Proactive Characterization of Wildfire Impacts on Drinking Water Treatability

by

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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

Soosan Bahramian was the primary author for all chapters of this thesis. Chapters 1 and 6 were not written for publication. The research presented in Chapters 2 to 5 was written for publication. Exceptions to sole authorship of material are described below. It should be noted that the co-authors' names, and consequently their listed contributions, are arranged alphabetically and do not reflect the authorship order.

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Abstract

Forested catchments are important sources of drinking water globally. They are increasingly threatened by disturbances, prominently climate shocks, including large wildfires. Wildfires alter watershed hydrology and biogeochemistry, leading to reduced infiltration, increased overland flow, and enhanced delivery of sediments, burned vegetation, and pyrogenic material into aquatic systems. Such inputs can alter drinking water source quality and challenge treatability.

Ash is the residual material from wildland fuel combustion, composed of mineral particles and organic matter that can leach into water. While inorganic dissolved compounds from ash can impact water quality by, for example, increasing ionic strength and alkalinity, water-extractable organic matter (WEOM) from wildfire ash contributes to increased post-fire dissolved organic carbon (DOC) concentrations. During drinking water treatment, higher DOC concentrations increase chemical demand (e.g., coagulant, disinfectant), enhance the formation of potentially harmful disinfection by-products (DBPs), cause taste and odor issues, and promote bacterial regrowth in distribution systems. These impacts may also necessitate new infrastructure to manage changes in source water quality, ultimately increasing overall treatment costs.

Although they cannot reflect all watershed processes, bench-scale evaluations provide valuable insights into wildfire impacts on drinking water treatability by isolating treatment-relevant mechanisms at controlled laboratory conditions. However, different approaches used to prepare wildfire ash-impacted waters (WAIWs) limit the inferences that can be drawn from them. Here, key factors (e.g., mixing duration and condition, ash-to-water ratio, and source water quality) that can impact organic matter leaching from wildfire ash to water were investigated. WEOM concentration increased within the first 24 hours of mixing before plateauing or declining as mixing progressed, regardless of ash type and background water source. Continuous mixing yielded higher WEOM concentrations than stagnant conditions, indicating that particle-particle interactions and surface exposure enhanced leaching. WEOM yield also decreased as ash-to-water ratios increased. Despite anecdotal suggestions, a relationship between wildfire ash color and WEOM concentration was not observed (Chapter 2).

Wildfire ash collection methods may also impact inferences drawn from bench-scale drinking water treatability assessments. Unburned vegetation, rocks, or other debris may have physico-chemical properties different from those of ash deposits; thus, increasing uncertainty in treatability assessments. Dry ash homogenization methods (i.e., manual separation, sieving, and pulverization) were investigated because they may mitigate these impacts. Sieving was shown to be the most practical and reliable

method for ensuring ash homogeneity. Pulverization enhanced organic matter release from large particles by increasing surface area, but it also generated aerosolized ash, complicating sample handling. In addition, pulverization altered WEOM character, potentially by increasing the availability of smaller organic matter compounds previously encapsulated within ash particles or by mechanically fragmenting larger organic molecules into smaller compounds (Chapter 3).

Subsequent investigations examined the role of settleable ash solids (SAS), a previously overlooked fraction of wildfire ash. SAS substantially increased water alkalinity and make pH control for coagulation extremely difficult. Although pH adjustment enhances DOC removal from WAIW, SAS increased acid demand substantially. The removal of SAS reduced both alkalinity and acid demand; however, as ionic strength was concurrently reduced, floc formation and turbidity reduction for a given coagulant dose decreased somewhat. A limited complementary analysis was conducted to evaluate whether atmospheric ash deposition could also act as a significant driver of source water quality and treatability change. While the impact of atmospheric deposition of ash on water alkalinity depends on the surface area of water body, only exceptionally high atmospheric ash loading could meaningfully alter source water alkalinity in reservoirs that hold large volume of water (Chapter 4).

Wildfire ash alters multiple aspects of water quality concurrently, including turbidity, DOC concentration and character, and alkalinity, so its overall implications for water treatment cannot be adequately assessed by examining individual mechanisms in isolation. Coagulation experiments with WAIWs demonstrated these interacting impacts. At low coagulant (i.e., alum) doses, turbidity was effectively reduced, yet DOC removal remained limited, despite pH adjustment to coagulant-specific optima. Enhanced coagulation combined with higher alum doses improved DOC removal but introduced trade-offs, as turbidity reduction declined somewhat because of reduced ionic strength associated with decreased alkalinity. The results indicated, while wildfire ash can severely deteriorate water quality by increasing turbidity, alkalinity, DOC concentration and aromaticity, which may increase coagulant demand or necessitate more advanced treatment methods, the underlying coagulation mechanisms for WAIW remain consistent with those in natural waters. Thus, wildfire ash does not present fundamentally new challenges to coagulation; rather, the magnitude of water quality changes following wildfire can pose risk to treatment performance and operational resilience (Chapter 5).

Collectively, this research demonstrates that while bench-scale studies cannot fully replicate the complexity of post-fire watershed processes and wildfire impacts on water quality, they remain essential for isolating and investigating the specific effects of wildfire ash on drinking water treatment processes.

Accordingly, it is practical to adopt methods that maximize the extraction of organic matter from wildfire ash and represent worst-case treatment scenarios. These methodological insights help ensure the comparability of bench-scale investigations. This work also shows that wildfire impacts coagulation primarily by complicating pH control and deteriorating drinking water source quality, increasing the need for more intensive treatment processes. Overall, this research establishes a robust methodological foundation for reliably assessing wildfire ash impacts on water quality and for informing the development of strategies to mitigate wildfire impacts on drinking water treatability.

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Dedication

To Toulooe, Kayhan, Mom, and Dad

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List of Abbreviations

%	Percentage
BDCM	Bromodichloromethane
$CaCO_3$	Calcium carbonate
CC	Cameron Creek
DBAA	Dibromoacetic acid
DBCM	Dibromochloromethane
DBP	Disinfection By-product
DBP-FP	Disinfection By-product Formation Potential
DCAA	Dibromoacetic acid
DC-P	Doctor Creek prescribed fire site
DC-S1	Doctor Creek sampling site 1
DC-S2	Doctor Creek sampling site 2
DOC	Dissolved organic matter
DPD	N-diethyl-p-phenylene diamine
DWTP	Drinking water treatment plant
E2:E3	UV absorbance at 250 nm divided by UV absorbance at 365 nm
ER	Elbow River
FDBP-UFC	Disinfection By-product Uniform Formation Conditions
FP	Formation potential
g cm^{-3}	Gram per cubic centimeter

$g\ mol^{-1}$	Gram per mol
$g\ L^{-1}$	Gram per liter
HAA	Haloacetic acids
HAA5	Total haloacetic acids
HCl	Hydrochloric Acid
kg	Kilogram
$kg\ m^{-2}$	Kilogram per square meter
$L\ mg^{-1}\ m^{-1}$	Liter pr milligram meter
LC-OCD	Liquid chromatography in combination with organic carbon detection
LMW	Low molecular weight
m	Meter
m^2	Square meter
m^3	Cubic meter
MBAA	Monobromoacetic acid
MCAA	Monochloroacetic acid
$mg\ cm^{-3}$	Milligram per cubic centimeter
$mg\ g^{-1}$	Milligram per gram
$Mg\ ha^{-1}$	Megagram per hectare
$mg\ L^{-1}$	Milligram per liter
MK	Minnekhada
mm	millimeter
$mS\ cm^{-1}$	Mili siemens per centimeter
NOM	Natural organic matter

NTU	Nephelometric Turbidity Units
OM	Organic Matter
PES	Polyethersulfone
RMWB	Regional Municipality of Wood Buffalo
S:L	Solids-to-liquid ratio
SAS	Settleable ash solids
SC	Scottie Creek
SD	Standard Deviation
SUVA	Specific ultraviolet absorbance at 254 nm
TBM	Tribromomethane
TC	Thuya Creek
TCAA	Trichloroacetic acid
TCM	Trichloromethane
THMs	Trihalomethanes
TOC	Total organic carbon
TTHMs	Total trihalomethanes
U. S. EPA	United States Environmental Protection Agency
UFC	Uniform formation conditions
UP	Ultrapure
UV_{254}	Ultraviolet absorbance at the wavelength of 254 nm
WAIW	Wildfire ash-impacted water
WEOM	Water extractable organic matter
wt	Weight

$\mu S\ cm^{-1}$	Micro siemens per centimeter
$\mu g\ L^{-1}$	Microgram per liter

Chapter 1
Introduction

1.1 Research motivation

The availability of safe drinking water is essential to the protection of public health. All natural water requires some level of treatment to make it safe for consumption (Edzwald, 2011)—even deep groundwater supplies require sufficient disinfection to mitigate threats from waterborne pathogens (Emelko et al., 2019). While drinking water treatment focuses on removing contaminants from untreated source water to make it safe for consumption and aesthetically pleasing, drinking water treatability reflects the difficulty and cost of providing safe drinking water; thus, it is linked to both current and future source water quality, which is governed by watershed condition and hydroclimate (Emelko et al., 2011).

Forested catchments are critical sources of drinking water globally, but they are increasingly threatened by a range of natural and anthropogenic disturbances (Dale et al., 2001; Emelko et al., 2011). Among these, large wildfires have emerged as one of the most pressing threats to water supply reliability (Delpla et al., 2009; Flannigan et al., 2013; Dennison et al., 2014). Prolonged droughts, warmer temperatures, and increased fuel availability have contributed to more frequent, large and severe wildfires (Westerling et al., 2006; USEPA, 2016; NRC, 2025). Wildfires can substantially deteriorate water quality (Smith et al., 2011; Bladon et al., 2014; Paul et al., 2022) and reduce drinking water source treatability, thereby threatening the provision of safe drinking water (Emelko et al., 2011).

Wildfire threats to drinking water supply reliability are underpinned by potential alterations to watershed hydrology and biogeochemistry. Loss of vegetation and the formation of hydrophobic soils reduce infiltration and increase overland flow, enhancing erosion and the delivery of sediments, burned vegetation, and pyrogenic material into receiving waters (DeBano, 1991; Doerr et al., 2000; Certini, 2005; Silins et al., 2009; Emelko et al., 2024). Ash inputs into water can increase turbidity, suspended solids, pH, alkalinity, and dissolved organic carbon (DOC) (Bladon et al., 2008; Emelko et al., 2011; Silins et al., 2014; Writer et al., 2014). Greater variability in these aspects of source water quality can challenge drinking water treatment operational response capacity (Emelko et al., 2011; Emelko & Sham, 2014; Blackburn et al., 2023). Once deposited in downstream receiving waters such as lakes and reservoirs, ash and wildfire-impacted sediments may act as a long-term internal source of nutrients such as phosphorus, even many years after wildfire when surface water appears visually clear (Watt et al., 2021; Francisgeli, 2022). This poses latent risks to drinking water treatment performance (McEachern et al., 2000; Silins et al., 2014; Emelko et al., 2016; Murphy et al., 2017; Rhoades et al., 2018; Martens et al., 2019; Paul et al., 2022).

While wildfire impacts on drinking water source quality and treatability can be readily characterized *after* wildfire, proactive assessment of potential impacts for risk management purposes is more challenging because it is difficult—if not impossible—to be predictive. Bench-scale experiments have been conducted at a wide range of experimental conditions in an attempt to proactively simulate wildfire effects on water quality (e.g., Santín et al., 2012; Hohner et al., 2017; Blackburn et al., 2023). Typically, such investigations involve preparation of wildfire ash-impacted water (WAIW), which involves adding post-fire ash or lab-heated biomass (to represent ash) to water. While these studies cannot fully replicate the complex hydrological and biogeochemical processes that occur at the watershed scale, they can provide valuable insights regarding treatment challenges and mechanisms. As treatability implications are directly related to source water quality, differences in experimental conditions and the lack of justification for chosen methods in preparing WAIW have hindered the ability to draw meaningful inferences across studies and highlighted the need for systematic evaluation of key methodological factors influencing WAIW quality. For example, the effects of preparation conditions, such as mixing duration and ash-to-water ratio, on the concentration and character of water-extractable organic matter (WEOM) have not been characterized (**Gap #1**).

Wildfire ash is a complex mixture of residual material from wildland fuel combustion, consisting of mineral particles and organic matter. It may also contain unburned vegetation, rocks, and other debris that do not share the characteristics of combusted fuels. Given the inherent heterogeneity of wildfire ash (Bodí et al., 2014; Garcia-Sanchez et al., 2023), various methods have been used to homogenize dry ash and improve experimental reproducibility. Common approaches include sieving, pulverization, and manual removal of large, non-representative materials. While these pretreatment methods are intended to enhance consistency, their effects on the rate and extent of WEOM leaching are unknown (**Gap #2**).

The extent and duration of wildfire ash impacts on water quality depend on factors such as fire severity, precipitation patterns, and watershed characteristics (Tecle & Neary, 2015; Nunes et al., 2018). For example, ash generated at higher combustion temperatures typically has smaller particle sizes, lower organic content, and a higher proportion of inorganic compounds, particularly carbonates, silica and metal oxides (Balfour & Woods, 2010; 2011; 2013; Bodí et al., 2014; Sapkota et al., 2025). These particles generally exceed 2.5 g cm^{-3} in density and can settle out of suspension (Balfour & Woods, 2013).

Alkaline minerals in wildfire ash can increase pH and buffering capacity, complicating pH-sensitive treatment processes such as chemical coagulation (Amirtharajah & Mills, 1982; Bratby, 2016). Changes

in water temperature, pH, alkalinity, turbidity, and organic carbon concentration can impact the efficiency of coagulation with metal salts in turbidity and DOC removal (Edzwald & Tobiason, 1999; Crittenden et al., 2012). Settleable ash solids (SAS) that deposit raw water reservoirs have the potential to serve as longer-term drivers of water quality change; however, their role in shaping WAIW chemistry and its implications for drinking water treatment are not understood (**Gap #3**).

Although watershed-scale responses vary due to dilution and hydrological factors, bench- and pilot-scale studies have consistently reported increases in DOC, turbidity, alkalinity, and pH after wildfire ash addition to water. Wildfire ash also tends to increase the proportion of low molecular weight (LMW) organic compounds in water (Hohner et al., 2019; Skwaruk, 2021), which are less amenable to removal by coagulation than higher molecular weight fractions (Dannett et al., 1996; Chow et al., 2009). Accordingly, reduced coagulation efficiency for DOC removal is expected for WAIWs; thus, enhanced coagulation is typically required for removed DOC from WAIW (Skwaruk et al., 2020; Farmer 2021). Because contaminants requiring treatment beyond conventional drinking water treatment methods are rarely reported after wildland fires (i.e., fires on non-urbanized landscapes) (Emmerton et al., 2020; ADD OTHERS), it is unlikely that WAIW would pose new treatment challenges to chemical pre-treatment processes (i.e., coagulation, flocculation, clarification) other than extremes in magnitude—this has not been demonstrated, however (**Gap #4**). Given that wildfire ash addition to natural water typically increases DOC, turbidity, alkalinity, and pH (depending on quality of the water matrix prior to ash addition), it is reasonable to expected that pre-treatment performance, especially coagulation, would be governed by the same, well-establish physico-chemical mechanisms as natural water; namely, adsorption and charge neutralization, double layer compression, enmeshment in precipitated metal hydroxides, and inter-particle bridging (Amirtharajah & Mills 1982; Duan & Gregory 2003; Ballantyne et al., 2024).

1.2 Research objectives

The overall goal of this research is to advance proactive characterization of wildfire impacts on drinking water source treatability. To this, the knowledge gaps identified above were investigated at bench-scale. Specific research objectives were to:

1) Characterize key factors impacting WEOM concentration and character after wildfire ash addition to water (addressing **Gap #1**);

2) Identify mixing conditions that maximize WEOM concentration in WAIW at bench-scale (addressing **Gap #1**);

3) Evaluate the impacts of wildfire ash attributes and pretreatment methods on WEOM leaching into water (addressing **Gap #2**);

4) Assess the impact of SAS on untreated water alkalinity and its implications for drinking water treatment (addressing **Gap #3**);

5) Demonstrate how and why wildfire ash implications for coagulation during drinking water treatment are universally consistent (addressing **Gap #4**).

Collectively, these objectives aim to provide guidance for WAIW preparation and characterization, while enhancing insight into the treatability of WAIW under varying environmental and operational conditions.

1.3 General research approach

To achieve the overall goal of advancing assessment of wildfire ash impacts on drinking water quality and treatability, this research was conducted in four phases. Figure 1-1 and the descriptions below detail the approach undertaken in each phase.

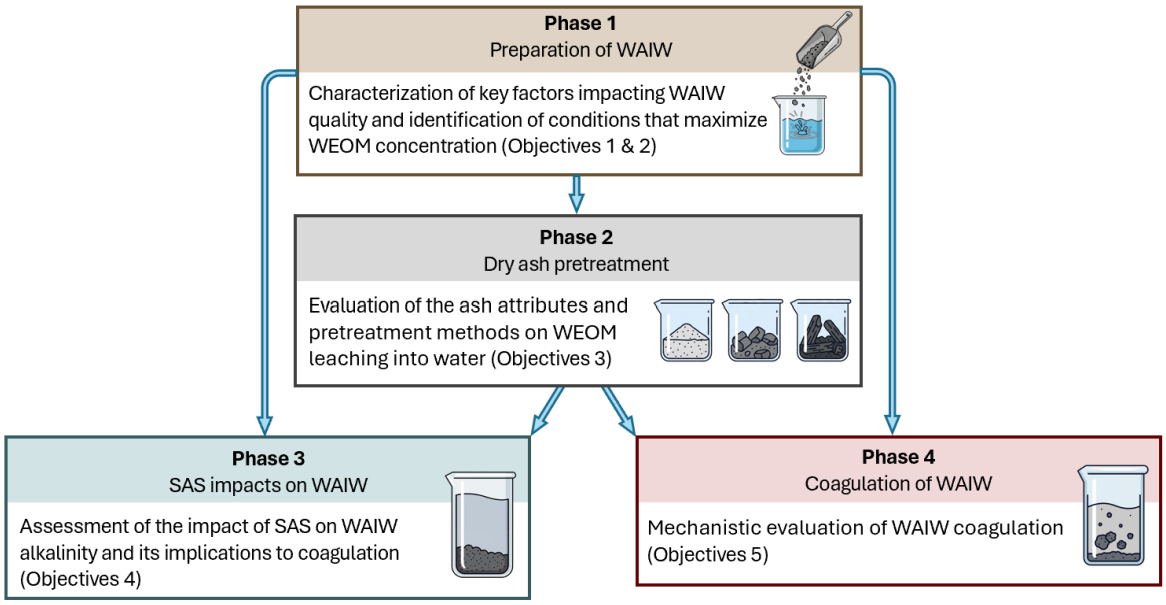


Figure 1-1 Research approach and corresponding objectives. The arrows show how specific objectives and outputs informed subsequent stages of the study. Phases 1 and 2 focused on the impact of wildfire ash-impacted water preparation and dry ash pretreatment techniques on wildfire ash water extractable organic matter (WEOM) concentration and character. These phases informed Phase 3, which studied the impact of settleable ash solids (SAS) on WAIW alkalinity and coagulation, and also guided the design of Phase 4.

In Phase 1, the impact of WAIW preparation conditions on WEOM concentration and character was evaluated (Objectives 1 and 2) and associated implications to interpreting wildfire impacts on water quality and treatability were discussed. Several experimental factors, including (i) ash type (several wildfires, prescribed fire), (ii) background water matrix (ultrapure, natural river water), (iii) ash-to-water ratio (from 0.5 to 5 g L^{-1}), (iv) mixing conditions, and (v) mixing duration were investigated. This led to recommendations for bench-scale testing methods so that generated data from nominal replicates are more reproducible and inter-study comparisons are possible. The work also provided strategies for maximizing WEOM leaching to water; this may be desirable for treatment technology challenge testing or pilot-scale evaluations of operational response capacity. The findings from this phase directly informed the experimental design of Phases 2, 3 and 4.

Phase 2 investigated the impact of different pretreatment methods used to homogenize dry ash on the extraction of organic matter from wildfire ash (Objective 3). Here, different ash types were homogenized using manual separation, sieving, and pulverization, and WEOM concentration and

character were monitored during different mixing times and at different ash-to-water ratios. By evaluating how these pretreatment approaches affect WEOM release, this work also led to recommendations for bench-scale testing methods so that generated data from nominal replicates are more reproducible and inter-study comparisons are possible. Coupled with findings from Phase 1, Phase 2 findings informed the design of Phases 3 and 4.

Phase 3 involved evaluating the effects of SAS on WAIW alkalinity and its implications for conventional and enhanced (i.e., reduced pH) coagulation (Objective 4). WAIWs were prepared using different ash fractions collected from multiple wildfires and a prescribed fire, representing a broad range of ash characteristics. Several ash-to-water ratios were tested.

Phase 4 involved evaluation of WAIW coagulation (Objective 5). Given that coagulation of natural water is governed by well-established physico-chemical mechanisms, this work was conducted to investigate if wildfire ash associated increases in DOC, turbidity, alkalinity, and pH would affect coagulation performance in a manner similar to natural water unaffected by wildfire. Turbidity and DOC removal by conventional and enhanced coagulation were investigated for WAIWs composed of different (i) ash types (representing a range of fire severities and combustion conditions) at (ii) source water matrices (ultrapure and natural river water).

1.4 Thesis organization

This thesis consists of six chapters. Chapters 2 through 5 are formatted as journal papers. Chapter 2 has been submitted to a refereed journal, and Chapters 3 to 5 have been submitted to co-authors for commentary, prior to submission for refereed journal publication.

Chapter 2 provides the results of the study that investigated key factors, including mixing conditions and duration, ash-to-water ratio, and source water quality, on wildfire ash WEOM concentration and character. Chapter 3 describes the impacts of different dry ash pretreatment techniques on WAIW quality metrics relevant to drinking water treatment. Chapter 4, valuates the relationship between SAS removal and WAIW alkalinity, and its implications for both conventional and enhanced coagulation processes. Chapter 5 evaluates WAIW coagulation performance and examines whether the wildfire ash affects coagulation differently compared to natural waters. Lastly, Chapter 6 provides a summary of the conclusions, major contributions, implications, and recommendations of this work. This is followed by a reference list and several appendices containing additional details.

