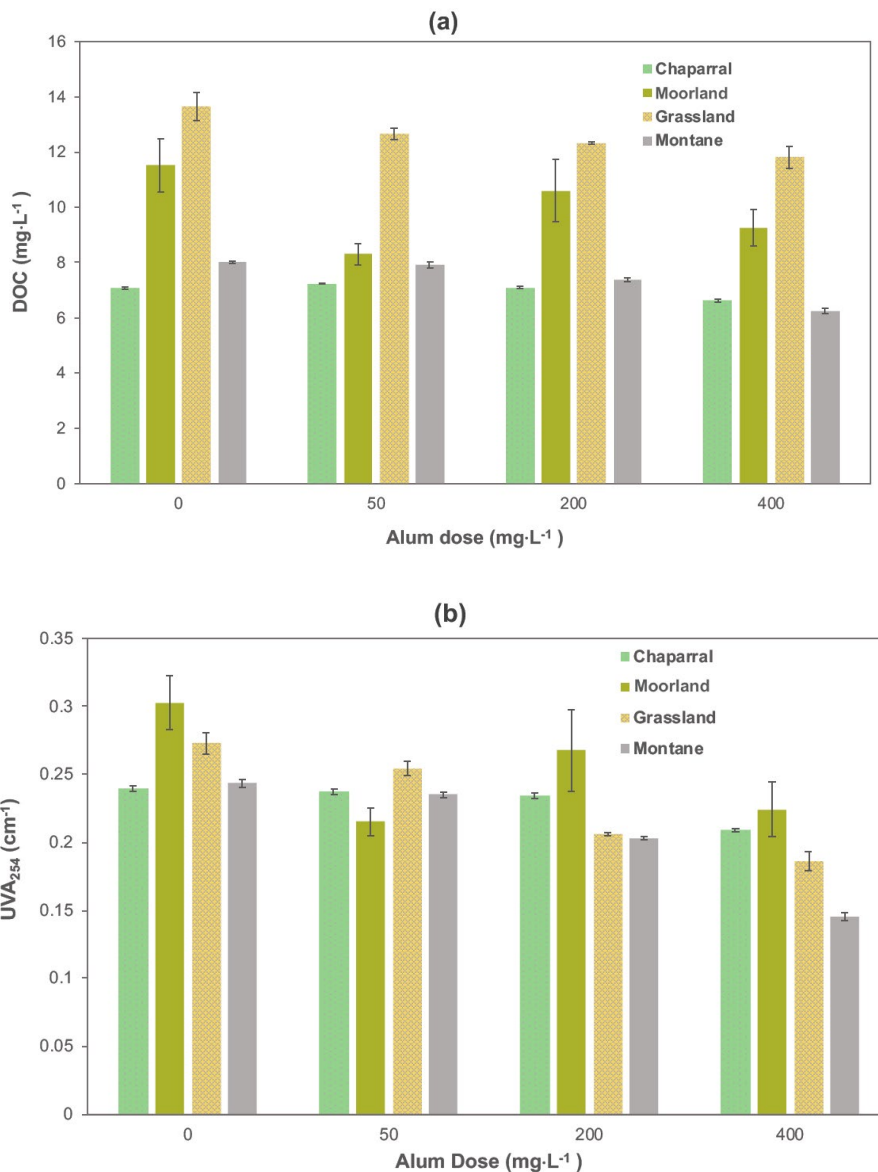
Figure 5.13: Dissolved organic carbon (DOC) (a), and ultraviolet absorbance at 254 nm (UVA_{254}) (b) following conventional chemical pre-treatment for deteriorated ash-impacted source waters prepared with ash from severe wildfires in different physiographic regions (chaparral, moorland, grassland, and montane). Treatment conditions were tested over a range of alum doses (0–400 $mg·L^{-1}$); mean values are indicated for each source water prepared with ash from severe wildfires in different physiographic regions with different predominant vegetation types; error bars specify standard error. All jar tests were completed in triplicate for each of the four ash-impacted source waters tested (i.e., n=3 in all cases). Parameters reported as mean ± standard error. P-values comparing DOC and UVA_{254} reductions in the various regions are provided in Table D8 for the highest alum dose condition (400 $mg·L^{-1}$).

In all cases, UVA_{254} reductions were higher than DOC at an alum dose of 400 mg·L^{-1} for the source waters prepared with ash from different physiographic regions, which is indicative of the preferential removal of aromatic DOC present in the ash-impacted source waters (Croué et al., 1993; Reckhow & Singer, 1990). The lowest UVA_{254} levels achieved following conventional treatment at the highest alum dose (400 mg·L^{-1}) for the chaparral, moorland, grassland, and montane source water conditions were 0.209 ± 0.001 cm^{-1}, 0.224 ± 0.016 cm^{-1}, 0.186 ± 0.007 cm^{-1}, and 0.145 ± 0.003 cm^{-1} (mean $\pm$ SE, n=3 in all cases), respectively. An ANOVA test comparing the UVA_{254} level in the clarified water follow treatment with the highest alum dose indicated a significant difference, where p=0.001. A post-hoc Tukey test revealed that in some instances there were not significant differences between the UVA_{254} levels in the treated water representative of different physiographic regions. An example of this was when the UVA_{254} from the grassland condition was compared to the UVA_{254} levels of the moorland or montane conditions after treatment, where p≥0.27 (see Table D8).

Following conventional chemical pre-treatment, the SUVA values decreased for all ash-impacted source water conditions representative of different physiographic regions, where the SUVA values for chaparral, moorland, grassland, and montane regions were 3.16 ± 0.01, 2.42 ± 0.02, 1.57 ± 0.01, 2.32 ± 0.02 L·mg^{-1}·m^{-1} (mean $\pm$ SE, n=3 in all cases), respectively. The reduction of SUVA for all source waters prepared with ash from different physiographic regions demonstrates that the aromatic portion of carbon following conventional chemical pre-treatment was decreased in all cases. In spite of the reductions in SUVA, the range of SUVA values after treatment across the source waters prepared with ash from different physiographic regions indicates that there was variability in aromaticity of the carbon present in different samples, where higher SUVA values are indicative of higher levels of aromatic carbon.

The analysis of DBP-FP was also completed on the ash-impacted source waters prepared with wildfire ash from different physiographic regions with different predominant vegetation types. DBP-FP was conducted for pre-treatment and post-treatment conditions (at an alum dose of 400 mg·L^{-1}) and provided a valuable indication of how effective conventional chemical pre-treatment was at removing the DOC which acts as DBP pre-cursor material. Due to the variation in DOC of the different samples, comparisons were made based on normalized DBP concentrations, where TTHMs and HAA5 were divided by the total DOC concentration to provide a value per mg of carbon present. An ANOVA test was completed to compare TTHM results (for normalized concentrations) and indicated that there was a statistically significant difference (p=0.01) between the pre-treated ash-impacted source waters (Figure 5.14), where mean TTHMs ranged 86.8–161.1 µg·mg_c^{-1}. In contrast, differences in the TTHM formation potentials after treatment were very similar, and not statistically significant (p=0.051; Table D9). Mean TTHM FPs ranged from 19.0 to 25.4 µg·mg_c^{-1} for ash form the different regions.
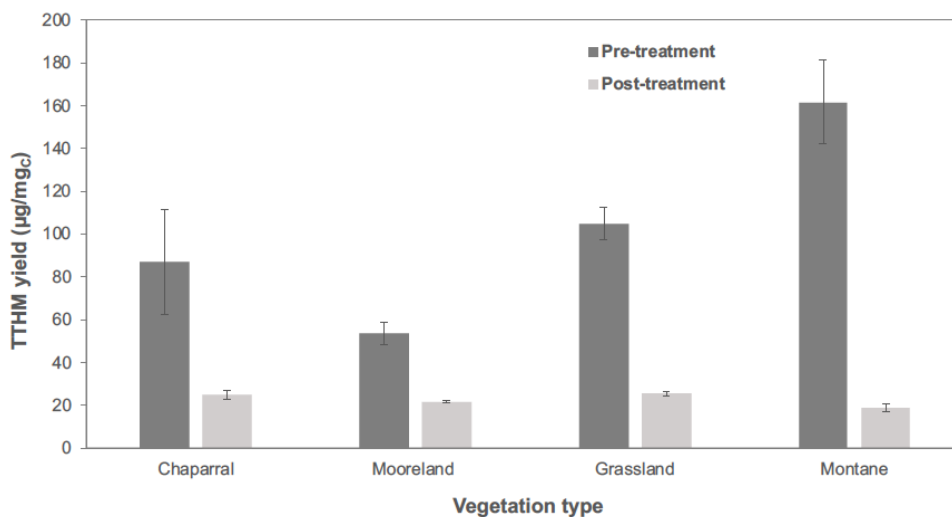
Figure 5.14: Comparison of normalized (per mg of DOC) total trihalomethanes (TTHMs) before and after conventional chemical pre-treatment with alum (400 mg·L^{-1}) of ash-impacted source waters representing deteriorated conditions prepared with Elbow River water and severe wildfire ash from different physiographic regions with different predominant vegetation types (chaparral, moorland, grassland, and montane) (mean ± SE, n=3 in all cases). All p-values comparing TTHMs between the different physiographic regions are provided in Table D9.

Although the DOC values in the pre-treated water varied, the UVA$_{254}$ values were similar, suggesting that the samples had comparable amounts of aromatic DOC. The similar results of the normalized TTHMs in the treated water for all the physiographic regions may be an indication that the DOC contributing to the formation of THMs was effectively removed in all cases, specifically the highly aromatic portion of DOC (Kitis et al., 2001). Although there was a substantial reduction in TTHMs in waters representing the various physiographic regions following treatment, the final levels (i.e., non-normalized per mg carbon) of TTHMs were above the USEPA maximum contaminant level (MCL) of 80 µg·L^{-1} (Federal Register, 2006), where the lowest level achieved was 118 µg·L^{-1} following treatment of wildfire-impacted source water prepared with ash from the montane region. The disinfection conditions used for the DBP-FP analysis involved chlorination levels that may be higher than typically applied at a full-scale WTP to provide an indication of true formation potential of DBPs where all DOC present is reacted with chlorine; as such TTHM levels may be expected to be lower than the values reported herein for actual conditions at a WTP following wildfire.

Similar to the reduction in TTHMs, convention chemical pre-treatment was also effective in removing a substantial portion of the HAA5 in the ash-impacted source waters prepared with ash from different physiographic regions with different predominant vegetation types. Normalized HAA5 results were

compared with an ANOVA test which indicated that there was a significant difference between the source waters representing different physiographic regions, where p=0.02 (Figure 5.15); the mean values for HAA5 ranged from 72.0–186.1 $\mu g \cdot mg_c^{-1}$. Following treatment, the values for the normalized HAA5 ranged 33.2–43.5 $\mu g \cdot mg_c^{-1}$; however, an ANOVA test comparing HAA5 levels in source waters representative of different physiographic regions revealed that there was a statistically significant difference in HAA5 levels, where p=0.001 (see Table D9). Although there were substantial reductions of HAA5 in all vegetation conditions following treatment, the final levels of HAAs were well above the MCL of 60 $\mu g \cdot L^{-1}$ (Federal Register, 2006), where the lowest level was achieved after treatment of the chaparral source water which resulted in an HAA5 level of 225.6 $\mu g \cdot L^{-1}$. As with the TTHM analysis, levels of HAA5 under full-scale WTP conditions would likely be lower due to lower doses of chlorine for disinfection.
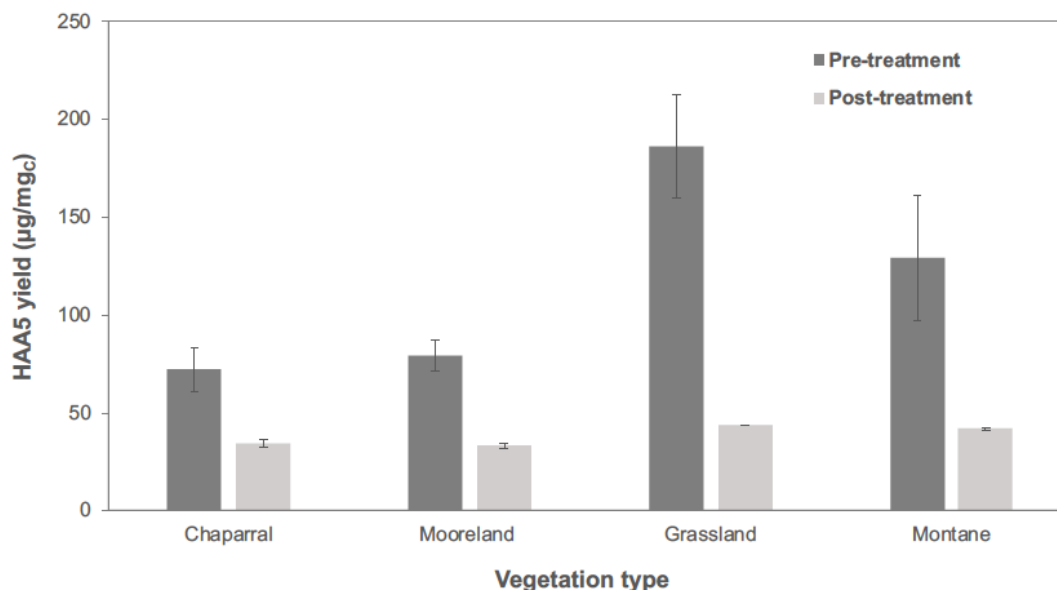
Figure 5.15: Comparison of normalized (per mg of dissolved organic carbon [DOC]) total haloacetic acids (HAA5) before and after conventional chemical pre-treatment (alum at 400 $mg \cdot L^{-1}$) of ash-impacted source waters representing deteriorated conditions prepared with Elbow River water and severe wildfire ash from different vegetation regions (chaparral, moorland, grassland, and montane) (mean ± SE, n=3 in all cases). All p-values comparing HAA5 between the different physiographic regions are provided in Table D9.

In spite of the differences in SUVA values (i.e., difference in aromaticity of carbon), the TTHM and HAA5 yields (i.e., mass formed per mass DOC) after coagulation were very similar, regardless of ash origin (Figures 5.14 and 5.15), where the values for TTHM and HAA5 for the four different source water types

were within 16% and 14%, respectively, of the mean values of the TTHM and HAA5 yields of the four different source waters. Thus, the character of the DOC remaining in solution after coagulation was also almost identical, regardless of ash origin after wildland fire, and excellent linear correlation was observed between TTHM and HAA5 formation potentials and DOC concentration (Figures 5.16). While there were good correlations between DBP formation potentials and DOC concentration in treated water, similar correlations were not observed prior to treatment, potentially as result of different levels of particulate matter (i.e., turbidity; see Figure 5.11) that reacted with chlorine during the DBP-FP analysis (Figure D5).

(a)

(b)
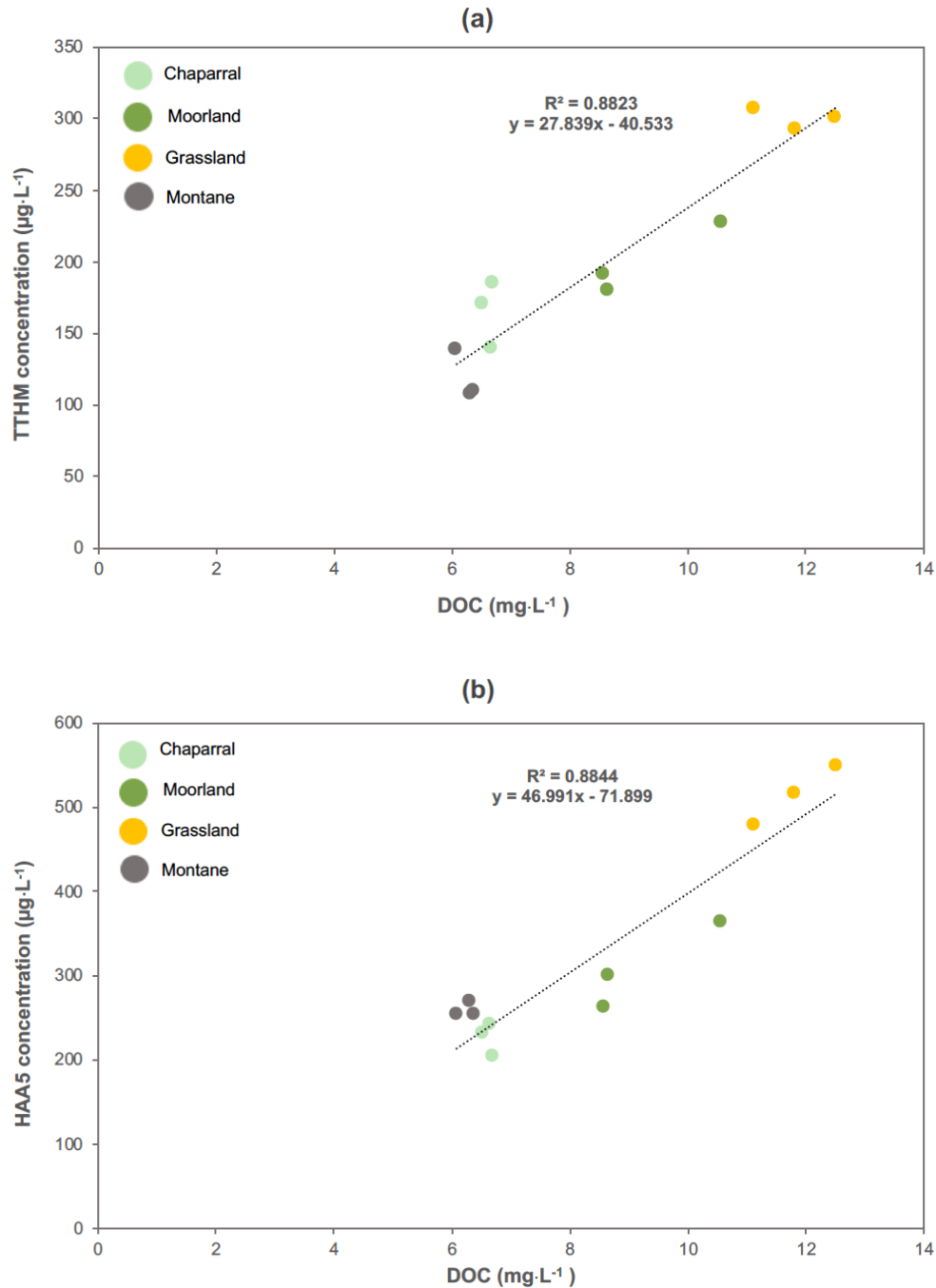
Figure 5.16: Linear correlation between dissolved organic carbon (DOC) and total trihalomethane (TTHM) yield **(a)**, and total haloacetic acid (HAA5) yield **(b)** after conventional chemical pre-treatment of ash-impacted source waters prepared with ash from severe wildfires in different physiographic regions with different predominant types of vegetation (chaparral, moorland, grassland, and montane).

In addition to examining the TTHMs and HAA5, specific THMs (four) and HAAs (five) were also compared between the different ash-impacted source waters. Of particular interest were the brominated THMs and HAAs which varied considerably between the ash-impacted source waters representing different physiographic regions. For instance, bromodichloromethane (BDCM) and dibromochloromethane (DBCM) are both brominated THMs that were present in high levels in the chaparral and moorland source waters both before and after treatment (Figure 5.17 and Figure 5.18). Similarly, elevated levels of dibromoacetic acid (DBAA), a brominated HAA, was also present in the ash-impacted source waters from the chaparral and moorland areas both before and after treatment (Figure 5.19 and Figure 5.20). The presence of brominated DBPs is of particular concern as these compounds are known to be more toxic than their chlorinated analogues (Plewa et al., 2010; Richardson et al., 1999). Interestingly, the proportions of the bromated DBPs to total DBPs increased after treatment, indicating that that these compounds were not amenable to removal with conventional pre-chemical treatment.
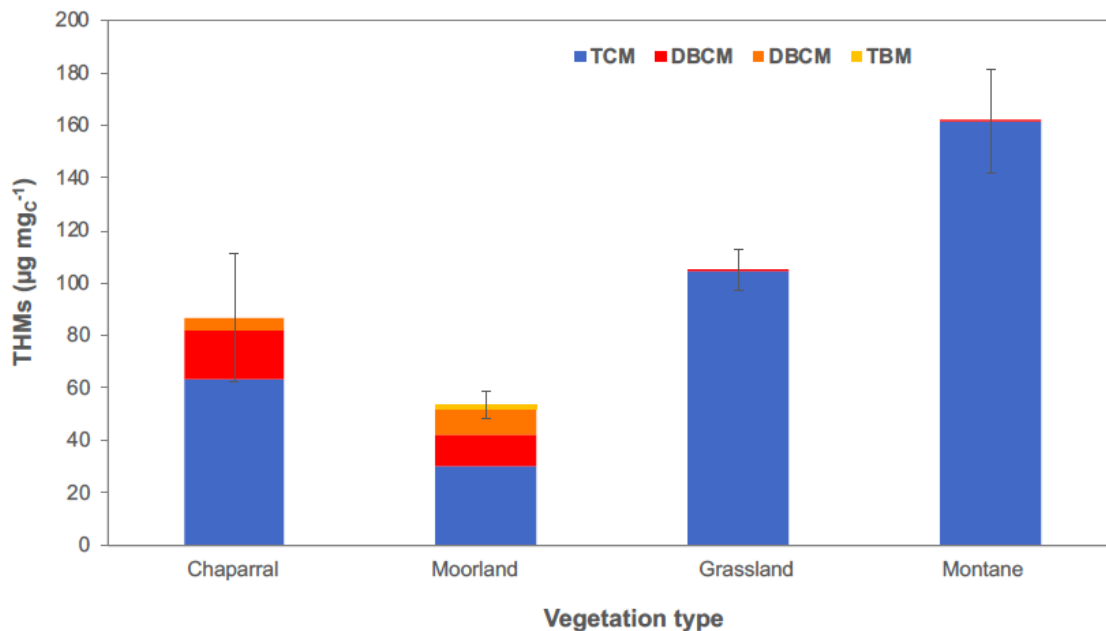
Figure 5.17: Pre-treatment comparison of normalized (per mg of DOC) trihalomethanes (THMs) for four specific THMs (trichloromethane [TCM], bromodichloromethane [BDCM], dibromochloromethane [DBCM], and tribromomethane [TBM]) for deteriorated ash-impacted source waters prepared with Elbow River water and ash from severe wildfires in different physiographic regions (chaparral, moorland, grassland, and montane); n=3 in all cases. Error bars are indicative of standard error of mean for total THMs, inclusive of TCM, BDCM, DBCM, and TBM.
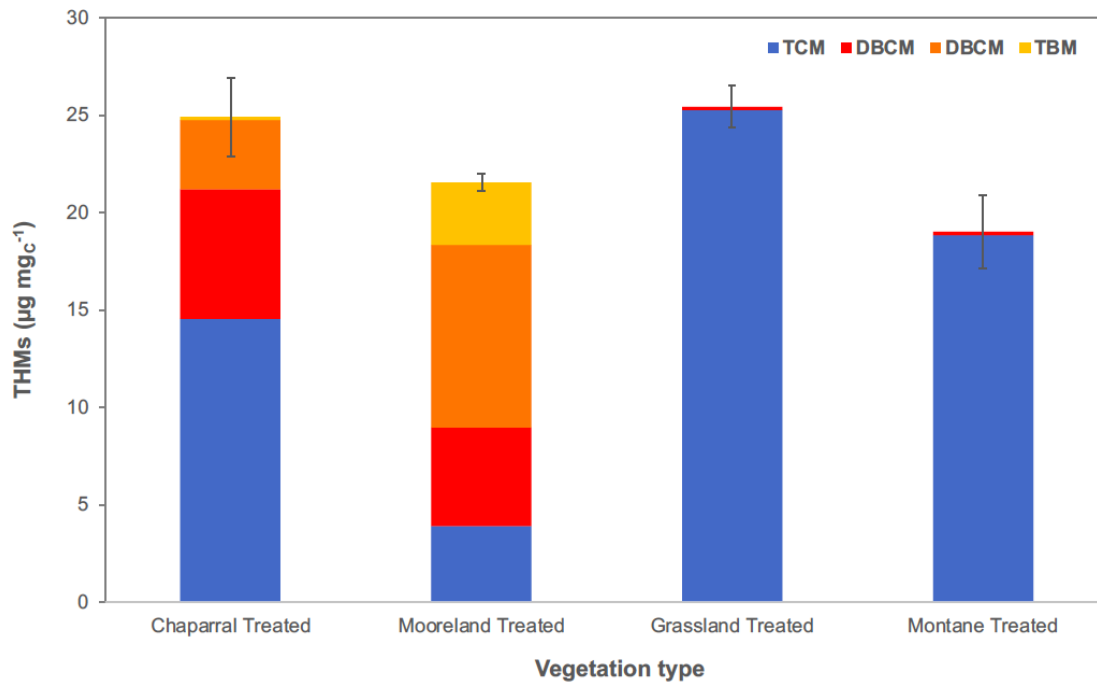
Figure 5.18: Comparison of normalized (per mg of DOC) trihalomethanes (THMs) after conventional chemical pre-treatment with alum (400 mg·L^{-1}). Four specific THMs were measured, including trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM) after treatment of ash-impacted source waters prepared with Elbow River water and ash from severe wildfires in different physiographic regions (chaparral, moorland, grassland, and montane); n=3 in all cases. Error bars are indicative of standard error of mean for total THMs, inclusive of TCM, BDCM, DBCM, and TBM.
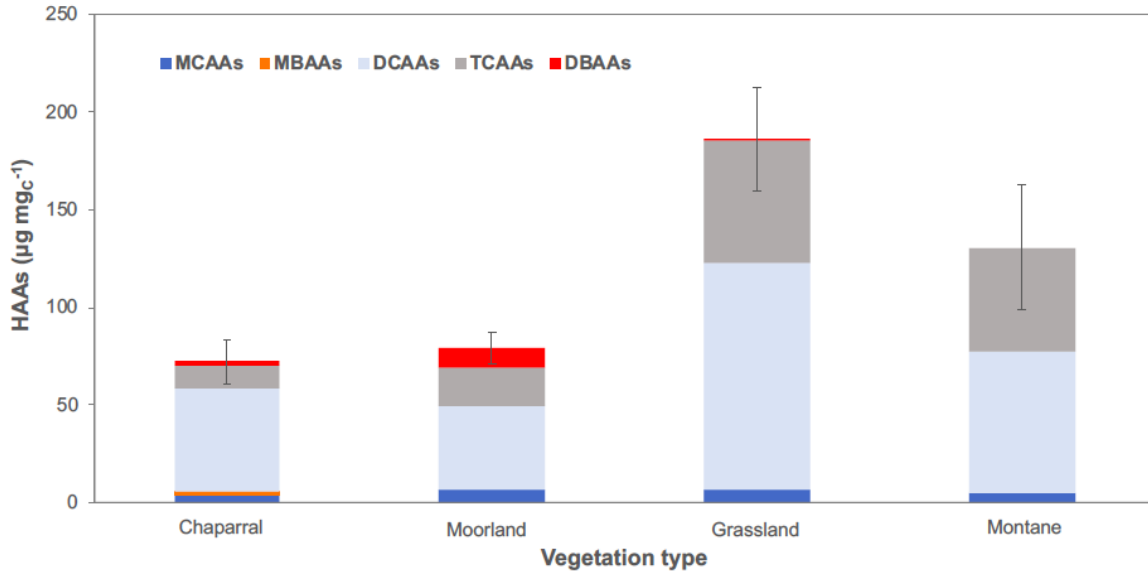
Figure 5.19: Pre-treatment comparison of normalized (per mg of DOC) haloacetic acids (HAAs) for five specific HAAs (monochloroacetic acid [MCAA], monobromoacetic acid [MBAA], dichloroacetic acid [DCAA], trichloroacetic acid [TCAA], and dibromoacetic acid [DBAA]) for deteriorated ash-impacted source waters prepared with Elbow River water and ash from severe wildfires in different physiographic regions (chaparral, moorland, grassland, and montane); n=3 in all cases. Error bars are indicative of standard error of mean for total HAAs, inclusive of MCAA, MBAA, DCAA, TCAA, and DBAA.
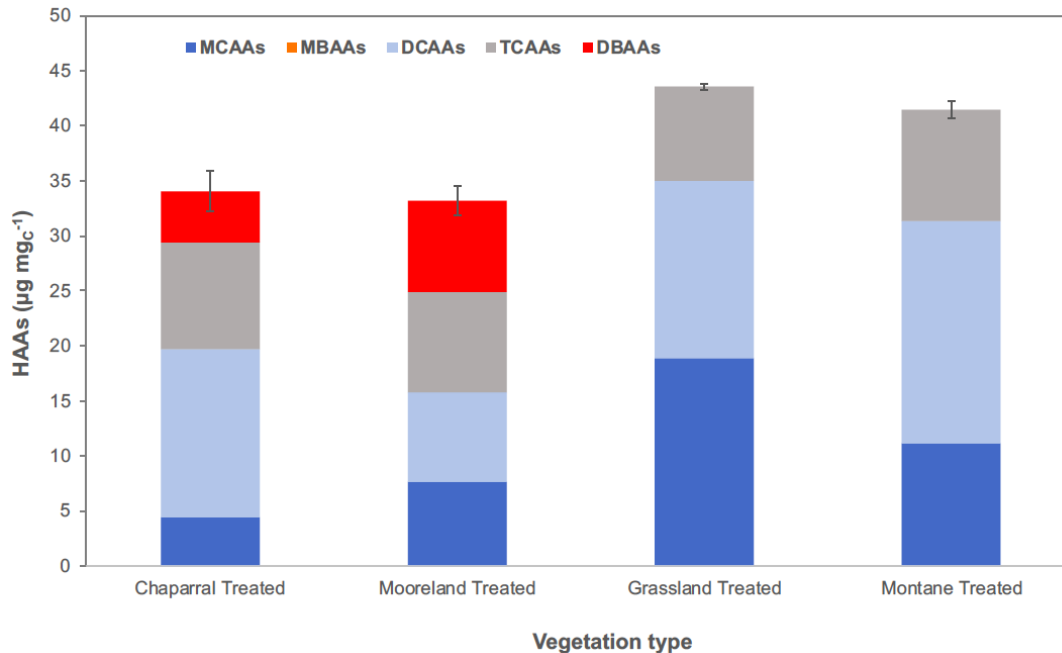
Figure 5.20: Comparison of normalized (per mg of DOC) haloacetic acids (HAAs) after conventional chemical pre-treatment with alum (400 mg·L^{-1}). Five specific HAAs were analyzed (monochloroacetic Acid [MCAA], monobromoacetic acid [MBAA], dichloroacetic acid [DCAA], trichloroacetic acid [TCAA], and dibromoacetic acid [DBAA]). The ash-impacted source waters which were treated were prepared with Elbow River water and ash from severe wildfires in different physiographic regions (chaparral, moorland, grassland, and montane); n=3 in all cases. Error bars are indicative of standard error of mean for total HAAs, inclusive of MCAA, MBAA, DCAA, TCAA, and DBAA.