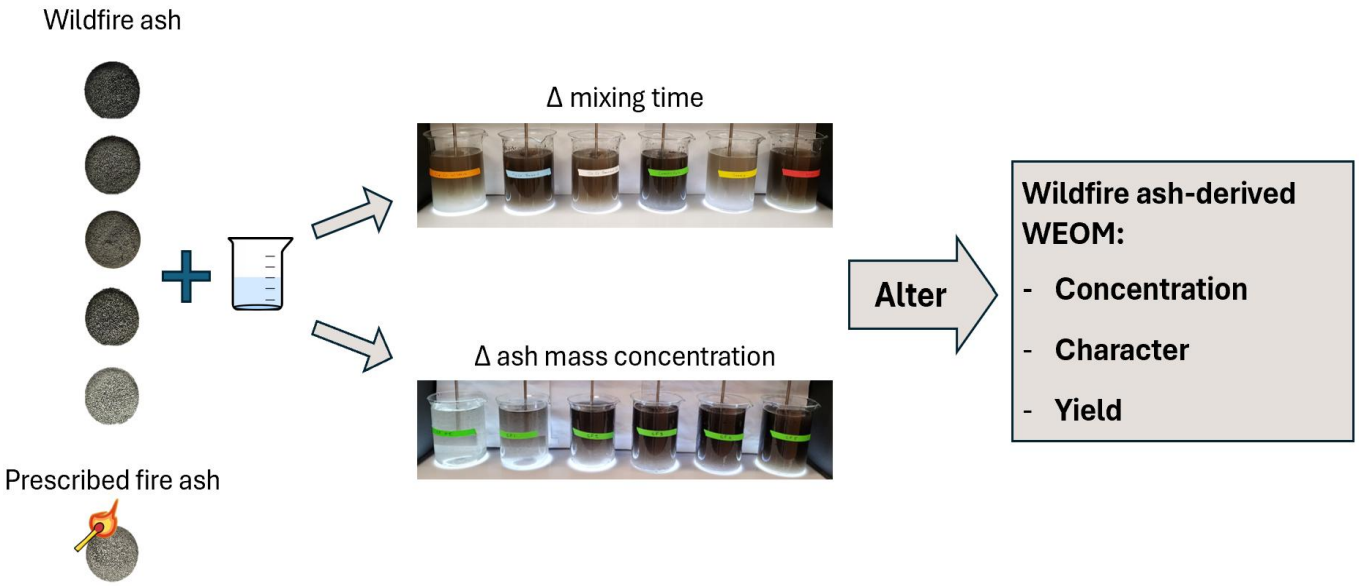
Chapter 2

Key considerations for assessing potential wildfire ash organic carbon threats to drinking water

Summary

To evaluate the impact of wildfire on drinking water treatability, wildfire ash is often added to source water to reflect post-fire source water quality change. The use of varying experimental conditions has led to conflicting inferences across studies and inconsistent results, even between nominal replicates. Here, mixing time and ash concentration effects on wildfire ash-impacted water (WAIW) quality were investigated, and their impacts on leached water extractable organic matter (WEOM) from wildfire and prescribed fire ash were characterized at bench-scale. The effects of mixing time and ash-to-water ratios were investigated using both natural river water and ultrapure water. Notably, WEOM concentration and character varied considerably within the first 24 hours of mixing, and water type and ash mass concentration limit the leaching of WEOM into water. These results highlight the critical role of careful experimental design and well-justified approaches to support meaningful interpretation and comparability across studies.

Graphical abstract



2.1 Introduction

Forested watersheds are critical sources of drinking water globally (UNFF, 2016; FAO, 2018). Anthropogenic and natural landscape disturbances, however, can deteriorate the high quality of water originating in these regions (Janetos et al., 1997; Christensen et al., 2004; Huntington et al., 2009; Whitehead et al., 2009; Watts et al., 2015). Although natural landscape disturbances are an integral part of ecosystem regulation, climate change has profoundly impacted the frequency and severity of such events (IPCC, 2018). Hotter and drier atmospheric conditions associated with climate change have contributed to the increased frequency of larger, more severe wildfires (U.S. EPA, 2016). Wildfires can alter the timing of snowmelt and increase stream temperature (Wagner et al., 2014; Williams et al., 2019). They can also change the structure of soils and lead to decreased infiltration capacity and increased runoff (DeBano, 1991).

Higher rates of runoff can increase the transport and delivery of sediments, nutrients, and other contaminants from hillslopes to receiving waters (Bladon et al., 2008; Silins et al., 2009; Emelko et al., 2011). Warming temperatures, hydroclimatic changes, and disturbances such as wildfire also alter the mobility and delivery of organic carbon to water supplies (Emelko et al., 2024). The change in concentration, character and flux of dissolved and particulate organic carbon in rivers can substantially challenge water treatment plant operations (Emelko & Sham, 2014; Hohner et al., 2016; Shams, 2018) and increase drinking water treatment costs (Emelko et al., 2011; Price et al., 2018). While nature-based solutions such as biological filtration may offer some resilience to these shifts, their performance may also be compromised depending on organic carbon character (Blackburn et al., 2023).

Shifts in organic matter concentration and character have been reported following wildfires (Emelko et al., 2011; Hohner et al., 2016; Uzun et al., 2020, Tshering et al., 2023). The resulting changes in organic matter concentration and character can strongly affect drinking water treatment needs and performance. Numerous bench-scale investigations of wildfire impacts on water quality and treatability have reported the use of a variety of ash types from burned landscapes and laboratory-simulated wildfires to produce WAIW at a wide range of experimental conditions, including ash-to-water ratios and mixing conditions (Table 2-1). Most frequently, they have focused on evaluating water extractable organic matter (WEOM) concentration and character and associated potential to form disinfection by-products. While these methods are reductionist simulations that do not reproduce the full complexity of landscape-scale abiotic and biotic biogeochemical processes that drive water quality change after wildfire and are thus far from predictive, they do enable controlled evaluation of key water quality and treatment responses to disturbance-associated inputs.

The use of diverse WAIW preparation methods can often lead to inconsistent and even contradictory results. For example, Wang et al. (2015a) and Chen et al. (2020) used fresh ash collected from the same wildfire but applied different mixing times (2 h vs. 24 h) and ash concentrations (200 g L^{-1} vs. 1.9 g L^{-1}, respectively). These methodological differences resulted in substantially different DOC yields: approximately 0.91 mg g^{-1} in Wang et al. (2015a) compared to 4.4 mg g^{-1} in Chen et al. (2020).

Given that systematic studies of methods for ash addition to water for investigation of wildfire threats to water quality and treatability are scant, the goal of this study was to (1) investigate the impact of mixing time and ash-to-water ratio on WEOM concentration and character after ash addition to water and (2) identify mixing conditions that maximize WEOM concentration in wildfire ash-impacted waters (WAIW).

Table 2-1 Experimental conditions in previously reported studies on ash impacts on surface water organic matter concentration and quality. In studies where more than two ash-to-water ratios were used, a range of ash-to-water ratios is presented.

Mixing duration	Type of burned ash/soil used & fire/burn severity	Type of water used	Ash condition	Ash concentration ($g\ L^{-1}$)	Source
5 min	wildfire, prescribed & lab burned	deionized	fresh & 1-year post-fire	50, 200	Ferrer et al. (2021)
5 min shake & 10 min settling	wildfire ash- low to high	ultrapure	fresh & older	50	S´anchez-García et al. (2023)
30 min shake & 20 min centrifugation	wildfire ash- low to extreme	ultrapure	2.5 to 3 months post-fire	50	Santín et al. (2012)
3 wet dry cycle (30 min wet)	wildfire ash- very low to high	deionized	fresh	-	Ahmed et al. (2023)
2 h	wildfire ash- moderate & high	ultrapure	fresh	200	Wang et al. (2015a)
2 h	lab burned ash- moderate & high	ultrapure	-	20	Wang et al. (2015b)
5 times leaching	wildfire ash- moderate & severe	ultrapure	fresh	200	Wang et al. (2016)
2 min	wildfire ash	river water	fresh	2 to 20	Skwaruk et al. (2020)
3 wet dry cycle (30 min wet)	wildfire ash- very low to high	deionized	fresh	-	Ahmed et al. (2023)
4 h	lab burned ash- moderate to high	ultrapure	-	4	Chen et al., 2022)
6 h	lab burned soil- low to high	ultrapure	-	5	Wilkerson & Rosario-Ortiz (2021)
12 h & 15 min centrifugation	wildfire ash & soil- high	lab-produced*	fresh	100	Wilkerson (2017)
18 h & 3 h settling	wildfire ash- high	river water	fresh	0.25 to 1	Blackburn et al. (2023)
16 h agitation & centrifuge	wildfire ash & soil	lab-produced*	fresh & 1-year post-fire	100	Lersche et al. (2025)
16+ h	wildfire ash	lab-produced*	fresh & 1-year post-fire	-	Fischer et al. (2023)
18 h mixing & 3 h settling	wildfire ash - high	river water	fresh	1	McGregor (2024)
24 h	wildfire ash- moderate & high	ultrapure	fresh	250	Tsai et al. (2019)
24 h	wildfire ash- moderate & high	rainwater	fresh & 1-year post-fire	1.35 to 52.7	Chen et al. (2020)
24 h	lab burned- low to high	deionized	-	100	Thurman et al. (2020)
24 h	wildfire ash- moderate & high	ultrapure	fresh	250	Chen et al. (2021)
24 h	wildfire ash- low to high	ultrapure	fresh	10	Rodela et al. (2022)
24 h	wildfire ash- moderate & high	rainwater	fresh & 1-year post-fire	1.35, 2.5	Chen et al. (2023)
24 h	lab burned soil- low to high	ultrapure	-	0.25	Dayaranthne et al. (2023)
24 h	lab burned ash- low to high	lab-produced*	-	25	Myers-Pigg et al. (2024)
24 h	lab burned ash- unburned to high	lab-produced*	-	25	Roebuck Jr et al. (2025)
24 h shake	wildfire ash- low to high	lab-produced*	fresh	10	Muñiz González et al. (2023)
2 min mixing & 24 h stagnant	wildfire affected sediment- low to high	river & low DOC tap water	-	13 to 64	Hohner et al. (2017)
2 min stirring & 24 h stagnant	lab burned soil- low to high	low DOC tap water	-	50	Cawley et al. (2018)
24 h stagnant & 10 min centrifugation	wildfire ash & lab burned ash- low to extreme	lab-produced*	fresh	15	Li et al. (2023)
2 min stirring & 6 or 24 h stagnant	wildfire affected sediment- low to high	river water	-	50	Cawley et al. (2017)
5 min & 24 h and up to 168 h settling	Wildfire ash	ultrapure & river water	fresh	2 to 30	Gifford et al. (2025)
48 h	wildfire ash- low to high	ultrapure	fresh & 2 years post-fire	10	Revchuk & Suffet (2014)
48 h	lab burned ash- moderate	reverse osmosis water	-	5	Wu et al. (2022)
48 h stagnant & 1 h slow stirring	wildfire burned soil	ultrapure	3 months post-fire	-	Olefeldt et at. (2013)
1, 24, & 72 h	ash (lab burned)- high	ultrapure	-	3	Cerrato et al. (2016)
4, 24, 72 h	lab burned ash- moderate to high	deionized	-	3.33	Rahman et al. (2018)
72 h	wildfire ash- moderate & high	ultrapure	fresh	250	Tsai et al. (2017)
72 h	lab burned ash- unburned to high	lab-produced*	-	20	Egan et al. (2023)
7 days	wildfire ash-very low to high	ultrapure	fresh	10	Numan et al. (2025)
-	wildfire ash- low to high	ultrapure	fresh	200	Thurman et al. (2023)
7 & 196 h & 66 days	lab burned ash & wildfire ash- high	deionized	fresh	2	Audry et al. (2014)

* lab-produced refers to a variety of water matrices, such as synthetic rainwater and hard water.

2.2 Materials and Methods

2.2.1 Experimental approach

A bench-scale study was conducted at controlled conditions to (1) investigate the impact of mixing time and ash-to-water ratio on WEOM concentration and character after ash addition to water and to (2) identify mixing conditions that maximize WEOM concentration in WAIW. Mixing conditions for maximizing WEOM concentration were expected to be approximately 24 h or less at room temperature because of the high potential for biodegradation (Brailsford et al., 2017; Rahman et al., 2018; Lloyd et al., 2022). The six ash samples collected from different wildfires and one prescribed fire reflect a range of fire severities and ash characteristics. WAIW matrices were prepared using a high-quality drinking water source (i.e., low turbidity and organic carbon concentration) collected from the Elbow River in Calgary, Alberta, Canada, as well as ultrapure water. The use of ultrapure water allows for benchmarking of organic matter leaching from wildfire ash between sites in the absence of water matrix effects, while the use of natural source water is more system specific because it includes matrix effects.

Several studies focusing on the impacts of wildfire and/or lab-produced ash on water quality have used the terms “extraction” and “leaching” interchangeably to describe the transfer of organic matter from ash to water. While extraction procedures typically include testing conditions that maximize the extraction of a targeted element or pollutant from the solid phase (e.g., Voegelin et al., 2003; Ran et al., 2007; Guigue et al., 2014), leaching tests usually intend to simulate the natural dissolution of compounds into water (e.g., Voegelin et al., 2003; Guigue et al., 2014). Thus, the release of organic matter from wildfire ash is described here as extraction, while the dissolution of organic matter into water is referred to as leaching, following the definitions provided in LEAF Methods 1313, 1315, and 1316 (U.S. EPA, 2023).

2.2.2 Experimental design

The overall design of the bench-scale experiments reported herein is presented in Figure 2-1 . The impacts of mixing conditions, mixing time and ash mass concentration on WEOM were evaluated using Elbow River (Calgary, Alberta, Canada) source water and ultrapure (Milli-Q®, 18.2 MΩ-cm, 25°C, TOC ≤ 5 ppb) water. WAIWs were prepared using a jar test apparatus (Phipps & Bird, PB-900 Series Programmable 6-Paddle Jar Tester). Controlling light exposure was beyond the scope of this study, thus all experiments were conducted under laboratory conditions, where samples exposed to approximately 16 h of light and 8 h of darkness per 24 h. Elbow River water samples were stored in sealed pails at

4 °C after collection until use. Nominal Elbow River water quality during the study is summarized in Supporting information Table A1. The temperature of the WAIW matrices was maintained at approximately 21°C throughout the experiments.

Experiment 1 investigated the impact of mixing on WEOM concentration and character after ash addition to water. In Phase I, to evaluate the impact of mixing, 2 g of ash (used by others in literature; Table 2-1) from two wildfires were each mixed in 1 L of ultrapure water at two conditions: (A) mixing for 5 minutes at 120 RPM followed by 24 h of settling; and (B) mixing for 24 h at 120 RPM. These mixing and settling times were selected to compare the most commonly reported mixing conditions (Table 2-1); a mixing speed of 120 RPM was selected to ensure thorough mixing and prevent particle breakage. Water samples were collected after 5 minutes of mixing and at the end of the experiment (i.e., after 24 h). WAIWs for each mixing condition were prepared in triplicates (i.e., 6 individual samples). The concentrations of total and dissolved organic carbon (i.e., TOC and DOC, respectively) were measured; dissolved organic matter was also characterized using specific ultraviolet absorbance at 254 nm (SUVA).

Based on the results from Phase I of the experiment, mixing conditions for Phase II were selected to maximize the concentration of WEOM from wildfire ash. Thus, WAIW matrices were prepared by mixing 2 g L^{-1} of each of six ash types with ultrapure and source water collected from Elbow River at 120 RPM for 24 h (to ensure thorough mixing without particle breakage) followed by 48 h of gentle mixing at 40 RPM (Figure 2-1). This gentler level of mixing (relative to Phase 1) was used to limit longer-term decreases in pH due to air entrainment. Although some biodegradation was expected after approximately 24 h of ash contact with water (Brailsford et al., 2017; Rahman et al., 2018; Lloyd et al., 2022), one set of WAIWs prepared using ultrapure water and one using Elbow River water were mixed for 7 days to confirm this so that a mixing time associated with maximum WEOM concentration could be recommended. Dilution effects attributed to evaporation were managed by adding ultrapure water to WAIW every 24 h based on volume lost. Subsequent samples were collected at the beginning of the experiment before ash addition to water (labeled as “initial”), and after the addition of ash when the suspension was mixed for 30 min, 6, 10, 24, and 48 hours. WAIWs were prepared in triplicate (i.e., 18 individual samples). DOC, conductivity, and pH were measured on all WAIW; dissolved organic matter was also characterized using SUVA and size exclusion liquid chromatography with organic carbon detection (LC-OCD) analyses. It should be noted that, due to the time-intensive nature of LC-OCD analysis, only one replicate of the collected WAIWs made with Elbow River water was analyzed using this method (i.e., 30 individual samples). In addition, disinfection by-product formation potential

(DBPFP) and uniform formation condition (UFC) tests were performed on the WAIWs prepared using Scottie Creek (SC) wildfire ash mixed with Elbow River water. Natural river water was used to account for matrix effects and to reflect more realistic conditions. Subsamples were collected after 30 min and 24 h of mixing to provide a confirmatory demonstration that observed differences in DOC concentration and character associated with WAIW mixing time would also correspond to differences in DBP-FP and -UFC, as would be expected given that DOC is a key DBP precursor (APHA, 2022). The DBP analyses are further described in Section 2.3.4.

In Experiment 2, the impact of ash mass concentration on WEOM concentration and character was evaluated. Two batches of WAIW with ash-to-water ratios of 0.5, 1, 2, 3, 4, and 5 g L^{-1} were made by mixing each of the six ash types with ultrapure and source water collected from the Elbow River in Calgary, Alberta, Canada (Figure 2-1). WAIWs for each ash mass concentration were prepared in triplicate (i.e., 108 individual samples). WAIW samples were collected after 24 h of mixing at 120 RPM, and their quality was characterized in the same manner as in the first set of experiments. Similar to Experiment 1 and due to the time-intensive nature of LC-OCD analysis, only one replicate of the collected WAIWs made with Elbow River water was characterized using LC-OCD (i.e., 36 individual samples).

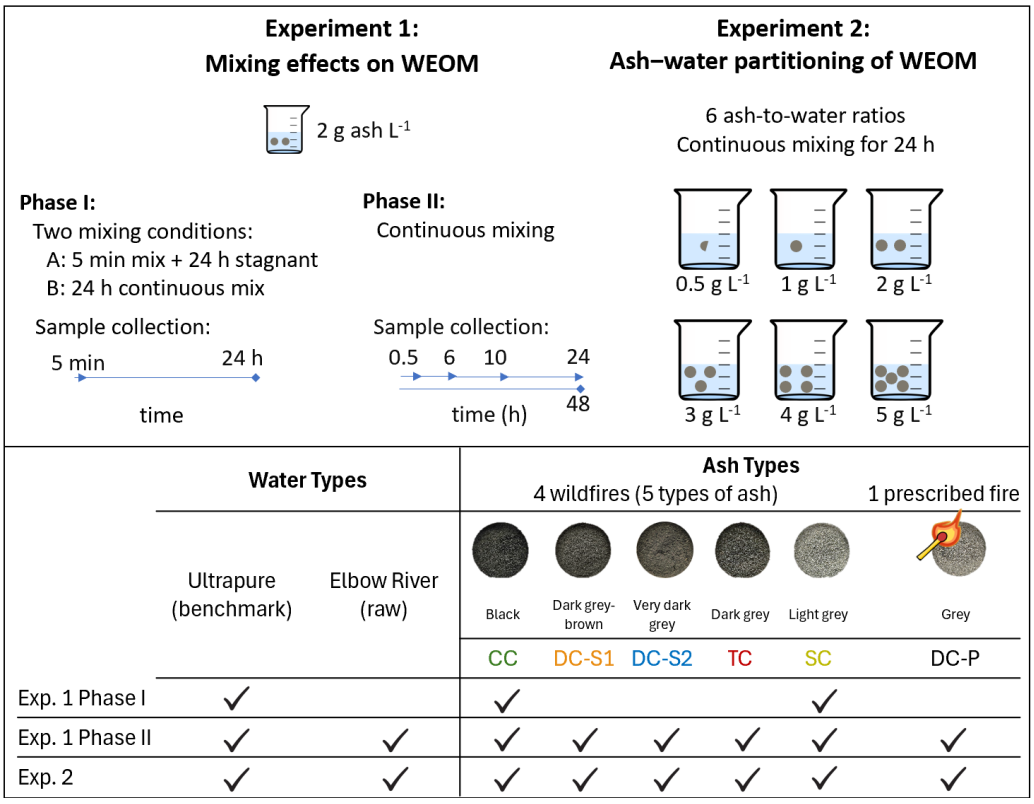


Figure 2-1 Experimental design for investigating effects of WAIW preparation methods on WEOM. The impact of mixing conditions and time (Experiment 1) and the effect of ash mass concentration (Experiment 2) on the concentration and characteristics of WEOM were investigated. Either ultrapure or natural untreated river water were used to prepare WAIW. Six different ash types were analyzed: CC (Cameron Creek), DC-S1 (Doctor Creek ash sampling site 1), DC-S2 (Doctor Creek ash sampling site 2), TC (Thuya Creek), SC (Scottie Creek), and DC-P (Doctor Creek prescribed fire).

2.2.3 Wildfire ash collection

Ash samples collected from four wildfires and one prescribed fire reflect a range of pyrogenic materials produced by different burn severities (Table 2-2). All ash types were air dried and sieved through a 1 mm screen to homogenize them and eliminate any large debris and conifer needles (Skwaruk et al., 2020; and Chapter 3). The color of different ash types was identified visually using a Munsell color chart. Processed samples were stored in closed containers at a controlled temperature of 21°C. Organic matter content of each ash type was measured using loss on ignition according to ASTM D7348 method.

Table 2-2 Ash collection location, date and fire information.

Ash type	Fire	Location (Canada)	Burn area (ha)	Fire start date (mm/yyyy)	Vegetation type	Burn severity	Ash collection date (mm/yyyy)
Cameron Creek (CC)	Kenow Wildfire[a]	Waterton, AB[a]	35,000[a]	09/2017[a]	Lodgepole Pine[1a], Subalpine Fir[2a]	High to extreme[b]	06/2018[b]
Doctor Creek sampling site 1 (DC-S1)	Doctor Creek Wildfire[c]					High[c]	
Doctor Creek sampling site 2 (DC-S2)	Doctor Creek Wildfire[c]	Canal Flats, BC[c]	7645[c]	08/2020[c]	Lodgepole Pine[1c] Douglas Fir[3c], Ponderosa Pine[4c], Western Larch[5c]	Medium[c]	09/2020
Doctor Creek prescribed fire site (DC-P)	Doctor Creek Prescribed Fire[c]					Medium[c]	
Thuya Creek (TC)	Little Fort Fire Complex[d]	Little Fort, BC[d]	556[d]	07/2017[d]	Lodgepole Pine[1d], Douglas Fir[3d], Spruce Hybrids[6d], Paper Birch[7d]	High[d]	08/2017[d]
Scottie Creek (SC)	Elephant Hill Fire Complex[e]	Ashcroft, BC[e]	191,865[e]	07/2017[e]	Douglas Fir[1d], Spruce Hybrids[6d], Yellow Pine[8d], Trembling Aspen[9d]	High[d]	08/2017[d]

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1- *Pinus contorta* var. *latifolia*
2- *Abies lasiocarpa*
3- *Pseudotsuga menziesii* var. *glauca*
4- *Pinus ponderosa*
5- *Larix occidentalis*
6- *Picea* spp.
7- *Betula papyrifera*
8- *Pinus ponderosa*
9- *Populus tremuloides*

a- Parks Canada- Kenow Wildfire timeline (2023)
b- U. Silins (Personal communication, March 20, 2025)
c- BC Wildfire Service Information Section (2020)
d- Skwaruk (2021)
e- BC gov news (2020)

2.2.4 Water quality analyses

Most water quality analyses were conducted according to Standard Methods 24th edition (APHA, 2022). Water quality metrics investigated included pH (Standard Method 4500H using a Fisher Scientific Accumet AB250 benchtop PH/ISE meter), alkalinity (titration method Standard Method 2320B using 0.1N HCl), conductivity (Malvern Panalytical Zetasizer Nano Z series with an accuracy of 10%) and maximum conductivity (200 mS cm^{-1}). DOC and TOC were measured using the combustion method (Standard Method 5310C) on a Shimadzu TOC-VCHP Analyzer (Shimadzu Corporation, Jiangsu, China) with a detection limit of 0.1 mg L^{-1}. UV absorbance at 254 nm was measured using a UV_{254} analyzer (RealTech P200B) following Standard Method 5910B. Specific ultraviolet absorbance at 254 nm (SUVA) was calculated by dividing UV_{254} by DOC concentration (Edzwald et al., 1985; Weishaar et al., 2003).