Bromide analysis indicated that there were elevated levels in both the chaparral and moorland ash-impacted source waters, which had mean values of 0.19 mg·L^{-1} (n=3) and 1.40 mg·L^{-1} (n=3), respectively. Following treatment, the mean bromine level did not change for the chaparral condition (0.19 mg·L^{-1} [n=3]) and there was only a minimal change in the moorland condition which had a post-treatment mean bromine concentration of 1.19 mg·L^{-1} (n=3). It is clear from the post-treatment results that the bromide present in the water was not effectively removed during conventional chemical pre-treatment, thereby resulting in elevated concentrations of brominated DBPs in the clarified water for the chaparral and moorland regions. The lack of bromine removal was not surprising as bromine is known to be recalcitrant to commonly employed drinking water treatment methods (Watson et al., 2015).

It is speculated that the high level of bromine in the ash-impacted source waters is as a result of the chaparral and moorland regions being in coastal areas, where elevated levels of bromine are known to be present in soil (Fuge, 1988) as a result of marine derived aerosols being mobilized from the sea (Fuge, 1988; Sander

et al., 2003). Although elevated levels of brominated DBPs have been previously reported in coastal regions in the absence of wildfire (Richardson et al., 1999; Chow et al., 2007), other reports have demonstrated the presence of brominated DBPs following wildfire in coastal regions (Chen et al., 2020; Uzun et al., 2020a). This study, however, is the first to provide a comparison of ash-impacted source waters prepared with ash from coastal regions (i.e., chaparral and moorland) and non-coastal regions (i.e., grassland and montane) on the formation of brominated DBPs. Although comparatively investigating coastal and non-coastal regions was not anticipated in of the original objectives of this work, it is recognized that this finding is consequential, as brominated DBPs are of significant health concern. As such, monitoring for brominated DBPs after wildfire in coastal regions should be considered to ensure they may be managed appropriately if present in high levels.

Overall, the results indicated that there were limited reductions in DOC following conventional chemical pre-treatment, regardless of the physiographic region from where wildfire ash originated. This result was expected due to post-fire DOC being recalcitrant to removal by conventional treatment due to shifts in carbon character and other water quality parameters which impacts coagulation efficacy (i.e., alkalinity and pH), which has been previously demonstrated in wildfire-impacted water (e.g., Chapter 3; Hohner et al, 2017). The limited reductions in DOC are likely attributable to changes in functionality and aromaticity of the carbon after wildfire (Gonzalez-Perez et al., 2004; Knicker et al., 2006; Knicker et al., 2007). The higher proportion of LMW carbon species may have also impacted the limited efficacy of DOC reduction, as LMW carbon compounds are known to be recalcitrant to removal through coagulation (Edzwald, 1993; Quang et al., 2015; Zhao et al., 2009). Other parameters, such as high alkalinity, also likely reduced the efficacy of DOC removal by coagulation by precluding shifts toward lower pH after coagulant addition, where lower pH levels are required to promote optimal DOC removal through coagulation (Crittenden et al., 2012). Thus, the multiple water quality parameters which shifted as a result of severe wildfire likely collectively led to the ineffective removal of DOC by ultimately precluding complexation of dissolved organic matter with metal hydroxide species or the direct adsorption of organic matter onto the surface of precipitated metal hydroxide solids (Ghernout et al., 2009). Given this, it was further anticipated that DBP formation potential in ash-impacted source waters representative of physiographic regions with different predominant vegetation types would be variable due to differences in DOC character and concentration. Despite these differences, TTHM and HAA5 yields after coagulation were very similar regardless of ash origin, indicating that the character of the DOC remaining in solution after coagulation may also be very similar—this was not surprising given that most of the DOC in the ash-impacted source water samples was a result of leaching from of pyrogenic materials derived from vegetation biomass and other forest floor materials, which are more similar to each other in composition relative to other sources of DOC (e.g., anthropogenic contaminants, municipal waste, etc.).

5.5 Conclusions and implications

The key conclusions of this study were:

(1) Wildfire ash runoff from hillslopes to receiving waters after severe wildfire may deteriorate source water quality (i.e., increase DOC concentration and alter DOC character) and challenge physico-chemical drinking water treatment more so than after moderate severity wildfire, while turbidity reduction appears readily achievable irrespective of burn severity;

(2) Low molecular weight (LMW) carbon compounds that are difficult to remove by coagulation were relatively elevated after severe wildfire ash addition to water (this observation was consistent with previous reports, Chapter 3);

(3) The delivery/addition of post-fire ash after severe wildfire in different physiographic regions (i.e., chaparral, moorland, grassland, montane) to the same source water resulted in very similar water quality impacts (i.e., increased turbidity, increased DOC concentration, increased UVA_{254}), though the magnitudes of those impacts differed when normalized to mass of ash. Despite these differences, the TTHM and HAA5 yields after coagulation were very similar (i.e., all yields were within 16% and 14%, respectively), regardless of ash origin. Thus, the character of the DOC remaining in solution after coagulation was also very similar, regardless of ash origin after wildland fire, and excellent linear correlation was observed between TTHM and HAA5 formation potentials and DOC concentration;

(4) Although UVA_{254} was generally consistent between the wildfire-impacted source waters prepared with the ash from the various physiographic settings, the resulting DOC concentrations varied considerably (see Figure 5.8) as did the DOC yield per gram of ash, thereby underscoring that ash mobilization is likely to have different impacts on receiving water quality and treatability that vary regionally depending on the setting. Water quality varies as a result of landscape characteristics including land cover, land use, land management, atmospheric deposition, geology and soil properties, climate, and topography. Catchment hydrology, which is strongly influenced by climate (e.g., rainfall intensity and duration, mean annual rainfall, temperature, evapotranspiration rates), geology (susceptibility of soil/bedrock to erosion/weathering, soil/bedrock nutrient content, soil/aquifer conductivity, soil sorption capacity), and soil type, can also play a significant role in the delivery of pollutants to receiving waters. Each of these characteristics involves several different factors that can contribute to observed water quality responses;

(5) Ash from wildfire in coastal regions is more likely to contribute to the formation of brominated DBPs, presumably due to the presence of bromide from atmospheric aerosols that deposit on vegetation; and

(6) Consistent with previous reports (Chapters 3 and 4), sufficient reductions in turbidity could be achieved irrespective of the physiographic region from where ash originated.

Chapter 6:

Preparing for and responding to wildfire impacts on drinking water treatment: A framework for risk management and adaptation

6.1 Summary

Wildfire threats to drinking water supplies are exacerbated by changing climate and are increasing globally. Although the impacts of wildfire on drinking water source quality may be episodic and relatively short-lived following major runoff events, long-term impacts may persist for several years following severe wildfire in some physiographic settings. Wildfire-associated shifts in source water quality can adversely impact drinking water treatment, especially when utilities are not prepared to manage and respond to more variable, episodically more-deteriorated source water quality. Although source water quality impacts of wildfire can range from none to severely deteriorated, and can vary substantially between regions, the major threats to drinking water treatment after wildfire on the natural landscape are universal. Critically, they include elevated levels of fine suspended solids/turbidity and organic carbon (which is often also more aromatic after wildfire), which are the main water quality drivers of drinking water treatment infrastructure design and operation. Source water alkalinity and pH can also be affected by wildfire—this is notable because collectively with dissolved organic carbon (DOC) and turbidity, they drive coagulant dosing requirements and chemical pre-treatment (i.e., coagulation, flocculation, clarification) performance prior to subsequent advanced oxidation (if relevant), filtration, and disinfection. Post-fire water quality may also be impacted by increases in fine sediment-associated bioavailable phosphorus, which can be released to the water column, promoting the proliferation of potentially toxin-forming cyanobacteria and other nuisance algae. Especially relevant to systems reliant on raw water storage reservoirs, these impacts may not occur immediately after wildfire and may persist for decades or longer in some regions. Additional source water quality concerns include sediment-associated polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), especially from urban landscapes, which can also release other anthropogenic organic contaminants from the built environment (e.g., benzene from distribution system pipes) to water supplies. While wildfire impacts on source water quality and drinking water treatment have been described, a framework that integrates (1) changes in source water quality and (2) understanding of the potential treatment implications of those changes to inform watershed- and plant-scale operational response strategies is not currently available. As such, the objective of this work was to synthesize the available scientific literature and industry reports to develop a framework to detail watershed- and plant-scale operational response actions for describing and mitigating the potential impacts of wildfire on drinking water treatment to ultimately enable risk management, operational resilience, and climate change adaptation planning for drinking water utilities in fire-prone regions.

6.2 Introduction

Wildfire is an increasingly significant threat to drinking water supplies globally, where the impacts to source waters originating in forested headwaters are being experienced with greater frequency (Bladon et al., 2014; Emelko et al., 2011; Robinne et al., 2016). Climate change has undermined water management by rendering the critical and historically reliable, basic assumption of stationarity—the idea that variability in natural systems does not change over time—is no longer valid (Koster et al., 2017; Milly et al., 2008); this has led to the inability to predict the potential implications of wildfire and other climate-exacerbated landscape disturbances on water sources. As such, drinking water utilities must adapt to changing climatic conditions, which are expected to increase in frequency in the future (Chikamoto et al., 2017; Westerling et al., 2006). Adaptation measures for drinking water systems in wildfire-prone regions must include increased resiliency, which is the capacity to maintain a system and recover operational processes following disturbance (McWethey et al., 2019). Improving the resiliency of water treatment plants (WTPs) in fire-prone regions will prepare utilities for managing the risks associated with wildfire; however, attempting to improve resilience requires planning and dedicated resources (e.g., financial, and human). Many WTPs may not be adequately prepared to manage extreme shifts in water quality that surpass design thresholds and may benefit from implementing strategies to identify and/or manage deteriorated water quality post-fire (Emelko et al., 2011) so that the potential for service disruptions or outages is reduced.

For effective management of risks to drinking water treatment, a holistic approach that integrates both watershed/forest management and in-plant treatment strategies for increasing resilience in the ability to provide safe drinking water is expected to be the most effective (Emelko & Sham, 2014). Relatively little guidance for managing wildfire risks to drinking water treatment exists. An evaluation of post‑fire water contamination risks from mobilized sediments and focused on landscape erosion mitigation and discussed several potential approaches for mapping dominant sediment and associated contaminant transport pathways to contribute to describing the delivery of eroded solids from the landscape to receiving waters after wildfire provides an important first step; however, it did not speak to changes in non-sediment water quality impacts of wildfire such as DOC, which is a key driver of the need for and operation of critical chemical pre-treatment (i.e., coagulation) processes, and only indicated that in-plant treatment could be modified, but did not indicate the types of modifications that might be required (as indicated in Figure 6.1; Nunes et al., 2018). While other investigations have linked wildfire effects on water quality to implications for drinking water treatment challenges and in-plant mitigation (Emelko et al., 2011; Becker et al., 2018) or distribution system contamination (Tran et al., 2021), coupled watershed and in-plant treatment planning and mitigation of wildfire impacts on the provision of safe drinking water has not been reported to date. Thus, although wildfire impacts on source water quality and drinking water treatment have been described,

a framework that integrates (1) changes in source water quality and (2) understanding of the potential treatment implications of those changes to inform and prioritize specific watershed- and plant-scale operational response strategies is not currently available. As such, the objective of this work was to develop a framework to provide details of watershed- and plant-scale operational response actions for describing and mitigating the possible impacts of wildfire on drinking water treatment to ultimately enable risk management, operational resilience, and climate change adaptation planning for drinking water utilities in regions prone to wildfire.
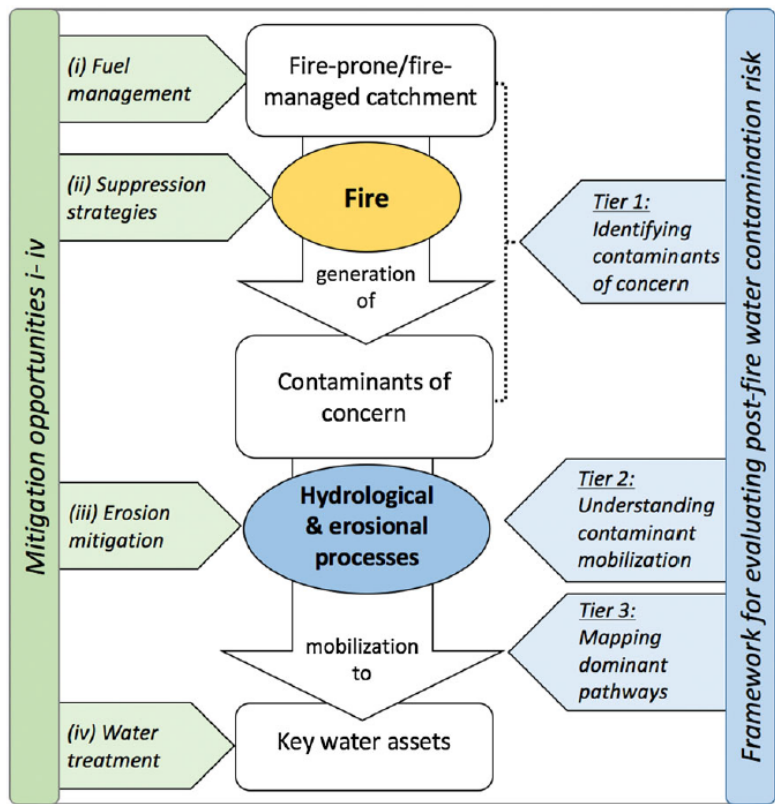
Figure 6.1: Framework for evaluation of post‑fire water contamination risks from mobilized sediments and identification of mitigation strategies (Nunes et al., 2018).

6.3 Approach

To develop a framework that details watershed- and plant-scale operational response actions so that drinking water utilities can prepare for and respond to potential impacts of wildfire on drinking water treatment, the scientific and applied literature was reviewed. Three practice areas were identified. These were:

(1)   Identification of potential wildfire-associated changes in source water quality;

(2)   Description of the drinking water treatment implications of wildfire-associated changes in source water quality; and,

(3)   Identification of watershed- and plant-scale operational response actions for describing and mitigating the potential impacts of wildfire on drinking water treatment.

The first two areas have been previously discussed in the literature. The key focus of this work was to address the third practice area by linking the first two areas to identifying priority watershed- and plant-scale operational response actions that can be implemented to identify and mitigate wildfire impacts on drinking water treatment in fire-prone regions. The operational response actions involve either monitoring and mitigation. A goal of the framework was to provide a rationale for these actions so that utilities may prioritize them based on system-specific needs. Critically, the framework includes actions relevant to either the source watershed or the water treatment plant that focus on not only ensuring technological capability (i.e., can the water be sufficiently treated?), but increasing operational resilience (i.e., are water managers and plant operators well-positioned to make decisions and best respond to deteriorated water quality events based on the combination of watershed management and treatment plant information and technologies available?).

The available scientific (i.e., academic research) and grey (i.e., professional conference) literature was reviewed and scientific and operational insights associated with proactive and reactive measures in response to water quality change were identified, organized, and synthesized. Wildfire impacts on water quality and their associated implications to drinking water treatability were evaluated according to the approach discussed by Emelko et al. (2011), which is summarized in Figure 6.2 below. Additional information regarding watershed-scale evaluations, reservoir management, and distribution system considerations was evaluated so that the developed framework would reflect wildfire impacts on water quality and treatability from source to tap. The available scientific and experiential knowledge was organized by area of impact (i.e., source water/watershed [including reservoir] or treatment plant) and action type (i.e., monitoring or mitigation), as linked to treatment implications. The identification of specific actions that enhance operational response capacity was the focus of the investigation. Operational response capacity was defined

herein as the ability to both identify the impact (e.g., source water quality change) and manage the consequence(s) (e.g., water supply or treatability challenge) of watershed disturbance (i.e., wildfire). The operational response actions were further categorized as proactive or reactive, and corresponded to actions that could be undertaken prior to or in response to watershed disturbance by wildfire. This framework can be especially useful for evaluating innovative or less common operational responses such as the techno-ecological nature-based solutions such as shown in Figure 6.3, which can be especially relevant for increasing operational response capacity in small systems that are often situated in rural and remote areas (Blackburn et al. 2021). For example, classical biological filtration might be implemented to increase removal of recalcitrant LMW fractions of DOC (Krzeminski et al., 2019; Kirisits et al., 2019). The selection of treatment technologies in these systems is necessarily case-specific (Blackburn et al. 2021) and thus would be advanced by guidance for linking process selection to actions for enhanced operational response capacity. Recognizing that some wildfires may have no measurable or operationally significant impacts on water quality and treatability is a further critical consideration; however, defining operational significance of disturbance impacts is necessarily case-specific and beyond the scope of the present investigation.

Impact on Treatment	Parameter					
	Turbidity	TP	DON and TKN	Hg	DOC	Chl.-a
Need for solids removal (C/F/S)	✔	✔			✔	✔
↑ Coagulant demand	✔				✔	✔
↑ Sludge production	✔				✔	✔
↑ Oxidant demand	✔		✔		✔	✔
↑ DBPs	✔		✔		✔	✔
↑ Fluence required for UV			✔		✔	✔
↑ microcystins		✔				✔
↑ Taste and odor concerns			✔		✔	✔
Compliance concerns	✔		✔	✔	✔	✔
↑ Operating costs	✔	✔	✔	✔	✔	✔

Figure 6.2: Water quality parameters impacted by wildfire and their potential implications to drinking water treatability (Emelko et al., 2011).

Figure 6.3: Framework for evaluation of green attributes of water supply, treatment, and distribution technologies often prioritized for use in rural and remote areas (Blackburn et al., 2021).

6.4 Results and Discussion

A simple framework was developed so that it concisely (i.e., on one page) connects source water quality to drinking water treatability impacts for the major treatment processes commonly associated with surface water treatment (Figure 6.4). Source water/reservoir and treatment plant monitoring and mitigation actions are then highlighted so that planners, managers, and operators can quickly access the relevant and current operational and scientific literature to inform decision-making. The sections below detail the main elements that comprise these specific actions.
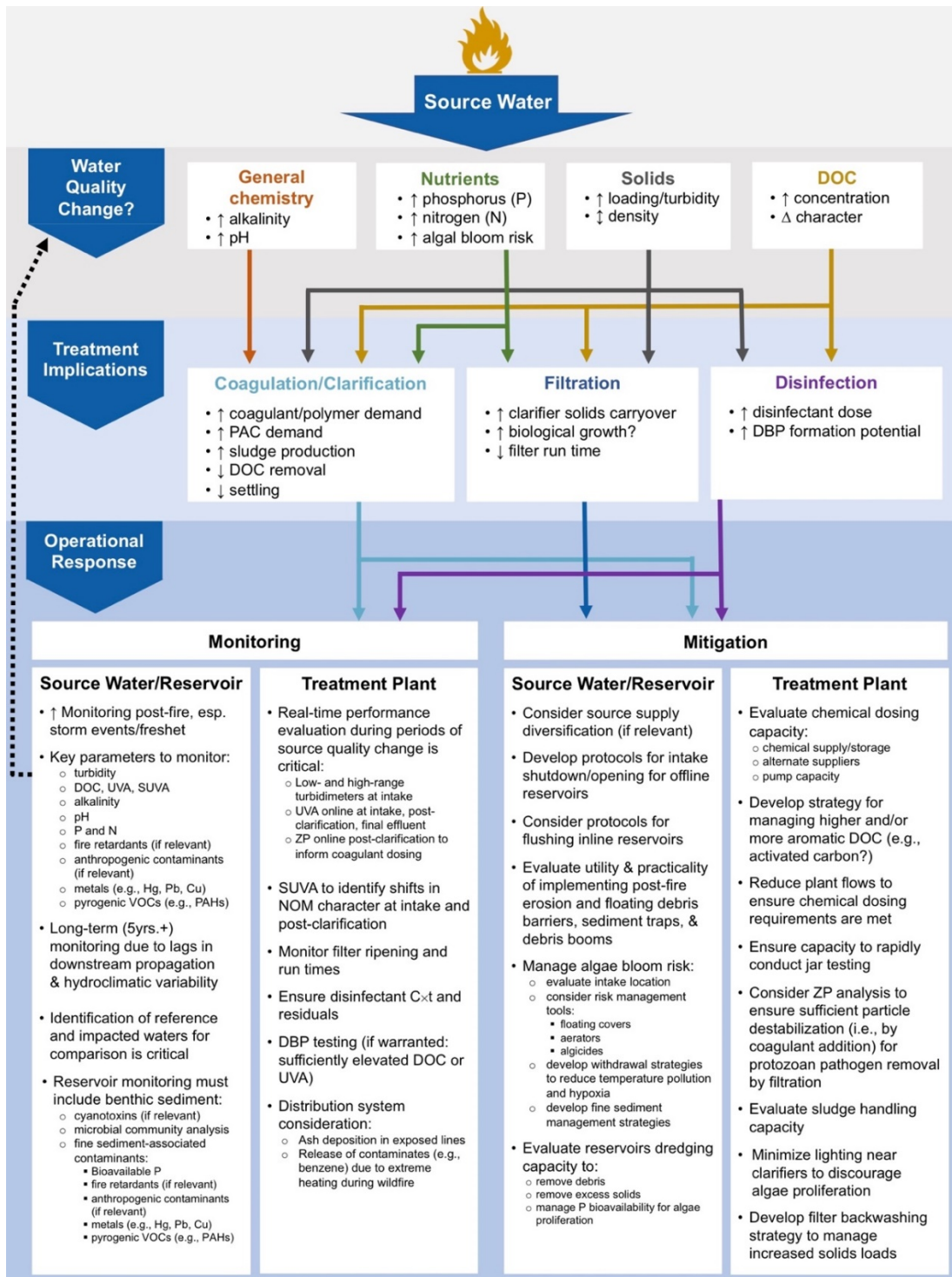
Figure 6.4: Proposed framework for adapting to and managing risks to source water quality in fire-prone regions. Three key categories are provided: the identification of the potential impacts of wildfire on source water quality; the impacts of post-fire shifts in water quality on treatment processes; and, operational response actions, specifically monitoring and mitigation strategies, which may be implemented to ensure utility preparedness for managing post-fire water quality and improving treatment system resilience.

6.4.1 Water quality change and treatment implications

Conventional drinking water treatment is composed of coagulation, flocculation, clarification (typically sedimentation), filtration, and disinfection processes. "Chemical pre-treatment" (i.e., the combination of coagulation, flocculation, and clarification processes), is the cornerstone of conventional drinking water treatment. As described by Crittenden et al. (2012), coagulation is designed to destabilize or "condition" suspended, colloidal, and dissolved matter in water by the addition of chemical coagulant(s) so that it can be subsequently flocculated and then removed from the water column. This material includes particles (minerals, clays, algae, etc., typically measured as turbidity), pathogens, and natural organic matter (NOM). By removing NOM, color and disinfection by-product (DBP) precursors are removed, and UV transmittance can be increased to improve the efficiency of UV disinfection. As described by Pernitsky and Edzwald (2006), coagulants remove dissolved-phase NOM by complexation reactions and then a phase change, so that the NOM either forms a solid or adsorbs onto a solid. Flocculation is the aggregation of (i) destabilized particles and (ii) precipitates formed as a result of coagulant addition into larger particles or "flocs," which are subsequently removed by gravity separation during sedimentation and/or physico-chemical, granular media filtration. The objectives of the coagulation process (e.g., turbidity removal, floc filterability, NOM removal) depend on the suspended, colloidal, and dissolved organic constituents that comprise water quality. Coagulation of water that contains both particles and NOM is complicated because several aspects of water quality contribute to process efficiency. Specifically, pH, alkalinity, and temperature, collectively affect (1) the surface charge of suspended particles/pathogens (i.e., turbidity), (2) the charge of NOM functional groups, (3) the charge of the dissolved-phase coagulant species, (4) coagulant solubility, and (5) the surface charge of flocs (Pernitsky and Edzwald, 2006). In general, lower pH (5-7) is better for ensuring coagulation performance because the coagulant demand of NOM is much higher at high pH. Elevated alkalinity may complicate coagulation further because it can preclude the ability to adjust pH during treatment (Crittenden et al., 2012). Thus, when both alkalinity and pH are elevated, a high coagulant dose or acid addition is required to reduce pH and enable effective coagulation.

As mentioned above, effective coagulation destabilizes suspended particles thereby enabling their removal during physico-chemical, granular media filtration. Critically, filtration is not a size exclusion process; it removes particles and pathogens because the electrostatic repulsion between them and filter media is overcome by coagulant addition that destabilizes particles and enable their deposition in the filters, thereby removing them from the water (Amirtharjah, 1988; Edzwald, 2011). In addition to serving as a polishing step for removing fine particles remaining in suspension after clarification, filtration is a critical barrier in the removal of waterborne enteric protozoan pathogens, including Cryptosporidium spp. and Giardia spp. (Crittenden, 2012).

In Canada, health-based turbidity limits have been established for different filtration technologies described in the Guideline Technical Document on enteric protozoa in drinking water (Health Canada, 2019) to help ensure that systems meet the minimum levels of pathogen removal required to protect public health. Analogous to the suite of Surface Water Treatment Rules in the United States (Federal Register, 1989), Health Canada (2012) indicates that "conventional and direct filtration systems should strive to achieve a treated water turbidity target of less than 0.1 NTU at all times". When this is not achievable, treated water turbidity from individual filters that is less than or equal to 0.3 NTU in at least 95% of measurements either per filter cycle or per month, and never to exceed 1.0 NTU is considered acceptable and thus, sufficiently protective of public health. The target of individual filter effluent turbidities less than 0.1 NTU and the upper threshold value of 0.3 NTU in at least 95% of measurements were set to indicate "well-operated" treatment and associated enteric protozoan pathogen removal expectations and the 1.0 NTU threshold was set to minimize the potential downstream interference to disinfection from elevated turbidity (Health Canada, 2012). After solids and other sources of oxidant demand (e.g., organics) have been sufficiently removed from water by chemical pre-treatment and subsequent filtration, any microorganisms remaining in the water are inactivated during primary disinfection, which typically involves the application of oxidants such as chlorine; thereafter, treated water in the distribution system maintains a disinfectant residual through secondary disinfection (Crittenden, 2012).

6.4.1.1 Wildfire impacts on water quality

Wildfire impacts on source water quality can range from none to severe deterioration. Major post-fire runoff events may lead to debris flows (Santi et al., 2008; Staley et al., 2014) in which massive amounts of post-fire material are mobilized from the landscape into receiving waters (Lyon & O'Connor, 2008; Sham et al., 2013). Significant amounts of sediment, (Kunze & Stednick, 2006; Silins et al., 2009) nutrients, (Bladon et al., 2008; Ranalli, 2004; Silins et al., 2014, Rhoades et al., 2019), heavy metals, (Kelly et al., 2006; Wolf et al., 2008) and other contaminants (Crouch et al., 2006; Kalabokidis, 2000) may be released to receiving waters as a direct result of wildfire. Dissolved organic carbon, including DBP precursors, can be elevated after wildfire (Emelko et al., 2011; Chen et al., 2020; Hohner et al., 2017; Uzun et al., 2020b); DOC can also be more aromatic (Uzun et al., 2020b). While most of these impacts are episodic and short-lived after major runoff events, typically lasting for a day to a week (Dahm et al., 2015; Leak et al., 2003; Lyon & O'Connor, 2008; Mast et al., 2016; Murphy et al., 2015; Writer & Murphy, 2012), they can nonetheless propagate downstream and last for decades in some cases (Emelko et al., 2016; Stone et al., 2014), leading to more variable source water quality (Stone et al., 2011). Increased variability and deterioration in source water quality can substantially challenge water treatment operations (Emelko et al., 2011; Hohner et al.,

2017) and increase treatment costs (Emelko et al., 2011; Price et al., 2017), though notably, recent work suggests that some wildfire-associated pollutants that are released from wildfire ash (e.g., DOC) are general consistent in composition, but not amount released across physiographic regions (Chapter 5).

6.4.1.2 Wildfire impacts on water quality and treatability

DOC. Following wildfire, elevated levels of DOC and ultraviolet absorption at 254nm (UVA$_{254}$), have been reported immediately after major runoff events, with DOC levels recorded in excess of 20 mg·L^{-1} (Emelko et al., 2011; Writer & Murphy, 2012). Such extreme levels, however, are only expected after major runoff events, which are episodic, short-lived, and are generally only anticipated after the first post-fire flush events (Clark, 2010; Minshall et al., 2001; Olivares et al., 2019; Writer & Murphy, 2012). Elevated levels of DOC have also been reported for extended periods following wildfire, where DOC levels were elevated in burned catchments for several years when compared to unburned catchments (Emelko et al., 2011). High DOC concentrations post-fire can impact coagulation-flocculation-clarification and require higher coagulant doses to remove DOC (Emelko et al., 2011).

In addition to high levels of DOC, the character of organic carbon may also shift after wildfire. For instance, DOC is often more aromatic following wildfire (Olefeldt et al., 2013; Uzun et al., 2020a) as indicated by elevated UVA$_{254}$ levels. Specific ultraviolet absorption (SUVA) is also a useful parameter for estimating the content of aromatic carbon (Weishaar et al., 2003) and has been used to demonstrate increases in the aromaticity of DOC in source waters impacted by wildfire (Hohner et al., 2016). Additional changes in DOC character following wildfire include the loss of side-chains and shifts in functionality, which may reduce the efficacy of DOC removal through coagulation-flocculation (Almendros et al., 1992; Chen et al., 2020; Knicker et al., 2007). Shifts in DOC toward lower molecular weight (LMW) species have also been observed after wildfire (Cawley et al., 2017; Hohner et al., 2016), and have also been reported in source water conditions representative of wildfires in different physiographic regions (Chapter 5).

As a result of increases in DOC concentrations and changes in DOC character post-fire, conventional chemical pre-treatment may require additional techniques to remove DOC following wildfire, such as the addition of powdered activated carbon (PAC) to adsorb DOC, or the use of cationic polymers to aid in effective floc formation (Chapters 3 and 4). High levels of DOC may also lead to reduced filter run times (Eikebrokk et al., 2004; Health Canada, 2020), which may be problematic following wildfire, where DOC may be considerably elevated (Emelko et al., 2011). Elevated levels of DOC also exert increased chemical oxidant demand to ensure pathogen inactivation can be effectively achieved (Crittenden et al., 2012).

Furthermore, the presence of high levels of DOC in source water after wildfire may lead to an increased potential of carbonaceous DBPs to form during disinfection (Emelko et al., 2011; Hohner et al., 2016).

Turbidity. Elevated levels of solids (i.e., turbidity) in source waters have been well documented following wildfire, where major runoff events post-fire may result in episodic degradation of source waters, leading to turbidity levels >1000 NTU (e.g., Emelko et al., 2011; Emmerton et al., 2020; Neary et al., 2005; Writer & Murphy, 2012). Such extreme turbidity events have been associated with debris flows after severe wildfire where massive amounts of material are mobilized from the landscape into receiving water bodies (Dham et al., 2015; Sham et al., 2013; Smith et al., 2012). While extreme levels of turbidity may be short-lived following major runoff events, long-term impacts on elevated solids have also been reported, where suspended solids have remained elevated in burned catchments years after a wildfire had occurred (Silins et al., 2009).

In addition to higher levels of solids being generated in post-fire conditions, the physical characteristics of solids remining after wildfire may be less dense and have lower settling velocities (Clark, 2014; Stone et al., 2011), which may float on the surface of the water and may not be removed by conventional chemical pre-treatment. Low-density material may remain on the surface of water in clarification basins and/or accumulate on the sides of basins, requiring basins to be thoroughly cleaned following treatment of post-fire source water (Chapter 4). If optimal coagulation cannot be achieved, increased solids loading is likely to occur on filters (Becker et al., 2018). Ineffective reductions in turbidity through coagulation-flocculation, may also lead to increased chlorine demand and reduced efficacy of chlorination, as high turbidity can shield microorganisms from chemical oxidants (LeChevallier et al., 1981; NHMRC, 2011). Effective coagulation-flocculation adversely impacted by elevated turbidity following wildfire may also lead to high sludge volumes (Emelko et al., 2011).

Alkalinity and pH. Source waters impacted by wildfire can also demonstrate shifts in both pH and alkalinity, both of which are key water quality parameters that impact the efficacy of coagulation-flocculation. Following wildfire, the pH of source waters may increase (e.g., Bodí et al., 2014; Harper et al., 2019; Pereira et al., 2012) and elevated levels of alkalinity may be present (e.g., Chapters 3, 4 & 5; Cerrato et al., 2016; Earl & Blinn, 2003; Hohner et al., 2018). The increase of both alkalinity and pH in source water is a result of alkaline post-fire material on the landscape entering water bodies where dissolution of base cations and carbonates may occur (Bodí et al., 2014; Lydersen et al., 2014). When both alkalinity and pH are elevated, a high coagulant dose or acid addition is required to reduce pH and enable effective coagulation (Pernitsky & Edzwald, 2006).

Nutrients. Post-fire source waters often have elevated levels of nutrients, such as phosphorus (P) and nitrogen (N) (Bladon et al., 2014; Lane et al., 2008; Rhoades et al., 2011; Silins et al., 2014). Total P concentrations in stream sediments, for instance, has been noted to remain 3–8 times higher in watersheds impacted by wildfire several years following the fire (Emelko et al., 2011). Similarly, the presence of N was found to be 4–5 times higher in burned watersheds in the first year after wildfire (Silins et al., 2016). Additionally, during high flow periods, high levels of nitrogenous species were found to be evident in the water column years after wildfire had occurred (Bladon et al., 2008). The occurrence of high levels of P and N in source waters can lead to an increased potential of eutrophication in freshwater systems following wildfire (Emelko et al., 2016; Silins et al., 2014; Santín et al., 2015) increasing the potential for algal blooms even years after a fire (Emelko et al., 2016; Silins et al., 2014). The potential of cyanobacteria growth has also been reported following landscape disturbance due to increased nutrient inputs (Charette & Prepas, 2003; Paerl & Huisman, 2008), which may occur in burned watersheds (Emelko et al., 2016).

Algae present in source water, resulting in high turbidity, may not be amenable to removal through conventional chemical pre-treatment, and require alternative forms of treatment, such as dissolved air flotation or contact clarification (Crittenden et al., 2012). The increased presence of algae in source water following wildfire may also lead to the presence of chemicals causing taste and odour issues (Emelko et al, 2011) or toxins, such as microcystin, produced by cyanobacteria (Paerl & Otten, 2013). These chemicals are generally not amenable to conventional chemical pre-treatment and would require additional measures, such as treatment with PAC (Donati et al, 1994; Ghernaout et al., 2010; Lambert et al., 1996). The possible implications of elevated nutrients after wildfire may not pose immediate challenges for the provision of potable water, as in the case with elevated turbidity or DOC following debris flows, but rather may have impacts which are manifested many years after a fire.

Other contaminants. Contaminants other than those discussed above may be present in impacted source waters after wildfire, including metals (Kelly et al., 2006; Wolf et al., 2008) and polycyclic aromatic hydrocarbons (PAHs) (Norwood et al., 2013; Santín et al., 2015; Vergnoux et al., 2011). In addition to naturally occurring contaminants post-fire, synthetic chemicals, such as fire retardants, also may be found (Crouch et al., 2006; Kalabokidis, 2000). When wildfire occurs on the urbanized landscape, numerous anthropogenic contaminants including various products of pyrolysis and combustion may be released to both source and treated water supplies. For example, the recent devastation in the United States that resulted from the 2017 Tubbs Fire in Sonoma and Napa Counties in California and the 2018 Camp Fire in Butte County, California underscored the risks that wildfire poses in wildland–urban interfaces in which combustion and pyrolysis of the built environment can lead to hazardous chemical (e.g., benzene) contamination of water supplies isolated in buried distribution networks (Isaacson et al., 2021; Macler et

al., 2020; Proctor et al., 2020). Distribution system water quality impacted by wildfire may also be contaminated due to the back-siphonage of smoke, ash, and soot due to loss of system pressure (Macler et al., 2020). Accordingly, onsite reconnaissance is critical for identifying the range of potential contaminants that may be delivered to both source and treated water supplies after wildfire on the urbanized landscape— an exhaustive list of potential contaminants is beyond the scope of the present framework.

6.4.2 Operational response in fire-prone regions

The effective implementation of operational responses in fire-prone regions will aid utilities in preparing for and responding to the potential impacts of wildfire on drinking water treatment. There is an array of measures which may be employed by utilities to manage risks associated with deteriorated water quality following wildfire. The following sections provide details of the operational response strategies that may be applied, where two key components are identified: (1) monitoring, which is necessary to identify potential shifts in post-fire water quality; and (2) mitigation strategies, which inform what may done to respond to changing water quality conditions.

6.4.2.1 Source water monitoring

Water quality monitoring strategies for source waters and reservoirs are needed to inform (i) any water quality shifts following wildfire and (ii) drinking water treatment process optimization in response to changing water quality. Monitoring activities should be augmented following wildfire, especially following major runoff events, such as storms and snow melt (i.e., freshet), where quality can be expected to shift rapidly in the first- or second-year following wildfire (Sham et al., 2013; Writer & Murphy, 2012). Increased source water monitoring after wildfire is especially important due to the shifts in stream flows which may impact water quality (Emelko et al., 2011; Sham et al., 2013).

Watershed monitoring activities should include increased testing for general water quality especially key drivers of drinking water treatability, including turbidity, DOC, UVA_{254}, alkalinity, and pH. Additionally, monitoring SUVA will provide an indication of potential shifts in the aromaticity of organic carbon in post-fire source waters, which can impact the efficacy of DOC removal during coagulation (Edzwald & Tobiason, 1999). Increased water quality monitoring for nutrients (e.g., N and P), is particularly important for reservoirs and can indicate if source water conditions are conducive to algal proliferation and, therefore, the potential for toxins and/or taste and odor compounds (Emelko et al., 2011). Additional parameters which should be monitored for are heavy metals, such as mercury (Hg), lead (Pb), copper (Cu), and chromium (Cr) as they can be elevated in post-fire source waters (Abraham et al., 2017; Emelko et al., 2011; Kelly et

al., 2006; Wolf et al., 2008) and may have adverse health impacts if not effectively removed during treatment. Carbonaceous by-products formed as a result of high heating temperatures, such as PAHs, may also be present following wildfire (Ferrer et al., 2021; Knicker et al., 2007) and should be monitored as they can pose a health concern as they are potentially carcinogenic (Menzie et al., 1992). Monitoring for anthropogenic chemicals, such as fire suppression compounds, should be considered if such chemicals were used in the vicinity of source waters (Crouch et al., 2006; Kalabokidis, 2000).

Long term monitoring programs (i.e. >5 years) should be implemented as lags in downstream propagation of deteriorated water conditions, including elevated levels of sediment, nutrients, and DOC, may not be evident immediately following a wildfire but manifested many years later (Emelko et al., 2016; Silins et al., 2014). Additionally, climate change related shifts in precipitation intensity and frequency can substantially impact streamflow conditions (Koster et al., 2017) and the intermittent impacts of wildfire on source waters may oscillate between wetter and drier years. Monitoring programs should necessarily run for multiple years to account for this hydroclimatic variability; they should also include the monitoring of reference (i.e., unimpacted) regions and receiving waters to enable comparison between burned and unburned catchments—these approaches are commonly referred to as paired catchment studies (Emelko et al., 2011; Silins et al., 2014; Silins et al., 2016). While protocols for reference site selection and paired catchment study design are beyond the scope of the present investigation, further information is widely available in the broader forest hydrology and watershed science literature (Neary et al., 2016; Brown et al. 2005; Underwood et al. 1992).

Reservoir monitoring of benthic sediment is an essential component of post-fire monitoring strategies if reservoirs are used for source water storage. Large quantities of sediment may be mobilized from landscapes and transferred into reservoirs following wildfire which would increase the likelihood of sediment-associated contaminants in reservoirs, such as bioavailable P or heavy metals (Emelko et al., 2011; Emelko et al, 2016). Notably, relatively small fractions of the landscape can release significant amounts of fine sediment and associated contaminants (Stone et al., 2014). Recently, a new framework for modelling fine sediment transport in rivers was developed to include Flocculation to inform reservoir management in wildfire impacted watersheds (Stone et al. 2021). This framework emphasized that a critical limitation of most existing sediment transport models is that they incorrectly assume that the transport characteristics of fine-grained cohesive sediment can be described using the approaches for coarse-grained non-cohesive sediment to evaluate reservoir storage capacity—those are inappropriate because they ignore the fundamental tendency of fine sediment to flocculate (Stone et al., 2021). Modeling platforms that couple hydrologic models like SWAT with the Hydro Basin water quality model also suffer from the same important limitation of disregarding the flocculation process; in all such cases, the result is the

underprediction of fine sediment and associated contaminant concentrations in rivers and reservoirs (Stone et al., 2021). Recognizing that even relatively small amounts of fine sediment can result in substantial source water quality and treatability impacts (Stone et al., 2011, 2014, 2021; Emelko et al., 2016), consideration of those impacts is critical. Sampling bottom sediment in reservoirs with corers can be used to evaluate pre- and post-fire nutrient loading to the reservoir and provide an early indicator of algal blooms due to internal loading of phosphorus release from sediment to the water column. In the event an algal bloom occurs, microbial community sampling may be conducted to identify the algae or cyanobacteria species present (Crittenden et al, 2012). Additional testing for taste and odour causing compounds and cyanotoxins is recommended if algal blooms occur after wildfire (Emelko et al., 2011).

6.4.2.2 Treatment plant monitoring

Increased post-fire monitoring upstream of treatment plants will assist utilities in identifying possible short- and/or long-term shifts in water quality, providing an early warning mechanism so that treatment operators may adapt and respond to changing source water conditions. While monitoring upstream of a WTP is crucial to informing the impacts of wildfire on source waters, increased in-plant monitoring at WTPs is also necessary to ensure shifts in water quality can be effectively managed. Having online measuring equipment (i.e., telemetry) at various points throughout the treatment process is extremely useful as it provides continuous data and enables appropriate treatment responses. This is especially critical during periods of rapidly changing source water quality (Emelko & Sham, 2014; Martin, 2016). For instance, WTPs should be equipped with both low- and high-range turbidimeters on raw water intakes to monitor for rapid shifts in turbidity. Changes in turbidity provide a primary signal that coagulant dose must be changed so that solids and pathogens are removed though coagulation to provide optimal conditions for subsequent disinfection. Online monitoring for UVA_{254} at the raw water intake and on clarified water (i.e., after coagulation-flocculation-sedimentation) will provide information to operators on the efficacy of DOC removal during treatment. Additionally, including online zeta potential (ZP) following clarification provides a valuable tool for managing post-fire water quality as it informs optimal coagulant dose (Sharp et al., 2005) and can be used to manage water treatment during algae blooms (Henderson et al., 2008; 2010). Monitoring SUVA will provide information about any potential shifts in the aromaticity of DOC and inform expected efficacy of DOC removal by coagulation (e.g., Edzwald & Tobiason, 1999). Regularly testing for pH and alkalinity will also inform coagulant dosing and ensure optimal pH conditions are present so that effective coagulation can be achieved, especially in the event of rapidly changing source water conditions.

Monitoring filter ripening and run times if deteriorated water quality occurs after a wildfire will alert operators to potential inefficacies of conventional chemical pre-treatment, where high levels of solids may be carried over to filters. Also, increased testing of disinfectant residuals and disinfection conditions (i.e., $C{\times}t$ value) when shifts in water quality occur will ensure effective inactivation of microbial pathogens (Crittenden et al, 2012). Testing for DBPs should also be increased in cases of elevated DOC and/or UVA_{254} following wildfire due to their potential health implications (Li & Mitch, 2018). Increased water quality testing in distribution systems should also be considered if wildfire has directly impacted water piping. For example, increased testing for contaminants, such as benzene, is warranted due to water lines being impacted by extreme heating during wildfire (Proctor et al., 2020). In the event that water lines rupture during wildfire and are exposed to atmosphere, monitoring for particulate matter (e.g., turbidity) in a distribution system should also be conducted.

6.4.2.3 Mitigation strategies for source waters

While effective monitoring strategies are essential to characterizing the potential impacts of wildfire on source water quality and drinking water treatment processes, it is also critical that mitigation strategies are developed and implemented to respond to shifting water conditions post-fire. If source waters are adversely affected by wildfire, unities should identify alternative water source supplies, if relevant (Emelko & Sham, 2014; Martin, 2016). Having multiple source supplies available (i.e. source diversification) will eliminate the need for utilities to treat deteriorated water quality (e.g., Dahm et al., 2015; Writer et al., 2014). If no alternate sources are available, protocols should be developed for intake shutdown and opening procedures when post-fire shifts in water quality occur, where plant intakes should be closed for as long as possible to allow source water quality to improve. In cases where reservoirs are relied upon for water storage, offline reservoirs may have the option to close an intake from a water source (e.g., river); however, inline reservoirs, where a WTP draws water directly from a reservoir, may not be able to simply shut the source flowing into a reservoir. In such cases, strategies may be used where reservoir flow is managed to ensure deteriorated water quality may be permitted to pass through a reservoir (Feldbauer et al., 2020; Weber et al., 2017).

Major runoff events after severe wildfire may result in debris flows where massive sediment loading to reservoirs may occur, which can adversely impact water quality and reduce reservoir storage capacity (Emelko & Sham 2014; Miller & Yates, 2005; Moody & Martin, 2004; Sham et al., 2013). To mitigate the impacts of debris flows on reservoirs, post-fire erosion control measures may be required, such as sediment traps and riparian treatments (Emelko & Sham, 2014; Neary et al., 2005). Additional measures may be needed to prevent floating debris from entering a reservoir, such as floating debris barriers or booms (Sham et al., 2013).

Post-fire reservoir management strategies should include protocols for managing algal blooms. Selecting an appropriate offtake depth from a reservoir into a WTP can be an important factor in reducing potential contamination due to algal cells (Hrudey et al., 1999). Additional strategies include the installation of floating covers (Herman et al., 2017), the installation of aerator systems (California State University, 2008), or the use of algicides, such as copper sulfate, to control the growth of cyanobacteria, reducing the potential of toxins in reservoirs (Crittenden et al., 2012; Hrudey et al., 1999). Developing withdrawal strategies from reservoirs to reduce temperature and hypoxia (Feldbauer et al., 2020; Weber et al., 2017) can also be useful in preventing conditions conducive to the proliferation of algae in reservoirs.

The accumulation of post-fire sediment in reservoirs following debris flows will likely require dredging to remove excessive sediment from a reservoir (Martin, 2016; Sham et al., 2013). Removing sediment by dredging can have a range of benefits for reservoirs, including increased reservoir capacity and reducing bioavailable nutrients which may contribute to algae proliferation (Peterson, 1982). As such, utilities relying on reservoirs should develop protocols for dredging in post-fire conditions which may be implemented if substantial amounts of sediment enter a reservoir, thereby minimizing risks such as the proliferation of algae or reduced reservoir capacity.

6.4.2.4 Mitigation strategies for treatment plants

In addition to mitigation strategies being necessary to manage the risks of wildfire on water sources, in-plant strategies are also crucial to ensuring WTPs can be adequately prepared to manage deteriorated water quality and improve resilience of drinking water treatment systems. By having in-plant mitigation protocols, WTPs will be able to adapt to shifts in water quality and ensure that the provision of safe drinking water is uninterrupted in the event of shifts in source water quality.

Deteriorated source water quality after wildfire may lead to increases in chemical demand (e.g., coagulant, polymer, PAC, acid, disinfectant) to ensure water can be effectively treated (Emelko et al., 2011). It is therefore crucial that adequate chemical supplies are available to meet high dosing conditions, which will require coordination with chemical supply companies to guarantee demand may be met. Furthermore, identifying alternative chemical providers to ensure redundancy in supplies should be considered (Tran et al., 2021). Chemical dosing systems should be tested to identify the limits of dosing capabilities, such as maximum chemical pump output capacity. By ensuring chemical supplies are available and that dosing conditions can be achieved, utilities will be better prepared to respond to deteriorated source water quality post-fire (e.g., high turbidity and DOC) where high levels of treatment chemical will be required. Having strategies in place to reduce plant flow will aid in meeting chemical dosing demands during deteriorated water quality after wildfire as reduced flows allow for higher chemical doses be applied.