Size exclusion liquid chromatography in combination with organic carbon detection (LC-OCD) was conducted according to Huber et al. (2011) using a Model 8 LC-OCD analyzer (DOC-Labor GmbH, Karlsruhe, Germany). A size exclusion column, a weak cation exchange column on a polymethacrylate basis (Toyopearl HW 50S, 250 mm x 20 mm, 30 µm from TOSOH Bioscience) was used for separation. The organic carbon detector was calibrated using potassium hydrogen phthalate. A customized software program (ChromCALC, DOC-LABOR, Karlsruhe, Germany) was used for data acquisition and processing. LC-OCD subdivides organic carbon into five fractions: biopolymers, humic substances, building blocks, LMW acids, and LMW neutrals based on molecular size (Huber et al., 2011).

Biopolymers are the largest DOC compounds with molecular weights higher than 20,000 g mol^{-1} (>10 kDa) that donot absorb 254 nm UV radiation, and they include polysaccharides, proteins, polypeptides, and amino sugars. Humic substances include humic and fulvic acids with a molecular weight range from 400 to 1100 g mol^{-1}. Building blocks are defined as humic substance-like material of lower molecular weight (300-500 g mol^{-1}). LMW acids consist of small aliphatic organic acids with molecular weights lower than 350 g mol^{-1}). LMW neutrals include weakly charged hydrophilic or slightly hydrophobic compounds such as alcohols, aldehydes, ketones, sugars, and amino acids. WAIW samples were filtered through 0.45 µm polyethersulfone (PES), Millipore Express® PLUS; Merck Millipore, Burlington, MA, for DOC, UV_{254} and LC-OCD analyses. Prior to sample collection, all PES filters were prerinsed with ultrapure water, followed by rinsing with WAIW.

DBP formation potential (FP) tests under standard conditions (Methods 5710 B and 5710 D (APHA, 2022), as well as uniform formation conditions (UFC) (Summers, 1996) were performed on the ash-

water matrices. DBPs (trihalomethanes (THMs) and haloacetic acids (HAAs)) precursors from the ash-water matrix and the potential for DBP formation in drinking water distribution systems after chlorination of ash-impacted waters were evaluated. While the uniform formation conditions test predicts DBP formation within drinking water distribution systems (Summers et al., 1996), the true FP test evaluates the reactivity of DBP precursors and allows for WEOM comparisons. For both DBP-FP and DBP-UFC tests, chlorine residuals after chlorination were measured according to colorimetric Method 4500-Cl G (APHA, 2012) using N,N-diethyl-p-phenylene diamine (DPD). Trihalomethanes (THMs) were analyzed using purge and trap extraction and gas chromatography with electron capture detection Method 501.1 (U.S. EPA, 1979). Total trihalomethanes (TTHMs) concentration was calculated as the sum of four THM compounds (trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM)). Five haloacetic acids including trichloroacetic acid (TCAA), dichloroacetic acid (DCAA), monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA)) were measured according to Method 552.3 (U.S. EPA, 2003), a liquid-liquid extraction and gas chromatography with electron capture detection method. HAA5 was calculated as the sum of the concentrations of these five compounds. Minimum reporting limits for the water quality metrics analyzed here are presented in Supporting information Table A2.

2.2.5 Statistical Analysis

Statistical analyses were conducted to evaluate whether extended mixing time (30 min vs. 6 h vs. 24 h) has a significant impact on WEOM concentration. It should be noted that because WAIW preparation was labor- and time-intensive, only three replicates were available for each ash type. Consequently, WEOM concentration of different ash types were grouped together to increase statistical power. As the data were not normally distributed in either sets of samples, non-parametric test (Wilcoxon signed rank test) with $\alpha = 0.05$ was used ($n = 18$).

2.3 Results and Discussion

2.3.1 Mixing effects on WEOM

2.3.1.1 Changes in WEOM concentration

The total and dissolved concentrations of extracted organic matter at different mixing conditions (Experiment 1 Phase I) are presented in Figure 2-2 a to d. TOC and DOC increased following ash addition to ultrapure water in all WAIWs. DOC concentrations increased more with continuous mixing relative to no mixing (i.e., stagnant conditions), especially in WAIW prepared using SC ash (Figures 2-2 a & b) which is likely due to enhanced particle interactions and increased surface area exposure, which facilitate more efficient leaching of WEOM.

DOC concentrations increased throughout the experimental period regardless of mixing conditions. In contrast, TOC concentrations decreased when WEOM was leached under stagnant conditions—TOC decreased by 93% and 22% in CC and SC WAIW, respectively (Figure 2-2 c & d). Such differences may be attributable to ash particle size distribution and particulate organic carbon density variability, which affect settling velocities. Accordingly, these findings underscore the importance of carefully considering how mixing conditions during bench- and pilot-scale investigations of WAIW either (i) connect to and reflect landscape conditions and processes relevant to wildfire ash impacts on water quality or (ii) maximize WEOM concentration so that treatment performance investigations can be conducted efficiently.

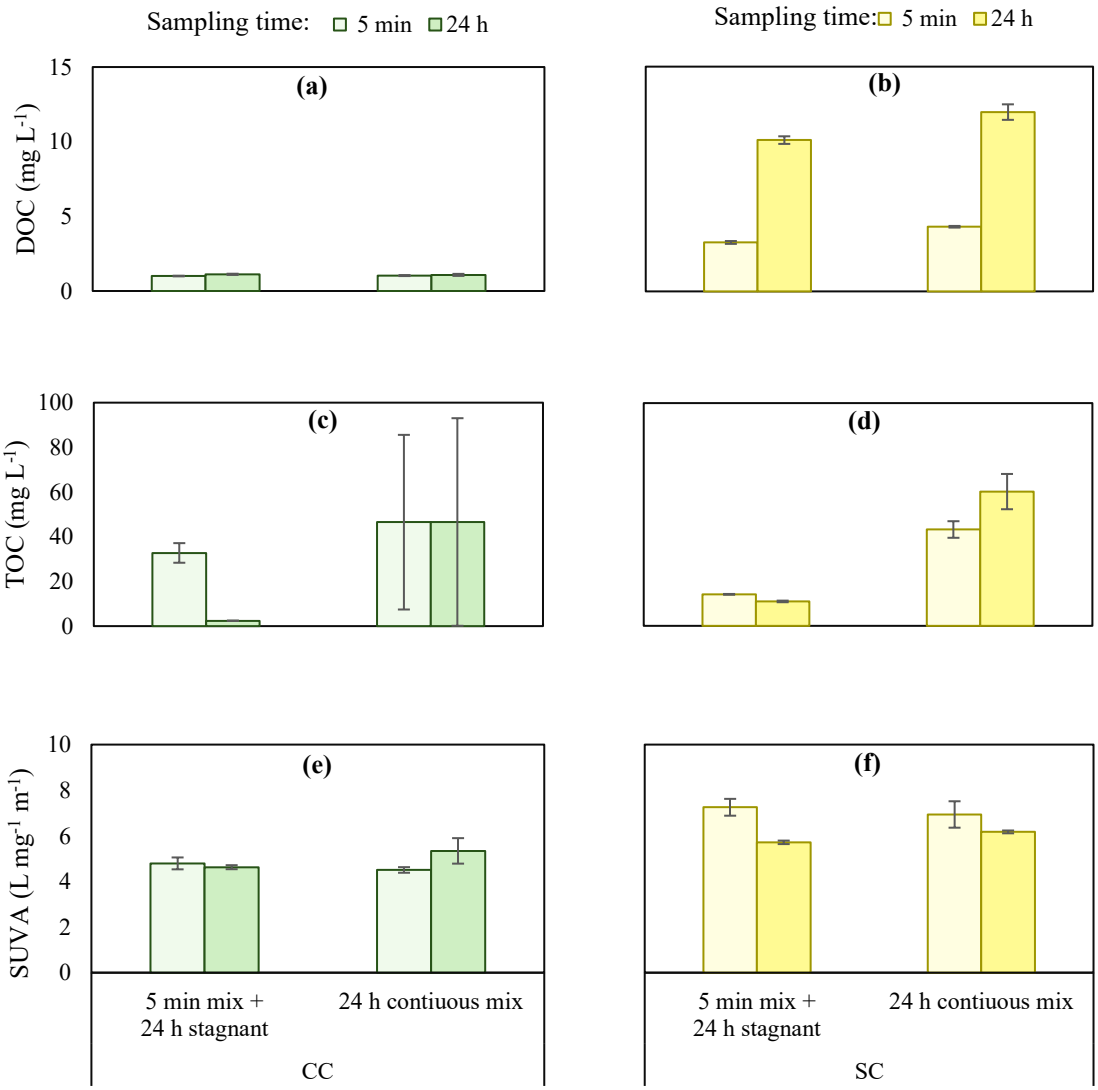


Figure 2-2 Change in (a & b) DOC concentration, (c & d) TOC concentration , and (e & f) SUVA for WAIW prepared using CC (Cameron Creek) and SC (Scottie Creek) ash mixed in ultrapure water at two different leaching conditions. Each bar represents average values (n = 3) with error bars representing standard deviation.

DOC concentrations of WAIWs in Phase II are shown in Figure 2-3a. These concentrations ranged from 0.85 ± 0.07 mg L^{-1} to 14.0 ± 1.02 mg L^{-1}. Consistent with the results presented above and reported elsewhere (e.g., Rahman et al., 2018), the addition of wildfire ash to both ultrapure and Elbow River water resulted in an immediate (i.e., within the first 30 minutes of mixing) increase in WEOM concentration, this trend continued for 24 hours regardless of ash type. Nonparametric statistical analysis (Wilcoxon signed-rank test) also indicated a significant difference between WAIW WEOM

concentration after 30 min, 6 h, and 24 h of mixing (all p-values << 0.05, n = 18, Supporting information Table A).

The changes in DOC concentration decreased during the second half (i.e., 24 to 48 h) of the experiment for all WAIWs (Table 2-4). This reduction continued for all ash types during the one-week experiment (Supporting information Figure A1). The observed shifts in extracted organic carbon concentration after 24 h of mixing may be associated with biodegradation (Bruun et al., 2008; Wagner et al., 2015; Brailsford et al., 2017; Lloyd et al., 2022); however, identification of a causal relationship was beyond the scope of the present investigation. Nonetheless, the substantial increase in DOC concentration, especially within the first 24 hours of the experiment, highlights the critical role of mixing time on the concentration of leached organic matter and the need for careful consideration of the objective of the WAIW preparation (i.e., reflecting landscape process vs. creating a WAIW matrix for treatment performance or other evaluation).

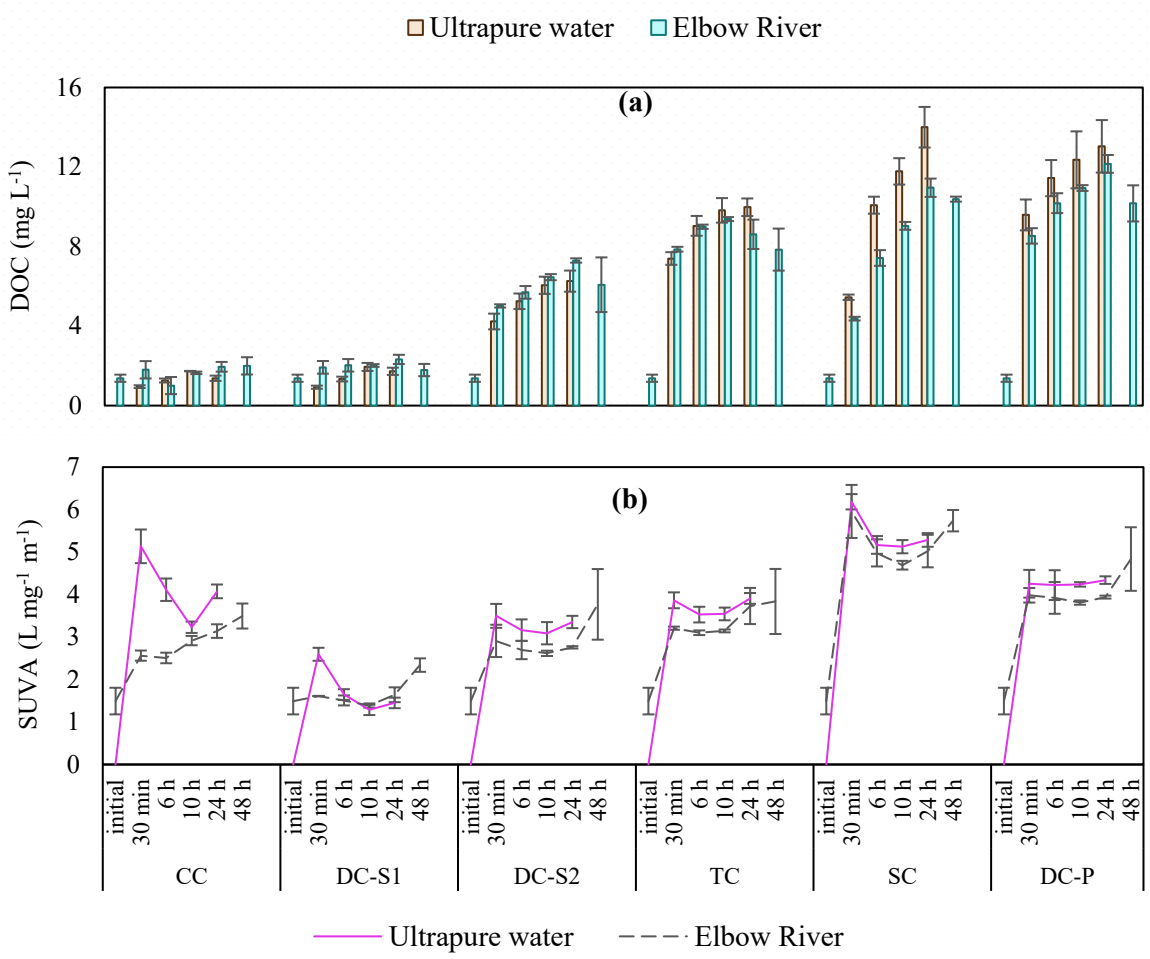
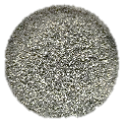


Figure 2-3 (a) Change in DOC concentration, and (b) SUVA during 48 hour experiment. Light brown and turquoise bars show the changes in DOC concentrations for WAIWs prepared using ultrapure and Elbow River water, respectively. Solid purple and dashed grey lines show SUVA in WAIWs prepared using ultrapure and Elbow River water, respectively. Initial sampling points represent values for ultrapure/raw water with no ash for both DOC and SUVA. Each bar/symbol represents the average values (n=3) with error bars representing standard deviation.

DOC concentration increases during the first 24 h of mixing varied among ash types (Figure 2-3a) with SC and CC ash demonstrating the highest and lowest rates (12.1 and 8.3 mg L^{-1} DOC for SC ash and 0.5 and 0.2 mg L^{-1} for CC ash in ultrapure and Elbow River water, respectively). Variable DOC release from different wildfire ash types suggests that multiple factors such as burn severity, antecedent rainfall, and/or presence of soil mixed with the ash may substantially impact WEOM leaching. While

such relationships are plausible and often suggested (e.g., Rahman et al., 2018; S´anchez -García et al., 2023), the findings of this study, along with those discussed in Chapter 3, show that differences in experimental design can confound these effects. It is worth noting that a weak correlation between ash color and burn severity has been suggested (Bodí et al., 2011). Often, lighter colored (e.g., white or light grey) ash is attributed to more complete combustion (Bodí et al., 2014; Rodela et al., 2022) and is thus expected to release less organic matter to water. It is also then suggested that darker-colored (e.g., black) ash will release more organic matter into water. In contrast, several studies have reported no appreciable differences in WEOM leached from white and black ash (Wang et al., 2015a; Tsai et al., 2017; Rodela et al., 2022), and in some cases, WEOM concentrations leached from white ash were substantially higher than those from black ash (Wang et al., 2016). Notably, in the present investigation, lighter-colored ash types (i.e., SC and DC-P) released the highest concentrations of organic carbon to the water (Table 2-3).

Table 2-3 Change in DOC concentration in different WAIWs prepared using Elbow River water. The increases in DOC after 0.5 h and during the first (i.e., 0.5 to 24 h) and second (i.e., 24 to 48 h) half of the experiment are shown here (n = 3).

Ash type	Initial increase in DOC within 30 min of the experiment $\Delta DOC_{0.5}$ (mg L^{-1})	Change in DOC between 30 min to 24 h of experiment $\Delta DOC_{0.5\text{-}24}$ (mg L^{-1})	Change in DOC within the second 24 h of experiment $\Delta DOC_{24\text{-}48}$ (mg L^{-1})	Ash color	Ash photo
CC	0.4± 0.3	0.2± 0.2	0.0± 0.2	Black	
DC-S1	0.5± 0.2	0.4± 0.1	-0.5± 0.2	Dark grey-brown	
DC-S2	3.6± 0.2	2.3± 0.1	-1.2± 1.5	Very dark grey	
TC	6.5± 0.3	0.8± 0.6	-0.8± 0.4	Dark grey	
SC	3.0± 0.2	6.6± 0.5	-0.6± 0.5	Light grey	
DC-P	7.2± 0.3	3.6± 0.1	-2.0± 1.3	Grey	

2.3.1.2 Changes in WEOM character: SUVA and LC-OCD

SUVA changes for CC and SC WAIW mixed at different conditions are presented in Figures 2-2 e & f. Ash addition to water resulted in an increase in SUVA regardless of ash type and mixing condition (Figure 2-2 e & f). This observation was expected and aligns with previously reported studies (Tsai et al., 2019; Chen et al., 2020; Skwaruk et al., 2020). Similar to Phase I, in Phase II an initial increase in SUVA was recorded for all ash types, regardless of the source water quality (Figure 2-3b).

Longer ash-water contact time generally resulted in decreased SUVA in SC WAIW (Figure 2-2f). In contrast, while SUVA slightly decreased in CC WAIW at stagnant conditions, it increased with continuous mixing (Figure 2-2e). Changes in WAIW SUVA during mixing were also different between ash types in Phase II (Figure 2-3), suggesting the potential for differential leaching dynamics between ash types.

Comparison of WAIWs prepared using ultrapure and Elbow River water shows that changes in SUVA values were more pronounced in WAIW matrices prepared with ultrapure water. Notably, SUVA was higher in WAIWs prepared using ultrapure water throughout the study period (Figure 2-3b). However, this difference became less noticeable for ash types with higher concentrations of leachable organic matter
(i.e., SC and DC-P). This could be attributed to the effect of the natural organic matter (NOM) from Elbow River on the SUVA of WAIW. The contribution of NOM from Elbow River water to the overall SUVA of WAIW was lower in WAIW with high WEOM/NOM ratios (SC and DC-P; Figure 2-3b).

Differential leaching dynamics associated with the molecular size and character indicated by the LC-OCD analysis are presented in Figure 2-4 and Supporting information Figure A2. Although humic substances remained the dominant fraction of dissolved organic matter in WAIWs across different mixing times (except in the 24 h sample from DC-P), changes in the concentrations of various carbon fractions suggest that the release of different molecular groups occurs over time and is not necessarily proportional (Figure 2-4). The concentrations of refractory fractions (including the predominant fractions of WEOM: humic substances and building blocks) changed at different mixing times in the various WAIW (Supporting information Figure A2). Notably, while the yield of refractory fractions (i.e., the sum of the concentrations of refractory fractions divided by DOC concentration) generally remained stable during mixing, SUVA increased, decreased, and then increased further in all cases, reflecting the nonlinearity and complexity of leaching dynamics and underscoring that results from

investigations reliant on prepared WAIWs must be interpreted cautiously (Supporting information Figure A2).

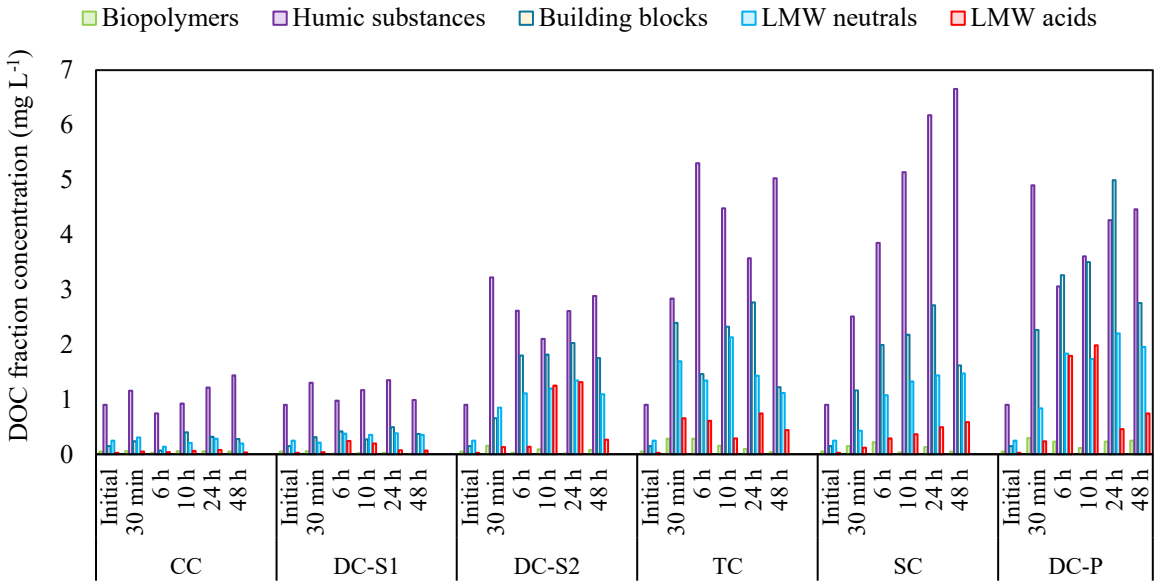


Figure 2-4 Change in different fractions of dissolved organic matter over time for WAIWs prepared in Elbow River water. These fractions are presented in descending order of molecular weight: biopolymers, humic substances, building blocks, LMW acids and LMW neutrals.

2.3.1.3 Changes in WEOM extraction: Source water quality impact

In addition to the effects of source water NOM concentration and character on wildfire ash WEOM leaching, the potential impacts of source water pH, alkalinity, and conductivity on WAIW quality were also investigated. Figure 2-5 shows the pH of WAIW prepared using ultrapure and Elbow River. The changes in pH of the WAIWs prepared using Elbow River water after the addition of ash were negligible, likely due to the high alkalinity of Elbow River water (Table 2-2 and Figure 2-5). In contrast, the absence of buffering capacity in ultrapure water resulted in a substantial increase in pH following ash addition. Additionally, the decrease in pH in the WAIW matrices prepared using ultrapure water towards the end of the 24 h experiment may be attributed to the increasing concentration of humic substances and dissolution of atmospheric CO_2 into the WAIWs (Figure 2-5).