Developing treatment strategies for managing higher levels and/or more aromatic DOC may be required to ensure DOC can be effectively removed in post-fire source waters. Using PAC, for instance, has been demonstrated to be effective in reducing elevated levels of DOC in severely deteriorated wildfire ash-impacted water (Chapters 3 and 4). Enhanced coagulation strategies are also beneficial for reducing DOC where the pH conditions are adjusted during coagulation (Chapters 3 and 4).

Having laboratory protocols in place to manage rapid shifts in water quality will allow utilities to adapt to post-fire water quality. For instance, ensuring that protocols are in place to rapidly conduct jar tests will be beneficial in responding to shifts in water quality which may occur during severe water conditions (Stanford et al., 2014). Effective jar testing protocols will inform chemical dosing requirements required to achieve effective coagulation (ASTM, 2013). Implementing ZP analysis and having laboratory protocols in place to monitor ZP may provide a means to ensure sufficient particle destabilization (i.e., by coagulant addition) for effective flocculation and enteric protozoan pathogen removal by filtration (Hsu & Huang et al., 2002), as well as removing elevated levels of DOC, including DBP precursors (Sharp et al., 2005). Incorporating ZP into a strategy for managing coagulant dosing may also reduce the need for jar testing (Morfesis et al., 2009).

Elevated levels of solids in source water following major runoff events will lead to the production of high levels of sludge during coagulation-flocculation-sedimentation. A strategy is needed to manage elevated levels of sludge due to high solids loading (Emelko et al., 2011), where specific protocols should be developed for removing high levels of sludge from clarification basins (Becker et al., 2018). A means for disposal of high levels of sludge should also be considered by utilities, where typical management protocols (e.g., dewatering, off-site hauling) may be insufficient to remove excessive levels of sludge following wildfire.

While the proliferation of algae has been highlighted as a concern for reservoirs after wildfire, algal growth can be a problem inside WTP facilities due to elevated nutrient levels. The proliferation of algae in clarifiers, for example, may be mitigated by minimize lighting near clarifiers or filters. This can include the installation of light screens over windows to minimize natural light needed by algae to proliferate. Reducing the potential for algal growth inside a WTP facility by managing light availability will mitigate the possibility of toxic or taste- and odour producing compounds, safeguarding the provision of safe, high quality drinking water.

Lastly, developing protocols for managing filters is an important consideration. For instance, having filter backwashing procedures to manage increases solids loads will ensure that filters can be rotated effectively

in times of deteriorated water quality. Such strategies will ensure the continuous filter operation and mitigate potential disruptions in WTP flow due to filters being offline.

6.5 Conclusions and implications

The risk of wildfire to drinking water sources is expected to increase with climate change related variability in the intensity and frequency of precipitation which may have negative consequences for the provision of potable water. Limited reports exist of WTPs treating deteriorated water following wildfire (see Table D2), as such, there is little first-hand knowledge available to inform post-fire water treatment. The framework described herein is the first to provide operational response strategies for drinking water treatment in wildfire-prone regions, where details of watershed- and plant-scale actions for mitigating the potential impacts of wildfire on drinking water treatment are provided. Specifically, the suggested recommendations include:

- Increase monitoring of source water quality upstream of WTPs is necessary to identify possible shifts in source water quality following wildfire, especially at high flow conditions during which the greatest shifts in water quality are most likely to occur. Evaluation of source water turbidity, DOC concentration and character (i.e., UVA_{254}, SUVA), pH, and alkalinity is especially important to minimize sub-optimal coagulation, which can subsequently lead to (i) poor filtration performance (including poor filter ripening, shortened filter run times, and the increased potential for enteric protozoan passage into treated water) and (ii) increased oxidant demand during disinfection;

- Augment in-plant monitoring of clarified water and filter effluent for turbidity and organic carbon (DOC concentration, UVA_{254}, and SUVA) to ensure utilities are able to implement appropriate treatment measures and respond to rapid shifts in source in water conditions;

- Ensure that source water mitigation strategies are developed prior to wildfire to prepare utilities for managing potentially deteriorated conditions if wildfire impacts drinking water sources;

- Developing in-plant mitigation strategies will allow WTPs to adapt to shifts in water quality after wildfire and improve treatment resilience;

- Augmenting in-plant monitoring of turbidity, organic carbon (through DOC and UVA_{254} analysis), alkalinity, and pH is necessary, as these parameters drive coagulation and will enable utilities to respond to rapid shifts in source in water conditions and ensure effective coagulation. Additional monitoring of filter performance (e.g., filter run times; filter to waste times) and disinfection

efficacity (e.g., chlorine residual; C×t) are required, especially if effective coagulation is not achieved, leading to adverse impacts on filtration (e.g., high solids loading) and disinfection due to high solids carry-over;

- Developing strategies to mitigate changes on source water quality will enable utilities to control the water that enters a WTP (e.g., source diversification; intake management); prevent source water from becoming contaminated (e.g., reservoir flushing; erosion and debris control), and respond to unfavourable source water conditions (e.g., algae management; dredging). Source water mitigation strategies will minimize the impacts of wildfire on water quality (e.g., turbidity and DOC) before it enters a WTP, promoting conditions for effective coagulation; and

- Developing in-plant mitigation strategies will enable WTPs to achieve effective coagulation and DOC removal by having adequate chemical dosing capacity and appropriate laboratory protocols. Strategies to manage clarifiers (e.g., sludge handling; algae mitigation) and filters will permit WTPs to respond to shifts in water quality mitigate disruptions to plant flow.

The framework provided here may be implemented as a decision-support tool for utilities planning for the potential impacts of wildfire on source water. While there is not a single strategy for all situations and all utilities, this framework provides information which may be generally applicable to a range of treatment systems. However, solutions for managing post-fire source water quality changes must be tailored to the needs and capacities of individual systems, where source water quality, drinking water treatment processes, and response capabilities must be holistically considered to meet the specific needs of a utility.

Although this framework may be used as guidance for utilities, the implementation of monitoring and mitigation strategies in fire-prone regions will require significant planning and necessitate the coordination and collaboration with watershed and wildfire authorities. By including a range of monitoring and mitigation strategies in planning for deteriorated water quality due to wildfire, drinking water providers in fire-prone regions will augment operational response capabilities, increase resiliency of treatment plant systems, and ultimately safeguard the provision of adequate quantities of safe drinking water.

Chapter 7:

Conclusions, Implications & Recommendations

7.1 Conclusions & Implications

The overall goal of this research was to enable risk management, operational resilience, and climate change adaptation planning for drinking water utilities in fire-prone regions. The key conclusions and associated implications of this work are:

(1)   While there are many possible approaches for collecting and characterizing wildfire ash, collection (by sweeping) and sieving of burned vegetation and forest floor materials can be used to reflect material that directly runs off the landscape to receiving waters. This material can be added to natural water can be conducted to generate wildfire ash-impacted source water that reflects the runoff and direct delivery of these materials to receiving waters and consistently yields water quality (e.g., DOC concentration, turbidity) that is significant to drinking water treatability. Here, DOC concentration or UVA_{254} was proposed as a target for generating wildfire ash-impacted source water because DOC is a key driver of coagulant demand and a precursor of regulated DBPs. Simple visual assessment of burn severity was further proposed to differentiate between moderate and severe burn conditions, recognizing that no one wildfire will ever be homogeneous in its impacts on the landscape. While more detailed and quantitative ash separation and burn severity assessment methods are available, their application would be useful for mechanistic insight, but less informative for drinking water treatability assessments that are more realistic when they reflect that natural variability associated with the delivery of post-fire ash to source water, which is likely to reflect mixed severity burning conditions at the watershed-scale (Chapter 2);

(2)   Elevated levels of post-fire DOC and turbidity are highly uncertain and episodic; they are frequently associated with increases in stream flows, but cannot be predicted because of the multiple factors that impact source water quality change (Chapter 2);

(3)   Conventional chemical pre-treatment (i.e., coagulation/flocculation/sedimentation) and high-rate clarification systems can adequately reduce very high source water turbidity resulting from direct wildfire ash runoff from hillslopes to receiving waters after severe wildfire (i.e., from 100s to 1000s NTUs to the less than ~3 NTU needed for efficient subsequent filtration) (Chapters 3 and 5). This ability to reduce extremely elevated turbidity resulting from post-fire ash delivery/addition to source water as consistently observed using several pre-treatment approaches (conventional, sand ballasted flocculation [SBF], SBF with enhanced coagulation, and SBF with PAC) (Chapters 3, 4, and 5) and appears independent of ash origin/burned vegetation type and wildfire severity (Chapter 5);

(4)   Shifts in post-fire pH, alkalinity, and dissolved organic carbon (DOC) concentration and character contribute to extremely high coagulant dosing requirements when wildfire ash severely deteriorates source water quality. While recognition of these potential impacts of severe wildfire on source water quality is not surprising, the chemical pre-treatment impacts and associated coagulant addition requirements that can result from these collective source water quality changes has not been previously documented. Here, it was demonstrated that they can comprise significant treatment challenges associated with DOC removal/carbonaceous disinfection by-product (DBP) precursor removal during conventional chemical pre-treatment and high-rate clarification by sand-ballasted flocculation (SBF), SBF with enhanced coagulation, and PAC pre-treatment with subsequent SBF (Chapters 3, 4 and 5);

(5)   Low molecular weight (LMW) carbon compounds that are difficult to remove by coagulation and various SBF approaches including powdered activated carbon (PAC) pre-treatment with subsequent SBF were relatively elevated after wildfire ash addition to water (Chapter 3, 4, and 5) and may especially contribute to coagulation challenges after direct delivery of wildfire ash to source water;

(6)   PAC pre-treatment with subsequent SBF not only effectively reduced turbidity levels in severely deteriorated wildfire-ash impacted water, but also reasonably reduced DOC concentration and UVA_{254}, as well as THM- and HAA- formation potentials at both bench- and pilot-scales (Chapters 3 and 4, respectively);

(7)   Treatment of wildfire ash-impacted, severely deteriorated source water by SBF technology was generally comparable in different physiographic regions (i.e., Montane Cordillera and Boreal Plain) with very different source water quality (i.e., typically high quality with low turbidity and low DOC, and degraded quality with high turbidity and high DOC, respectively). Thus, while wildfire on that natural landscape has the potential to (i) impact all of the key drivers of physico-chemical drinking water treatment (i.e., turbidity, organic carbon, pH, and alkalinity) and (ii) result in extremely deteriorated source water quality that is challenging to treat using conventional approaches, it does not lead to unusual water quality deterioration that would necessitate a paradigm shift in water treatment process design and optimization (Chapters 3 and 4). Rather, it (i) underscored that extreme source water quality requires extreme treatment, and (ii) emphasized that while technology is available to treat even the most severely deteriorated water, the highly uncertain and typically episodic nature of wildfire-associated shifts in source water quality require particular consideration in treatment infrastructure design and planning,

(8)   Wildfire ash runoff from hillslopes to receiving waters after severe wildfire may deteriorate source water quality (i.e., increase DOC concentration and alter DOC character) and challenge physico-chemical drinking water treatment more so than after moderate severity wildfire, while turbidity reduction appears readily achievable irrespective of burn severity (Chapter 5),

(9)   The delivery/addition of post-fire ash after severe wildfire in different physiographic regions (i.e., chaparral, moorland, grassland, montane) to the same source water resulted in very similar water quality impacts (i.e., increased turbidity, increased DOC concentration, increased UVA_{254}), though the magnitudes of those impacts differed when normalized to mass of ash. Despite these differences, the TTHM and HAA5 yields after coagulation were almost identical (i.e., all yields were within 16% and 14%, respectively), regardless of ash origin. Thus, the character of the DOC remaining in solution after coagulation was also almost identical, regardless of ash origin after wildland fire, and excellent linear correlation was observed between TTHM and HAA5 formation potentials and DOC concentration (Chapter 5).

(10) Post-fire ash originating in different physiographic settings does not have the same impacts on drinking water treatability (i.e., coagulant demand, THM- and HAA DBP formation potential) on a mass basis when added to the same source water; however, in absence of unique contaminants such as those that might occur as a result of combustion or pyrolysis in the built environment, the addition of different types of wildfire ash to Elbow River water yielded similar drinking water treatment challenges and extent of treatment largely due to elevated DOC, pH and alkalinity, the latter of which can be attributed to mineralized alkaline materials rich in base cations and carbonates. Consistent with previous reports (Chapters 3 & 4), sufficient reductions in turbidity could be achieved irrespective of ash origin (Chapter 5),

(11) Ash from wildfire in coastal regions appears more likely to contribute to the formation of brominated DBPs, presumably due to the presence of bromide from atmospheric aerosols that deposit on vegetation (Chapter 5),

(12) The major threats to drinking water treatment after wildfire on the natural landscape are universal (Chapter 6). They include elevated levels of fine suspended solids/turbidity and organic carbon (which is often also more aromatic after wildfire), which are the main water quality drivers of drinking water treatment infrastructure design and operation. In combination with pH and alkalinity,

these parameters drive coagulant dosing requirements and chemical pre-treatment (i.e., coagulation, flocculation, clarification) performance prior to subsequent advanced oxidation (if relevant), filtration, and disinfection. They also include increases in fine sediment-associated bioavailable phosphorus, which can be released to the water column, promoting the proliferation of potentially toxin-forming cyanobacteria and other nuisance algae—especially relevant to systems reliant on raw water storage reservoirs. These impacts may not be experienced immediately after wildfire and may persist for decades or longer in some regions. Additional source water quality concerns include sediment-associated polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), especially from urban landscapes, which can also release other anthropogenic organic contaminants from the built environment (e.g., benzene from distribution system pipes) to water supplies (Chapter 6),

(13) Increased, targeted source water and in-plant monitoring after wildfire, especially during high flow events, will enable utilities to be aware of possible shifts in water quality and inform them of potential implications to coagulation (e.g., increased coagulant dosing) and downstream treatment processes (i.e., filtration and disinfection) when elevated turbidity and DOC are present in source waters (Chapter 6),

(14) To enable risk management, operational resilience, and climate change adaptation planning for drinking water utilities in fire-prone regions, watershed- and plant-scale operational response actions for describing and mitigating the potential impacts of wildfire on drinking water treatment should be based on the recognition that although source water quality impacts of wildfire can range from none to severely deteriorated, and can vary substantially between regions, the major threats to drinking water treatment after wildfire on the natural landscape are universal. Source diversification, landscape erosion and debris barrier deployment, reservoir intake or flushing protocol development (for offline and inline reservoirs, respectively), algae mitigation, and reservoir dredging can mitigate treatment threats from wildfire impacts on source watersheds and reservoirs. Several strategies for increasing treatment resilience can further mitigate wildfire threats to drinking water treatment. These include ensuring sufficient chemical dosing/sludge handling capacity, ability to rapidly conduct jar tests, real-time evaluation of sufficiency of coagulant addition for particle destabilization using zeta potential analysis, minimizing lighting near clarifiers to discourage algae proliferation, and developing filter backwashing strategies to manage increased slides loads (Chapter 6).

7.2 Major Contributions

The overall goal of this research was to enable risk management, operational resilience, and climate change adaptation planning for drinking water utilities in fire-prone regions. The research approach that was used to address this goal was summarized in Figure 1.1. This work contributes to the general advancement of the available body of scientific and practical knowledge associated with this goal and delivers several novel components that comprise the major contributions of this dissertation research. These are described below.

Phase 1 of this research focused on protocol development to address Objective 1, which was to develop protocols for (i) post-fire ash collection and (ii) wildfire ash-impacted source water preparation. The major contributions of Phase 1 were:

- A protocol for post-fire ash collection was developed. It provides general information and guidance regarding important aspects of ash collection that can affect drinking water treatment assessments, including composition of post-fire ash and how it is described/characterized, simple approaches for differentiating burn severity, discussion regarding ash amounts that might be required for different types of treatability assessments, and discussion regarding spatio-temporal variability considerations within and between regions and before and after precipitation events. Key references where more detailed information can be found are highlighted. Prior to this work, no such guidance for ash collection for the purpose of evaluating wildfire ash impacts on water quality and treatability was available globally.

- A protocol for wildfire ash-impacted source water preparation was developed to enable experimental evaluation of wildfire impacts on water quality and treatability at bench- and pilot-scales. The protocol was developed to enable evaluations of conditions that represent a worst-case scenario for drinking water treatment after wildland fire, which include direct delivery of wildfire ash to source water after major runoff events. The development of this protocol is essential to enabling rigorous experimental evaluations that provide a linkage to the delivery of pyrogenic material from the landscape to receiving waters. To date, investigations of wildfire impacts on drinking water treatability have assumed some pre-treatment of wildfire-impacted water by settling or filtration; however, the pre-treatments were applied without validation of any connection to what may reasonably be expected either on the landscape (e.g., settling) or within treatment plants. Moreover, assumptions of pre-treatment preclude assessment of worst-case scenarios such as direct delivery of wildfire ash to source water after major runoff events. Guidance for wildfire ash-impacted water preparation was not available globally prior to this work.

- The highly uncertain and typically episodic nature of wildfire-associated potential shifts in key aspects of source water quality that impact treatment were summarized and synthesized. Critical for water treatment managers, this work synthesized the available literature to highlight that extreme increases in post-fire DOC and turbidity are episodic and frequently associated with increases in stream flows. Notably, it was emphasized that the multiple factors that impact source water quality change may render prediction of such events difficult or infeasible. Nonetheless, the recognition that the occurrence of such events is not certain and typically episodic over periods of years to more than a decade, can help to inform decision-making regarding watershed and in-plant resiliency planning and investment.

Phase 2 of this research focused on treatment focused on treatment evaluation to address Objectives 2 and 3. Objective 2 focused on evaluating the capacity to treat severely deteriorated, wildfire ash-impacted source water using commonly available water treatment technologies; it was conducted at bench-scale. Objective 3 focused on evaluating the capacity to treat severely deteriorated, wildfire ash-impacted source water at pilot-scale in regions of markedly different source water quality. The major contributions of Phase 2 were:

- Proof-of-concept bench-scale evaluations of the treatment of worst-case scenario, severely deteriorated, wildfire-ash impacted water by commonly available drinking water treatment technologies (conventional chemical pre-treatment and high-rate clarification [specifically, SBF], SBF with enhanced coagulation, and SBF with PAC) were conducted. Although evaluations of the impacts of deteriorated post-fire water quality on drinking water treatability are increasingly available, they typically provide limited or no information about treatment technology capabilities. Furthermore, most studies to date have assumed some pre-treatment of wildfire-impacted water by settling or filtration; therefore, they have not informed the ability to treat severely deteriorated water resulting from direct delivery of wildfire ash to source water after major runoff events. Although raw water intakes ideally would be closed or alternative source water supplies would be used when water quality is deteriorated, these options are not always available, and severely deteriorated source water may require treatment to prevent service disruptions. This work emphasized that DOC concentration and character, turbidity, alkalinity, and pH are key aspects of source water quality change that should all be considered after severe wildfire because they have the potential to compromise chemical pre-treatment by coagulation, flocculation and clarification processes that preclude adequate subsequent treatment—it is these types of upsets that can lead to service disruptions and outages. This demonstration highlighted that common treatment technologies are available to treat even the most severely deteriorated source water quality that can occur after wildfire. This was the first such investigation reported to date globally; it provides key information for water managers and decision makers to help evaluate the costs associated with

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investment in this level of treatment response capability, which likely need to be weighed carefully given the highly uncertain and typically episodic (i.e., relatively short episodes that might last for days and might occur with increased frequency over periods of a year to a decade or longer) nature of wildfire-associated shifts in source water quality.

- Proof-of-concept pilot-scale evaluations of the treatment of worst-case scenario, severely deteriorated, wildfire-ash impacted water by commonly available drinking water treatment technologies (SBF high-rate clarification, SBF with enhanced coagulation, and SBF with PAC) were conducted. These evaluations comprised the first pilot-scale investigation of wildfire impacts on drinking water treatment that has been reported to date globally. Critically, they confirmed the conclusions drawn from the bench-scale investigations and built upon them to demonstrate that worst-case scenario deteriorated source water quality after wildland fire could be treated using the same technology approaches in different environmental settings (i.e., Montane Cordillera and Boreal Plains regions) with very different course water quality. Because they were conducted at pilot-scale, these investigations were able to inform the extreme extent to which treatment technologies would have to be modified with either additional commercially available infrastructure and/or operational response capacity (e.g., coagulant availability, PAC availability, rapid analytical capacity to inform chemical dosing, sludge management capacity) to treat worst-case scenario severely deteriorated, wildfire-ash impacted water. This work was novel because although evaluations of the impacts of deteriorated post-fire water quality on drinking water treatability are increasingly available, they typically provide limited or no information about treatment technology capabilities. More importantly, however—and perhaps more novel, this work highlighted key operational response needs that would be required to effectively treat water at such challenging operational conditions in order to eliminate or reduce the potential for service disruptions or outages.

Phase 3 of this research focused on wildfire type and regional effects of wildfire on drinking water treatability to address Objective 4, which was to assess the impacts of wildfire in different physiographic regions with different predominant vegetation types and wildfire burn severity on drinking water treatability after wildfire. Drinking water treatability was evaluated using forest floor and post-fire materials that can runoff and affect source water quality and treatability. It was also evaluated after severe wildfire in chaparral, moorland, grassland, and montane regions was also investigated. The major contributions of Phase 3 were:

- A bench-scale evaluation demonstrating that ash-derived from severe wildfires challenged conventional drinking water treatment more than that derived from moderate severity wildfire. This work is novel because it provides the first report of burn severity impacts on drinking water treatability

based on the use of actual post-fire ash. These findings can directly inform proactive and reactive risk assessment, resiliency planning, and other associated planning and decision-making.

- A bench-scale evaluation demonstrating that although the composition of ash derived from wildland fire on different vegetated landscapes can vary considerably and the extent to which water quality changes after wildfire may vary between regions, the potential source water quality impacts and the associated treatment implications of wildland fire are consistent and generalizable between regions. Notably, differences in water quality impact magnitudes that vary across regions have not been well characterized and cannot be attributed to vegetation type. These findings can directly inform proactive and reactive risk assessment, resiliency planning, and other associated planning and decision-making because they demonstrate that the drinking water treatability implications of wildland fire that pertain to chemical pre-treatment (i.e., coagulation, flocculation, clarification) are generalizable in potential impacts across regions, but not in the magnitudes of those impacts.

Lastly, Phase 4 of this research focused on wildfire planning and response to address Objective 5, which was to develop a framework to detail watershed- and plant-scale operational response actions for describing and mitigating the potential impacts of wildfire on drinking water treatment. The novel insights from the first three research phases were synthesized in conjunction with a literature review to develop a framework to detail watershed- and plant-scale operational response actions for describing and mitigating the potential impacts of wildfire on drinking water treatment. The major contribution of Phase 4 was:

- A framework detailing watershed- and plant-scale operational response strategies focused on the monitoring and mitigation of potential wildfire impacts on the provision of safe drinking water was developed. Although wildfire impacts on source water quality and drinking water treatment have been described in available reports, they had not been previously synthesized to recommend and enable prioritization of specific actions at watershed- and plant-scales for drinking water risk management, operational resilience, and climate change adaptation planning in fire-prone regions.

7.3 Recommendations

(1) Evaluate the efficacy of a range of PACs (i.e., coal-, wood-, coconut-based; steam-, chemically-activated, etc.) for removing/adsorbing DOC from severely deteriorated wildfire ash-impacted water;

(2) Evaluate DOC removal from wildfire ash-impacted water across the entire treatment process at pilot-scale;

(3) Explore the applicability of industrial burn residual material (e.g., fly ash) as a potential surrogate for wildfire ash in the preparation of source waters that may be used to conduct bench- and pilot-scale treatability studies, replacing the need to collect ash from actual wildfires, which can be costly and extremely challenging logistically;

(4) Investigate the impacts of light rainfall on the removal of water extractable organic matter (WEOM) from different ash types (e.g., different burn severities; different vegetation types) to inform how organic matter in ash that remains on the landscape following wildfire for extended periods (e.g., months or years) may be impacted (i.e., reduced) prior to entering receiving waters;

(5) Conduct further evaluations of burn severity and vegetation types using ash from natural wildfires to investigate how these parameters may impact different types of treatment (e.g., enhanced coagulation, pre-treatment with PAC, sand-ballasted flocculation) at different scales (i.e., bench- and pilot-scale) to inform the implications across different types of wildfire in different regions globally;

(6) Evaluate the potential frequency of severely deteriorated source water conditions (i.e., episodic events) after wildfire to inform decision-makers of the risk that such events may have on drinking water treatment and the possible measure which may need to be implemented to mitigate such risks (e.g., different treatment technologies; new infrastructure); and

(7) Evaluate the costs and benefits of implementing watershed-based management approaches for mitigating the potential impacts of wildfire on source water quality compared to the implementation of additional treatment infrastructure (i.e., green vs gray infrastructure).

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Appendices

Appendix A: Supporting information for Evaluating wildfire impacts on drinking water treatment: Guidance for post-fire ash collection and preparation of wildfire ash-impacted water

Table A1: Set points for parameters selected for preparation of wildfire ash-impacted source water.

Set point parameter	Set point(s) selected	Specific details	Justification/comments
Ash type	Thuya Lake Road (TLR) ash	• Collected near Little Fort, British Columbia; Thuya Lake Road wildfire was part of the Little Fort fire complex.	• Ash was collected from a severe wildfire site to provide material which could be used to prepare synthetic wildfire ash-impacted source water representative of severely deteriorted conditions following major runoff events. • Site selected based on accessibility to fire site and coordination with regional wildfire authorities (see Governemnt of British Columbia, 2017 for site details).
Water type	Elbow River	• Collected in Calgary, Alberta, Canada at Glenmore reservoir.	• Elbow River water was selected as it is repreentative of a high quality source water origiating in a fire-prone region (e.g., Beers & Sosiak, 1993). • Selected due to availability through partnership with City of Calgary. • Mixed with TLR to prepare synthetic ash-impacted source water.
Ash concentrations tested	• 2 g/L • 5 g/L • 10 g/L • 20 g/L	• TLR ash mixed with Elbow River water.	• Ash was mixed with Elbow River water at different concentrations to determine the amount of ash required to reach targets for 'severely deteriorated' water quality (i.e., DOC >15 mg/L and turbidity >500 NTU; see Chapter 2, Section 2.2 for additional details). **• A range of concentrations were analyzed for DOC and turbidity to determine the impacts of adding different quantities of ash on water quality.** • 5 g/L was selected as the ideal concentration as this was the minimum amount of ash required to meet the desired water quality targets which were then used for subsequent drinking water treatment studies (i.e., Chapter 3).
Mixing time	• 2 min • 30 min	• Ash was mixed with Elbow River water using programable jar tester.	• Prelimary invesigation to determine approximate amounts of ash required to reach targets were mixed for 2 min; once desired target parameters were achieved (i.e., using 5 g/L) subsequent samples were mixed for 30 min to provide additional time for effective mixing and DOC leaching from ash.