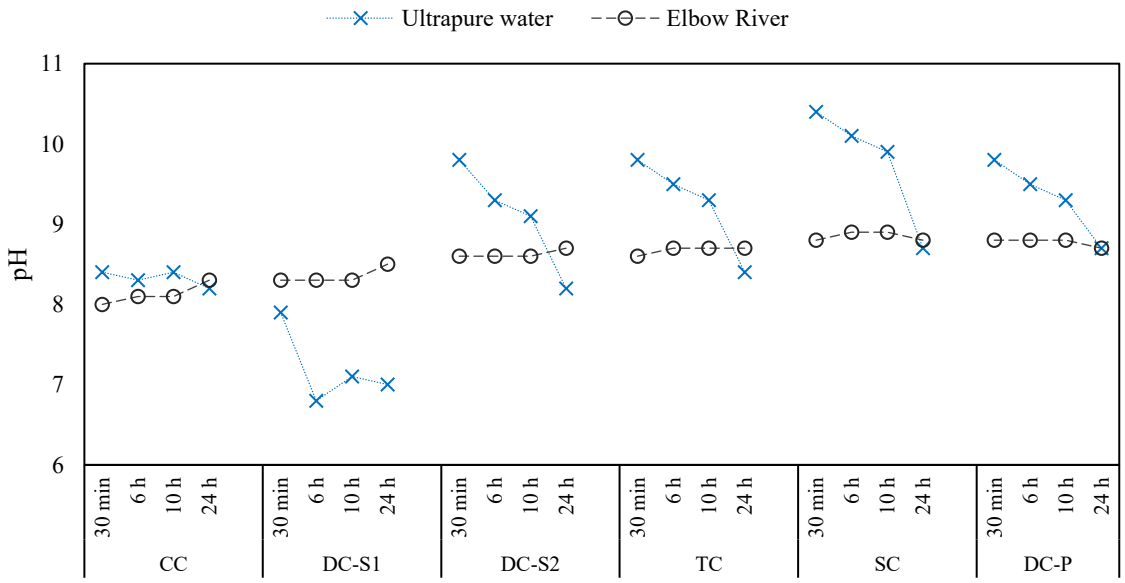


Figure 2-5 pH for all WAIWs prepared in ultrapure and Elbow River water during the first 24 h of the experiment. Blue crosses and grey circles indicate the pH of the WAIWs prepared in ultrapure and Elbow River water, respectively. The initial pH of Elbow River water was 8.3 ± 0.1 (n = 3).

Table 2-5 presents conductivities of WAIWs prepared with 2 g L^{-1} of ash after 24 hours of mixing. Conductivities of WAIWs prepared using ultrapure water were consistently lower than those prepared with Elbow River water, primarily due to the higher initial conductivity in the Elbow River matrix. The net change in WAIW conductivity was consistently lower in the Elbow River matrix. While the impact of source water conductivity on organic matter extraction from wildfire ash has not been documented, but an inverse relationship between source water conductivity and the dissolution of organic matter from soils has been previously reported (Kalbitz et al., 2000; Säurich et al., 2017; Tiemeyer et al., 2017). Consequently, a greater change in DOC concentrations over time was expected in WAIWs prepared with ultrapure water, relative to those prepared with Elbow River water (Figure 2-6).

Table 2-4 Conductivity (mean ± SD- n=3) of the WAIWs made with 2 g L^{-1} of each ash type after 24 h of mixing a) shows conductivities for WAIWs prepared in ultrapure water, and b) provides conductivity values for those prepared in Elbow River water, as well as the average change in conductivity from ash alone (calculated by subtracting conductivity of WAIWs from initial conductivity of Elbow River water).

(a)

WAIW in ultrapure water	Conductivity (µS cm^{-1})
Ultrapure	0.00 ± 0.005
CC	0.05 ± 0.002
DC-S1	0.03 ± 0.001
DC-S2	0.14 ± 0.03
TC	0.13 ± 0.05
SC	0.23 ± 0.06
DC-P	0.21 ± 0.02

(b)

WAIW in Elbow River water	Conductivity (µS cm^{-1})	Δ Conductivity (µS cm^{-1})
Elbow River	0.50 ± 0.03	-
CC	0.51 ± 0.08	0.01
DC-S1	0.51 ± 0.04	0.01
DC-S2	0.61 ± 0.03	0.11
TC	0.55 ± 0.04	0.05
SC	0.66 ± 0.03	0.16
DC-P	0.69 ± 0.05	0.19

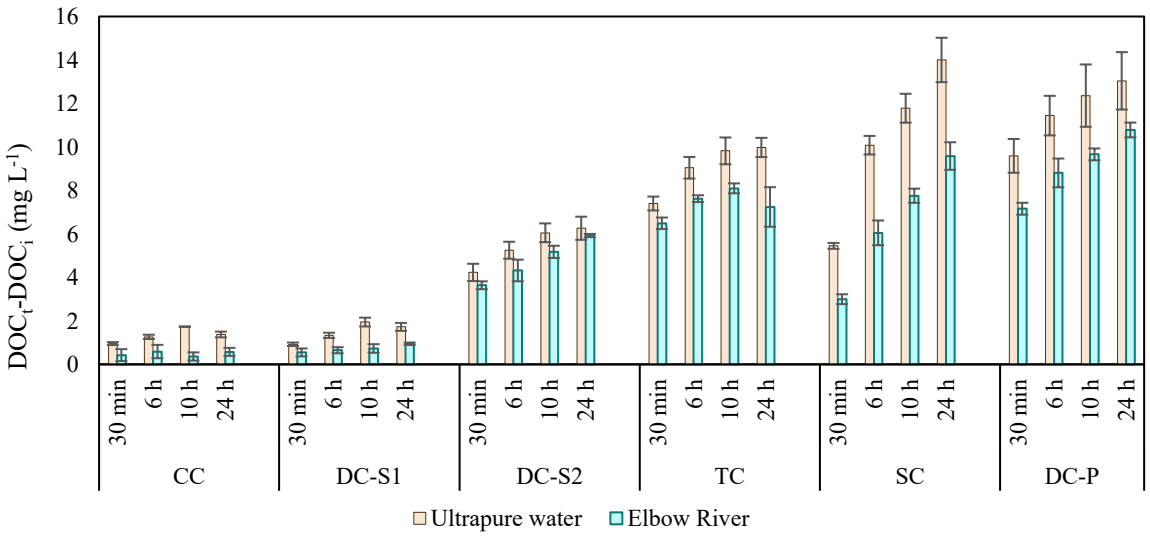


Figure 2-6 Change in DOC concentration (DOC at time t - source water initial DOC) and pH for all WAIWs during the first 24 h of the experiment. Light brown and turquoise bars show the changes in DOC concentrations for WAIWs prepared with ultrapure and Elbow River water, respectively. Changes in DOC concentrations were calculated by subtracting the DOC of WAIW at each sampling time (DOC_t) from the initial DOC of source water (DOC_i). Initial DOC concentrations of ultrapure and Elbow River water were equal to zero and 1.47 ± 0.08 (mean ± SD, n = 6), respectively.

2.3.1.4 Changes in disinfection by-product precursors

DBP formation of WAIWs prepared using 2 g L^{-1} SC ash mixed in Elbow River water was measured after 30 min and 24 h of mixing. True formation potential (i.e., DBP-FP) and formation under uniform formation conditions (i.e., DBP-UFC) were evaluated. DBP precursor concentrations increased by approximately three times (i.e., from 3.99 ± 0.12 mg L^{-1} to 10.9 ± 0.40 mg L^{-1}; Figure 2-7) and led to a generally proportional increase in DBP formation, as expected. Notably, WAIWs mixed for 24 h had almost three times higher concentrations of DBPs compared to those mixed for 30 min, irrespective of DBP type (i.e., THM or HAA) and chlorination conditions (FP or UFC; Figure 2-7). Shorter reaction times and lower chlorine doses at UFC (Summers et al., 1996; APHA, 2022) resulted in generally lower DBP-UFC compared to DBP-FP (Figure 2-7). This aligns with what has been reported previously (Yang et al., 2005).

Collectively, the results presented herein demonstrate that mixing time can substantially affect DBP precursor concentration and character and the concentration of DBPs produced during chlorination of WAIW. Accordingly, it is critical that evaluations of *prepared* WAIW matrices (as opposed to wildfire-impacted source waters) explicitly outline experimental conditions and justify the selected methodology, present a range of outcomes across various leaching conditions, or acknowledge that findings may not be quantitatively meaningful for decision-making and might be exploratory or comparative.

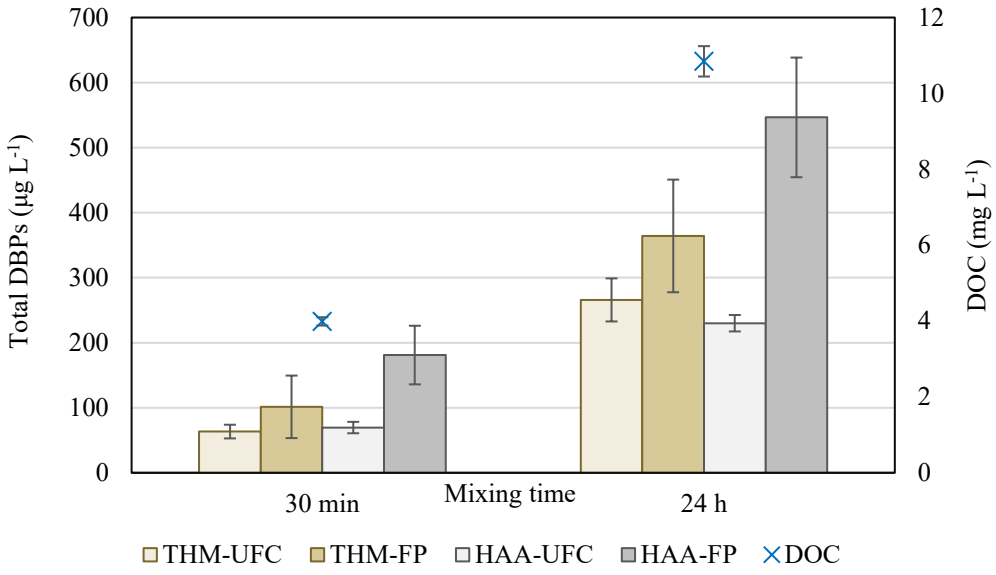


Figure 2-7 Change in DOC and DBP concentration in WAIWs prepared using SC (Scottie Creek) ash after 30 minutes and 24 hours of mixing in Elbow River water. Brown and grey bars represent concentrations of THMs and HAAs, respectively, and blue crosses indicate DOC concentration at each mixing time. Each bar/symbol represents the average values (n = 3) with error bars representing standard deviation.

2.3.2 Ash–water partitioning of WEOM

2.3.2.1 Changes in WEOM concentration

Figures 2-8 a & b show leached WEOM in WAIWs (i.e., DOC concentration) after 24 h of mixing with ash-to-water ratios ranging from 0.5 to 5 g L^{-1}. Notably, the lowest ash mass concentration (i.e., 0.5 g L^{-1}) resulted in a considerable increase in DOC concentration for some ash types such as SC and DC-P; Figure 2-8 a & b). Suggesting ash characteristics can substantially impact the extraction of organic matter from wildfire ash. This aligns with previously reported studies (e.g., Rahman et al., 2018; S´anchez-García et al., 2023). Additionally, a positive relationship between ash-to-water ratio and DOC concentration was observed over the ash-to-water ratios investigated (i.e., WEOM saturation was not reached). For the same ash mass concentration, the highest WEOM concentration was measured in WAIWs prepared using SC and DC-P ash types, while it was considerably lower in WAIWs prepared with CC and DC-S1 ash, regardless of the water used (i.e., ultrapure or Elbow River; Figure 8 a & b).

Although this observation did not align with color-based classification of ash and its WEOM content, it was consistent with the findings of the previous experiment (Section 2.4.1).

Ash organic matter content and WEOM concentration for the investigated ash types are presented in Table 2-6. Organic matter content ranged from 3.7 ± 0.1% to 21 ± 1.9 % for DC-S1 and CC, respectively (Table 2-6). Notably, the lowest DOC concentrations were measured in WAIWs prepared using the same ash types. This suggests that ash organic matter content is not a reliable indicator of its leachable organic carbon concentration.

At ash-to-water ratios ranging from 0.5 to 2 g L^{-1}, the normalized concentration of extracted organic matter (expressed as mg of DOC extracted per g of ash) was highly sensitive to ash-to-water ratio. WEOM yield decreased with an increase in ash mass concentration in all WAIW (Figures 2-8 c & d). For ash-to-water ratios exceeding 2 g L^{-1}, the normalized WEOM concentration stabilized, showing minimal further change, however. This behavior might be attributed to changes in ionic strength following the addition of ash to water (e.g., Brito et al., 2021), which can influence the solubility of organic matter (Lawrence & Roy, 2021). Specifically, this observation can be attributed to dissolution chemistry differences between dilute and non-dilute systems (Logan, 2012; Klučáková & Věžníková, 2016). In concentrated solutions and suspensions, ionic strength increases, and electrostatic interactions become stronger, leading to deviations from ideality. The reasons for these deviations at higher ionic strength may include increased (i) competition between inorganic ions and organic molecules for water molecules that reduce the hydration shell around organic molecules rendering them less soluble and more likely to aggregate or precipitate (i.e., “salting out”), (ii) compression of the electric double layer around negatively charged organic matter leading to its destabilization and aggregation thereby preventing or reducing its dissolution, (iii) cation bridging between negatively charged organic functional groups reducing solubility and promoting the formation of organic complexes (flocs) that limit dissolution, and (iv) reduced hydrophobic dissolution as a result of increased solution/suspension polarity at higher ionic strength making it less favorable for non-polar, hydrophobic organic molecules (e.g., aromatic and lipid-like components of DOC) to dissolve. Similar trends have been observed in studies examining the leaching of various inorganic elements from soils and fly ash. These studies consistently reported a decrease in leaching efficiency for multiple metals as the solids-to-liquid (S : L) ratio increases, highlighting the broader influence of solid concentration on solute mobility (Koralegedara et al., 2017; Cao et al., 2018; Ghosh & Kartha, 2025). The increase in S : L ratio reduces the available free water molecules to interact with solute particles, thereby hindering the solubility of various compounds, ultimately decreasing extraction efficiency.

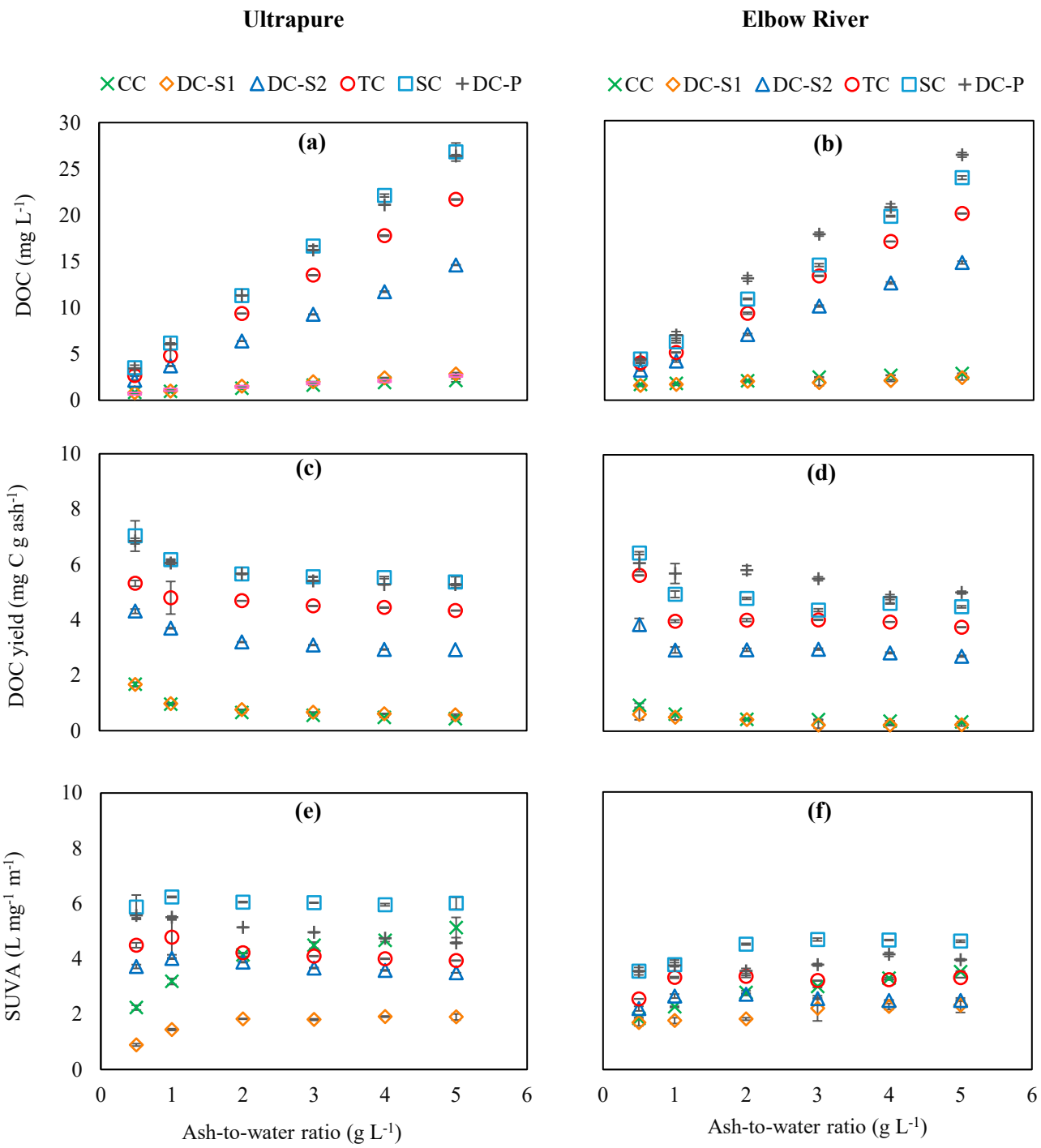


Figure 2-8 Change in (a & b) DOC concentration, (c & d) DOC yield, and (e & f) SUVA for different WAIWs prepared using ultrapure and Elbow River water across a range of ash-to-water ratios. Each symbol represents the average values (n = 3) with error bars representing standard deviation.

Table 2-5 Organic matter content, DOC concentration in WAIW containing 2 g L^{-1} of ash mixed in ultrapure water (mixed continuously for 24 h- n = 3). The table is organized in descending order of organic matter content for different ash types.

Ash type	Organic matter content (Moist Free %wt)	Moisture Content (%wt)	DOC (mg L^{-1})
CC	21.0 ± 1.9	3.9 ± 0.1	1.3 ± 0.04
DC-P	20.7 ± 0.1	1.6 ± 0.03	11.9 ± 1.0
DC-S2	17.0 ± 0.5	4.2 ± 0.01	6.3 ± 0.1
TC	14.7 ± 0.7	5.0 ± 0.02	9.6 ± 0.3
SC	14.6 ± 0.4	4.6 ± 0.1	12.2 ± 1.6
DC-S1	3.7 ± 0.1	3.9 ± 0.04	1.6 ± 0.1

2.3.2.2 Changes in WEOM character: SUVA and LC-OCD

Figure 2-8 e & f presents the changes in SUVA for WAIWs prepared using different ash-to-water ratios. Regardless of the ash type, SUVA values increased WAIW at lower ash-to-water ratios (i.e., 0.5 to 2 g L^{-1}). However, at ash-to-water ratios greater than 2 g L^{-1}, SUVA stabilized for almost all ash types, except for CC (Figure 2-8 e & f). SUVA values were higher in WAIWs prepared using ultrapure water, for almost all ash types (except for DC-S1), this could be attributed to the initial SUVA in Elbow River water and its potential impact on the overall WAIW SUVA.

LC-OCD analysis confirmed changes in WEOM character with increasing ash mass concentration, as shown in Figure 2-9 and Supporting information Figure A3. The data shows that increasing ash-to-water ratio leads to an increase in the concentration of all organic matter fractions. Consistent with the results of Experiment 1 (Section 2.4.1) and previously reported studies (Skwaruk et al., 2020; Blackburn et al., 2023), the greatest increases in organic matter fractions were in refractory fractions of DOC (i.e., humic substances and building blocks). However, there is no apparent proportionality among increases of different fractions at each ash mass concentration (Figure 2-9). In contrast to SUVA, refractory fractions yield generally remained stable in all WAIWs across different ash-to-water ratios (Supporting information Figure A3). This discrepancy emphasizes that different methods of analysis may capture distinct aspects of the organic matter present and highlights the critical need for careful interpretation of results.

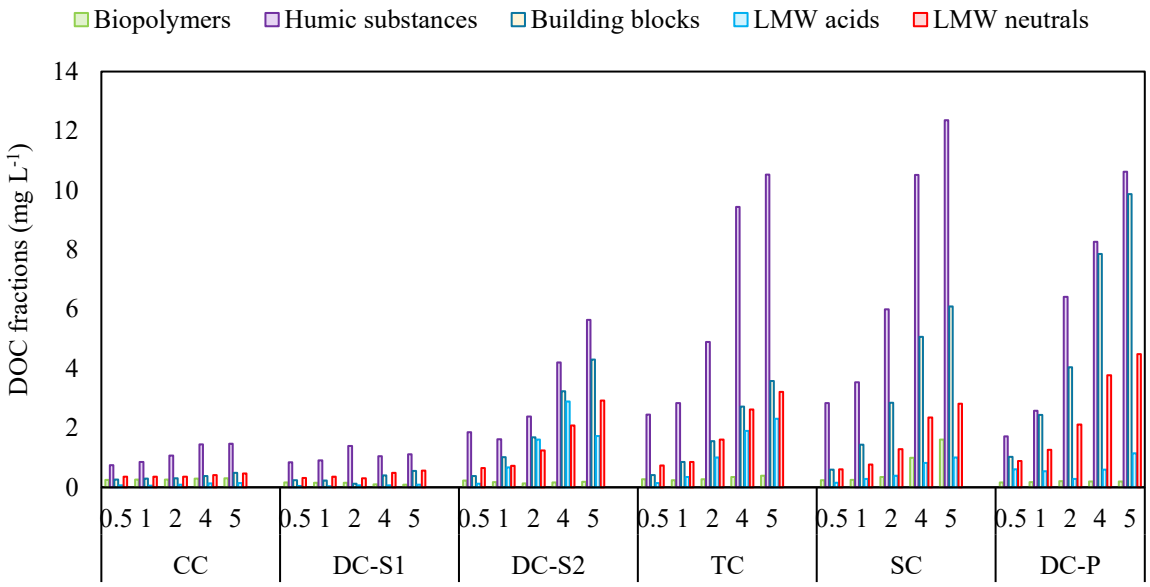


Figure 2-9 Organic matter character over time as indicated by LC-OCD for different ash types across a range of ash-to-water ratios mixed in Elbow River water. a) DOC fractions are presented in descending order of molecular weight: biopolymers, humic substances, building blocks, LMW neutrals and LMW acids; and b) Comparison between refractory fractions (including humic substances and building blocks) yield mg refractory fraction divided by mg DOC and SUVA.

2.3.2.3 Changes in WEOM extraction: Source water quality impact

The impacts of initial pH and alkalinity of source water on the overall WAIW pH were also assessed. Figure 2-10 shows changes in pH for all WAIWs prepared using different ash-to-water ratios mixed in ultrapure and Elbow River water. The largest changes in pH were observed in WAIWs prepared using ultrapure water. In contrast, changes in pH in Elbow River water were negligible, due to its high initial alkalinity (140-170 mg L^{-1}; Supporting information Table A1).

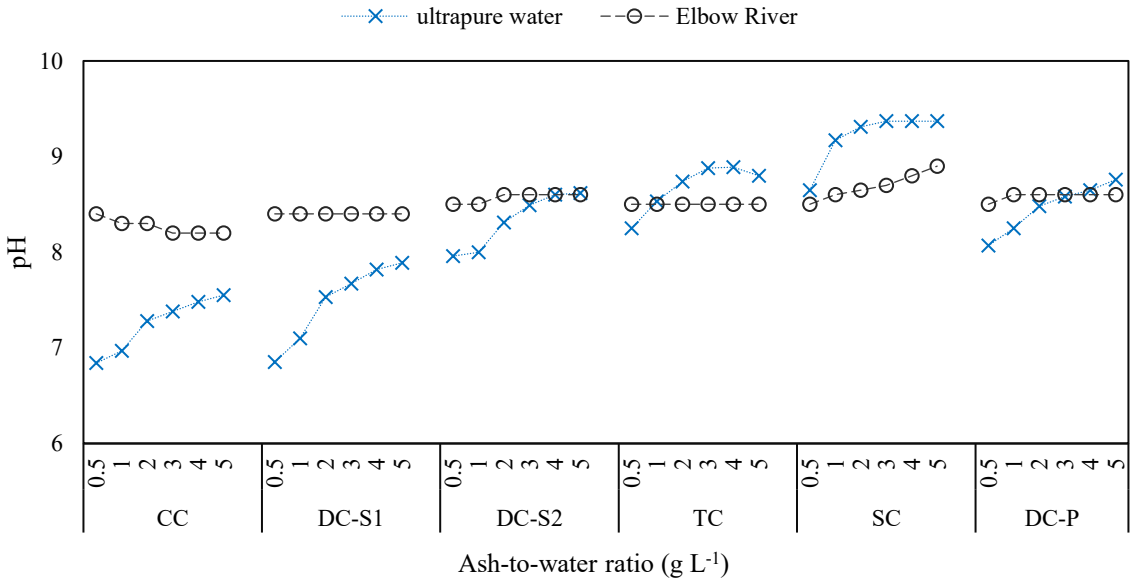


Figure 2-10 Change in pH for all ash types mixed in ultrapure and Elbow River water across a range of ash-to-water ratios. Blue crosses and grey circles indicate pH of WAIWs prepared in ultrapure and Elbow River water, respectively. The initial pH of Elbow River water was 8.3 ± 0.1 (n=3).

2.4 Conclusions

The effects of mixing conditions, time, and ash mass concentration on water extractable organic matter (WEOM) release from wildfire ash to water were investigated to demonstrate that experimental approach affects water quality and treatability assessments when using prepared wildfire ash-impacted water (WAIW) matrices (i.e., water matrices to which pyrogenic material is added to infer wildfire implications to water quality or treatability). Key conclusions from this research are:

- The impacts of wildfire on WEOM characteristics were generally consistent across different ash types. A higher DOC concentration consisting of mainly humic substances was measured in all WAIWs, regardless of mixing condition and ash mass concentration in the suspension.

- WEOM concentrations in ash leachates and ash organic content do not necessarily correlate with the ash color classification scheme.

- Substantial changes in organic matter concentration and character occur during the first 24 h of WAIW mixing and can thus impact inferred implications of wildfire ash on drinking water source quality and treatability (e.g., DBP formation).

- Source water quality and different concentrations of ash used to prepare WAIW impact WEOM solubility, and therefore inferred implications of wildfire ash on drinking water quality and treatability.

- In the absence of conducting a system-specific characterization of WEOM leaching from wildfire ash with different mixing conditions (or developing an alternative leaching method), a 24-hour mixing time is recommended for WAIW preparation for investigations (e.g., treatment performance evaluations) focused on maximizing WEOM concentration.

The conclusions above highlight several important considerations for conducting investigations of wildfire impacts on water quality and treatability in situations where wildfire impacts cannot be directly investigated. Most notably, they collectively emphasize the importance of (i) specifying experimental conditions and providing rationale for the WAIW preparation approach utilized (e.g., demonstrating a worst-case scenario of maximal leaching of WEOM from wildfire ash, reflecting watershed conditions), (ii) providing a range of results obtained at different leaching conditions, or alternatively (iii) clarifying that results may be exploratory or comparative, but not necessarily quantitatively meaningful or relevant for decision-making.

Chapter 3

Mechanical processing of ash affects bench-scale assessments of wildfire impacts on organic carbon threats to drinking water treatment

Summary

Wildfires can severely deteriorate drinking water source quality. Wildfire ash is a highly mobile mixture of organic and inorganic combustion residues, and its characteristics (e.g., leachability of different compounds) depend strongly on fuel availability and burn severity. However, reported ash properties and the quality of wildfire ash-impacted water (WAIW) vary widely across studies, partly due to differences in ash handling and pretreatment methods. As a result, it is often unclear whether observed differences in WEOM concentration and character in WAIW reflect true variations associated with differences in wildfire severity and fuel conditions or they are related to sample preparation, limiting cross-studies comparisons and drawing reliable inferences about wildfire ash impacts on drinking water source quality and treatability. This study systematically evaluated the effects of three commonly used dry ash pretreatment techniques (manual separation, sieving into coarse [> 1 mm] and fine [< 1mm] fractions, and pulverization) on the concentration and character of water-extractable organic matter (WEOM) in WAIW. Six ash types, representing a range of fire severities, were processed and analyzed at different mixing times and ash-to-water ratios. Ash particle size distribution, organic matter, total organic carbon (TOC), and carbonate (CO_3^{2-}) content were characterized. Water quality analyses included dissolved organic carbon (DOC) concentration, specific ultraviolet absorbance (SUVA), and organic matter fractionation. Following manual sieving, coarse fractions (> 1mm) showed a greater range of differences in DOC and SUVA compared to fine fractions (< 1mm). Pulverization decreased nominal samples variability but also affected WEOM character and introduced handling challenges due to aerosolization. These findings demonstrate that ash pretreatment techniques can impact WEOM concentration and character in ash-water matrices and should be carefully considered when assessing wildfire impacts on drinking water quality and treatability. Overall, sieving is recommended for the preparation of WAIWs to minimize variability among nominal replicates.

3.1 Introduction

Wildfire is among the most catastrophic natural disturbances changing landscapes (Santi et al., 2013), and its adverse effect on drinking water source quality is increasingly being recognized as a challenge for the provision of safe drinking water (Smith et al., 2011; Raoelison et al., 2023). Post-fire removal of vegetation and subsequent changes to soil properties can alter hydrological and biogeochemical processes (DeBano, 1991; Wagner et al., 2014; Williams et al., 2019). Wildfire ash is defined as highly

mobile solid residue remaining after the combustion of vegetation, surface fuels, and soil organic matter during a wildfire (Bodí et al., 2014).

Ash is composed of partially combusted organic matter, inorganic mineral particles, soluble ions, and other thermally altered residues (Ulery et al., 1993; Ferreira et al., 2005; Brito et al., 2017; Sánchez-García et al., 2023). Fuel type and availability, burn severity, and combustion duration and completeness can substantially impact ash characteristics and result in producing ash with highly heterogeneous physical and chemical properties (Bodí et al., 2014; Sánchez-García et al., 2023).

The delivery of wildfire ash to receiving waters can alter the concentration, character, and transport dynamics of nutrients, contaminants, and organic matter in surface waters (Bladon et al., 2008, 2014; Silins et al., 2009; Emelko et al., 2011; Rhoades et al., 2019; Emelko et al., 2024), challenging drinking water treatment processes (Emelko & Sham, 2014; Hohner et al., 2016; Shams, 2018) and increasing treatment costs (Emelko et al., 2011; Price et al., 2018). Wildfire impacts on drinking water source quality and treatability have been widely studied at bench, pilot, and full scales (e.g., Emelko et al., 2011; Wang et al., 2015a; Hohner et al., 2016; Uzun et al., 2020; Skwaruk et al., 2020; Blackburn et al., 2023; Tshering et al., 2023). Although it is not feasible to replicate the biogeochemical processes that ash and runoff undergo in natural landscapes within a laboratory setting, several studies have utilized either wildfire ash or laboratory-produced ash under controlled combustion conditions to assess the impacts of wildfire on water quality and treatability (e.g., Tsai et al., 2017; Chen et al., 2022; Blackburn et al.; 2023, Li et al., 2023).

Ash can differ substantially in key characteristics such as mineral composition, organic matter content, and particle size distribution, even among nominal replicates. Other materials such as unburned soil, rocks or debris are often unintentionally included during ash collection, further contributing to variability. Various techniques have been utilized to decrease variability within the collected ash samples. Different methods used across various studies for dry ash pretreatment prior to mixing with water are summarized in Table 3-1. These methods include manual separation, sieving, and grinding or pulverization. These pretreatment methods might alter ash physical structure, surface area, and particle composition, thereby impacting leaching behaviour of different compounds, especially organic matter, from ash to water.

Sieving is the most commonly used processing method to increase homogeneity of a sample within specific particle size ranges. Finer fractions of wildfire ash typically contain a higher proportion of pyrogenic materials formed through more complete combustion at elevated temperatures (Balfour &

Woods, 2013) and are therefore expected to yield lower concentrations of organic carbon. The method selected for dry ash pretreatment can substantially impact the concentration and quality of leached organic matter in wildfire-ash-impacted water (WAIW) and can consequently affect inferences from such studies and ultimately impact decisions regarding wildfire mitigation strategies.

Cerrato et al. (2016) and Rahman et al. (2018) used laboratory-generated ash from the same tree species, burned under identical conditions and mixed with ultrapure water at comparable mass concentrations. While one used ash resulting from burning whole branches (Cerrato et al., 2016), the other grounded unburned branches into a fine powder before combustion (Rahman et al., 2018). This difference in dry material pretreatment led to a variation of over 50% in dissolved organic carbon (DOC) concentrations, with ranges of 0.3 to 0.8 mg L^{-1} and 1.1 to 2.8 mg L^{-1}, respectively. Such inconsistencies underscore the importance of recognizing how experimental approaches impact the results obtained.

Despite the potential substantial impact from such pretreatment methods on WEOM concentration and character in prepared WAIWs, these techniques have not been systematically investigated. Dry ash pretreatment techniques may increase variability among replicates, complicate cross-study comparisons, and ultimately weaken the reliability of inferences drawn from bench- and pilot-scale evaluations of wildfire impacts on water quality and treatability.

Given the need for consistent and well-defined methods to evaluate the release of dissolved organic carbon and character from pyrogenic materials in water, this study systematically evaluates how different dry ash pretreatment techniques impact water quality metrics relevant to drinking water treatment. While not intended to standardize methods, it specifically investigates the effects of (1) manual separation, (2) sieving, and (3) pulverization on temporal changes on water extractable organic matter (WEOM) concentration and character, as well as its leaching potential across different ash mass concentrations.

Table 3-1 Methods employed for processing dry ash.

Processing method		Source
Manual separation (unburned vegetation, larger pyrogenic materials and rocks)		Tomkin et al. (1991); Olefeldt et al. (2013); Santín et al. (2015); Wan et al. (2021); Wirth et al. (2024)
Sieving to specified mesh size (mm)		
	4.75	Revchuk & Suffet (2014)
	2.00	Etiégni & Campbell (1991); Khanna et al. (1994); Hageman et al. (2007); Plumlee et al. (2007); Hageman et al. (2008); Certini et al. (2011); Son et al. (2015); Burton et al. (2016); Silva et al. (2016); Wang et al. (2016); Otieno (2017); Tsai et al. (2017); Ku et al. (2018); Tsai et al. (2019); Chen et al. (2020); Murphy et al. (2020); Chen et al. (2021); Chen et al. (2022); Li et al. (2022); Mesquita et al. (2022); Rodela et al. (2022); Alshehri et al. (2023); Chen et al. (2023); Fischer et al. (2023); Muñiz González et al. (2023); Alam et al. (2024); Megremi et al. (2024); Wu et al. (2024); Alshehri et al. (2025); Lersche et al. (2025).
	1.00	Brito et al. (2017); Oliveira-Filho et al. (2018); Harper et al. (2019); Skwaruk et al. (2020); Brito et al. (2021); Skwaruk (2021); Blackburn et al. (2023); Sánchez-García et al. (2023); McGregor (2024)
	0.991	Hohner et al. (2017); Cawley et al. (2018)
	0.850	Cawley et al. (2017); Thurman et al. (2020)
	0.840	Murphy et al. (2006); Kwan et al. (2024)
	0.630	Ahmed et al. (2023)
	0.212	Li et al. (2023)
	0.200	Doufexi et al. (2022); Numan et al. (2025)
Pulverization (using mills, mortar and pestle, or grinders)		Durgin & Vogelsang (1983); Úbeda et al. (2009); Pereira et al. (2013); Audry et al. (2014); Rahman et al. (2018); Quigley et al. (2019); Calderon (2020); Myers-Pigg et al. (2024); Johnson & Mansfeldt (2025)

3.2 Materials and methods

3.2.1 Experimental approach

A bench-scale investigation using three pretreatment methods (i.e., manual separation, sieving, and pulverization) was conducted to evaluate the effect of dry ash pretreatment methods on WEOM concentration and character. Six ash types from four wildfires and one prescribed fire were collected to represent a spectrum of burn severities and ash properties. Each ash type was separated into two size fractions using sieves: coarse (> 1 mm) and fine (< 1 mm). Subsequently, a portion of each fraction was further processed using a mortar and pestle to yield pulverized coarse and pulverized fine ash. To eliminate any potential impacts of source water natural organic matter (NOM) on WEOM leaching from the ash, WAIW matrices were prepared using ultrapure water (Bahramian et al., 2025- Chapter 2). This approach ensured consistent sample pretreatment across experiments and enabled meaningful comparisons with other studies.

3.2.2 Experimental design

The impacts of dry ash pretreatment methods, specifically mixing duration and ash-water ratio (i.e., ash mass concentration [mg/L]) on WEOM concentration and character were evaluated (Figure 3-1). To investigate the potential link between ash organic carbon leachability and its characteristics, ash particle size, organic matter content, TOC proportions, and ash density were measured in all coarse (retained on 1 mm sieve and rocks and unburned materials separated manually) and fine (passed through 1 mm sieve) samples.

Phase 1- Mixing Duration: WAIW matrices were prepared by adding 2 g L^{-1} of each ash sample to ultrapure water. WAIWs were mixed at 120 RPM (as described in Bahramian et al., 2025- Chapter 2), and water samples were collected at predetermined intervals: 0.5 h, 6 h, and 24 h. DOC, UV_{254}, and SUVA were measured for all samples.

Phase 2- Ash-to-Water Ratio: WAIW matrices were prepared with ash-to-water ratios ranging from 0.5 g L^{-1} to 5 g L^{-1}. Each ash type was mixed with ultrapure water at 120 RPM for 24 hours. Water samples were analyzed for water quality metrics including DOC, UV_{254}, and SUVA. In Phase 2, organic carbon was further characterized using liquid chromatography with organic carbon detection (LC-OCD), described in section 3.3.5.

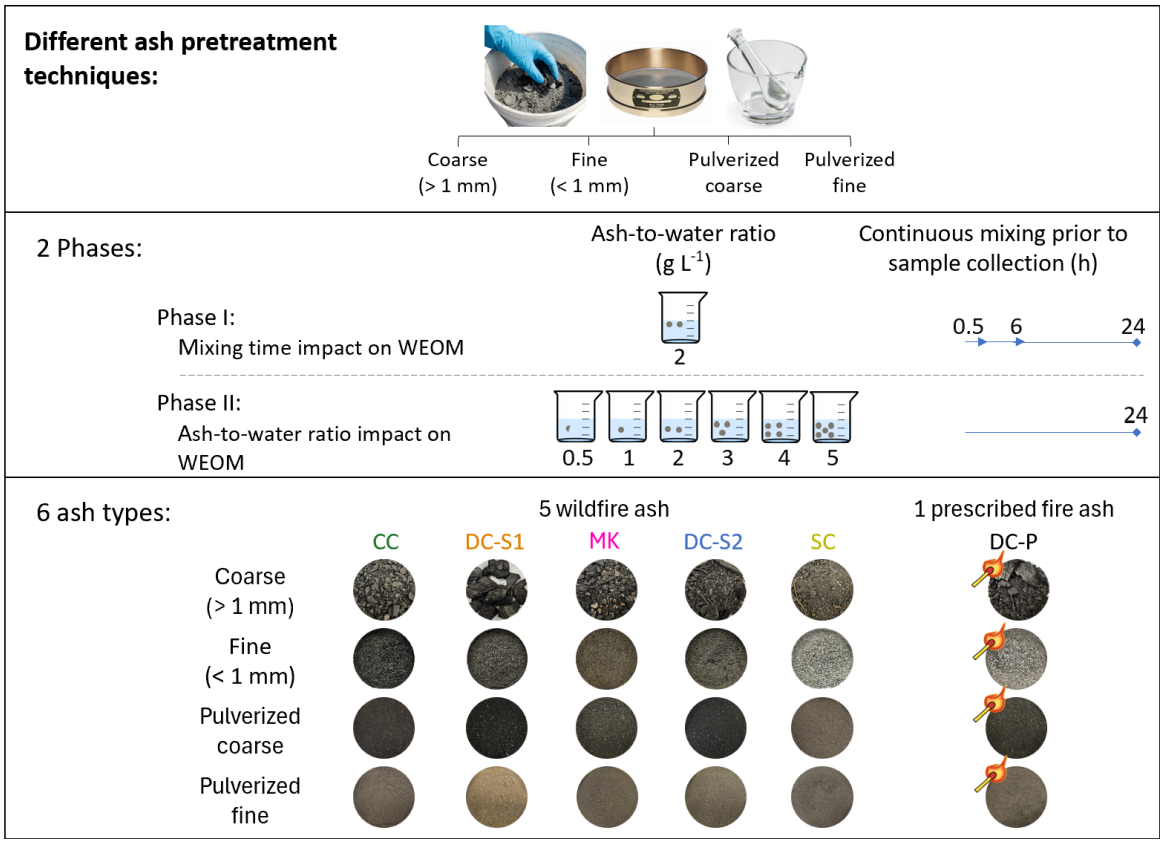


Figure 3-1 Experimental design to evaluate the impact of dry ash pretreatment methods on WEOM concentration and character. For this study, different ash samples were sieved through a 1 mm mesh and portion retained on sieve was labeled as coarse and the portion passed through the sieve was labeled as fine ash. Rocks and unburned material were manually separated from coarse fractions. A subset of both coarse and fine fractions was further ground using a mortar and pestle to produce pulverized coarse and pulverized fine ash, respectively. The leaching behavior of 24 ash samples was assessed in two experimental phases: Phase 1 examined the effect of mixing duration, and Phase 2 evaluated the influence of ash mass concentration on the concentration and character of water-extractable organic matter (WEOM). In all experiments, ultrapure water was used to prepare water-extractable ash-induced water (WAIW). The ash samples analyzed were collected from five wildfire sites and one prescribed burn site: Cameron Creek (CC), Doctor Creek sampling site 1 (DC-S1), Minnekhada (MK), Doctor Creek sampling site 2 (DC-S2), Scottie Creek (SC), and the Doctor Creek prescribed fire site (DC-P).

3.2.3 Wildfire ash collection

Ash samples were collected from four wildfires and one prescribed fire that represent pyrogenic materials produced by different burn severities in Western Canada. Fire locations, burned area, fire severity, vegetation type, and ash condition for each study site are listed in Table 3-2. Except for Cameron Creek ash (CC), all other ash samples were collected prior to any major precipitation event. All ash samples were air dried and stored in closed containers at 21 °C.

Table 3-2 Ash collection location, date, and fire information.

Ash type	Fire	Location	Burn area (ha)	Fire start date (mm/yyyy)	Vegetation type	Burn severity	Ash collection date (mm/yyyy)
Cameron Creek (CC)	Kenow Wildfire[a]	Waterton, AB[a]	35,000[a]	09/2017[a]	Lodgepole Pine[1a], Subalpine Fir[2a]	High to extreme[b]	06/2018[b]
Doctor Creek sampling site 1 (DC-S1)	Doctor Creek Wildfire[c]	Canal Flats, BC[c]	7645[c]	08/2020[c]	Lodgepole Pine[1c] Douglas Fir[3c], Ponderosa Pine[4c], Western Larch[5c]	High[c]	09/2020
Doctor Creek sampling site 2 (DC-S2)	Doctor Creek Wildfire[c]					Medium[c]	
Doctor Creek prescribed fire site (DC-P)	Doctor Creek Prescribed Fire[c]					Medium[c]	
Minnekhada (MK)	Minnekhada Park Fire[d]	Coquitlam, BC, Canada[d]	14[d]	10/2022[d]	Douglas fir[3d], Western Red Cedar[6d]	High[d]	10/2022[d]
Scottie Creek (SC)	Elephant Hill Fire Complex[e]	Ashcroft, BC[e]	191,865[e]	07/2017[e]	Douglas Fir[1f], Spruce Hybrids[6f], Yellow Pine[8f], Trembling Aspen[9f]	High[f]	08/2017[f]

1- *Pinus contorta* var. *latifolia*
2- *Abies lasiocarpa*
3- *Pseudotsuga menziesii* var. *glauca*
4- *Pinus ponderosa*
5- *Larix occidentalis*
6- *Thuja plicata*
7- *Picea* spp.
8- *Populus tremuloides*

a- Parks Canada- Kenow Wildfire timeline (2023)
b- U. Silins (Personal communication, March 20, 2025)
c- BC Wildfire Service Information Section (2020)
d- Gifford et al. (2025)
e- BC gov news (2020)
f- Skwaruk (2021)

3.2.4 Dry ash pretreatment

Ash samples were sieved through a 1 mm mesh to separate the homogenized fine (< 1 mm) ash from the coarser (> 1 mm) fraction (e.g., Cawley et al., 2018; Oliveira-Filho et al., 2018; Harper et al., 2019; Skwaruk et al., 2020; Sánchez-García et al., 2023). Large inorganic materials (sands and gravel) and unburned materials were separated from the sieved burned fraction manually, following previously reported methodologies (Tomkin et al., 1991; Olefeldt et al., 2013; Santín et al., 2015; Wirth et al., 2024).

After sieving and manual separation, 200 g of each ash type, both coarse and fine fractions, were collected and divided into four portions. Two portions were randomly selected as untreated samples, while the remaining two were pulverized manually under a fume hood using a mortar and pestle to obtain superfine particles. Pulverization is assumed to further homogenize the samples and minimize the variability in obtained experimental results (U.S. EPA, 2004).

Notably, varying particle size distributions were observed in the coarse fraction of different ash types. While some samples showed a broad range of particle sizes with charred and burned materials' diameters ranging from just over 1 mm to several centimeters (e.g., DC-P), distributions of other samples were more uniform (e.g., SC). In some samples, the coarse fraction contained clumps of burned soil (e.g., CC). Additionally, some samples contained larger sand and pebble sized materials. It was not always possible to remove non-pyrogenic (e.g., rocks and unburned biomass) materials in those samples. For example, the MK ash contained numerous rocks of varying sizes, making it impractical to isolate only charred materials. Similarly, the SC coarse sample retained unburned needles due to their overwhelming presence in the collected ash. Due to these variations in coarse ash samples, collecting three separate untreated samples with identical profiles and selecting a representative sample for pulverization could not be assured.

3.2.5 Ash characteristics and water quality analyses

The particle size distribution of coarse and fine ash samples was determined using a series of 26 sieves ranging from 0.075 mm to 19 mm (ASTM D6913). Organic matter content was measured using loss on ignition according to ASTM Method D7348. TOC in dry ash samples was measured using high-temperature combustion (ASTM Method D7573). The carbonate content of each ash type was measured following the ASTM Method D4373. Additionally, following A volumetric flask method outlined by Flint & Flint (2002) was used to determine ash density.