Appendix B: Supporting information for Treatment of severely-deteriorated post-fire runoff: Comparison of conventional and high-rate clarification demonstrates key drinking water treatment capabilities and challenges

B1: Jar testing protocol summary

The conventional pre-treatment evaluation followed ASTM method D2035-13 (ASTM, 2013), where alum was simultaneously added to four 1-L beakers containing the pre-mixed severely-deteriorated wildfire ash-impacted source water and flash mixed for one minute at 120 RPM. Cationic polymer was then added (0.5 mg·L^{-1}), followed by flash mixing for one minute at 120 RPM. Samples were then flocculated at 40 RPM for 20 minutes. The paddles were then removed and the treated water settled for 15 minutes.

The SBF jar tests involved a modified jar-test protocol (Actiflo®, Veolia Water, Saint-Laurent, Canada) following the same chemical dosing sequence used in previous studies (Desjardins et al., 2002). Alum was simultaneously added to four 1-L beakers containing the pre-mixed, severely-deteriorated source water; 10.0 g of microsand (silica quartz sand, 85μm diameter, uniformity coefficient of 2.07, Veolia Water, Saint-Laurent, Canada) and a total 0.5 mg·L^{-1} of cationic polymer were also added. The paddles were then removed and the treated water was settled for 3 minutes. Treated water samples were then siphoned from 3 cm below the surface to avoid any low-density material remaining on the surface; a modified 60-mL syringe was used for carefully syphoning samples to prevent the re-suspension of any settled material.

The SBF with enhanced coagulation jar tests involved pH adjustment to enhance DOC removal, which optimally occurs with alum coagulation when pH is between 5 and 6 (Anderson et al., 1995; Edzwald & Van Benschoten, 1990). Although coagulation conditions at lower pH using alum may lead to elevated levels of dissolved residual aluminum (Pernitsky & Edzwald, 2003), especially under high alum dosing conditions such as those tested herein, it must be highlighted that severely deteriorated water conditions post-fire would be short-lived following major runoff events and not require such extreme treatment measures for extended periods. Preliminary acidification titrations indicated that 1.0 mL of 3.2 mol L^{-1} hydrochloric acid (HCl) would lower the severely deteriorated source water pH from 8.71 ± 0.05 (mean ± SE, n=10) to 5.83 ± 0.01 (mean ± SE, n=4). Despite initial decreases pH after acid addition, pH began to increase after approximately one minute. Alum addition at the doses used during the investigation further decreased pH; however, the pH remained in the optimal pH range for enhanced coagulation. Thus, HCl was added to each 1-L beaker one minute prior to the addition of alum to ensure both adequate mixing of the acid and coagulation at low pH. The SBF jar test procedure described above was then followed.

SBF jar tests comparing the treatment efficacy of pre-treatment with PAC at varying doses of PAC were conducted with bituminous coal PAC (Norit PAC 20BF M2334, supplied by Veolia Water, Saint-Laurent, Canada). Additional jar tests were completed to collect samples for LC–OCD and DBP analysis using 1000 mg·L^{-1} of wood-based PAC (Aquasorb MP23, supplied by Veolia Water, Saint-Laurent, Canada). Although different PACs were used due to availability, preliminary tests indicated that PAC performance was very

similar regarding DOC reduction, with < 4.0% (n=4) difference between the PAC types used (see Figures B1 and B2). PAC was prepared as slurry at a concentration of 10.0 g of dry PAC per 100 mL of Milli-Q® ultra-pure water. This was mixed on a stir plate for a minimum of 24 hours to ensure it was fully hydrated prior to use. This slurry (100, 200, 400, or 1000 mg) was added to the 1-L beakers containing untreated severely-deteriorated source water following AWWA-M12 (AWWA, 2002). The samples were then mixed at 150 RPM for 30 minutes to allow adequate time for DOC adsorption on the PAC. The pre-treatment contact time was not intended to be replicative of a specific WTP configuration, but rather provide a general demonstration of the efficacy of PAC pre-treatment at bench-scale. The SBF jar test procedure described above was then followed using alum and polymer doses of 400 mg·L^{-1} and 0.5 mg·L^{-1}, respectively.

Table B1: Set points for parameters selected for bench-scale drinking water treatability study of wildfire ash-impacted source water.

Set point parameter	Set point(s) selecte	Specific details	Justification/comments
Ash type	Thuya Lake Road (TLR) ash	• Collected near Little Fort, British Columbia; Thuya Lake Road wildfire was part of the Little Fort fire complex.	• Ash was collected from a severe wildfire site to provide material which could be used to prepare synthetic wildfire ash-impacted source water that is representative of severely deteriorted conditions following major runoff events. • Site selected based on accessibility to fire site and coordination with regional wildfire authorities (see Governemnt of British Columbia, 2017 for site details).
Source water	Elbow River	• Collected in Calgary, Alberta, Canada from the Glenmore reservoir.	• Elbow River water was selected as it is reprentative of a high quality source water origiating in a fire-prone region (e.g., Beers & Sosiak, 1993). • Selected due to availability through partnership with City of Calgary. • Mixed with TLR to prepare synthetic ash-impacted source water.
Synthetic ash-impacted source water concentration	5 g/L	• TLR ash mixed with Elbow River.	• Ash was mixed with Elbow River water to reach targets for 'severely deteriorated' water quality (i.e., DOC >15 mg/L and turbidity >500 NTU; see Chapter 2, Section 2.2 for additional details).
Mixing time	30 min	• Ash was mixed with river water using programable jar tester at 150 RPM.	• Ash was mixed for 30 min to provide time for effective mixing to occur and to provide an opportunity for DOC to leach from ash. • Conditions were designed to represent a scenario where ash is mobilized off the landscape following a major runoff event into a recieving stream for a short period (i.e., 30 min) prior to reaching a WTP, where it would then be treated.
Treatment technology	Conventional chemical pre-treatment	• Conducted according to ASTM jar test protocol (ASTM, 2013) with alum and cationic polymer; consist of cogulation, flocculation, and sedimentation; coagulant added and mixed for 1 min at 120 RPM; polymer added and mixed for additional 1 min at 120 RPM; 20 min mixing at 40 RPM; settled for 15 min.	• Conventional chemical pre-treatment was selected as this is the most commonly employed treatment technology in Canada (Statistics Canada, 2013) and is capable of tretating water quality with turbidity >20 NTU and DOC >4 mg/L (Crittenden et al., 2012).
	Sand-ballasted flocculation (SBF)	• Conducted with modified jar test protocol (e.g., Desjardins et al., 2002; Ghanem et al., 2007); settling time of 3 min; additional details in Appendix A, Section A1.	• SBF treatment was selected as it is known to be an effective technology for responding to rapid shifts in source water quality and can respond to high solids loading (Edzwald, 2011); additionally, SBF has been tested in post-fire scenarios (e.g., Emelko et al., 2020); however, not under the severely deteriorted watet quality conditions tested in this study.
	SBF with enhanced coagulation	• Conducted with SBF protocol (noted above) and the addition of acid (HCl) to lower the pH into optimal range for coaguation; 1 mL of acid was added 1 min prior to coagulant; additional details in Appendix A, Section A1.	• SBF with enhanced coagulation through pH adjustment was investigated to determine if the efficacy of DOC removal was improved from SBF in the absence of pH adjustment; enhanced coagulation through pH adjustment is an established means to improve DOC reduction (USEPA, 1999).
	SBF with PAC pre-treatment	• PAC added as slurry to untreated water and mixed for 30 min at 150 RPM prior to treatment with SBF (as noted above); additional details in Appendix A, Section A1.	• Pre-treatment with PAC followed by SBF treatment was investigated to determine if PAC would improve the efficacy of DOC removal; 30 min contact time was selected to ensure sufficient time was available for DOC to adsorb to PAC and to provide treatment conditions indicative of subsequent pilot-scale testing with PAC pre-treatment (Chapter 4).

Table B1: Set points for parameters selected for bench-scale drinking water treatability study of wildfire ash-impacted source water (continued).

Set point parameter	Set point(s) selecte	Specific details	Justification/comments
Treatment chemicals	Aluminum sulfate (alum)	• Four alum doses were tested throughout the treatment experiments: 100, 200, 300, and 400 mg/L (as commercial product); additional details in Appendix A, Section A1.	•Alum was selected as a coagulant as it is a commonly availble chemical and is the most widely used coagulant in North America (Crittenden et al., 2012). • Turbidity was effectively removed at the lowest alum dose (100 mg/L); however, this study investigated the concurrent reduction of both turbidity and DOC, as such, doses > 100 mg/L of alum were tested. • Coagulant doses were increased at equal increments to provide an indication of DOC removal efficacy across a wide range of dose conditions, where a maximum value of 400 mg/L was selected which is the NSF guidleine for alum dose (NSF, 2017).
	Cationic polymer	• Polymer was dosed consisently at 0.5 mg/L for all treatment technologies tested.	• Polymer was used concurrently with alum to increase the efficacy of floccultion during treatment; SBF requires the addition of polymer to increase the weight of floc particles, which include ballasting sand (Desjardins et al., 2002).
	Powdered activated carbon (PAC)	• Four PAC doses were tested throughout treatment testing: 100, 200, 400, 1000 mg/L; additional details in Appendix A, Section A1.	• The minimum PAC dose (100 mg/L) was selected based on previous reports of PAC doses for treating less deteriorted post-fire water than he conditions tested herein; the highest evel of PAC tested in a previous study was 60 mg/L for water with a DOC concentration of < 10 mg/L (Hohner et al., 2017). • The highest dose of PAC tested was 1000 mg/L was the same the maximum dose tested in previous studies where deteriorated water quality wth high DOC was treated (Najm et al., 1991). • Increments of PAC doses were doubled between each of the first three doses and the maximum dose was chosen as per note above (e.g. Najm et al., 1991).
	Hydrochloric acid (HCl)	• Dosed 1 mL of 10% HCl (3.2. mol/L) into 1L of synthetic ash-impacted source water prior to treatment; additional details in Appendix A, Section A1.	• Preliminary titrations were conducted to determine the approprite volume of HCl required to reduce the pH into an optimal range for coagulation. • HCl was selected as acid due to it being suggested as a means to lower pH conditions for enhanced coagulation (USEPA, 1999) and due to availablilty.

Table B2: Ash composition analysis for dry Thuya Lake Road ash sample collected in August, 2017 prior to any precipitation events.

Parameter	Result	Detection limit	Unit
Moisture	2.11	0.10	%
Carbon total	5.81	0.10	%
Carbonate	1.1	0.10	%
Aluminum (Al)	6190	50	ug/g
Arsenic (As)	4.54	0.10	ug/g
Cadmium (Cd)	0.772	0.020	ug/g
Calcium (Ca)	33100	50	ug/g
Copper (Cu)	31.9	0.50	ug/g
Iron (Fe)	17000	50	ug/g
Lead (Pb)	32.2	0.50	ug/g
Magnesium (Mg)	14400	20	ug/g
Manganese (Mn)	5720	1.0	ug/g
Mercury (Hg)	0.0185	0.0050	ug/g
Phosphorus (P)	2210	50	ug/g
Potassium (K)	3120	100	ug/g
Sodium (Na)	234	50	ug/g
Sulfur (S)	1000	1000	ug/g
Titanium (Ti)	515	1.0	ug/g

Table B3: Treated water turbidity after treatment with different coagulant doses using conventional chemical pre-treatment, sand-ballasted flocculation (SBF), SBF with enhanced coagulation, and SBF with powdered activated carbon pre-treatment.

Treatment	Alum dose (mg/L)	PAC dose (mg/L)	Number of samples (n)	Turbidity (NTU)	
				Mean	Standard error
No treatment (water matrix)	0	0	12	1400	60
Conventional pre-treatment	100	0	3	2.03	1.17
	200	0	3	1.67	0.96
	300	0	3	1.28	0.74
	400	0	3	2.05	1.18
Sand-ballasted flocculation (SBF)	100	0	3	1.87	1.08
	200	0	3	1.19	0.69
	300	0	3	0.95	0.55
	400	0	3	1.87	1.08
SBF with enhanced coagulation	100	0	3	3.36	1.94
	200	0	3	2.94	1.70
	300	0	3	2.57	1.48
	400	0	3	1.70	0.98
SBF with powdered activated carbon	400	100	3	2.33	0.16
	400	200	3	1.50	0.06
	400	400	3	0.98	0.02
	400	1000	3	0.81	0.01

Table B4: Treated water dissolved organic carbon (DOC) after treatment with different coagulant doses using conventional chemical pre-treatment, sand-ballasted flocculation (SBF), SBF with enhanced coagulation, and SBF with powdered activated carbon pre-treatment.

Treatment	Alum dose (mg/L)	PAC dose (mg/L)	Number of samples (n)	DOC (mg/L)	
				Mean	Standard error
No treatment (water matrix)	0	0	11	16.01	0.22
Conventional pre-treatment	100	0	2	15.12	0.07
	200	0	3	14.66	0.17
	300	0	3	13.86	0.06
	400	0	3	13.47	0.28
Sand-ballasted flocculation (SBF)	100	0	3	14.99	0.34
	200	0	3	14.43	0.26
	300	0	3	14.01	0.18
	400	0	3	14.05	0.43
SBF with enhanced coagulation	100	0	3	15.52	0.20
	200	0	3	14.48	0.29
	300	0	3	13.59	0.15
	400	0	3	12.82	0.05
SBF with powdered activated carbon	400	100	3	11.41	0.15
	400	200	3	10.50	0.48
	400	400	3	8.43	0.05
	400	1000	3	6.82	0.34

Table B5: Treated water ultraviolet absorbance at 254 nm (UVA_{254}) after treatment with different coagulant doses using conventional chemical pre-treatment, sand-ballasted flocculation (SBF), SBF with enhanced coagulation, and SBF with powdered activated carbon pre-treatment.

Treatment	Alum dose (mg/L)	PAC dose (mg/L)	Number of samples (n)	UVA_{254} (cm^{-1})	
				Mean	Standard error
No treatment (water matrix)	0	0	11	0.479	0.009
Conventional pre-treatment	100	0	3	0.445	0.007
	200	0	3	0.420	0.005
	300	0	3	0.354	0.014
	400	0	3	0.353	0.005
Sand-ballasted flocculation (SBF)	100	0	3	0.453	0.017
	200	0	3	0.417	0.013
	300	0	3	0.393	0.014
	400	0	3	0.388	0.021
SBF with enhanced coagulation	100	0	3	0.445	0.015
	200	0	3	0.388	0.010
	300	0	3	0.336	0.004
	400	0	3	0.293	0.007
SBF with powdered activated carbon	400	100	3	0.238	0.006
	400	200	3	0.193	0.005
	400	400	3	0.137	0.000
	400	1000	3	0.089	0.011

Table B6: Treated water specific ultraviolet absorbance at 254 nm (SUVA) after treatment with different coagulant doses using conventional chemical pre-treatment, sand-ballasted flocculation (SBF), SBF with enhanced coagulation, and SBF with powdered activated carbon pre-treatment.

Treatment	Alum dose (mg/L)	PAC dose (mg/L)	SUVA (L/mg•m)
No treatment (water matrix)	0	0	2.99
Conventional pre-treatment	100	0	2.94
	200	0	2.87
	300	0	2.55
	400	0	2.62
Sand-ballasted flocculation (SBF)	100	0	3.02
	200	0	2.89
	300	0	2.80
	400	0	2.76
SBF with enhanced coagulation	100	0	2.87
	200	0	2.68
	300	0	2.47
	400	0	2.28
SBF with powdered activated carbon	400	100	2.09
	400	200	1.84
	400	400	1.63
	400	1000	1.31

Table B7: Post-hoc tukey test p-value results comparing different coagulant doses (0-400 mg·L^{-1}) on treatment efficacy of three drinking water treatment methods: conventional chemical pre-treatment **(a)**, sand-ballasted flocculation [SBF] **(b)**, and SBF with enhanced coagulation **(c)** on reducing turbidity, dissolved organic carbon (DOC), and ultraviolet absorbance at 254 nm (UVA$_{254}$).

(a)

Coagulant dose multiple comparisons (mg/L)		Conventional		
		Turbidity p value	DOC p value	UVA$_{254}$ p value
0	100	7.99E-11	0.335	0.241
	200	7.95E-11	0.021	0.013
	300	7.91E-11	4.78E-04	3.00E-06
	400	7.99E-11	5.60E-05	3.00E-06
100	0	7.99E-11	0.335	0.241
	200	1.00	0.914	0.736
	300	1.00	0.242	0.002
	400	1.00	0.061	0.002
200	0	7.95E-11	0.021	0.013
	100	1.00	0.914	0.736
	300	1.00	0.591	0.028
	400	1.00	0.178	0.027
300	0	7.91E-11	4.78E-04	3.00E-06
	100	1.00	0.242	0.002
	200	1.00	0.591	0.028
	400	1.00	0.903	1.00
400	0	7.99E-11	5.60E-05	3.00E-06
	100	1.00	0.061	0.002
	200	1.00	0.178	0.027
	300	1.00	0.903	1.00

(b)

Coagulant dose multiple comparisons (mg/L)		SBF		
		Turbidity	DOC	UVA$_{254}$
		p value	p value	p value
0	100	7.97E-11	0.176	0.639
	200	7.91E-11	0.014	0.027
	300	7.89E-11	0.002	0.002
	400	7.97E-11	0.002	0.001
100	0	7.97E-11	0.176	0.639
	200	1.00	0.836	0.546
	300	1.00	0.406	0.113
	400	1.00	0.443	0.078
200	0	7.91E-11	0.014	0.027
	100	1.00	0.836	0.546
	300	1.00	0.939	0.83
	400	1.00	0.956	0.724
300	0	7.89E-11	0.002	0.002
	100	1.00	0.406	0.113
	200	1.00	0.939	0.83
	400	1.00	1.00	1.00
400	0	7.97E-11	0.002	0.001
	100	1.00	0.443	0.078
	200	1.00	0.956	0.724
	300	1.00	1.00	1.00

(c)

Coagulant dose multiple comparisons (mg/L)		SBF+EC		
		Turbidity	DOC	UVA$_{254}$
		p value	p value	p value
0	100	8.12E-11	0.72	0.234
	200	8.08E-11	0.008	1.43E-04
	300	8.04E-11	6.20E-05	3.43E-07
	400	7.96E-11	2.00E-06	5.72E-09
100	0	8.12E-11	0.72	0.234
	200	1.00	0.247	0.063
	300	1.00	0.007	2.60E-04
	400	1.00	2.56E-04	4.00E-06
200	0	8.08E-11	0.008	0.000143
	100	1.00	0.247	0.063
	300	1.00	0.39	0.109
	400	1.00	0.024	0.001
300	0	8.04E-11	6.20E-05	3.43E-07
	100	1.00	0.007	2.60E-04
	200	1.00	0.39	0.109
	400	1.00	0.536	0.225
400	0	7.96E-11	2.00E-06	5.72E-09
	100	1.00	2.56E-04	4.00E-06
	200	1.00	0.024	0.001
	300	1.00	0.536	0.225

Table B8: Post-hoc tukey test p-value results comparing three drinking water treatment methods (conventional chemical pre-treatment, sand-ballasted flocculation [SBF], and SBF with enhanced coagulation) on reducing turbidity, dissolved organic carbon (DOC), and ultraviolet absorbance at 254 nm (UVA_{254}). The post-hoc tukey test was conducted after a two-ANOVA test was completed where both alum dose and treatment type were used as independent variables.

Treatment multiple comparisons		Turbidity p value	DOC p value	UVA_{254} p value
Conventional	SBF	0.011	0.603	0.085
	SBF+EC	7.11E-09	0.842	0.015
SBF	Conventional	0.011	0.603	0.085
	SBF+EC	5.14E-09	0.281	5.80E-05
SBF+EC	Conventional	7.11E-09	0.842	0.015
	SBF	5.14E-09	0.281	5.80E-05

Table B9: Post-hoc tukey test p-value results comparing different powdered activated carbon (PAC) doses (0-1000 mg·L^{-1}) on treatment efficacy using sand-ballasted flocculation [SBF] with PAC pre-treatment on reducing turbidity, dissolved organic carbon (DOC), and ultraviolet absorbance at 254 nm (UVA$_{254}$).

PAC doses multiple comparisons (mg/L)		SBF with PAC pre-treatment		
		Turbidity	DOC	UVA$_{254}$
		p value	p value	p value
0	100	8.02E-11	2.81E-08	2.85E-11
	200	7.94E-11	1.57E-09	2.37E-12
	400	7.89E-11	8.33E-12	1.01E-12
	1000	7.87E-11	1.20E-12	9.71E-13
100	0	8.02E-11	2.81E-08	2.85E-11
	200	1.00	0.462	0.145
	400	1.00	2.43E-04	2.87E-04
	1000	1.00	8.57E-07	2.00E-06
200	0	7.94E-11	1.57E-09	2.37E-12
	100	1.00	0.462	0.145
	400	1.00	0.009	0.051
	1000	1.00	1.80E-05	2.05E-04
400	0	7.89E-11	8.33E-12	1.01E-12
	100	1.00	2.43E-04	2.87E-04
	200	1.00	0.009	0.051
	1000	1.00	0.053	0.108
1000	0	7.87E-11	1.20E-12	9.71E-13
	100	1.00	8.57E-07	2.00E-06
	200	1.00	1.80E-05	2.05E-04
	400	1.00	0.053	0.108
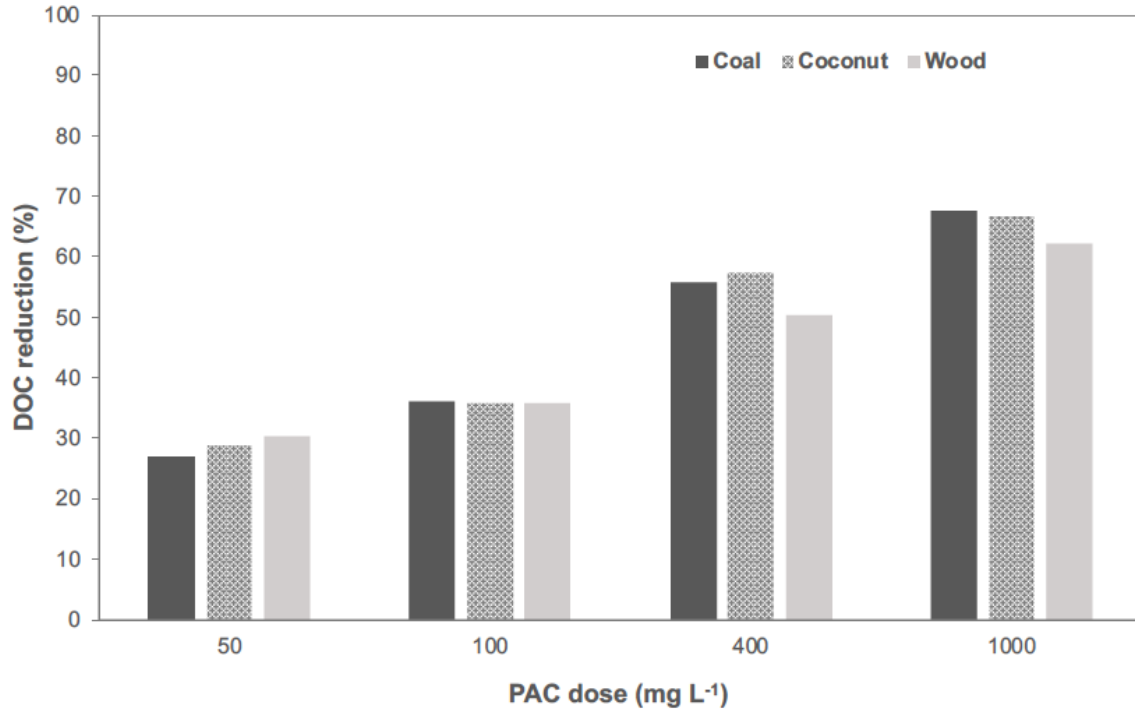
Figure B1: Percent reduction of dissolved organic carbon (DOC) in severely deteriorated wildfire ash-impacted source water comparing different types of powdered activated carbon (PAC) at varying dosages (50–1000 mg·L^{-1}). The types of PAC compared are coal-based (Norit 20BF M, Veolia Water), coconut-based (Aquasorb CB1-MW, Veolia Water), and wood-based (Aquasorb MP23, Veolia Water). All PACs were prepared as slurries and were mixed for >24 h to ensure slurry was effectively hydrated. All tests were conducted using a severely deteriorated wildfire ash-impacted source water which was pre-treated with PAC by mixing for 30 minutes followed by sand-ballasted flocculation with a 400 mg·L^{-1} dose of alum and 0.5 mg·L^{-1} of cationic polymer (Magnafloc LT22S).

Figure B2: Percent reduction of ultraviolet absorbance at 254 nm (UVA$_{254}$) in severely deteriorated wildfire ash-impacted source water comparing different types of powdered activated carbon (PAC) at varying dosages (50–1000 mg·L^{-1}). The types of PAC compared are coal-based (Norit 20BF M, Veolia Water), coconut-based (Aquasorb CB1-MW, Veolia Water), and wood-based (Aquasorb MP23, Veolia Water). All PACs were prepared as slurries and were mixed for >24 h to ensure slurry was effectively hydrated. All tests were conducted using a severely deteriorated wildfire ash-impacted source water which was pre-treated with PAC by mixing for 30 minutes followed by sand-ballasted flocculation with a 400 mg·L^{-1} dose of alum and 0.5 mg·L^{-1} of cationic polymer (Magnafloc LT22S). Singular samples were taken for each treatment scenario.