The WAIWs were analyzed according to Standard Methods for the Examination of Water and Wastewater (APHA, 2022). DOC concentration in WAIW was measured using the combustion method (Standard Method 5310C) on a Shimadzu TOC-VCHP Analyzer (Shimadzu Corporation, Jiangsu, China) with a detection limit of 0.1 mg L^{-1}. UV absorbance at 254 nm was measured with a UV-Vis analyzer (Agilent Cary 3500 UV-Vis Spectrophotometer, Santa Clara, United States) following Standard Method 5910B. Additionally, the specific ultraviolet absorbance at 254 nm (SUVA) was calculated by dividing the UV_{254} absorbance by the DOC concentration, as described by Edzwald et al. (1985).

Size exclusion LC-OCD analysis was performed in accordance with Huber et al. (2011) using a Model 8 LC-OCD analyzer (DOC-Labor GmbH, Karlsruhe, Germany). This method used a size exclusion column and a weak cation exchange column made of polymethacrylate (Toyopearl HW 50S, 250 mm x 20 mm, 30 µm from TOSOH Bioscience). The organic carbon detector was calibrated using potassium hydrogen phthalate. Data acquisition and processing were carried out using a specialized software program (ChromCALC, DOC-LABOR, Karlsruhe, Germany). LC-OCD subdivides dissolved organic matter into five fractions: biopolymers, humic substances, building blocks, low molecular weight (LMW) acids, and LMW neutrals based on the molecular size (Huber et al., 2011).

Biopolymers represent the largest molecules of dissolved organic matter compounds, with molecular weights exceeding 20,000 g mol^{-1} (>10 kDa), and include polysaccharides, proteins, polypeptides, and amino sugars. These compounds do not absorb UV at 254 nm. Humic substances consist of humic and fulvic acids, with molecular weights ranging from 400 to 1100 g mol^{-1}. Building blocks are defined as humic-substance-like material of lower molecular weight (300–500 g mol^{-1}); these compounds are breakdown products of humic substances. LMW acids comprise small aliphatic organic acids with molecular weights below 350 g mol^{-1}, while LMW neutrals include weakly charged or slightly hydrophobic compounds such as alcohols, aldehydes, ketones, sugars, and amino acids (Huber et al., 2011). For DOC, UV_{254} and LC-OCD analyses, WAIWs were filtered through pre-rinsed 0.45 µm polyethersulfone filters (PES, Millipore Express® PLUS; Merck Millipore, Burlington, MA). Minimum reporting limits for the water quality metrics analyzed here are presented in Supporting information Table B1.

3.2.6 Statistical Analysis

Statistical analyses were conducted to evaluate whether specific dry ash characteristics were associated with the concentration of leachable WEOM. Least square linear regression was used to examine

potential relationships between dry ash characteristics (i.e., organic matter, TOC, and carbonate content) and leachable WEOM concentration for each ash type. To evaluate the effects of different pretreatment techniques (i.e., sieving and pulverization) on WEOM concentrations, analysis of variance (ANOVA with $\alpha = 0.05$) was applied to samples that met ANOVA assumptions, while samples that did not meet these assumptions were analyzed using a non-parametric Mann–Whitney test ($\alpha = 0.05$). It should be noted that because both ash pretreatment and WAIW preparation were labor- and time-intensive, only three replicates were available for each ash type and pretreatment condition. Consequently, to increase statistical analysis power WEOM concentration of WAIW prepared at varying ash-to-water ratios of each ash type were grouped together (n=18).

3.3 Results and discussion

3.3.1 Ash particle size separation by sieving

The following section presents the results of dry ash characterization and changes in WEOM concentration and character in WAIW prepared using sieved ash fractions. Ash retained on the 1 mm sieve is referred to as the coarse fraction, while ash that passed through is classified as the fine fraction. Coarse ash was further manually sorted to remove rocks and unburned material prior to WAIW preparation. Ash characteristics, mixing time, and ash-to-water ratio impacts on WEOM are presented in Sections 3.1.1, 3.1.2, and 3.1.3, respectively.

the proportion of ash retaine coarse and fine ash (> 1 mm and < 1 mm, respectively) are described below. Ash characteristics, mixing time, and ash-to-water ratio impacts on WEOM are presented in Sections 3.1.1, 3.1.2, and 3.1.3, respectively.

3.3.1.1 Ash characteristics

The particle size distributions of all ash types are presented in Figure 3-2, Supporting information Figure B1 and Table B2. For all ash types, most particles were < 1 mm, comprising approximately 60% to 90% of the total mass (D50 ranged from 0.078 to 0.44 mm, Supporting information Table B2). Some ash types showed variability in the coarser fraction (> 1 mm) and contained very large particles (> 12 mm, e.g., DC-S1 and DC-P), while others had a smaller percentage (e.g., SC and MK; Supporting information Table B2). Although combustion temperature data are not available for the ash types used in this study, an inverse relationship between combustion temperature (up to 900 °C) and ash particle

size has been reported (Ulery et al., 1993; DeBano et al., 1998; Goforth et al., 2005; Liodakis et al., 2005; Pereira et al., 2012; Balfour & Woods, 2013; Bodí et al., 2014; Alshehri et al., 2022; Paul et al., 2022; Sapkota et al., 2025). Accordingly, it is typically assumed ash types with a higher proportion of smaller particles are likely produced at higher combustion temperatures, while finer fractions have lower organic matter content (Bodí et al., 2014).

The organic matter content and ash particle density for coarse and fine fractions of all ash types are presented in Figure 3-3. Organic matter content of fine fractions was consistently lower than coarse fractions. However, no correlation was observed between the proportion of fine particles and organic matter content (i.e., ash types with a higher percentage of small particles did not necessarily have less organic matter content- Supporting information Figure B2). While this observation aligns with what has been reported for wildfire ash (Wirth et al., 2024), it differs from reported studies for lab-produced ash (Balfour & Woods, 2013). This suggests that other factors, such as the presence of unburned material, mineral soil components, and variations in combustion conditions, may account for the differences between field-collected wildfire ash and lab-produced ash.

The particle density of different ash types used here ranged from 0.37 to 3.30 g cm^{-3} and 0.91 to 2.41 g cm^{-3} for coarse and fine ash, respectively. The fine ash density range is comparable to previously reported values (1 to 2.80 g cm^{-3} - Cerdà & Doerr, 2008; Moody et al., 2009; Bodí et al., 2011; Balfour & Woods, 2013). In contrast, the density values for coarse ash fall outside of the reported range (1 to 2.80 g cm^{-3}), reflecting the heterogeneity of coarse samples. The presence of charred wood, which may float in water, can lower particle density, while the inclusion of rocks in the sample can result in substantially higher values. Notably, higher particle density was measured for ash types with a higher proportion of very fine particles (< 0.105 mm)—including DC-S1, MK, DC-S2, and SC—than the other ash types (i.e., CC and DC-P). This aligns with the previously reported inverse correlation between ash particle size and particle density (Balfour & Woods, 2013).

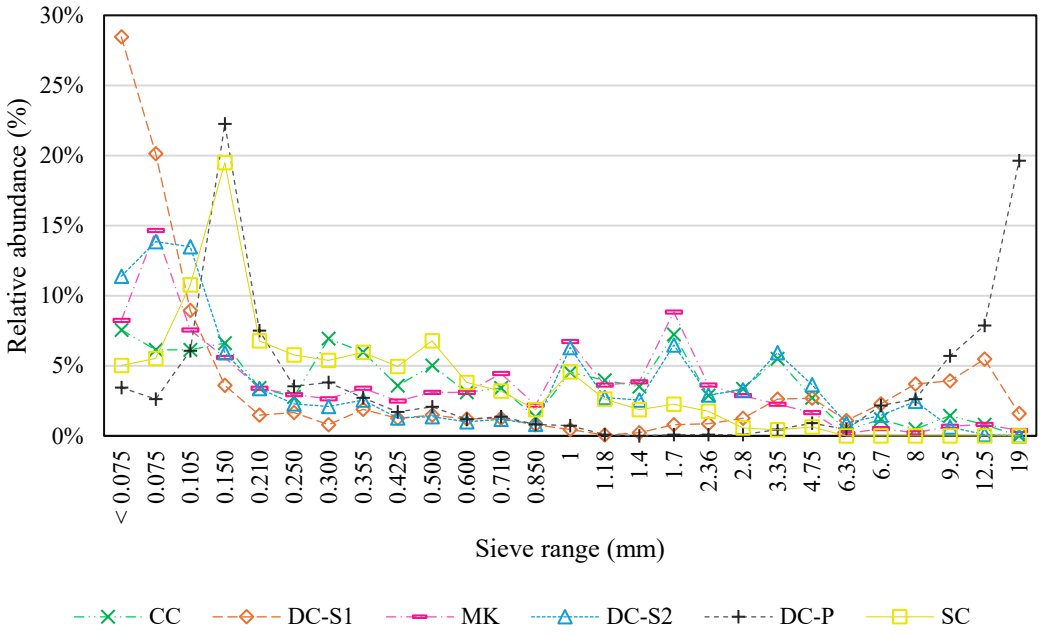


Figure 3-2 Particle size distribution of different ash types.

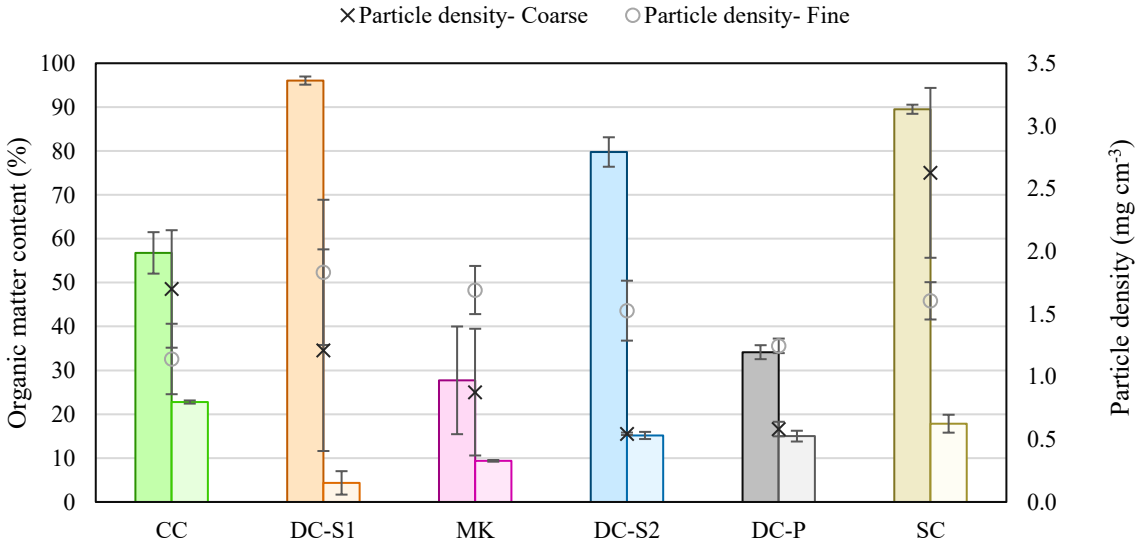


Figure 3-3 Organic matter content and particle density for coarse and fine fractions of different ash types. Darker bars on the left and lighter bars next to them show organic matter content percentage for coarse and fine ash, respectively. Particle density for coarse and fine ash is shown using crosses and circles, respectively. Each bar/symbol represents the average value (n = 3) with error bars representing standard deviation.

3.3.1.2 Mixing time impact on WEOM

Changes in WEOM concentration and character (i.e., DOC and SUVA) for bench experiments are shown in Figure 3-4. Coarse ash showed greater variability in DOC concentrations and SUVA values compared to fine ash, demonstrating that sieving increases ash homogeneity and leads to more consistent attributes, including WAIW quality, as would be expected. WAIW DOC concentrations ranged from 0.6 to 23.2 mg L^{-1} and 1.0 to 12.3 mg L^{-1} for coarse and fine ash, respectively. Longer mixing times (24 h vs. 30 min) substantially increased WEOM concentrations for some ash types (e.g., DC-S2, DC-P, and SC), regardless of the fraction of the ash (i.e., coarse and fine), suggesting extended mixing time enhances leaching of WEOM from wildfire ash. This is in good agreement with previously reported studies (Rahman et al., 2018; Bahramian et al., 2025- Chapter 2).

For some ash types, fine ash initially leached higher concentrations of organic carbon (i.e., (MK, DC-S2, DC-P), but for others coarse ash released more WEOM (i.e., CC, DC-S1, SC). While greater surface area in fine ash can lead to a more rapid initial leaching of WEOM, other factors such as burn severity, combustion completeness, and vegetation type also contribute to WEOM (Bodí et al., 2014; Roebuck Jr et al., 2025). The relative increase in DOC concentration after 24 h of mixing, calculated as ($DOC_{24\ h}$ - $DOC_{30\ min}$) / $DOC_{30\ min}$, was generally higher for coarse ash (> 1 mm) compared to fine ash, except for CC (Table 3-3). This suggests that readily soluble organic matter in fine ash is extracted more quickly during early leaching stages.

SUVA values showed minimal change during the study period, though they slightly increase with longer mixing of fine ash, indicating greater extraction of aromatic compounds. In contrast, SUVA in coarse ash varied considerably between ash types. The wide standard deviations of the SUVA in WAIWs prepared using coarse ash reflect the relatively greater heterogeneity of coarse ash.

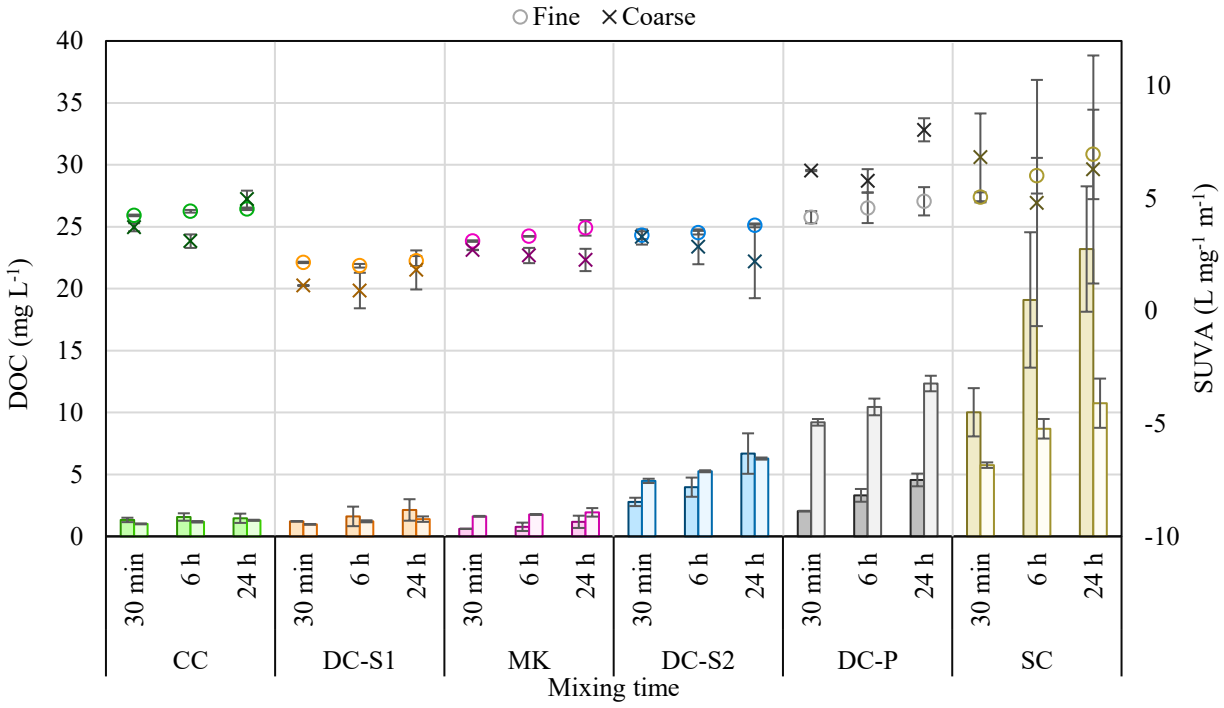


Figure 3-4 Changes in WEOM concentration and character (i.e., DOC and SUVA) for coarse and fine WAIWs at different sampling times during a 24 hour experiment. For each sampling time, darker and lighter bars show DOC concentrations for coarse and fine WAIWs, respectively, and crosses and circles show SUVAs for coarse and fine WAIWs, respectively. Each bar/symbol represents the average value (n = 3) with error bars representing standard deviation.

Table 3-3 Relative DOC increase during the experimental period for all ash types. The relative change is calculated as $(DOC_{24\ h} - DOC_{30\ min}) / DOC_{30\ min}$.

Ash type	Relative DOC change in 24 h (%)	
	Coarse	Fine
CC	10.1	28.9
DC-S1	75.9	43.5
MK	92.7	19.8
DC-S2	140.3	40.2
DC-P	123.5	34
SC	131.6	86.9

3.3.1.3 Ash-to-water ratio impact on WEOM

Figure 3-5 shows WEOM concentration and character (i.e., DOC and SUVA) for different ash types across varying ash-to-water ratios. WEOM concentrations ranged from 0.4 to 54.7 mg L^{-1} and 0.7 to 29.0 mg L^{-1} for coarse and fine ash, respectively. Comparison of DOC concentrations in WAIWs prepared using coarse and fine ash indicates that sieving increased ash homogeneity and reduced WEOM variability in certain ash types, including CC, MK, and DC-S1. However, in contrast to Section 3.1.2, no appreciable variability was observed in the coarse fractions of DC-S2 and SC (Figures 3-4, 3-5, and Supporting information Figure B3). These findings further underscore the inherent variability of coarse ash and the challenges associated with working with such heterogeneous materials.

Statistical comparisons between coarse and fine fractions of different ash types indicated significant difference for DC-S1, MK, DC-P, and SC, and no significant difference was observed for CC and DC-S2 (Supporting information Table B3). Comparing WEOM concentrations shows that the differences in coarse and fine DC-P and SC ash leachates exceeded 11 mg L^{-1} on average, while the corresponding differences for CC, DC-S1, MK, and DC-S2 were all less than 1 mg L^{-1} (Figure 3-5). This shows the magnitude of differences between coarse and fine fractions varies considerably across ash types.

It is worth noting that the WEOM concentration in WAIW prepared from coarse DC-P ash was, on average, 7.3 ± 4.1 mg L^{-1} lower than that from fine DC-P ash across all ash-to-water ratios. In contrast, the WEOM concentration in WAIW from coarse SC ash was, on average, 16.4 ± 10.4 mg L^{-1} higher than that from fine SC ash across all ash-to-water ratios. These observations do not align with the generally accepted direct correlation between ash particle size and its WEOM concentration whereby finer ash—resulting from higher combustion temperatures and/or longer burn durations—typically contains less organic carbon and thus releases lower WEOM concentration (e.g., Bodí et al., 2014; Sapkota et al., 2025). These data demonstrate that they present a more complex relationship and suggest that sieving impact is not uniform for all ash types.

The SUVA of WAIW produced using coarse ash showed greater variability across most ash types, except for MK and SC (Figure 3-5). SUVA stabilized at ash-to-water ratios above 2 g L^{-1}, with the exception of CC ash. Similarly, DOC yield (i.e., DOC concentration per gram of ash; Supporting information Figure B4) also stabilized for ash-to-water ratios exceeding 2 g L^{-1}. In contrast, for WAIWs containing ash-to-water ratios below 2 g L^{-1}, SUVA increased while DOC yield decreased with increasing ash concentration. These trends are consistent with previous findings (Bahramian et al., 2025- Chapter 2) and suggest a consistent leaching mechanism across various ash particle sizes. In

addition, shifts in SUVA and DOC yield suggest that at ash-to-water ratios below 2 g L^{-1}, WEOM concentration and character are highly dependent on ash mass concentration, which may introduce higher variability in water quality and challenge drinking water treatment processes.

Figure 3-6 shows the proportions of different fractions of DOC, obtained from LC-OCD, in WAIWs prepared using coarse and fine ash across different ash-to-water ratios. LC-OCD results show that WEOM from coarse ash generally contained higher proportions of smaller molecules (e.g., building blocks, LMW neutrals, and LMW acids; Figure 3-6). Although different factors such as fuel type impact ash characteristics, finer pyrogenic materials typically result from longer combustion at higher temperatures (Woods & Balfour, 2010; Balfour & Woods, 2013). In these conditions, less thermally stable compounds decompose, leaving behind more thermally stable and aromatic compounds (e.g., humic substances; González-Pérez et al., 2023).

Additionally, DOC concentrations of WAIWs prepared using 1 g L^{-1} of ash, along with the proportions of TOC, carbonate and organic matter content for different ash types, are presented in Table 3-4. As expected, all coarse ash types had higher TOC and organic matter proportions. However, only DC-P and SC ash showed substantial difference between coarse and fine WAIWs, suggesting DOC concentrations in WAIW are not directly determined by the TOC or organic matter content of the ash. Linear regression analysis indicated a very weak correlation between DOC concentration and dry ash TOC ($R^2 = 0.0586$) and organic matter content ($R^2 = 0.008$; Supporting information Figure B5 a & b). In contrast, carbonate content in dry ash showed a stronger relationship and may serve as a useful predictor of DOC concentration in WAIW ($R^2 = 0.5447$; Supporting information Figure B6).

The DOC-to-TOC ratios ranged from 0.2% to 7.9% for coarse ash and from 1.0% to 18.3% for fine ash. These values were generally higher than those reported by Santín et al. (2012) for twelve ash types across a range of burn severities (< 1%). This can be attributed to differences in experimental conditions. The present study used lower ash-to-water ratios and 24 h mixing duration, whereas Santín et al. (2012) employed a 50-min mixing time. The extended mixing duration in this study enabled leaching to approach equilibrium, resulting in higher concentration of WEOM from wildfire ash, as discussed in Bahramian et al. (2025)- Chapter 2.

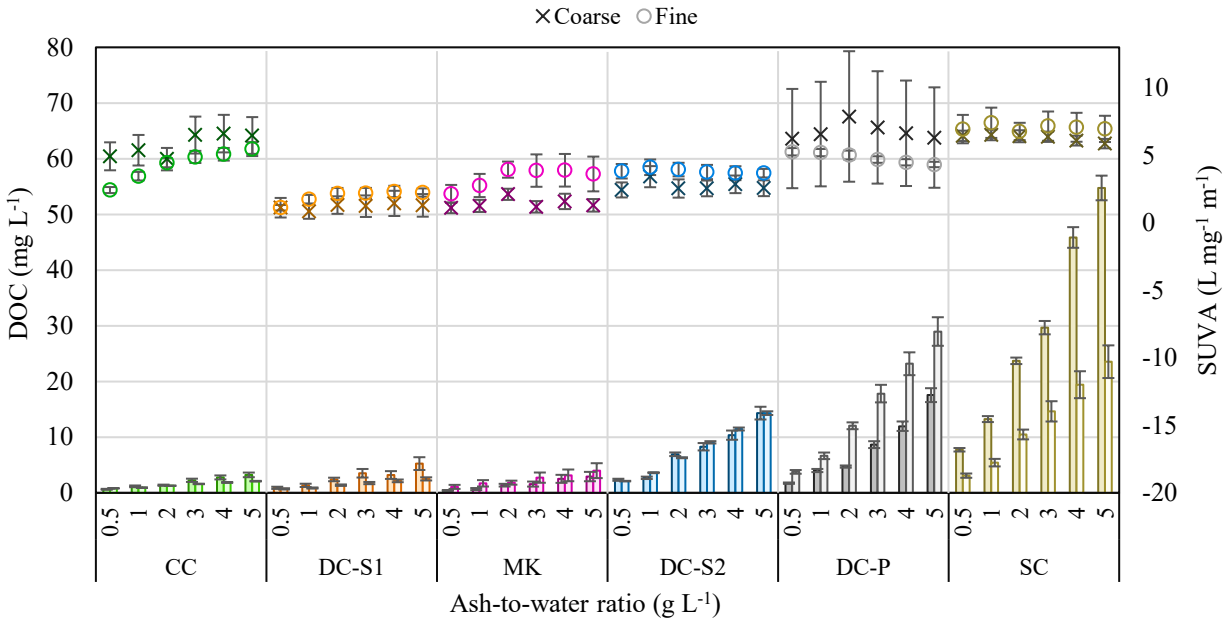


Figure 3-5 Changes in WEOM concentration and character (i.e., DOC and SUVA) for coarse and fine WAIWs across a range of ash mass concentration. For each ash concentration, darker and lighter bars show DOC concentrations for coarse and fine WAIWs, respectively, and crosses and circles show SUVAs for coarse and fine WAIWs, respectively. Each bar/symbol represents the average value (n = 3) with error bars representing standard deviation.