Appendix C: Supporting information for Pilot-scale evaluation of the treatment of two different wildfire ash-impacted source waters

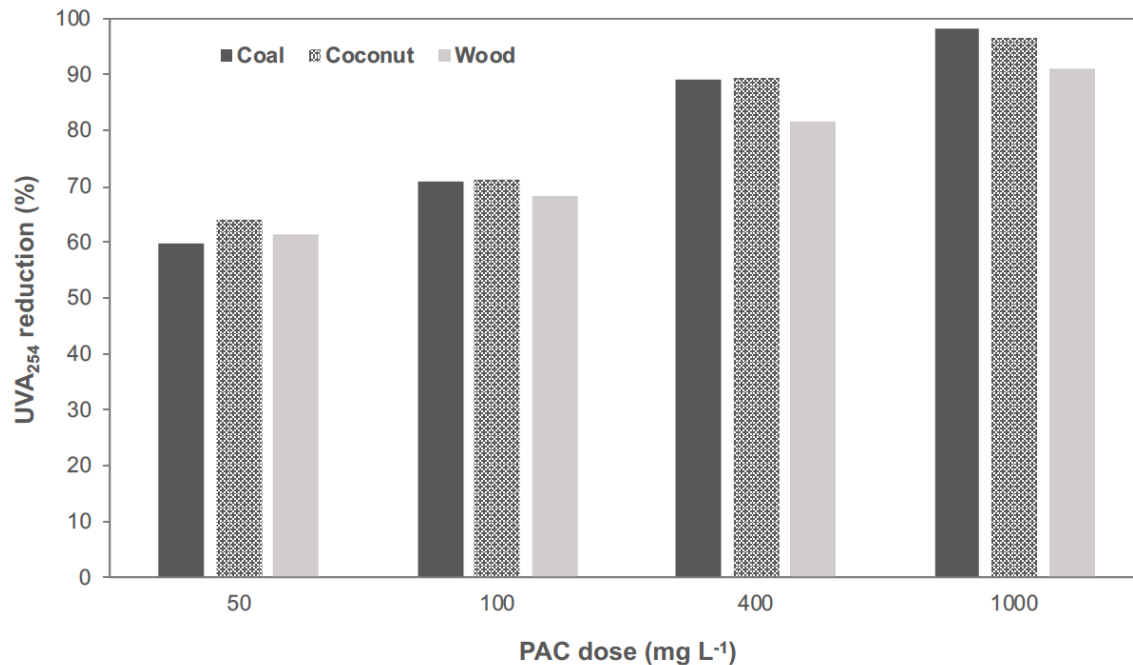Table C1: Set points for parameters selected for pilot-scale drinking water treatability studies of wildfire ash-impacted source water.

Set point parameter	Set point(s) selected	Specific details	Justification/comments
Ash type	Thuya Lake Road (TLR) ash	• Collected near Little Fort, British Columbia; TLR wildfire was part of the Little Fort fire complex (August, 2017).	• TLR ash was collected from a severe wildfire site to provide material which could be used to prepare synthetic wildfire ash-impacted source water representative of severely deteriorted conditions following major runoff events. A total off 40, 19 L pails were collected. • Site was selected based on accessibility and coordination with regional wildfire authorities (see Govemernmt of British Columbia, 2017).
	Scottie Creek Road (SCR) ash	• Collected near Ashcroft, British Columbia; SCR wildfire was part of the Elephant Hill fire complex (September, 2017).	• SCR ash was collected from a severe wildfire; ash was used to prepare synthetic wildfire ash-impacted source water (as noted above). A total of 61, 19 L pails were collected. • Sample collection site was selected based on coordination with regional wildfire authorities and ease of accessibility.
Source water	Elbow River	• Source water taken from Calgary, Alberta, Canada from the Glenmore reservoir.	• Elbow River water was selected as it is representative of a high quality source water originating in a fire-prone region (Beers & Sosiak, 1993) in the Montane Cordillera region. • This water was used in the GMWTP pilot studies it was the source water available at the WTP.
	Athabasca River	• Source water taken from Fort McMurray, Alberta, Canada.	• Athabasca River water used as it is a source with challenged water quality (e.g., high turbidity and DOC) and starkly contrasts the high-quality Elbow River. The Athabasca River at Ft. Mcmurray is also representative of a source water in the Boreal Plains, which is a region prone to wildfire. • This water was used in the FMWTP pilot studies as it was the source water available at the WTP.
Synthetic ash-impacted source water concentration	5 g/L	• TLR ash and Elbow River water	• Bench-scale assessments (i.e., Chapter 2 and 3) demonstrated that the target for DOC and turbidity, (>15 mg/L and >500 NTU, respectively) were achieved using 5 g/L. • Natural variability in the ash and mixing conditions at pilot-scale resulted in difficulties in maintaining a consistent source water matrix. • This source water matrix was used for GMWTP1 and GMWTP2.
	10 g/L	• SCR ash and Athabasca River water	• Preliminary bench-scale assessment where SCR ash and Athabasca River water were mixed for 30 min demonstrated that the target for DOC and turbidity, (>15 mg/L and >500 NTU, respectively) were achieved using 10 g/L. • Natural variability in the ash and mixing conditions at pilot-scale resulted in difficulties in maintaining a consistent water matrix used for FMWTP pilot testing. • SCR ash was also used in the GMWTP2 pilot study at 10 g/L using Elbow River.
Mixing time	Minimum of 1 h prior to testing; variable times	• Ash was mixed with river water using submersible pumps in 5000L tanks.	• Mixing times varied in tanks after the addition of ash due to additional residence time in the tank while water flowed from the tank to the pilot system (~3 h of flow volume per tank). Additionally, at times, tanks were mixed for longer periods due to having to stabilize conditions of the pilot plant before testing could commence.

Table C1: Set points for parameters selected for pilot-scale drinking water treatability studies of wildfire ash-impacted source water (continued).

Set point parameter	Set point(s) selected	Specific details	Justification/comments
Treatment technology	Sand-ballasted flocculation (SBF)	• Conducted acording to Actiflo pilot plant design where coagulant, polymer, and microsand are added to process (see Figure 4.2); residence time of water in the pilot system was ~15 min.	• SBF was conducted as it is known to be an effective technology for responding to rapid shifts in source water quality and can respond to high solids loading (Edzwald, 2011); additionally, SBF has been tested in post fire scenarios at full-scale (e.g., Emelko et al., 2020); however, not under the severely deteriorted watet quality conditions tested in this study. • SBF was tested based on results from Chapter 3. • The flow rate through the pilot plant was set to the minimum flow based on plant spcifications of 1.4 m^3/h for GMWTP1 and FMWTP or 1.3 m^3/h for GMWTP2; the minium flow was used as the set point as to conserve the sythetic ash-impacted source water due to limited quantites to test.
	SBF with enhanced coagulation	• Conducted acording to Actiflo pilot plant design where coagulant, polymer, and microsand are added to process (see Figure 4.2); HCI was added prior to coagulant to decrease pH. • GMWTP1 pilot study maintained constant pH (~5.8) and coagulant doses were varied (~100–400 mg/L). • FMWTP pilot study maintained a constant coagualnt dose (~400 mg/L) and pH levels were varied (~5–6.5).	• SBF with enhanced coagulation through pH adjustment was investigated to determine if the efficacy of DOC removal was improved from SBF in the absence of pH adjustment; enhanced coagulation through pH adjustment is an established means to improve DOC reduction (USEPA, 1999). • Addition of HCl for pH adjustment was based on previous jar testing to achieve desired pH (5-6) (Chapter 3) and has been suggested as a means to achieve lower pH conditions (USEPA, 1999). • SBF with enhanced coagulation was investigated during GMWTP1 to determine the impacts of a constant, but lower, pH on treatment efficacy; where as the FMWTP pilot study investigated the efficacy of DOC removal at different pH levels while maintaining a controlled coagulant dose.
	SBF with PAC pre-treatment	• Pre-treatment of the ash-impacted matrix with PAC in a continuous flow reactor with a contact time of ~45 min prior to passing the through the SBF pilot system (for GMWTP1 and FMWTP pilot studies).	• PAC pre-treatment was tested as this is a well-know method to reduce high DOC (Crittenden et al., 2012) and had been previously demonstraed to be effective in removing elevated DOC in post-fire water (Chapter 3).
	Dual-stage SBF with PAC	• Ash-impacted source water matrix was passed through SBF system once; claified water then passed through a PAC contact reactor (continuous flow) with a contact time of ~15 min prior to entering the SBF system for a second time. • Both fresh PAC and recirculted/recycled PAC were added to the contact reactor.	• Dual-stage SBF was selected as it has the capacity to remove high solids (stage 1), then PAC is used as polishing phase (stage 2) to remove high levels of DOC. • Extremely high dose conditions of PAC can be achievd due to the recycling of PAC in the system.

Table C1: Set points for parameters selected for pilot-scale drinking water treatability studies of wildfire ash-impacted source water (continued).

Set point parameter	Set point(s) selected	Specific details	Justification/comments
Treatment chemicals*	Aluminum sulfate (alum)	• Used at GMWTP1 and GMWTP2, where four doses ranged from ~100–400 mg/L (commercial product) for GMWTP1. A constant alum dose of ~200 mg/L for the first stage in GMWTP2 and ~25 mg/L in second stage (see Table B8 in Appendix B for specific details).	•Alum was used as a coagulant as it is a commonly available chemical is the most widely used coagulant in North America (Crittenden et al., 2012); also, alum was readily available at the WTP where GMWTP piloting was conducted. • Turbidity was effectively removed at the lowest alum dose; however, pilot studies investigated the concurrent reduction of both turbidity and DOC, as such, doses >100 mg/L of alum were tested. • Dose conditions for GMWTP1 were selected based on bench-scale investigations (see Chapter 3). • Coagulant doses were increased at equal increments to provide an indication of DOC removal efficacy across a wide range of dose conditions, where a maximum value of 400 mg/L was selected which is the NSF guideline for alum dose (NSF, 2017). • Alum dose was maintained at a constant level for GMWTP2 as to achieve maximum solids removal; subsequent DOC reductions were antipated with addition of PAC, due to DOC reductions through alum coagulation were minimal (Chapter 3).
	Polyhydroxy aluminum chloride (PACl)	• PACl was used for the FMWTP pilot study, where four doses ranged ~100–400 mg/L (commercial product) during SBF testing; for SBF+EC and SBF+PAC, PACl dose was maintained at ~400 mg/L.	• PACl doses were selected based on bench-scale investigations where doses were increased at equal increments for SBF testing. • High dose condition was above the NSF guidline limit (200 mg/L) as to demonstate that extreme dosing conditions may be required treat water in post-fire scenarios. • PACl was selected as the coagulant for the FMWTP pilot due to availabiliy at the WTP where pilot plant was located.
	Cationic polymer (LT22S)	• LT22S polymer was used during the GMWTP1 and GMWTP2 pilot studies. For GMWTP1, an approximate consistant dose was maintained during piloting SBF and SBF+PAC testing (~1.0 mg/L); however a higher dose was required to reduce solids during SBF+EC (~1.5 mg/L).	• This polymer was tested as it was previously used for bench-scale assessment; additionally, this was the polymer available at the WTP where GMWTP piloting was conducted. • Polymer was used concurrently with coagulant to increase the efficacy of floccultion during treatment; SBF required the addition of polymer to increase the weight of floc particles, which include ballasting sand (Desjardins et al., 2002).
	Cationic polymer (Hydrex 3613)	• Hydrex 3613 polymer was used during the FMWTP pilot study and was dosed consistently at ~1.0 mg/L; except in the case of the SBF+PAC study where polymer was increased to manage high solids loading due to high solids loading due to high levels of PAC being added (polymer dosed at ~1.0–2.0 mg/L, increasing as PAC dose increased).	• This polymer was tested as it was the polymer available at the WTP where FMWTP piloting was conducted and is required for the SBF process (see note above).

*See Table C3 for additional chemical details

Table C1: Set points for parameters selected for pilot-scale drinking water treatability studies of wildfire ash-impacted source water (continued).

Set point parameter	Set point(s) selected	Specific details	Justification/comments
Treatment chemicals*	Hyrochloric acid (HCl)	• HCl was added at ~1mL/L of source water; dosing conditions were variable.	• Dosing conditions were based on bench-scale assessment (Chapter 3); however, due to shifts in water quality, acid doses were adjusted to meet desired set point conditions required for enhanced coagulation for GMWTP1 and FMWTP pilot studies, which were monitored with an online pH meter. • HCl was diluted prior to addition to 10% (3.2 mol/L) from commercial strength. • HCl was selected as acid to use due to availablilty (i.e. muriatic acid) and has been noted to be effective for reducing pH for enhanced coagulation (USEPA, 1999).
	Powdered activated carbon (PAC)	• Three doses of PAC were tested during GMWTP1 pilot study (50, 100, 250 mg/L); Four PAC doses were tested during FMWTP pilot study (100, 200, 400, 1000 mg/L); PAC doses for GMWTP2 were >2000 mg/L where fresh and recirculted PAC were added (see Tables B2 & B8).	• PAC doses were selected based on bench-scale investigations (Chapter 3); where minimum PAC doses was selected based on previous reports of PAC doses for treating less deteriorted post-fire water, where the highest value tested in a previous study was 60 mg/L for water with a DOC concentration of < 10 mg/L (Hohner et al., 2017); since the water that was tested herein had a higher DOC (e.g., >15 mg/L), the lowest dose tested was 100 mg/L. • The highest dose of PAC tested was 1000 mg/L during the FMWTP pilot study was the same the maximum dose tested in previous studies where deteriorated water quality with high DOC was treated (Najm et al., 1991); 1000 mg/L was tested to demonstrate extreme water quality may require extreme treatment measures; dosing at such a high level (i.e., 1000 mg/L) is not generally feasible at full-scale due to the high costs and the need for approprate infrastructure to dose (e.g., pumps, batch tanks). • A maximum dose of 250 mg/L was achieved for GMWTP1 pilot study due to limited pump capacity for dosing PAC. • The PAC type used for piloting were based on conclusions from bench-scale investigations where all PAC types that were tested performed similarly on DOC reductions in severely deteriorted source water indicative of post-fire scenarios (see Figure A1 in Appendix A).

*See Table C3 for additional chemical details

Table C2: Ash composition analysis for dry Scottie Creek Road (SCR) and Thuya Lake Road (TLR) ash samples collected in 2017 prior to any precipitation events.

Parameter	SCR ash	TLR ash	Detection limit	Unit
Moisture	4.22	2.11	0.10	%
Carbon total	5.04	5.81	0.10	%
Carbonate	1.8	1.1	0.10	%
Aluminum (Al)	9190	6190	50	ug/g
Arsenic (As)	3.27	4.54	0.10	ug/g
Cadmium (Cd)	0.691	0.772	0.020	ug/g
Calcium (Ca)	44100	33100	50	ug/g
Copper (Cu)	37.4	31.9	0.50	ug/g
Iron (Fe)	27700	17000	50	ug/g
Lead (Pb)	7.45	32.2	0.50	ug/g
Magnesium (Mg)	26900	14400	20	ug/g
Manganese (Mn)	807	5720	1.0	ug/g
Mercury (Hg)	0.0132	0.0185	0.0050	ug/g
Phosphorus (P)	2930	2210	50	ug/g
Potassium (K)	10100	3120	100	ug/g
Sodium (Na)	1050	234	50	ug/g
Sulfur (S)	2700	1000	1000	ug/g
Titanium (Ti)	1190	515	1.0	ug/g

Table C3: Summary information for three pilot-scale studies investigating the performance efficacy of drinking water treatment technologies on severely deteriorated wildfire ash-impacted source water representative of post-fire water conditions. Wildfire ash-impacted source water were prepared using Thuya Lake Road (TLR) or Scottie Creek Road (SCR) ash and river water from the location where piloting was conducted (e.g., Elbow River or Athabasca River).

Pilot study	Source water matrix treated	Pilot plant information	Treatment chemicals/products
GMWTP1 October, 2018 Calgary, Canada	TLR ash + Elbow River	• Portable mini-Actiflo unit • Flow rate: 1.4 m^3/h • Online instrumentation: turbidity (Hach, 1720E) pH (Hach, SC 100 transmitter)	• Alum sulfate (Al$_2$[SO$_4$]$_3$•14H$_2$O, SG=1.33, 8.3% Al$_2$O$_3$; Chemtrade, Toronto, Canada) • Cationic polyacrylamide polymer (Magnafloc® LT22S; BASF, Florham Park, NJ) • Hydrochloric acid (muriatic acid, 31.45%; Ro-Tyme, Oakville, Canada) • Powdered activated carbon (Hydrodarco W, lignite coal-based; Cabot Norit Canada Inc., Estevan, Canada) • Microsand (Actisand, silica quartz, 85μm diameter, uniformity coefficient of 2.07; Veolia^{TM}, Saint-Laurent, Canada)
FMWTP May, 2019 Ft. McMurray, Canada	SCR ash + Athabasca River	• Portable mini-Actiflo unit • Flow rate: 1.4 m^3/h • Online instrumentation: turbidity (Hach, 1720E) pH (Hach, SC 100 transmitter)	• Polyhydroxy aluminum chloride (Isopac, SG=1.37, 17.2% Al$_2$O$_3$; Klearwater Equiptment & Technologies, Calgary, Canada) • Cationic polyacrylamide polymer (Hydrex^{TM} 3613; Veolia Water Technologies, Saint-Laurent, Canada) • Hydrochloric acid (muriatic acid, 31.45%; Ro-Tyme, Oakville, Canada) • Powdered activated carbon (Hydrodarco W, lignite coal-based; Cabot Norit Canada Inc., Estevan, Canada) • Microsand (Actisand, silica quartz, 85μm diameter, uniformity coefficient of 2.07; Veolia^{TM}, Saint-Laurent, Canada)
GMWTP2 October, 2020 Calgary, Canada	TLR ash + Elbow River SCR ash + Elbow River	• Permanent Actiflo unit • Flow Rate: 1.3 m^3/h • Online instrumentation: turbidity (Solitax Immersion t-line sc), pH (HACH, SC 200 transmitter)	• Alum (Al$_2$[SO$_4$]$_3$•14H$_2$O, SG=1.33, 8.3% Al$_2$O$_3$; Chemtrade, Toronto, Canada) • Cationic polyacrylamide polymer (Magnafloc® LT22S; BASF, Florham Park, NJ) • Powdered activated carbon (AquaSorb CB1-MW, coconut-based; Jacobi, Columbus, OH) • Microsand (Actisand, silica quartz, 85μm diameter, uniformity coefficient of 2.07; Veolia^{TM}, Saint-Laurent, Canada)

Table C4: Summary of analytic methods and instrumentation used for water quality analysis throughout the three pilot-scale studies investigating the performance efficacy of drinking water treatment technologies on severely deteriorated wildfire ash-impacted source water. Dissolved organic carbon and total organic carbon are indicated as DOC and TOC, respectively. Disinfection by-product (DBP) analysis included measurements for trihalomethanes (THMs) and haloacetic acids (HAAs). Water quality analysis for all samples during the Fort McMurray water treatment plant pilot study were conducted by a third-party accredited laboratory.

Water quality parameter	Standard method	Instrumentation*	Notes
Turbidity	APHA SM 2130B	HACH 2100 N turbidimeter (Loveland, CO) HACH TU5200 turbidimeter (Loveland, CO)	none
pH	APHA SM 4500-H$^+$ B	Orion 720A pH meter, Thermo Fisher (Waltham, MA) HACH HQ411d pH meter (Loveland, CO)	none
DOC and TOC	APHA 5310-C	Shimadzu TOC-V CPH analyzer (Kyoto, Japan)	DOC filtered through pre-rinsed 0.45 µm membrane filter
UVA$_{254}$	APHA SM 5910B	Hach DR 5000 Spectrophotometer (Loveland, CO) RealTech, UV254 P200B (Whitby, Canada)	1 cm^{-1} quartz cell; filtered through pre-rinsed 0.45 µm membrane
Alkalinity	APHA SM 2320B	Orion 720A pH meter, Thermo Fisher (Waltham, MA)	titration method with pH endpoint of 4.5
Conductivity	APHA SM 2510	Radiometer Analytical CDM230 Conductivity Meter (Copenhagen, Denmark)	filtered through pre-rinsed 0.45 µm membrane filter
DBPs (THMs)	EPA 501.1	Teledyne Tekmar Atomax purge and trap instrument (Mason, OH) connected to an Agilent, 6890 Series gas chromatograph with electron capture detector (Santa Clara, CA)	analysis of four THMs: trichloromethane, bromodichloromethane, dibromochloromethane, and bromoform
DBPs (HAA5)	EPA 552.3	Agilent, 6890 Series gas chromatograph with electron capture detector (Santa Clara, CA)	analysis of five HAAs: monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, dibromoacetic acid.
Chlorine	APHA 4500-Cl$^-$ G	HACH DR2000 multimeter (Loveland, CO)	using N, N-diethyl-p-phenylene diamine (DPD)

*Multiple instruments are reported for some parameters due to different equipment used at different pilot study locations for water quality analysis.

Table C5: Post-hoc tukey test p-value results for ANOVA test comparing different alum doses (100–400 mg·L^{-1}) on treatment efficacy of sand-ballasted flocculation (SBF) during the Glenmore water treatment plant pilot study in 2018 (GMWTP1). Alum doses provided in table are rounded to nearest 100 mg·L^{-1}; actual alum dose conditions were 107, 206, 295, 407 mg·L^{-1}. Differences between treatment conditions for dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UVA$_{254}$) are provided. Statistical analysis was conducted on the percent removal values for each water quality parameter which indicated differences in pre-treatment and post-treatment conditions; this method was used due to variability in water quality in the severely deteriorated wildfire ash-impacted source water.

Alum dose (mg L^{-1}) comparisons*		SBF treatment	
		DOC	UVA$_{254}$
		p value	p value
100	200	0.75	0.015
	300	0.46	6.60E-05
	400	1.00E-06	1.00E-05
200	100	0.75	0.015
	300	0.95	0.0040
	400	2.00E-06	1.20E-05
300	100	0.46	6.60E-05
	200	0.95	0.004
	400	3.0E-06	0.001
400	100	1.00E-06	1.00E-06
	200	2.00E-06	1.20E-05
	300	3.00E-06	0.0010

Table C6: Total organic carbon (TOC) compared to dissolved organic carbon (DOC) for a range of samples collected during pilot-scale studies at Glenmore water treatment plant (GMWTP2) and Fort McMurray water treatment plant (FMWTP), where severely deteriorated wildfire ash-impacted source water were tested that were prepared from river water and Thuya Lake Road (TLR) or Scottie Creek Road (SCR) ash samples.

Sample	TOC (mg L^{-1})	DOC (mg L^{-1})	DOC/TOC (%)
Source water matrix (Elbow River +TLR ash)	20	19	93
Source water matrix (Elbow River +TLR ash)	21	19	90
Source water matrix (Elbow River +TLR ash)	20	19	92
Source water matrix (Athabsca River +SCR ash)	27	27	100
Source water matrix (Athabsca River +SCR ash)	26	26	100
Source water matrix (Athabsca River +SCR ash)	28	24	86
Clarified water following Dual-stage SBF	6	6	100
Clarified water following Dual-stage SBF	6	6	100
Clarified water following Dual-stage SBF	6	6	100

Table C7: Post-hoc tukey test p-value results for ANOVA test comparing three drinking water treatment methods during the Glenmore water treatment plant pilot study in 2018 (GMWTP1), including: sand-ballasted flocculation (SBF), SBF with enhanced coagulation (SBF+EC), and SBF with powdered activated carbon (PAC) pre-treatment (SBF+PAC) at three different dose conditions (50, 100, 250 mg·L^{-1}). All alum dose conditions were maintained approximately constant (~400 mg·L^{-1}); slight variability in alum was due to chemical pump precision. Differences between treatment conditions for dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UVA$_{254}$) are provided. Statistical analysis was conducted on the percent removal values for each water quality parameter which indicated differences in pre- treatment and post-treatment conditions; this method was used due to variability in water quality in the severely deteriorated wildfire ash-impacted source water.

Treatment multiple comparisons		DOC p value	UVA$_{254}$ p value
SBF	SBF+EC	0.254	1.68E-09
	SBF+PAC 50 mg/L	0.927	0.016
	SBF+PAC 100 mg/L	9.80E-08	6.98E-12
	SBF+PAC 250 mg/L	5.71E-10	1.98E-12
SBF+EC	SBF	0.254	1.68E-09
	SBF+PAC 50 mg/L	0.636	3.93E-10
	SBF+PAC 100 mg/L	3.81E-07	2.03E-08
	SBF+PAC 250 mg/L	1.27E-09	1.85E-10
SBF+PAC 50 mg/L	SBF	0.927	0.016
	SBF+EC	0.636	3.93E-10
	SBF+PAC 100 mg/L	1.57E-07	3.77E-12
	SBF+PAC 250 mg/L	7.55E-10	1.77E-12
SBF+PAC 100 mg/L	SBF	9.80E-08	6.98E-12
	SBF+EC	3.81E-07	2.03E-08
	SBF+PAC 50 mg/L	1.57E-07	3.77E-12
	SBF+PAC 250 mg/L	3.00E-06	2.00E-06
SBF+PAC 250 mg/L	SBF	5.71E-10	1.98E-12
	SBF+EC	1.27E-09	1.85E-10
	SBF+PAC 50 mg/L	7.55E-10	1.77E-12
	SBF+PAC 100 mg/L	3.00E-06	2.00E-06

Table C8: Post-hoc tukey test p-value results for ANOVA test comparing three drinking water treatment methods during the Fort McMurray water treatment plant pilot study in 2019 (FMWTP), including: sand-ballasted flocculation (SBF), SBF with enhanced coagulation (SBF+EC), and SBF with powdered activated carbon (PAC) pre-treatment (SBF+PAC) at four different doses (100, 200, 400, and 1000 mg·L^{-1}). All coagulant (PACl) dose conditions were maintained approximately constant (~400 mg·L^{-1}); slight variability in alum was due to chemical pump precision. Differences between treatment conditions ultraviolet absorbance at 254 nm (UVA$_{254}$) are provided; data for DOC was not available for all samples. Statistical analysis was conducted on the percent removal values for each water quality parameter which indicated differences in pre-treatment and post-treatment conditions; this method was used due to variability in water quality in the severely deteriorated wildfire ash-impacted source water.