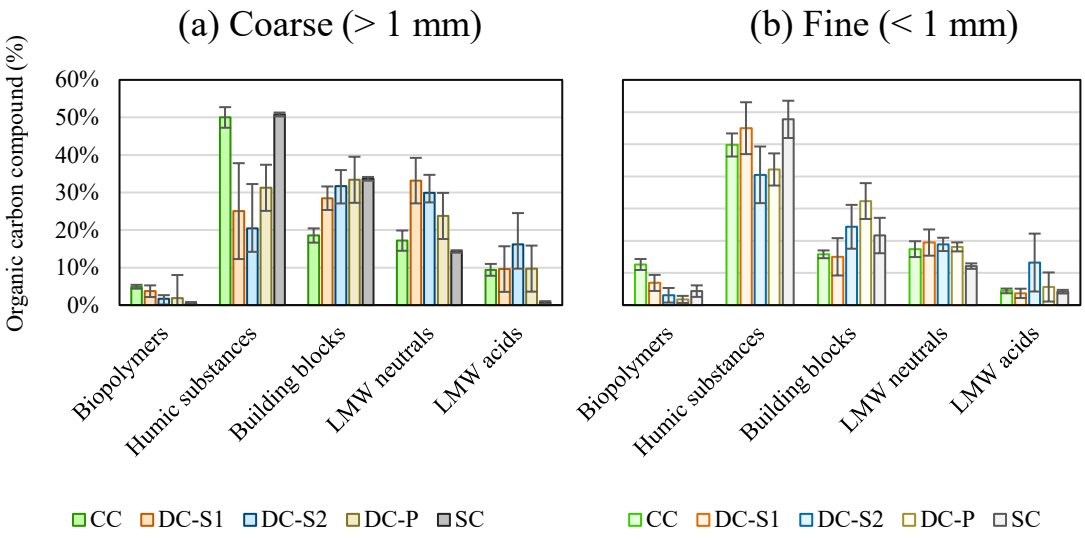


Figure 3-6 The proportion of different organic matter compounds in the total DOC concentration for (a) coarse and (b) fine ash WAIWs. Each bar represents the average value (n = 6) with error bars representing standard deviation.

Table 3-4 WEOM concentration (as indicated by DOC) in 1 g L^{-1} WAIW suspensions, TOC, carbonate, and organic matter content in dry ash for different ash types used in this experiment. DOC concentration and organic matter content show the average values with standard deviations (n = 3), however the TOC and carbonate proportions were measured in one sample.

	Coarse				**Fine**			
	DOC (mg L^{-1})	TOC (wt %)	Carbonate (wt %)	OM content (wt %)	DOC (mg L^{-1})	TOC (wt %)	Carbonate (wt %)	OM content (wt %)
CC	1.2 ± 0.2	37.8	< 0.04	56.8 ± 4.7	0.9 ± 0.0	8.9	4.1	22.8 ± 0.4
DC-S1	1.3 ± 0.3	> 40	< 0.04	96.0 ± 0.9	0.9 ± 0.1	1.3	0.9	4.3 ± 2.7
MK	0.7 ± 0.2	> 40	< 0.04	27.7 ± 12.3	3.6 ± 0.1	4.3	3.2	15.2 ± 0.8
DC-S2	2.7 ± 0.2	32.5	< 0.04	79.8 ± 3.4	1.7 ± 0.6	3.7	7.7	9.4 ± 0.2
DC-P	4.0 ± 0.3	> 40	< 0.04	89.5 ± 1.0	6.6 ± 0.6	3.8	13.8	17.8 ± 2.0
SC	13.2 ± 0.5	16.8	11.3	34.1 ± 1.6	5.4 ± 0.7	3.0	12.1	15.0 ± 1.2

3.3.2 Ash fragmentation: Pulverized vs. non-pulverized

Below the impact of pulverization of ash on water quality is described. Mixing time, and ash-to-water ratio impact on WEOM are presented in Sections 3.2.1, and 3.2.2, respectively.

3.3.2.1 Mixing time impact on WEOM

Figure 3-7 shows the variations in WEOM concentration and character (i.e., DOC and SUVA) over time for WAIWs prepared using coarse, pulverized coarse, fine, and pulverized fine ash. Consistent with the findings in Section 3.4.1 and previous studies (Ahmad et al., 2018; Bahramian et al., 2025-Chapter 2), DOC concentrations increased for all ash types as leaching time progressed (Figure 3-7 a & b). The extent of this increase varied among ash types, however. Non-pulverized coarse and fine WAIWs showed greater changes in DOC concentration over time, suggesting that pulverization results in higher initial reaction rates and leaching due to the increased surface area of the particles. In contrast, the leaching of organic carbon from Non-pulverized coarse and fine WAIWs occurred more gradually.

At the end of the experiment (after 24 h of mixing), coarse WAIWs showed greater variability in DOC concentrations, suggesting that coarse ash contains organic molecules with a broad range of leaching potentials and that the release of organic carbon from coarse ash occurs over an extended period. Conversely, fine and pulverized fine ash contain more homogenized particles, leading to a more consistent leaching of WEOM over time with less variability.

In general, SUVA in WAIWs prepared from fine and pulverized fine ash changed minimally (Figure 3-7d), whereas Non-pulverized coarse ash WAIWs showed substantial variation for all ash types (Figure 3-7c), further highlighting the heterogeneous nature of coarse ash. Over time, the average SUVA in fine and pulverized fine WAIWs increased slightly, but it generally decreased in pulverized coarse WAIWs, except for DC-P. Non-pulverized coarse WAIWs did not show a clear trend in changes in SUVA (Figure 3-7 c & d). These results suggest that pulverization has little effect on the extraction of aromatic compounds from fine ash but may substantially influence their leaching from coarse ash.

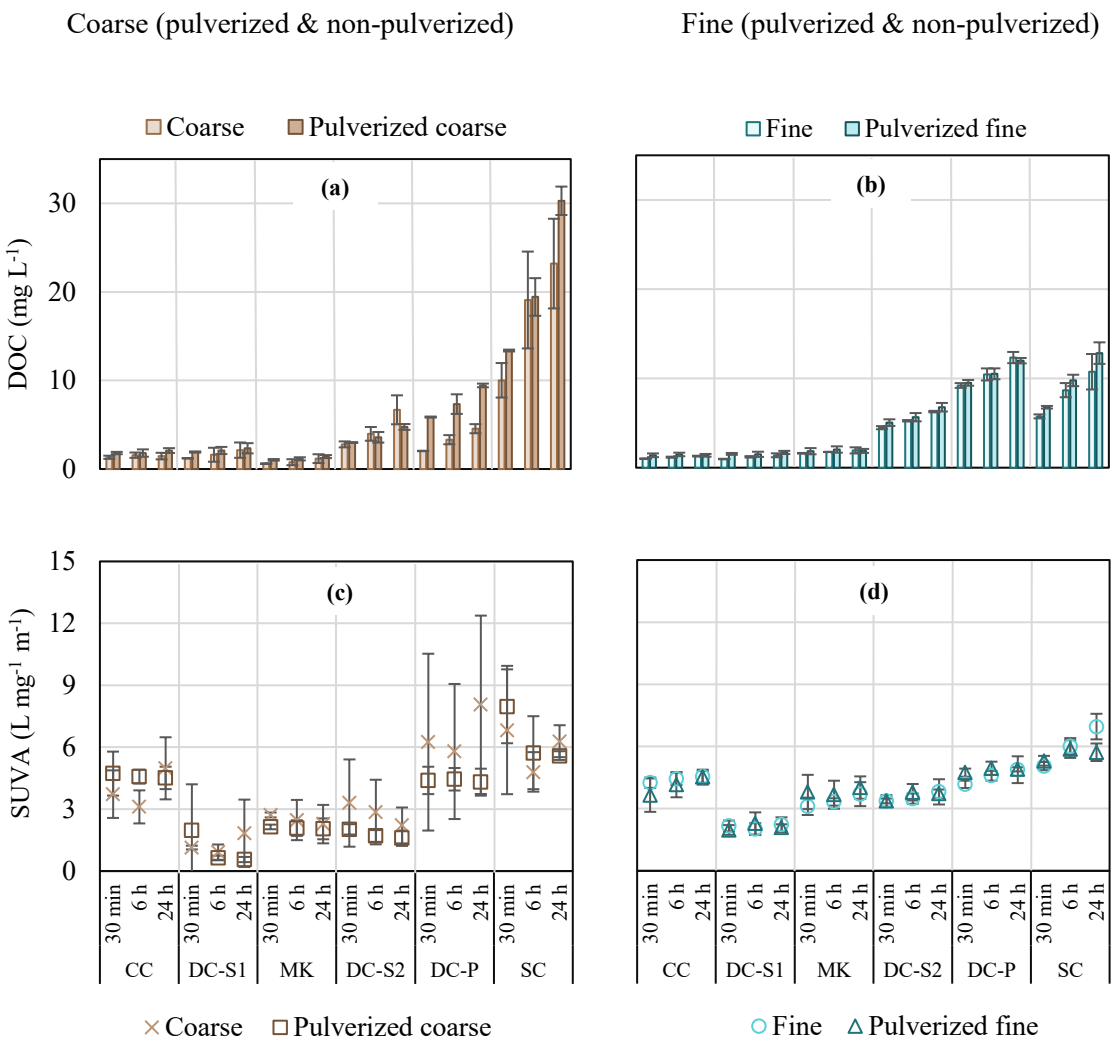


Figure 3-7 Changes in (a & b) DOC concentrations and (c & d) SUVA values for coarse, pulverized coarse, fine and pulverized fine WAIWs at different sampling times during 24 h of the experiment. The graphs on the left (a, c, and e) represent coarse and pulverized coarse WAIWs, while those on the right (b, d, and f) correspond to fine and pulverized fine WAIWs. The experiments were run in triplicate, and the average values with standard deviations are shown. Lighter bars on the left indicate DOC concentrations for coarse and fine ash, while darker bars on the right represent corresponding pulverized WAIWs. Crosses and circles indicate SUVA values for coarse and fine ash, while squares and triangles indicate values for pulverized coarse and pulverized fine ash, respectively.

3.3.2.2 Ash-to-water ratio impact on WEOM

Figure 3-8 shows changes in WEOM concentration and character (i.e., DOC and SUVA) across a range of ash-to-water ratios for different ash types subjected to different homogenization methods. It should be noted that while the experiments investigated six different ash-to-water ratios ranging from 0.5 to 5 g L^{-1}, only three ash-to-water ratios (0.5, 2, and 5 g L^{-1}) are shown to simplify data presentation; the full data set is provided in supplementary information (Supporting information Figures B7 and B8).

Fine ash WAIWs showed minimal variation in both DOC concentration and SUVA values, suggesting that fine ash is inherently more homogeneous (Figure 3-8). In contrast, coarse ash WAIWs showed substantial variability in WEOM concentration and character. This variability was considerably reduced through pulverization in some ash types. Statistical analysis further supported a range of responses: significant differences in WEOM between pulverized and non-pulverized WAIWs were observed for some ash types (i.e., CC and DC-S2), while no significant differences were found for others (i.e., MK and DC-P), regardless of ash fraction (coarse or fine; Supporting information Table B4). Notably, pulverization led to significant differences in WEOM concentration between fine and pulverized fine ash for certain ash types, but no significant difference was observed between coarse and pulverized coarse ash for others (i.e., DC-S1 and SC; Supporting information Table B4). These results indicate that improvements in ash homogeneity through pulverization are both ash-type and fraction dependent.

It is also important to note that sieving and pulverization do not replicate the natural post-fire particle size distribution and instead artificially suppress natural heterogeneity. As such, these methods cannot fully represent field conditions; instead, they allow for more controlled comparisons across different ash types and experimental setups.

DOC yield for different ash types decreased with an increase in ash-to-water ratio up to 2 g L^{-1}; beyond this concentration, DOC yield remained relatively constant, suggesting a decline in leaching efficiency at higher ash-to-water ratios (Figure 3-8 c & d). The observed reduction in DOC yield with increasing ash-to-water ratio for all ash types handled with a variety of homogenization methods (i.e., manual separation, sieving, and pulverizing; Figure 3-8 c & d) aligns with the findings of Section 3.1.3 and what has been reported previously (Bahramian et al., 2025- Chapter 2).

Contrary to previous observations (Section 3.3.2.1), pulverization did not consistently reduce WEOM concentration variability in WAIWs. This was particularly evident in WAIW prepared using SC ash and at higher ash-to-water ratios (i.e., 4 and 5 g L^{-1}; Supporting information Figure B7). The

observed variability in WEOM concentration in pulverized ash WAIWs may be attributed to losses during sample preparation. Superfine particles produced through pulverization were prone to aerosolization. Thus, even small differences in ash mass may therefore lead to substantial shifts in WEOM concentration at higher ash-to-water ratios (Figure 3-8 c & d), however this was not further investigated in the current study.

Figure 3-9 shows the proportions of different fractions of organic carbon in different WAIWs obtained from LC-OCD analysis. The LC-OCD results suggests that pulverization increases the availability of smaller, more labile DOC molecules (i.e., LMW compounds) by the mechanical breakdown of ash particles and increasing the available surface area. It is also possible that pulverization results in the breakdown of larger WEOM molecules, potentially increasing the relative abundance of building blocks and LMW compounds. Building blocks are products of the breakdown of humic substances (Huber et al., 2011). Thus, it is reasonable to infer that pulverization enhances the relative proportion of these smaller organic compounds in the ash samples by facilitating the disintegration of larger organic structures. This suggests that grinding and pulverization may alter the molecular composition of WEOM and underscores the critical role of sample preparation and pretreatment methods in obtaining reliable and reproducible results in studies of wildfire ash impacts on water quality.

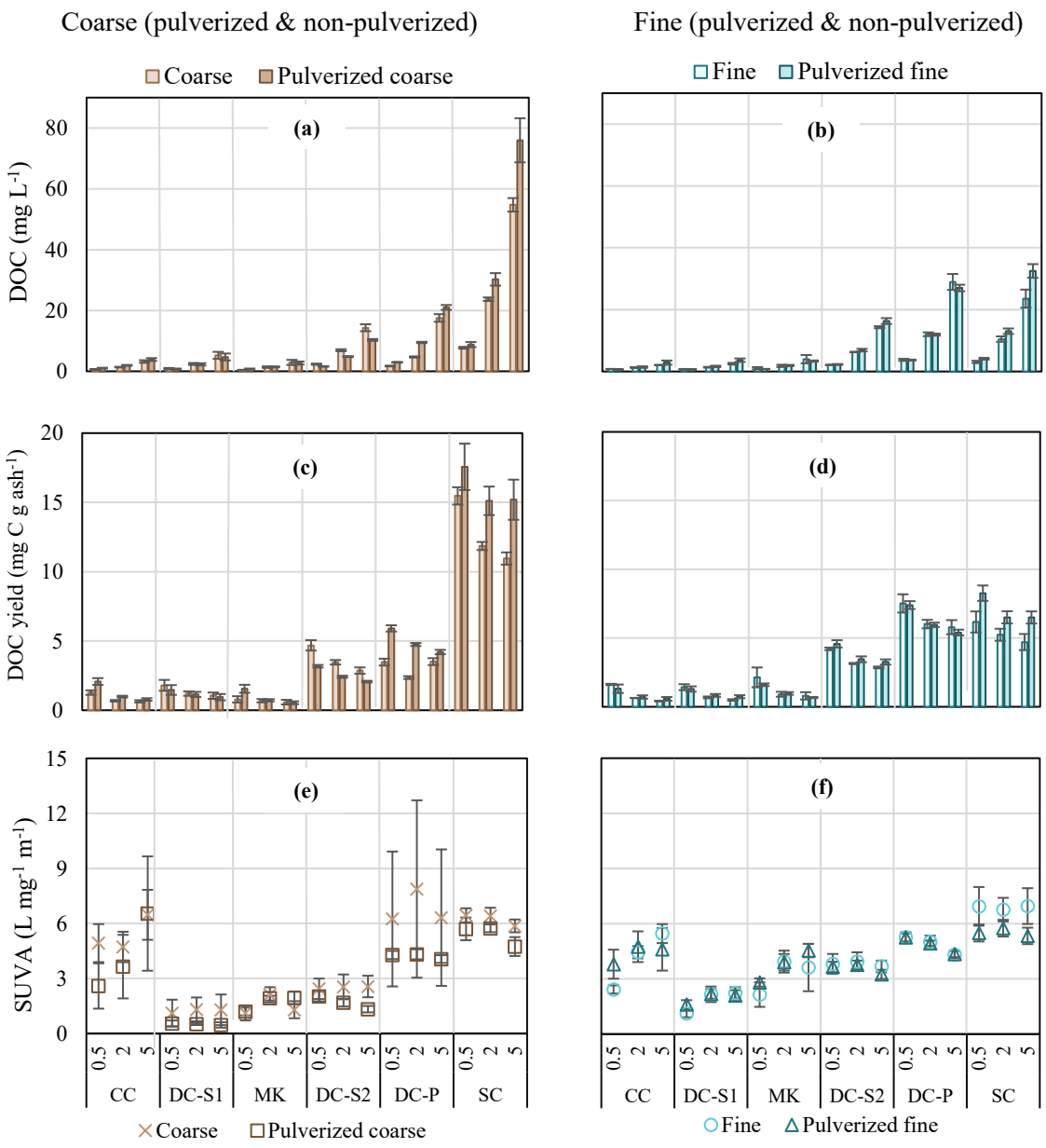


Figure 3-8 Changes in (a & b) DOC concentrations, (c & d) DOC yield, and (e & f) SUVA values for coarse, pulverized coarse, fine and pulverized fine WAIWs across a range of ash-to-water ratios. The graphs on the left (a, c, and e) represent coarse and pulverized coarse WAIWs, while those on the right (b, d, and f) correspond to fine and pulverized fine WAIWs. The experiments were run in triplicate, and the average values with standard deviations are shown. Lighter bars on the left indicate DOC concentrations/yields for coarse and fine ash, while darker bars on the right represent corresponding pulverized WAIWs. Crosses and circles indicate SUVA values for coarse and fine ash, while squares and triangles indicate values for pulverized coarse and pulverized fine ash, respectively.

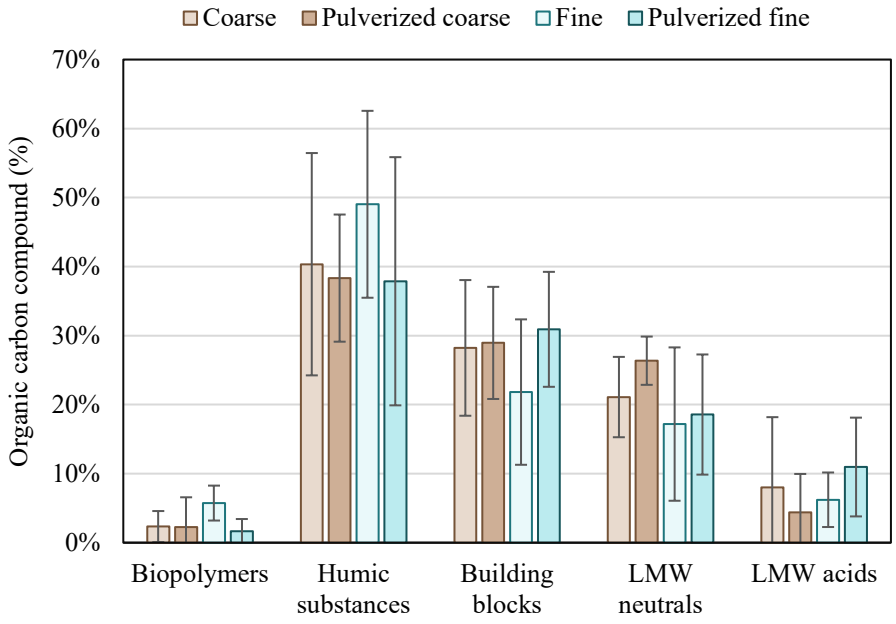


Figure 3-9 The proportion of different organic matter compounds in the total DOC concentration for coarse, pulverized coarse, fine, and pulverized fine ash WAIWs. Each bar represents the average value (n = 30) with error bars representing standard deviation.

3.4 Conclusions

This study demonstrates that different ash pretreatment techniques can substantially influence the release of water-extractable organic matter (WEOM) from wildfire ash when preparing wildfire-ash-impacted water (WAIW) matrices. These effects must be carefully considered when interpreting the impacts of wildfire ash on drinking water quality and treatability. Key conclusions of this study are:

- Different size fractions (i.e., coarse and fine) of the same ash can have distinctly different physicochemical properties (e.g., organic matter content, leachable WEOM) and yet have similar impacts on water quality and treatability (i.e., all tend to increase DOC and alter SUVA).

- Ash organic matter and TOC contents do not necessarily correlate with the concentration of leachable WEOM from ash. However, some correlation was found between ash carbonate proportions and WEOM concentration in WAIW.

- Higher particle size variability in coarse ash results in more variable available surface area for leaching, therefore contributing to greater variability in WEOM concentrations in WAIW.

- Pulverization increases sample size distribution uniformity and WEOM leaching (by increasing the available surface area); however, it concurrently alters WEOM character.

- Pulverized ash is easily aerosolized, posing challenges in WAIW preparation, potentially increasing variability among nominal replicates.

- Although sieving ash does not replicate the natural particle size distribution found on the landscape after fire, it allows for more controlled comparisons across different ash types and experimental setups. Applying a consistent particle size threshold (e.g., 1 mm) helps reduce variability in ash properties that can impact WEOM leaching. Preparing WAIW with sieved ash is therefore recommended to improve consistency among nominal replicates and enhance the comparability of results across bench-scale studies.

Recognizing the impact of ash pretreatment techniques on WAIW quality is critical when justifying selected experimental methods and for accurately interpreting the implications of wildfire ash on drinking water quality and treatability. Thorough documentation of the pretreatment methods employed is critical for improving comparability, and overall reliability of studies investigating wildfire impacts on drinking water quality and treatability.