Treatment multiple comparisons		UVA$_{254}$ p value
SBF	SBF+EC	8.72E-09
	SBF+PAC 100 mg/L	0.036
	SBF+PAC 200 mg/L	0.336
	SBF+PAC 400 mg/L	3.71E-08
	SBF+PAC 1000 mg/L	5.25E-12
SBF+EC	SBF	8.72E-09
	SBF+PAC 100 mg/L	1.19E-07
	SBF+PAC 200 mg/L	3.91E-08
	SBF+PAC 400 mg/L	0.368
	SBF+PAC 1000 mg/L	2.32E-08
SBF+PAC 100 mg/L	SBF	0.036
	SBF+EC	1.19E-07
	SBF+PAC 200 mg/L	0.716
	SBF+PAC 400 mg/L	7.21E-07
	SBF+PAC 1000 mg/L	1.68E-11
SBF+PAC 200 mg/L	SBF	0.336
	SBF+EC	3.91E-08
	SBF+PAC 100 mg/L	0.716
	SBF+PAC 400 mg/L	2.02E-07
	SBF+PAC 1000 mg/L	1.01E-11
SBF+PAC 400 mg/L	SBF	7.21E-07
	SBF+EC	0.368
	SBF+PAC 100 mg/L	7.21E-07
	SBF+PAC 200 mg/L	2.02E-07
	SBF+PAC 1000 mg/L	5.73E-09
SBF+PAC 1000 mg/L	SBF	5.25E-12
	SBF+EC	2.32E-08
	SBF+PAC 100 mg/L	1.68E-11
	SBF+PAC 200 mg/L	1.01E-11
	SBF+PAC 400 mg/L	5.73E-09

Table C9: Chemical dose conditions during the Glenmore water treatment plant second pilot study (GMWTP2) where dual-stage sand-ballasted flocculation (SBF) was evaluated. Chemical dose conditions are provided for treatment using SBF process in the absence of powdered activated carbon (PAC), indicated as 'SBF treatment (first pass).' The clarified water from the first pass of SBF was the treated again with the SBF process following PAC pre-treatment, indicated as 'Dual-stage SBF (second pass)'. In Trials 1 and 2 severely deteriorated wildfire ash-impacted source water were prepared with Elbow River water and ash from Thuya Lake Road (TLR) and Scottie Creek Road (SCR), respectively.

| Trial | SBF treatment (first pass) | | Dual-stage SBF (second pass) | | |
	Alum (mg L^{-1}) (mean ± SE)	Polymer (mg L^{-1}) (mean ± SE)	Alum (mg L^{-1}) (mean ± SE)	Polymer (mg L^{-1}) (mean ± SE)	PAC (mg L^{-1})* (mean ± SE)
Trial 1 (TLR ash and Elbow River water)	161 ± 33 (n=3)	1.2 ± 0.1 (n=3)	24 ± 0 (n=3)	1.1 ± 0.0 (n=3)	2200 (n=1)
Trial 2 (SCR ash and Elbow River water)	250 ± 0 (n=3)	1.1 ± 0.0 (n=3)	26 ± 0 (n=3)	1.1 ± 0.0 (n=3)	2600 (n=1)

* PAC doses are approximate combined total of fresh PAC slurry added and recirculted PAC sludge.

Table C10: Water quality results for dual-stage sand-ballasted flocculation (SBF) for Trial 1 and Trial 2 where severely deteriorated wildfire ash-impacted source water were prepared with Thuya Lake Road (TLR) and Scottie Creek Road (SCR), respectively. Water quality data (mean ± SE, n=9 in all cases) is provided for turbidity, dissolved organic carbon (DOC), and ultraviolet absorbance at 254 nm (UVA$_{254}$). Three water quality scenarios are provided: untreated severely deteriorated ash-impacted source water, identified as 'No treatment'; clarified water after it had passed through the SBF process a first time in the absence of powdered activated carbon (PAC), indicated as 'SBF treatment (first pass)'; and, final clarified water after it had passed through the SBF process a second time following PAC pre-treatment, indicated as 'Dual-stage SBF (second pass)'.

| GMWTP2 Trial | No tretatment | | | SBF treatment (first pass) | | | Dual-stage SBF (second pass) | | |
	Turbidity (NTU) (mean ± SE)	DOC (mg L^{-1}) (mean ± SE)	UVA (cm^{-1}) (mean ± SE)	Turbidity (NTU) (mean ± SE)	DOC (mg L^{-1}) (mean ± SE)	UVA (cm^{-1}) (mean ± SE)	Turbidity (NTU) (mean ± SE)	DOC (mg L^{-1}) (mean ± SE)	UVA (cm^{-1}) (mean ± SE)
Trial 1 (TLR ash and Elbow River water)	691 ± 18	19.9 ± 0.2	0.617 ± 0.004	5.3 ± 0.2	18.8 ± 0.1	0.558 ± 0.02	1.8 ± 0.1	6.9 ± 0.3	0.063 ± 0.007
Trial 2 (SCR ash and Elbow River water)	396 ± 8	17.4 ± 0.1	0.531 ± 0.003	3.5 ± 0.1	15.6 ± 0.1	0.449 ± 0.002	0.6 ± 0.02	7.9 ± 0.04	0.123 ± 0.03
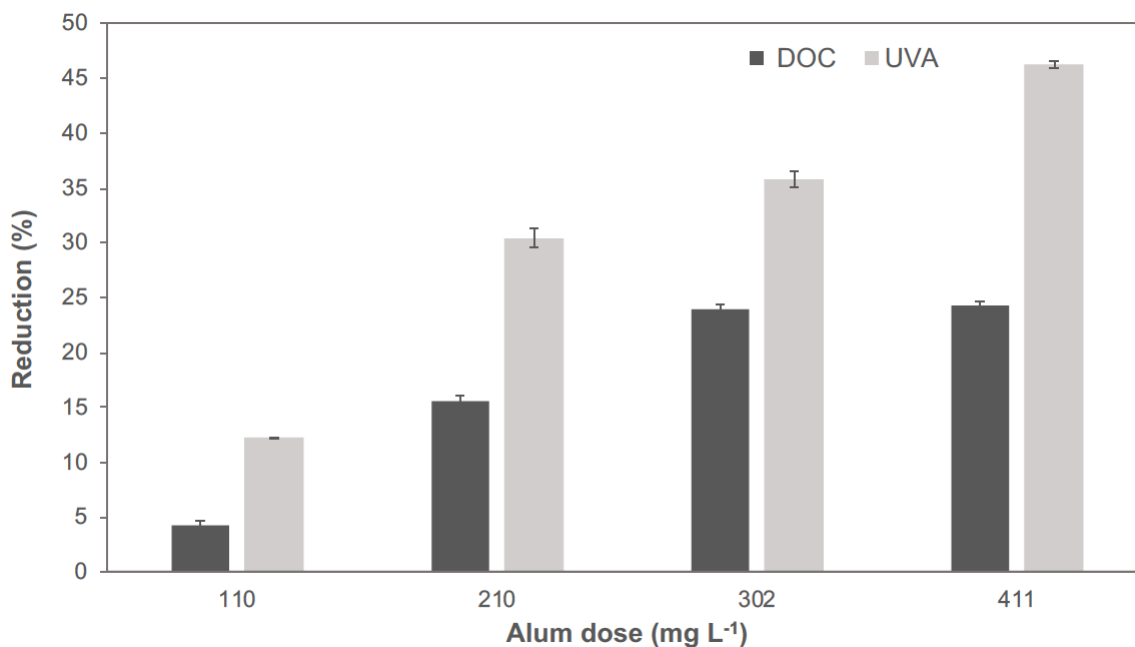
Figure C1: Percent reductions of dissolved organic carbon (DOC), and ultraviolet absorbance at 254 nm (UVA$_{254}$) in treated water after sand-ballasted flocculation (SBF) with enhanced coagulation through pH adjustment at different alum doses during the Glenmore water treatment plant pilot study in 2018 (GMWTP1). Treatment performance was evaluated on a severely deteriorated wildfire ash-impacted source water which was prepared with ash from the Thuya Lake Road severe wildfire and Elbow River water representing a "worst-case scenario," where wildfire ash is transported directly from hillslopes to source water supplies. All parameters reported as mean $\pm$ standard error (SE), n=3 in all cases; error bars indicate SE.
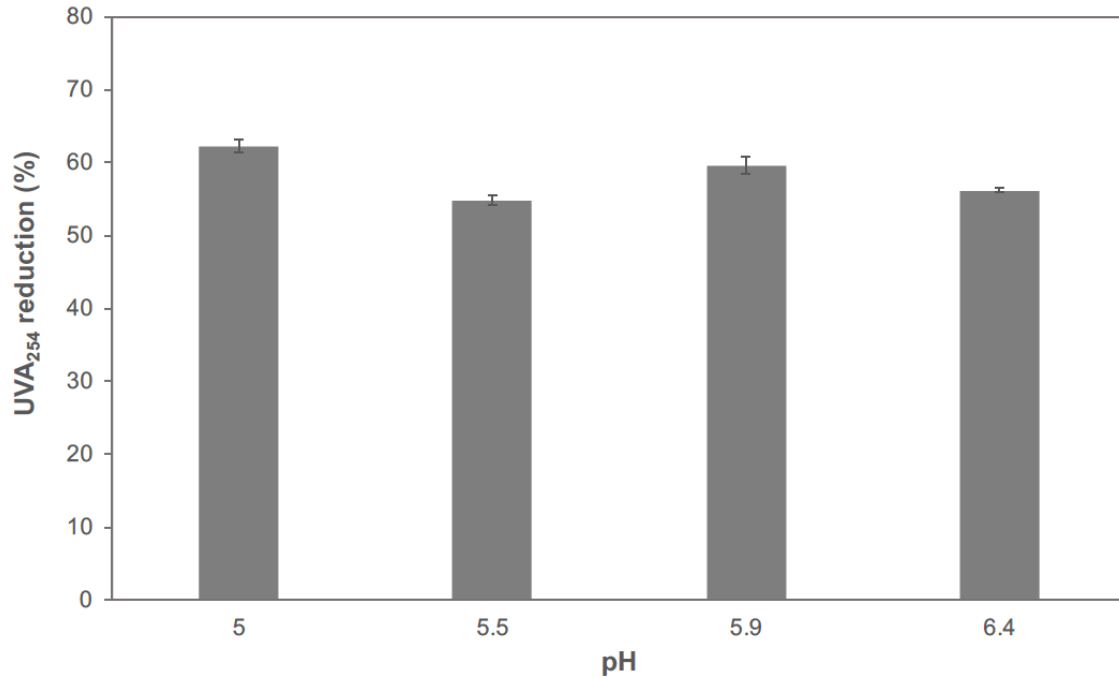
Figure C2: Percent reductions of ultraviolet absorbance at 254 nm (UVA_{254}) in treated water after sand-ballasted flocculation (SBF) with enhanced coagulation through pH adjustment during the Fort McMurray water treatment plant pilot study in 2019 (FMWTP). Treatment performance is indicated for clarified water after coagulation at pH ranging from 5.0-6.4. Treatment performance was evaluated on a severely deteriorated wildfire ash-impacted source water which was prepared with ash from the Scottie Creek Road severe wildfire and Athabasca River water representing a "worst-case scenario" following severe wildfire. UVA_{254} reduction reported as mean ± standard error (SE), n=3 in all cases; error bars indicate SE.
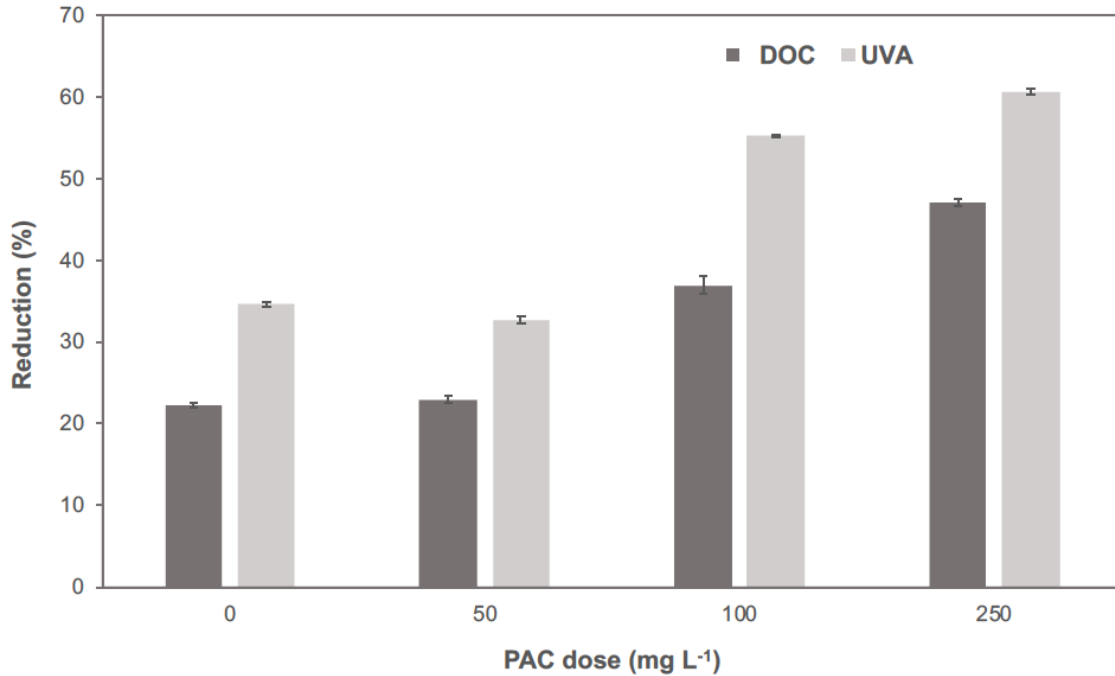
Figure C3: Percent reductions in treated water for DOC and UVA_{254} after powdered activated carbon (PAC) pre-treatment followed by sand-ballasted flocculation (SBF) treatment during the Glenmore water treatment plant pilot study in 2018 (GMWTP1). PAC doses ranging from 50–250 mg·L^{-1}were evaluated where treatment performance was evaluated on a severely deteriorated wildfire ash-impacted source water which was prepared with ash from the Thuya Lake Road severe wildfire and Elbow River water (indicated as '0' PAC dose condition). Parameters reported as reported as mean ± standard error (SE), n=3 in all cases; error bars indicate SE.
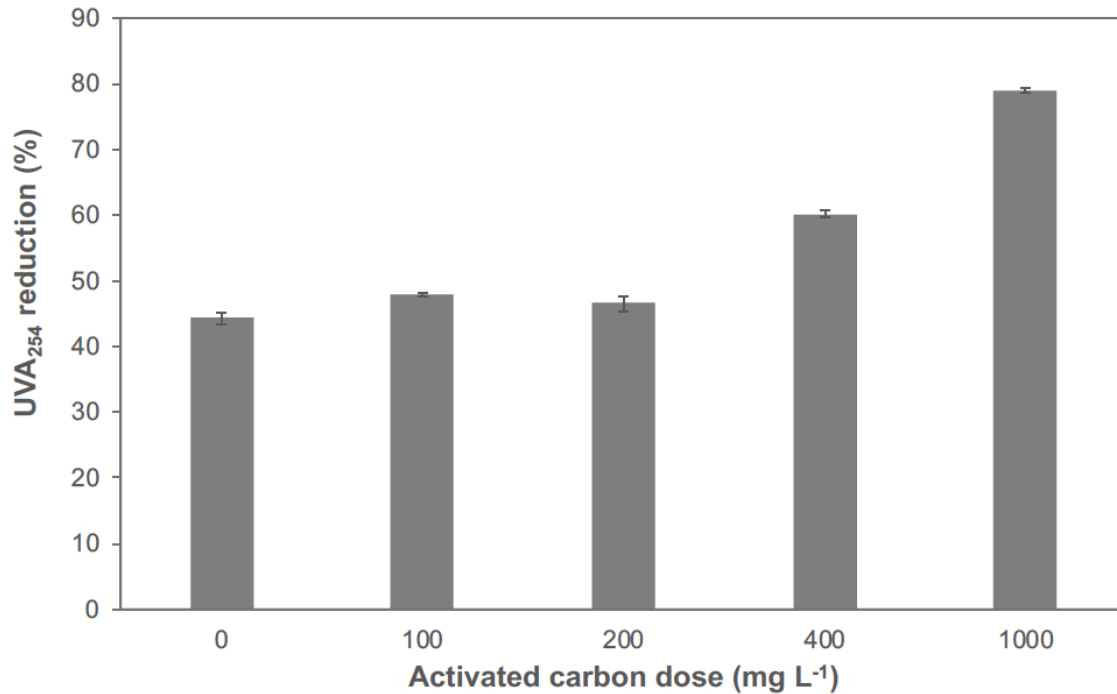
Figure C4: Percent reductions in treated water for UVA_{254} after powdered activated carbon (PAC) pre-treatment followed by sand-ballasted flocculation (SBF) treatment during the Fort McMurray water treatment plant pilot study in 2019 (FMWTP). PAC doses ranging from 100–1000 mg·L^{-1} were evaluated where treatment performance was evaluated on a severely deteriorated wildfire ash-impacted source water which was prepared with ash from the Scottie Lake Road severe wildfire and Athabasca River water (indicated as the '0' PAC dose condition). UVA_{254} reduction reported as mean ± standard error (SE), n=3 in all cases; error bars indicate SE.

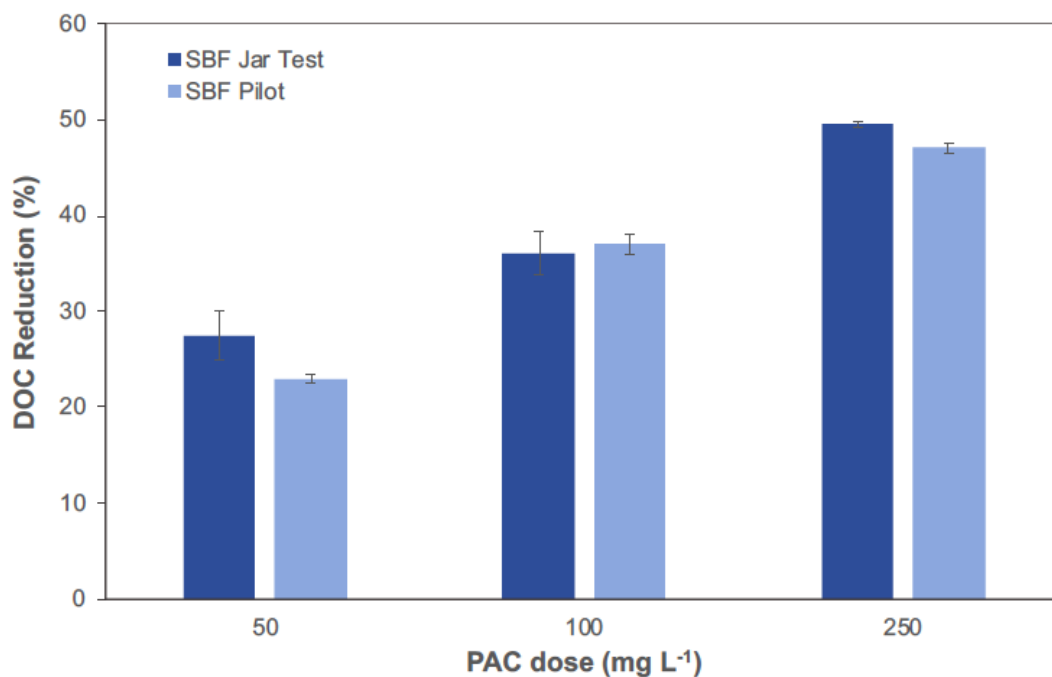Figure C5: Post-fire treatment performance evaluation using sand-ballasted flocculation with powdered activated carbon (PAC): comparing results of bench-scale (jar test) and pilot-scale treatment under the sample conditions. Similar results are demonstrated for both bench- and pilot-scale treatment, providing an indication that jar testing can be used as a valuable tool for predicting larger-scale treatment performance.

Appendix D: Supporting information for Treatment of wildfire ash-impacted water: Insights to the impacts of burn severity and physiographic setting

Table D1: Set points for parameters selected for drinking water treatability studies comparing wildfire-impacted source water prepared with material from different burn severities and different vegetation types.

Set point parameter	Set point(s) selected	Specific details	Justification/comments
Material/Ash type*	Unburned material (near Thuya Lake Road [TLR] wildfie site)	• Collected near Little Fort, British Columbia; material was collected on perimeter of burn site; TLR wildfire was part of the Little Fort fire complex (August, 2017).	• Unburned material used as a control to compare moderate and severe burn conditions on treatment efficacy.
	Moderate burned ash (TLR wildfire)	• Collected near Little Fort, British Columbia; sample was collected from area where moderate burning had occurred; TLR wildfire was part of the Little Fort fire complex (August, 2017).	• Ash was used to prepare synthetic ash-impacted source water as part of a comparative investigation of burn severity on post-fire treatment efficacy (moderate burn condition).
	Severe burn ash (TLR wildfire)	• Collected near Little Fort, British Columbia; sample was collected from area where severe burning had occurred; TLR wildfire was part of the Little Fort fire complex (August, 2017).	• Ash was used to prepare synthetic ash-impacted source water as part of a comparative investigation of burn severity on post-fire treatment efficacy (severe burn condition).
	Chaparral wildfire (United States)	• See Table 5.1 for collection site details.	• Ash was used to prepare synthetic ash-impacted source water as part of a comparative investigation of vegetation type on post-fire treatment efficacy as an indication of a chaparral wildfire.
	Moorland wildfire (United Kingdom)	• See Table 5.1 for collection site details.	• Ash was used to prepare synthetic ash-impacted source water as part of a comparative investigation of vegetation type on post-fire treatment efficacy as an indication of a moorland wildfire.
	Grassland wildfire (Canada)	• See Table 5.1 for collection site details.	• Ash was used to prepare synthetic ash-impacted source water as part of a comparative investigation of vegetation type on post-fire treatment efficacy as an indication of a grassland wildfire.
	Montane wildfire (Canada)	• See Table 5.1 for collection site details.	• Ash was used prepare synthetic ash-impacted source water as part of a comparative investigation of vegetation type on post-fire treatment efficacy as an indication of a montane wildfire.
Source water	Elbow River	• Collected in Calgary, Alberta, Canada, from the Glenmore reservoir.	• Elbow River water was selected as it is reprentative of a high quality source water origiating in a fire-prone region (e.g., Beers & Sosiak, 1993). • Selected due to availability through partnership with City of Calgary. • Mixed with ash (or unburned material) prepare synthetic source water matrices.
Synthetic ash-impacted source water concentration	Burn severity comparison study: 5.0 g/L for unburned, moderate burn, and severe burn.	• Mixed with Elbow River	• Concentration was kept constant (e.g., 5.0 g/L) for all burn conditions (unburned, moderate burn, severe burn) to compare scenarios following major runoff events when the same amount of material would be mobilized into a water source.
	Vegetation type comparison: variable, where chaparral 7.0 g/L, moorland 6.5 g/L, grassland 2.5 g/L, and Montane 1.5 g/L.	• Mixed with Elbow River	• Varying amounts of ash from the four wildfire sites to achieve similar UVA_{254} values to provide a baseline for comparing treatment efficacy; UVA_{254} was selected as baseline parameter due to being well-correlated with DOC (Chapter 2) and due to it being easier and faster to analyze compared to DOC.

*See Chapter 5, Table 5.1 for additional details

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Table D1: Set points for parameters selected for drinking water treatability studies comparing wildfire-impacted source water prepared with material from different burn severities and different vegetation types (continued).

Set point parameter	Set point(s) selected	Specific details	Justification/comments
Mixing time	30 min (for burn severity comparison study)	• Samples were mixed with river water using programable jar tester at 150 RPM in 1 L beaker.	• Ash was mixed for 30 min to provide time for effective mixing to occur to provide an opportunity for DOC to leach from ash. • Conditions were designed to represent a scenario where ash is mobilized off the landscape following a major runoff event into a recieving stream for a short period (i.e., 30 min) prior to reaching a WTP, where it would then be treated.
	12 h (for vegetation comparison study)	• Samples were mixed with river water using programable jar tester at 150 RPM in 1 L beaker.	• Ash was mixed for 12h to provide an opportunity for DOC to leach from ash for an extended period of time (i.e., >30 min). • Conditions were designed to represent a scenario where ash is mobilized off the landscape following a major runoff event into a recieving stream for a longer period (i.e., >30 min) prior to reaching a WTP, where it would then be treated.
Treatment technology	Conventional chemical pre-treatment	• Conducted according to ASTM jar test protocol (ASTM, 2013) with alum and cationic polymer; treatment consisted of cogulation, flocculation, and sedimentation; coagulant added and mixed for 1 min at 120 RPM; polymer added and mixed for additional 1 min at 120 RPM; 20 min mixing at 40 RPM; settled for 15 min.	• Conventional chemical pre-treatment was selected as this is the most commonly employed treatment technology in Canada (Statistics Canada, 2013) and is capable of tretating water quality with turbidity >20 NTU and DOC >4 mg/L (Crittenden et al., 2012).
Treatment chemicals**	Aluminum sulfate (alum)	• Four dose conditions for Burn Severity comparison study (50, 100, 200, and 400 mg/L) • Three dose conditions for Vegetation Type comparison study (50, 200, and 400 mg/L)	•Alum was used as a coagulant as this a commonly availble chemical and is the most widely used coagulant in North America (Crittenden et al., 2012). • Turbidity was effectively removed at the lowest alum dose; however, this study investigated the concurrent reduction of both turbidity and DOC, as such, doses >100 mg/L of alum were tested. • Coagulant doses were increased at equal increments to provide an indication of DOC removal efficacy across a wide range of dose conditions, where a maximum value of 400 mg/L was selected which is the NSF guideline for alum dose (NSF, 2017). • Four alum doses were tested for burn severity comparison to inicate increments where doses were doubled. • Three alum doses were tested for the vegetation comparison as an indication of high, medium, and low dose conditions; only three dose conditions were tested due to limited availability of ash samples to prepare synthetic ash impacted source waters
	Cationic polymer	• Polymer was dosed consistently at 0.5 mg/L for all treatment technologies tested.	• Polymer was used concurrently with alum to increase the efficacy of floccultion during treatment (Crittenden et al., 2012) and was used to be consistent with previous studies conducted on deteriorated water quality representative of post-fire scenarios (Chapter 3).

**See Chapter 5, Section 5.5.3 for additional details

Table D2: Summary of previous studies investigating post-fire treatment performance and speculated treatment implications.

Scale of evaluation	Water type	Treatment performance evaluated			Treatability speculated		References
		Turbidity	DOC/DBP-FP	Algae	Phosphorous/Algae	DOC/DBP-FP	
Full-scale	Natural	✓					Leak et., al., 2003
		✓	✓	✓			Emelko et al., in preparation
Pilot-scale	Natural	✓	✓				Skwaruk et al., 2021b
Bench-scale	Natural	✓	✓				Clark, 2010
	Natural	✓	✓				Emelko et al., 2011
	Natural		✓				Writer et al., 2014
	Synthetic					✓	Majidzadeh et al, 2015
	Natural replicated					✓	Wang et al., 2015a
	Synthetic					✓	Wang et al., 2015b
	Natural		✓				Hohner et al., 2016
	Synthetic				✓	✓	Tsai & Chow, 2016
	Natural replicated					✓	Wang et al., 2016
	Natural replicated					✓	Cawley et al., 2017
	Natural replicated	✓	✓				Hohner et al., 2017
	Natural replicated				✓	✓	Tsai et al., 2017
	Natural replicated					✓	Cawley et al., 2018
	Natural replicated				✓	✓	Tsai et al., 2019
	Natural					✓	Chow et al., 2019
	Synthetic		✓				Hohner et al., 2019b
	Natural replicated					✓	**Majidzadeh et al., 2019**
	Natural replicated		✓				Chen et al., 2020
	Natural					✓	Uzun et al., 2020a
	Natural replicated		✓				Uzun et al., 2020b
	Natural replicated	✓	✓				Skwaruk et al., 2021a
	Natural replicated				✓	✓	Chen et al., 2021
	Natural					✓	Olivares et al., 2021
	Synthetic					✓	Wilkerson & Rosario-Ortiz, 2021

Table D3: Summary of analytical methods and instrumentation used for water quality analysis for tests investigating the efficacy of conventional chemical pre-treatment treatment on deteriorated wildfire ash-impacted source water representative of different burn severity scenarios and different physiographic regions with different predominant vegetation types.

Water quality analysis	Standard method	Instrumentation	Notes
Alkalinity	APHA SM 2320B	Accumet AB 250 pH meter, Thermo Fisher (Waltham, MA)	titration method with pH endpoint of 4.5
Conductivity	APHA SM 2510	WTW Multi 350i conductivity Meter (Weilheim, Germany)	filtered through pre-rinsed 0.45 µm polyethersulfone (PES) membrane filter (Millipore Express® PLUS; Merck Millipore, Burlington, MA)
DOC	APHA 5310-B	Shimadzu TOC-V CPH analyzer (Kyoto, Japan)	DOC filtered through pre-rinsed 0.45 µm PES membrane filter
pH	APHA SM 4500-H$^+$ B	Accumet AB 250 pH meter, Thermo Fisher (Waltham, MA)	none
Turbidity	APHA SM 2130B	HACH 2100Q turbidimeter (Loveland, CO)	none
UVA$_{254}$	APHA SM 5910B	RealTech, UV254 P200B (Whitby, Canada)	1 cm^{-1} quartz cell; filtered through pre-rinsed 0.45 µm PES membrane
DBPs (THMs)	USEPA 501.1	Teledyne Tekmar Atomax purge and trap instrument (Mason, OH) connected to an Agilent, 6890 Series gas chromatograph with electron capture detector (Santa Clara, CA)	analysis of four THMs: trichloromethane, bromodichloromethane, dibromochloromethane, and bromoform
DBPs (HAA5)	USEPA 552.3	Agilent, 6890 Series gas chromatograph with electron capture detector (Santa Clara, CA)	analysis of five HAAs: monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid.
Chlorine	APHA 4500-Cl$^-$ G	HACH DR2000 multimeter (Loveland, CO)	N, N-diethyl-p-phenylene diamine (DPD) method
LC-OCD	Huber et al., 2011	DOC-Labor GmbH LC-OCD system (Karlsruhe, Germany)	chromatographs processed using ChromCALC, DOC-LABOR (Karlsruhe, Germany)

Table D4: Water quality results for Elbow River water and the ash-impacted source water prepared with Elbow River water and material from different burn severity conditions (unburned, moderate burn, severe burn); all wildfire ash-impacted source waters were prepared at a concentration of 5.0 g·L^{-1}. Mean ± standard error (SE) are indicated for each condition, where n=3 in all cases, unless otherwise specified.

Water sample	Turbidity (NTU) (mean ± SE)	DOC (mg L^{-1}) (mean ± SE)	UVA$_{254}$ (cm^{-1}) (mean ± SE)	pH (mean ± SE)	Alkalinity (mg L^{-1} as CaCO$_3$) (mean ± SE)	Conductivity (µS cm^{-1}) (mean ± SE)
Elbow River sample (n=3)	2.7 ± 0.8	4.2 ± 0.7	0.107 ± 0.004	8.1 ± 0.0	179 ± 1	387 ± 3 (n=2)
Unburned source water matrix (n=3)	149 ± 8	10.6 ± 0.2	0.218 ± 0.005	7.5 ± 0.1	177 ± 0.3	350 ± 0.4
Moderate burned source water matrix (n=3)	487 ± 62	7.2 ± 0.7	0.177 ± 0.004	8.0 ± 0.1	196 ± 1	370 ± 0.3
Severe burn source water matrix (n=3)	771 ± 49	25.8 ± 2.3	0.641 ± 0.022	9.1 ± 0.03	409 ± 4 (n=6)	496 ± 4

Table D5: Post-hoc tukey test p-value results comparing different burn severity conditions (unburned, moderate burn, and severe burn) for reductions of dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UVA$_{254}$) after conventional chemical pre-treatment (alum dose of 400 mg·L^{-1}). Comparisons were completed using the percent reduction from pre-treatment conditions in each case.

Burn severity		DOC p value	UVA$_{254}$ p value
Unburned	Moderate burn	7.13E-05	1.96E-04
	Severe burn	3.00E-06	2.49E-07
Moderate burn	Unburned	7.13E-05	1.96E-04
	Severe burn	3.81E-07	2.50E-07
Severe burn	Unburned	3.00E-06	2.49E-07
	Moderate burn	3.81E-07	2.50E-07

Table D6: Water quality results for Elbow River water and wildfire ash-impacted source waters prepared with Elbow River water and ash from severe wildfires in different vegetation regions (chaparral, moorland, grassland, and montane). Wildfire ash-impacted source water were prepared at varying concentrations to achieve similar UVA_{254} values: chaparral (7.0 $g·L^{-1}$), moorland (6.5 $g·L^{-1}$), grassland (2.5 $g·L^{-1}$) and Montane (1.5 $g·L^{-1}$). Mean ± standard error (SE) are indicated for each condition.

Water sample	Turbidity (NTU) (mean ± SE)	DOC (mg L^{-1}) (mean ± SE)	UVA_{254} (cm^{-1}) (mean ± SE)	pH (mean ± SE)	Alkalinity (mg L^{-1} as $CaCO_3$) (mean ± SE)	Conductivity ($\mu S\ cm^{-1}$) (mean ± SE)
Elbow River water* (n=6)	1.1 ± 0.1	1.6 ± 0.1	0.022 ± 0.001	8.2 ± 0.1	166 ± 1	469 ± 2
Chaparral source water matrix (n=3)	2648 ± 98	7.1 ± 0.04	0.240 ± 0.002	10.2 ± 0.03	207 ± 1	740 ± 1
Moorland source water matrix (n=3)	1195 ± 43	11.5 ± 1.0	0.303 ± 0.021	8.6 ± 0.1	115 ± 5	860 ± 32
Grassland source water matrix (n=3)	193 ± 5	13.7 ± 0.5	0.273 ± 0.008	8.5 ± 0.03	164 ± 3	472 ± 0
Montane source water matrix (n=3)	464 ± 7	8.0 ± 0.03	0.243 ± 0.003	8.7 ± 0.00	173 ± 2	496 ± 1

* Note the Elbow River water used for comparing the treatability of source water matrices representative of different vegetation regions varied slightly from that which was used in the burn severity comparison study due to samples being collected at different times of the year.

Table D7: Post-hoc tukey test p-value results comparing the UVA$_{254}$ of ash-impacted source waters prepared with Elbow River water and ash from severe wildfires in different vegetation regions (chaparral, moorland, grassland, and montane) prior to conventional chemical pre-treatment.

Vegetation type		UVA$_{254}$
		p value
Chaparral	Moorland	0.018
	Grassland	0.24
	Montane	1.00
Moorland	Chaparral	0.018
	Grassland	0.31
	Montane	0.024
Grassland	Chaparral	0.24
	Moorland	0.31
	Montane	0.32
Montane	Chaparral	1.00
	Moorland	0.024
	Grassland	0.32

Table D8: Post-hoc tukey test p-value results comparing DOC and UVA$_{254}$ of the ash-impacted source waters prepared with Elbow River water and ash from severe wildfires in different vegetation regions (chaparral, moorland, grassland, and montane) following treatment with conventional chemical pre-treatment using an alum dose of 400 mg·L^{-1}. Tests were conducted on percent reduction values for DOC following treatment due to a wide range of DOC values in the pre-treated wildfire ash-impacted source water; for statistical tests comparing UVA$_{254}$ levels, final UVA$_{254}$ values following treatment were used as similar values of UVA$_{254}$ were achieved in the pre-treated ash-impacted source water.

Vegetation type		DOC*	UVA$_{254}$**
		p value	p value
Chaparral	Moorland	0.08	0.056
	Grassland	0.48	0.0085
	Montane	0.04	8.68E-04
Moorland	Chaparral	0.08	0.056
	Grassland	0.57	0.53
	Montane	0.95	0.040
Grassland	Chaparral	0.48	0.0085
	Moorland	0.57	0.53
	Montane	0.32	0.27
Montane	Chaparral	0.04	8.68E-04
	Moorland	0.95	0.040
	Grassland	0.32	0.27

*Statistical tests completed using percent reduction values for DOC after treatment.

**Statistical tests completed using final UVA$_{254}$ values after treatment.

Table D9: Post-hoc tukey test p-value results comparing total trihalomethanes (TTHMs) and total haloacetic acids (HAA5) of the ash-impacted source waters prepared with Elbow River water and ash from severe wildfires in different vegetation regions (chaparral, moorland, grassland, and montane) following conventional chemical pre-treatment using an alum dose of 400 mg·L^{-1}. All tests were completed on normalized TTHM and HAA5 values (i.e., µg·L^{-1} of carbon), where total values were of TTHM and HAA5 were divided by DOC the concentrations of each sample. Although an ANOVA tests indicated that there was not a statistically significant difference between TTHMs (p=0.051), a post-hoc Tukey was still conducted to compare post-treatment TTHMs levels between the various wildfire ash-impacted source waters representative of different vegetation regions.

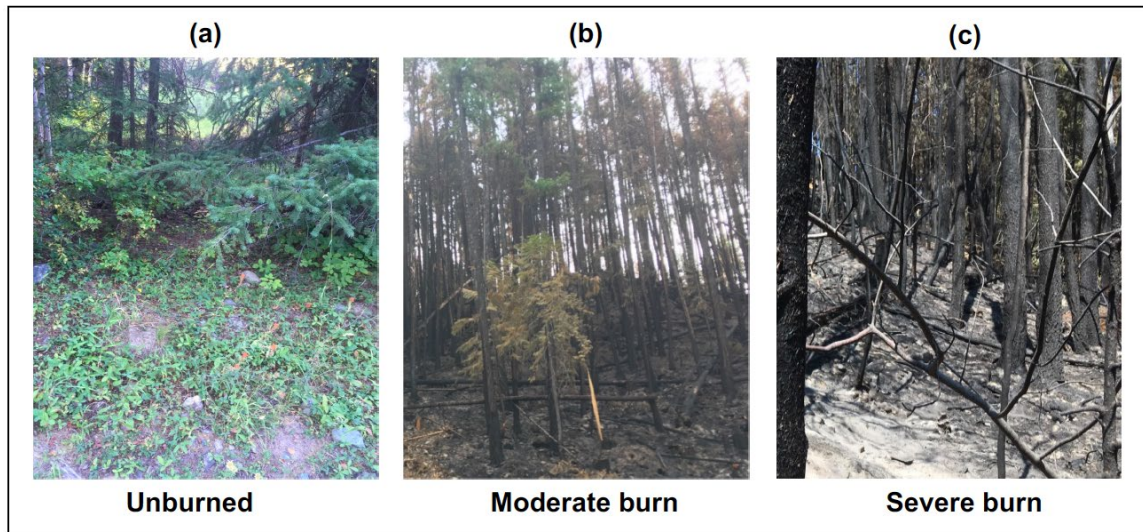| Vegetation type		TTHMs p value	HAA5 p value
Chaparral	Moorland	0.44	0.96
	Grassland	1.00	0.0030
	Montane	0.090	0.012
Moorland	Chaparral	0.44	0.96
	Grassland	0.33	0.0020
	Montane	0.65	0.01
Grassland	Chaparral	1.00	0.0030
	Moorland	0.33	0.0020
	Montane	0.065	0.66
Montane	Chaparral	0.090	0.012
	Moorland	0.65	0.0060
	Grassland	0.065	0.66

Figure D1: Landscape images of the sample collection sites where material was collected from unburned **(a)**, moderate burn **(b)**, and severe sites **(c)**. The difference in burn severity conditions was indicated by level of vegetation consumed during the wildfire. The materials collected were used to prepare the wildfire ash-impacted source waters for comparing treatability under different burn severity conditions.
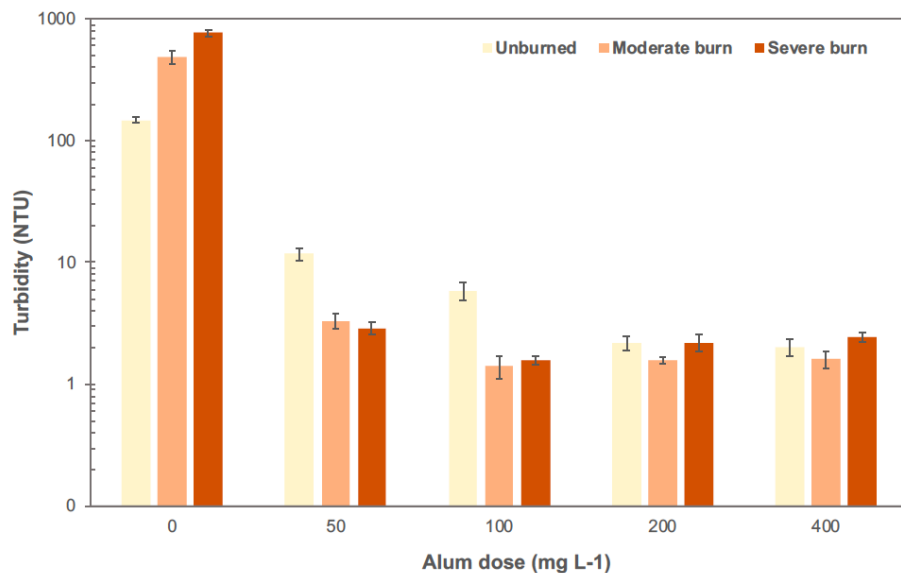
Figure D2: Turbidity reduction following conventional chemical pre-treatment for deteriorated ash-impacted source waters prepared with material from different burn severities (unburned, moderate burn, and severe burn). Treatment conditions were tested over a range of alum doses (0–400 mg·L^{-1}); mean values are indicated for each burn conditions; error bars specify standard error, where n=3 in each case.
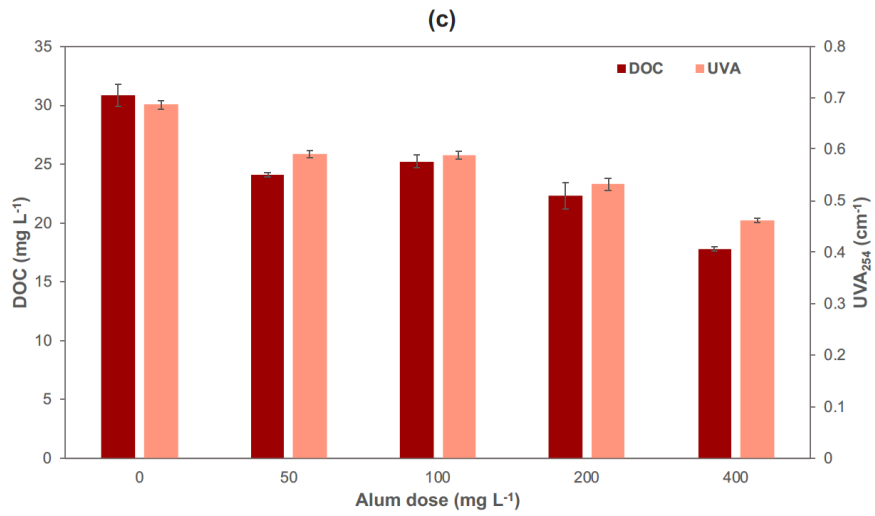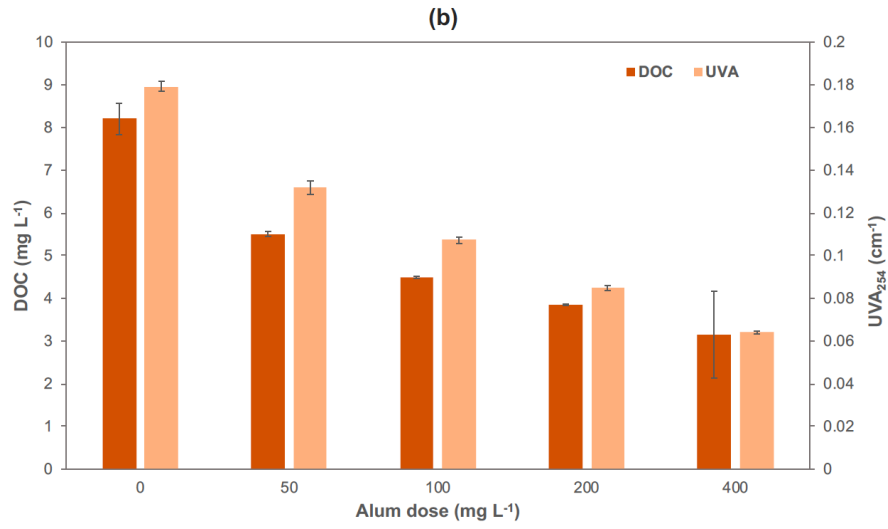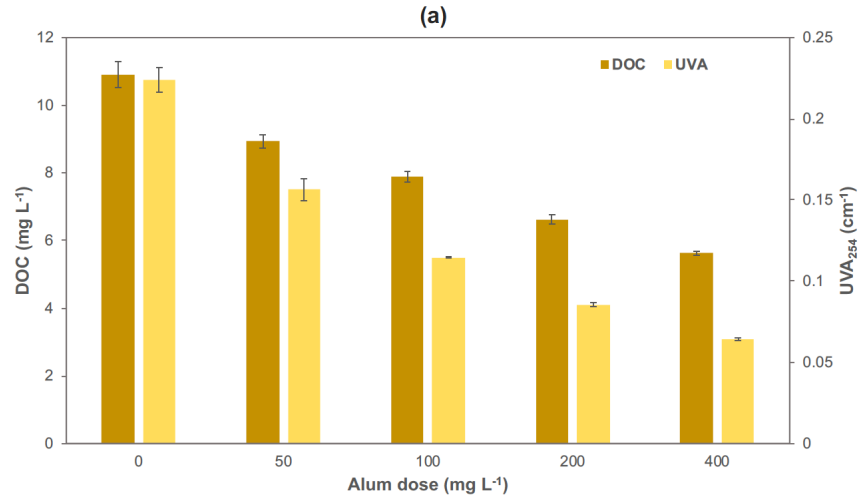
(a)

(b)

(c)

Figure D3: DOC and UVA$_{254}$ after conventional chemical pre-treatment over a range of alum dose conditions (0–400 mg·L^{-1}). Treatment results are provided for wildfire ash-impacted source waters representative of different burn severity conditions: **(a)** unburned; **(b)** moderate burned; and, **(c)** severe burned. All wildfire ash-impacted source waters were prepared at a concentration of 5 g·L^{-1}. All jar tests were completed in triplicate for each burn condition (i.e., n=3 in all cases). Parameters reported as mean ± standard error (SE), n=3 in all cases; error bars indicate SE.
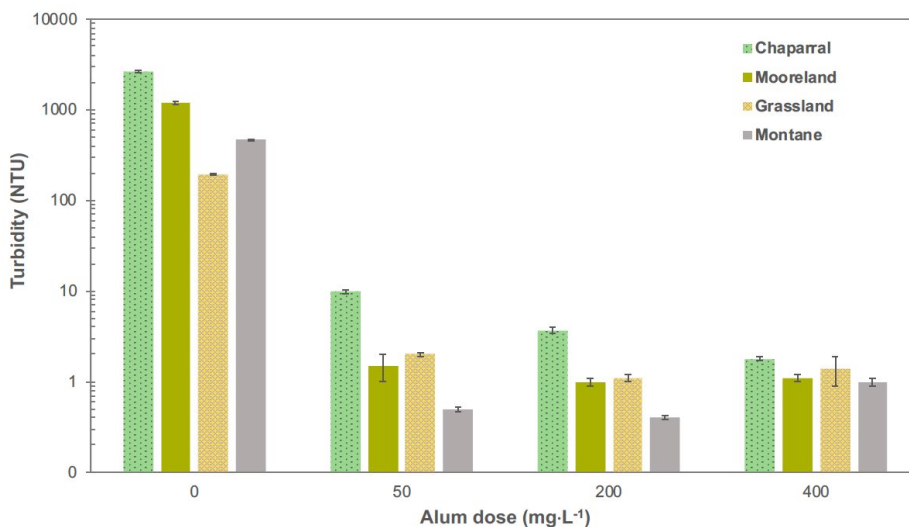

Figure D4: Turbidity reduction following conventional chemical pre-treatment for deteriorated ash-impacted source waters prepared with ash from severe wildfires in different vegetation regions (chaparral, moorland, grassland, and montane). Treatment conditions were tested over a range of alum doses (0–400 mg·L^{-1}); mean values are indicated for each burn conditions; error bars specify standard error. All jar tests were completed in triplicate for each vegetation type (i.e., n=3 in all cases). Parameters reported as mean ± standard error.
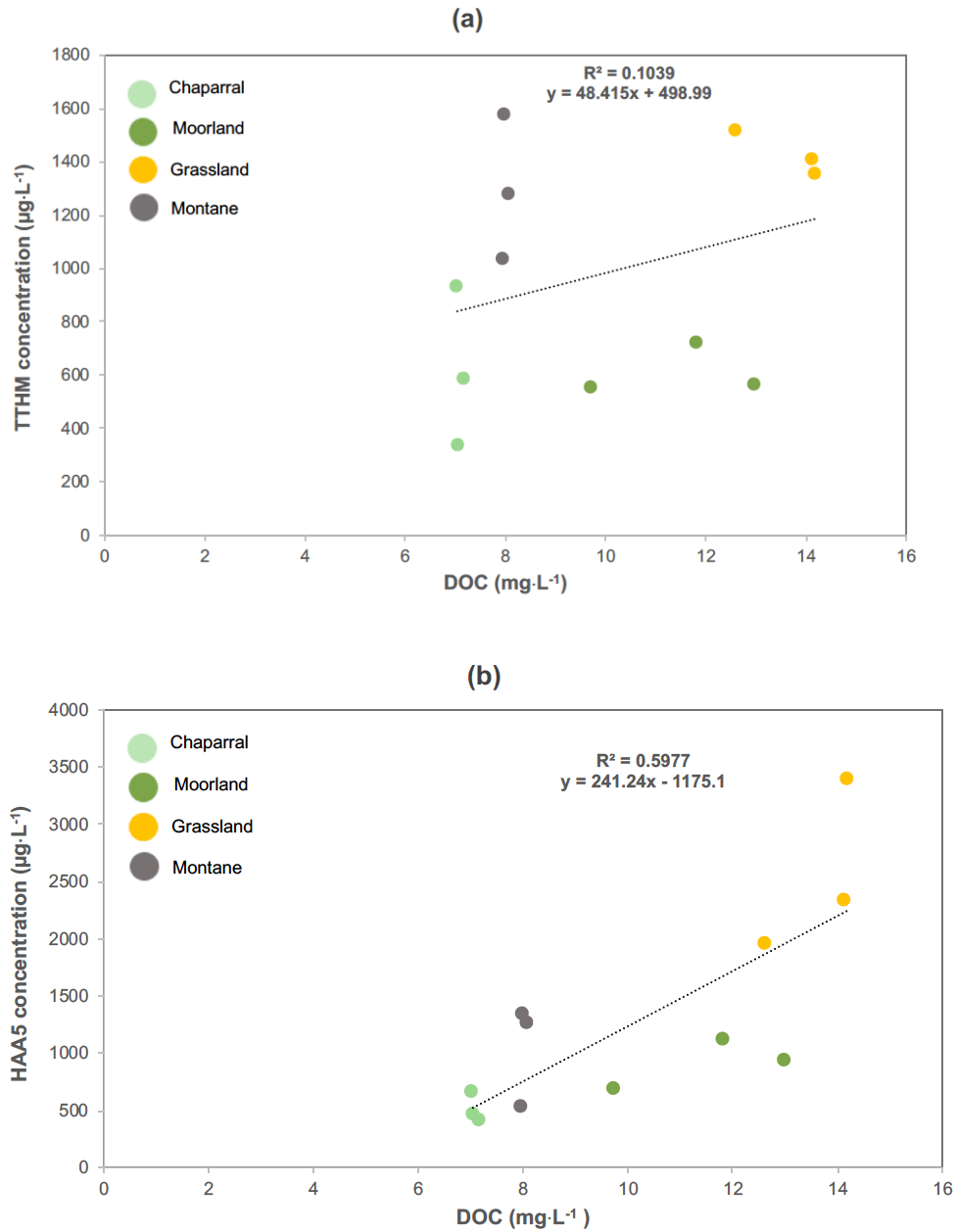
(a)

(b)

Figure D5: Linear correlation between dissolved organic carbon (DOC) and total trihalomethane (TTHM) yield **(a),** and total haloacetic acid (HAA5) yield **(b)** for wildfire-impacted source waters prepared with ash from severe wildfires in different physiographic regions with different predominant vegetation types (chaparral, moorland, grassland, and montane).