Chapter 4

Mitigating wildfire impacts on drinking water treatability: Recognizing the importance of settleable ash solids

Summary

Wildfires threaten drinking water source quality and treatability by mobilizing pyrogenic material into aquatic systems. While previous studies have primarily focused on the impacts of wildfire ash water-extractable organic matter (WEOM) on water treatability, some have also reported increases in water alkalinity following wildfires. Biomass combustion often produces alkaline particles, such as calcium and potassium carbonates, which are typically denser than water and settle quickly. Due to their high alkaline content, these particles may serve as long-term sources of alkalinity. However, the role of settleable ash solids (SAS) in altering water alkalinity and its implications for coagulation remains poorly understood. Bench-scale experiments were conducted to investigate SAS effects on wildfire ash-impacted water (WAIW) pH and alkalinity as well as coagulation performance. One set of experiments assessed the impacts of SAS on water alkalinity by mixing coarse and fine fractions of multiple ash types with ultrapure water across a range of ash-to-water ratios. Another set evaluated the effect of SAS removal—via settling and decanting—on coagulation performance under both conventional and enhanced conditions, using natural river water. Fine ash fractions substantially increased alkalinity, likely due to higher surface area and alkaline mineral content. Removing SAS reduced acid demand by over 60% and improved pH control during enhanced coagulation, although it also lowered turbidity removal efficiency. These findings highlight the importance of implementing solids management strategies to mitigate the adverse effects of wildfire ash on drinking water treatment processes. They also underscore the need for further research to fully understand their short- and long-term impacts on water quality and treatability in diverse environmental settings.

4.1 Introduction

The frequency of large wildfires has increased markedly over the past few decades (Dennison et al., 2014), which can profoundly impact water quality, particularly in forested regions that typically serve as high-quality drinking water sources (Emelko et al., 2011; Hohner et al., 2019a). Wildfires transform landscapes into highly erodible terrains where ash, charred vegetation, and loose sediments are easily mobilized by precipitation and wind. Post-fire rainfall events can trigger rapid runoff and erosion, delivering large quantities of sediment, nutrients, and contaminants to stream networks (Bladon et al., 2014; Nunes et al., 2018). These inputs often lead to substantial increases in turbidity, dissolved organic carbon (DOC), and other nutrient concentrations in surface waters (Hohner et al., 2016; Evans et al., 2017; Rhoads et al., 2019a; Paul et al., 2022). In turn, these changes increase coagulant demand, generate more sludge, necessitate frequent filter backwashing, and elevate the formation of disinfection by-products (DBPs; Emelko et al., 2011; Writer et al., 2014; Paul et al., 2022; Emelko et al., 2024).

Upon delivery to surface waters, wildfire ash particles partition into dissolved compounds, suspended particles, and settleable ash solids (SAS), each exerting distinct effects on water quality. For example, dissolved compounds can cause pulses in DOC concentration (S´anchez-García et al., 2023; Bahramian et al., 2025- Chapter 2). While most of the existing research has focused on the concentration and character of water-extractable organic matter (WEOM), the impact of SAS on water alkalinity and the associated treatment implications have been overlooked.

Biomass combustion produces a wide range of particles that often contain high proportions of alkaline compounds, including oxides, carbonates, and silicates—many of which are denser than water and tend to settle rapidly (Cerdà & Doerr, 2008; Moody et al., 2009; Bodí et al., 2011; Balfour & Woods, 2013). These settleable solids may serve as persistent sources of alkalinity, potentially having longer-time effects on drinking water treatment performance.

Alterations in source water pH and alkalinity can impact the efficiency of coagulation processes in drinking water treatment. Coagulants such as aluminum and ferric salts can reduce organic matter (OM) concentration most effectively within specific pH ranges (Amirtharajah & Mills, 1982; Crittenden et al., 2012). High alkalinity levels can hinder these hydrolysis reactions by resisting the necessary pH shifts required for optimal coagulant performance, leading to lower coagulation efficiency and increased chemical demand (Crittenden et al., 2012). The U.S. Environmental Protection Agency (EPA) mandates enhanced coagulation as a strategy to improve OM removal and minimize DBP formation. This process requires maintaining pH within coagulant-specific optimal ranges, typically through acid addition or buffering adjustments (U.S. EPA, 1999). Therefore, good control of pH and alkalinity is essential for achieving efficient coagulation and minimizing treatment costs and by-product formation.

To limit wildfire ash solids transport into water, various solids management strategies have been employed. These strategies include erosion control measures (e.g., mulching, silt fences, contour wattles), hydraulic interventions (e.g., sediment forebays, offline settling reservoirs), and the restoration of riparian buffer zones (Emelko et al., 2011; Bladon et al., 2014; Paul et al., 2022). However, the effectiveness of these methods in mitigating the impacts of solids on downstream chemical treatment processes remains poorly quantified. Accordingly, the goal of this study was to evaluate the impact of SAS removal as a potential solid management strategy to improve the treatability of wildfire-impacted source waters. Specifically, this work aimed to: (1) assess how SAS influences water alkalinity, a key metric impacting coagulation, and (2) investigate how the removal of SAS through decanting—used here as a proxy for offline settling reservoirs—affects coagulation performance and the formation

potential of DBPs. This study is anticipated to inform watershed management and utility response strategies to enhance drinking water treatment resilience in fire-prone regions.

4.2 Materials and methods

4.2.1 Experimental approach

To systematically evaluate the potential impact of SAS on the coagulation process, a series of bench-scale experiments were conducted. The first set of experiments investigated the influence of SAS on water alkalinity, while the second set assessed the effect of solids on coagulation performance to inform the value of solids management. For the first set, WAIW matrices were prepared by mixing two fractions of six ash types—collected from four wildfires and one prescribed fire—with ultrapure water. These ash types and fractions represented a range of burn severities and properties. The use of ultrapure water allowed for the assessment of alkalinity associated with wildfire ash without interference from background water chemistry. In the second set, WAIWs were prepared using one wildfire ash type and high-quality drinking water source (i.e., low turbidity and DOC) from the Elbow River in Calgary, Alberta. Natural river water from a fire-prone forested landscape was used to simulate more realistic conditions, accounting for potential matrix effects and thus enhancing the applicability of the findings.

4.2.2 Experimental design

The experimental design for this study is presented in Figure 4-1. Two sets of experiments aimed to address 1) the impact of SAS on water alkalinity and 2) the impact of ash solids on coagulation and DBP formation. The temperature of WAIW matrices was maintained at approximately 21°C throughout the experiments, and all WAIW were mixed for 24 h, as suggested in Bahramian et al. (2025)- Chapter 2).

Experiment 1 included the measurement of pH and alkalinity in WAIWs prepared using a range of ash concentrations, from 0.5 to 5 g L^{-1} to ultrapure water (Milli-Q®, 18.2 MΩ·cm at 25 °C, TOC ≤ 5 ppb). Six ash types (CC, DC-S1, MK, DC-S2, TC, SC, and DC-P)—collected from four wildfires and one prescribed fire—were used in this experiment. Ash samples were sieved into two fractions: coarse (>1 mm) and fine (<1 mm), and WAIWs were prepared for each of these fractions. These fractions were selected because finer ash particles are typically produced at higher combustion temperatures and tend to contain greater concentrations of inorganic constituents (Balfour & Woods, 2013; Bodí et al., 2014). WAIWs were mixed for 24 hours, after which samples were collected for pH and alkalinity

measurements. Each WAIW was then allowed to settle for 2 hours, and the supernatant was decanted for further pH and alkalinity analyses.

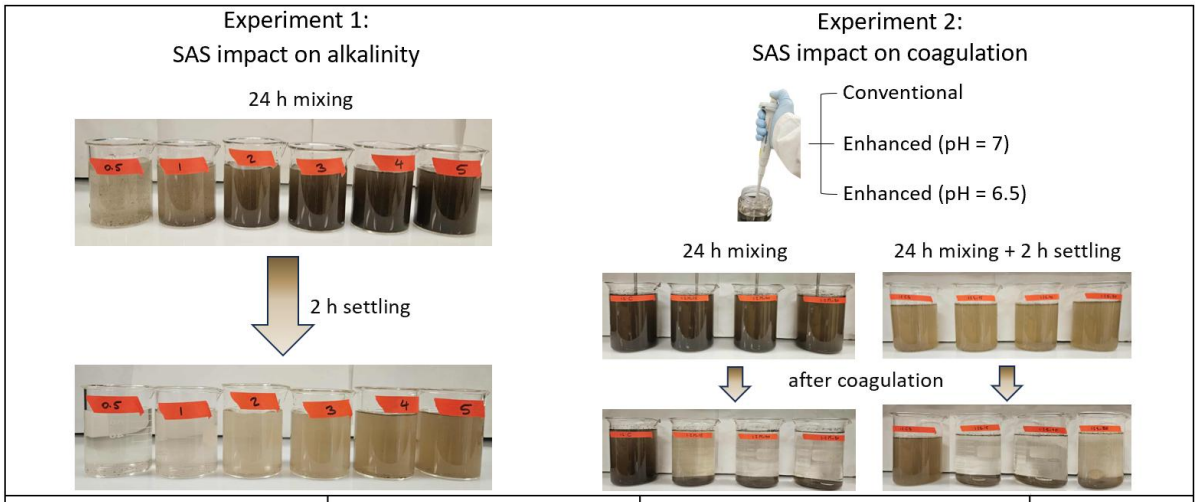
Experiment 2 included jar testing of WAIWs using different doses of aluminum sulfate ($Al_2(SO_4)_3.16H_2O$). WAIW matrices were prepared using TC ash (due to limited availability of other ash samples). To prepare WAIWs 1.2 g L^{-1} of the fine fraction of TC ash was added to source water collected from the Elbow River in Calgary, Alberta, Canada. Elbow River water samples were stored in sealed pails at 4°C after collection until use. Nominal Elbow River water quality during the study is summarized in Supporting information Table C1. This ash concentration was selected to yield a DOC concentration of approximately 5-6 mg L^{-1}. While this increase in DOC concentration does not represent a worst-case scenario, it reflects typical DOC increases reported in streams and source waters following wildfires (Uzun et al., 2020; Richardson et al., 2022; Hickenbottom et al., 2023) and can pose challenges to drinking water treatment processes (Emelko et al., 2011). Notably, to compare the impact of fine fraction of TC ash on alkalinity relative to the other ash types, varying ash-to-water ratios of this ash were added to ultrapure water. The alkalinity of the suspensions was then measured.

Two WAIW preparation conditions were used for the jar tests: (i) "unsettled", in which ash suspensions were mixed for 24 hours before coagulant addition, and (ii) "decanted", where suspensions were mixed for 24 hours, settled for 2 hours, and the supernatant was decanted prior to coagulant addition. A 2-hour settling time was selected based on Stokes' law calculations for ash particles with silt-sized diameters as described in (Montgomery, 1985).

Jar tests were conducted with water from the conventional and enhanced coagulation conditions using three alum doses—15, 40, and 80 mg L^{-1}—corresponding to 1.28, 3.43, and 6.85 mg L^{-1} of Al^{3+}, respectively. Enhanced coagulation was performed at two target pH values: 6.5 and 7. These pH levels were selected based on EPA guidelines, which recommend a minimum pH of 7 for enhanced coagulation in waters with alkalinity greater than 120 mg $CaCO_3$ L^{-1} (U.S. EPA, 1999). Additionally, pH 7 falls within the optimal range for turbidity removal with alum, while pH 6.5 is more effective for dissolved organic matter (DOM) removal (Amirtharajah & Mills, 1982).

To adjust pH, 1.0 N HCl was added prior to alum dosing. The acid volumes required to reach pH 7 and 6.5 were 1.5 and 2.8 mL L^{-1} for unsettled WAIWs, and 0.6 and 0.8 mL L^{-1} for decanted WAIWs, respectively. Notably, unsettled WAIWs required a minimum of 30 minutes after acid addition for pH stabilization due to the high alkalinity of the source water and the added alkalinity from SAS.

Following coagulant addition, WAIWs were mixed at 120 revolutions per minute (RPM) for 1 minute, followed by 40 RPM for 20 minutes, and then allowed to settle for 15 minutes (Skwaruk et al., 2020). Each jar test also included a control sample with no coagulant addition at the end of each test, pH, alkalinity, turbidity, DOC, UV_{254}, and SUVA were measured. Additionally, selected samples from enhanced coagulation tests with the highest OM removal percentage and their corresponding control WAIWs (both unsettled and decanted) were analyzed for DBP under uniform formation conditions and formation potential (DBP-UFC and DBP-FP, respectively). While DBP-UFC allows for direct comparison of DBP formation across different waters under standardized conditions (Summers et al., 1996), DBP-FP reflects the maximum potential concentrations of DBPs that could form in a system.



	Water type		Ash-to-water ratio (g L^{-1})							Ash type							Ash fraction	
										4 wildfire & 1 prescribed fire							Coarse	Fine
	Ultrapure	Elbow River	0.5	1	1.2	2	3	4	5	CC	DC-S1	DC-S2	DC-P	MK	TC	SC	≥ 1 mm	< 1 mm
Experiment 1	✓		✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓
Experiment 2		✓			✓										✓			✓

Figure 4-1 Experimental design to assess SAS impacts on water quality and treatability. Experiment 1 evaluated the effect of SAS removal on the alkalinity of WAIW using six ash types (Cameron Creek [CC], Doctor Creek sites 1 and 2 [DC-S1, DC-S2], Doctor Creek prescribed fire site [DC-P], Minnekhada [MK], and Scottie Creek [SC]) at varying ash-to-water ratios (g L^{-1})in ultrapure water. Experiment 2 assessed the impact of SAS removal on coagulation performance using alum at three doses (15, 40, and 80 mg L^{-1}) at conventional and enhanced conditions (pH = 7 & 6.5). These WAIWs were prepared by mixing Thuya Creek (TC) ash with natural river water. All tests were conducted in triplicate.

4.2.3 Wildfire ash collection

Ash samples collected from five different wildfires and one prescribed fire reflect the range of pyrogenic material (e.g., charcoal and burned vegetation) generated under varying burn severities. Detailed information on ash collection sites, burn extent and severity, vegetation types, and ash conditions is provided in Table 4-1. Except for the Cameron Creek ash (CC), all other ash types were

collected before any major precipitation events. To investigate the impact of different ash fractions on the alkalinity of WAIW, air-dried ash samples were sieved to separate the fine fraction (<1 mm) from coarser material. A similar method has been used previously (e.g., Cawley et al., 2018; Oliveira-Filho et al., 2018; Harper et al., 2019; Skwaruk et al., 2020; Sánchez-Garcia et al., 2023). The coarse fractions were manually sorted to remove rocks and unburned debris, following previously reported methodologies (Tomkin et al., 1991; Olefeldt et al., 2013; Santín et al., 2015; Wu et al., 2022). Following collection, all processed ash fractions were stored in sealed containers at a controlled temperature of 21°C. The carbonate content of each ash type was measured following the ASTM D4373 method.

Table 4-1 Ash collection location, date and fire information for the ash types used.

Ash type	Fire	Location (Canada)	Burn area (ha)	Fire start date (mm/yyyy)	Vegetation type	Burn severity	Ash collection date (mm/yyyy)
Cameron Creek (CC)	Kenow Wildfire[a]	Waterton, AB[a]	35,000[a]	09/2017[a]	Lodgepole Pine[1a], Subalpine Fir[2a]	High to extreme[b]	06/2018[b]
Doctor Creek sampling site 1 (DC-S1)	Doctor Creek Wildfire[c]					High[c]	
Doctor Creek sampling site 2 (DC-S2)	Doctor Creek Wildfire[c]	Canal Flats, BC[c]	7645[c]	08/2020[c]	Lodgepole Pine[1c] Douglas Fir[3c], Ponderosa Pine[4c], Western Larch[5c]	Medium[c]	09/2020
Doctor Creek prescribed fire site (DC-P)	Doctor Creek Prescribed Fire[c]					Medium[c]	
Minnekhada (MK)	Minnekhada Park Fire[d]	Coquitlam, BC, Canada[d]	14[d]	10/2022[d]	Douglas fir[3d], Western Red Cedar[6d]	High[d]	10/2022[d]
Thuya Creek (TC)	Little Fort Fire Complex[e]	Little Fort, BC[e]	556[e]	07/2017[e]	Lodgepole Pine[1f], Douglas Fir[3f], Spruce Hybrids[6f], Paper Birch[7f]	High[e]	08/2017[e]
Scottie Creek (SC)	Elephant Hill Fire Complex[f]	Ashcroft, BC[f]	191,865[f]	07/2017[f]	Douglas Fir[1e], Spruce Hybrids[6e], Yellow Pine[8e], Trembling Aspen[9e]	High[e]	08/2017[e]

1- *Pinus contorta* var. *latifolia*
2- *Abies lasiocarpa*
3- *Pseudotsuga menziesii* var. *glauca*
4- *Pinus ponderosa*
5- *Larix occidentalis*
6- *Thuja plicata*
7- *Picea* spp.
8- *Betula papyrifera*
9- *Populus tremuloides*

a- Parks Canada- Kenow Wildfire timeline (2023)
b- U. Silins (Personal communication, March 20, 2025)
c- BC Wildfire Service Information Section (2020)
d- Gifford et al. (2025)
e- Skwaruk (2021)
f- BC gov news (2020)

4.2.4 Water quality analyses

Standard Methods for the Examination of Water and Wastewater (APHA, 2022) was used to conduct most of the water quality analysis. Metrics measured included pH (Method 4500H) using an Accumet AB250 benchtop pH/ISE meter (Thermo Fisher Scientific, Seoul, Korea) and alkalinity (Method 2320B) via titration with 0.1 N HCl. Turbidity was measured according to Method 2310 on a 2100Q Portable Turbidimeter (HACH, Loveland, Colorado, USA). DOC concentrations were quantified using the high-temperature combustion method (Method 5310C) on a TOC-VCHP Analyzer (Shimadzu Corporation, Kyoto, Japan), with a detection limit of 0.1 mg L^{-1}. Ultraviolet absorbance at 254 nm (UV_{254}) was measured using a P200B portable UV_{254} analyzer (Real Tech Water, Whitby, Canada) with a detection limit of 0.005 cm^{-1}, following Standard Method 5910B. The specific ultraviolet absorbance at 254 nm (SUVA) was calculated by dividing UV_{254} by the corresponding DOC concentration (Edzwald et al., 1985). For DOC, UV_{254} and LC-OCD analyses, WAIWs were filtered through 0.45 µm polyethersulfone filters (PES, Millipore Express® PLUS; Merck Millipore, Burlington, MA). Prior to sample collection, all PES filters were first rinsed with ultrapure water, followed by rinsing with WAIW.

DBP formation potential (FP) and uniform formation conditions (UFC) tests were conducted following Methods 5710B and 5710D (APHA, 2022) and procedures outlined in Summers (1996), respectively. These tests evaluated the formation potential of trihalomethanes (THMs) and haloacetic acids (HAAs) in WAIW matrices following chlorination, with the UFC method simulating conditions in drinking water distribution systems and the FP test used to assess DBP precursor reactivity and allow for comparisons of OM in treated and untreated WAIWs. Chlorine residuals were determined using the DPD (N,N-diethyl-p-phenylenediamine) colorimetric method (Method 4500-Cl G). THMs and HAAs were quantified based on EPA Method 501.1 (U.S. EPA, 1979), and Method 552.3 (U.S. EPA, 2003), respectively, using an Agilent 6890 Series Gas Chromatograph (United States) equipped with an electron capture detector. Minimum reporting limits for the water quality metrics analyzed here are presented in Supporting information Table C2.

4.2.5 Statistical Analysis

Statistical analyses were conducted to determine whether SAS removal led to significant differences in alkalinity across samples. For this analysis, WAIWs prepared from different coarse or fine ash types were grouped accordingly, and alkalinity levels were compared between samples with and without SAS. As the data was not normally distributed in either sets of samples, non-parametric test (Wilcoxon signed-rank test) with $\alpha = 0.05$ was used ($n = 108$).

4.3 Results and discussion

4.3.1 Settleable ash solids impact on alkalinity

Figure 4-2 presents the pH and alkalinity of WAIWs across a range of ash mass concentrations for both coarse and fine ash. The data are available in Supporting information Tables C3 and C4. The initial pH of ultrapure water was measured as 5.5 ±0.07 and WAIWs ranged from 5.7 to 8.9 and 6.8 to 9.4 for coarse and fine ash, respectively. Even low ash concentrations (e.g., 0.5 g L^{-1}) substantially affected WAIW pH, particularly when fine ash types were used—likely due to the lack of buffering capacity in ultrapure water.

The more pronounced effect of ash on increasing WAIW pH prepared using fine ash can be attributed to (i) its higher surface area, which can enhance the dissolution of inorganic alkaline compounds, and (ii) higher content of inorganic alkaline compounds such as carbonates and oxides resulting from higher combustion temperatures (Etiégni & Campbell, 1991; Balfour & Woods, 2013; Bodí et al., 2014). While extensive ash characterization was beyond the scope of this study, Table 4-2 shows the results of carbonate content measurements for coarse and fine fractions of different ash types. This table indicates that fine ash generally contained more carbonates than the coarse fraction.

Alkalinity in unsettled WAIW ranged from 3 to 447 mg L^{-1} as $CaCO_3$ and 8 to 1175 mg L^{-1} for coarse and fine ash, respectively. Although the impacts on alkalinity varied by ash type, most showed minimal change at concentrations below 1 g L^{-1}—except for DC-P fine ash (Supporting information Table C3). Consistent with the impacts on pH, fine ash had a greater effect on alkalinity.

Following the removal of settleable ash solids (SAS), the alkalinity of decanted wildfire ash-impacted waters (WAIWs) decreased substantially. In these decanted samples, alkalinity ranged from 18 to 180 mg $CaCO_3$ L^{-1} for coarse ash and from 5 to 101 mg $CaCO_3$ L^{-1} for fine ash (Figure 4-2). Statistical analysis confirmed significant difference between the alkalinity of WAIWs with and without SAS, which was consistent across ash fractions (for WIWs prepared using either coarse or fine ash, $p << 0.05$, n = 108).

This reduction highlights the removal of alkaline ash particles—produced during combustion—and the associated decrease in leachable inorganic compounds that contribute to alkalinity. Among these, metal oxides such as CaO, MgO, and K_2O can react with water to form bases like $Ca(OH)_2$, $Mg(OH)_2$, and KOH. While KOH dissolves readily and releases hydroxide ions (OH^-) directly, $Ca(OH)_2$ and

$Mg(OH)_2$ primarily contribute to alkalinity over time by reacting with atmospheric CO_2 to form carbonates (Equations 4.1–4.5). Additionally, factors such as soil characteristics, vegetation type, and burn intensity can impact ash composition, potentially introducing other proton-accepting constituents such as phosphate and boron compounds—both of which can also elevate alkalinity (Brito et al., 2017; Zhang et al., 2020). The presence of all these compounds in SAS can provide a sustained source of alkalinity in undisturbed WAIWs, underscoring the importance of SAS removal in mitigating longer-term alterations in source water chemistry.

$CaO + H_2O \rightarrow Ca(OH)_2$	Equation 4.1
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$	Equation 4.2
$MgO + H_2O \rightarrow Mg(OH)_2$	Equation 4.3
$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$	Equation 4.4
$K_2O + H_2O \rightarrow 2KOH \rightarrow 2K^+ + 2OH^-$	Equation 4.5

Alkalinity reductions increased at higher ash-to-water ratio, however, the extent of this effect varied notably among ash types. For example, WAIWs prepared with MK fine ash showed a noticeable increase in alkalinity reduction between the 1 and 5 g L^{-1} WAIWs, indicating a strong concentration-dependent effect. In contrast, WAIWs prepared using CC fine ash showed minimal change across the same concentration range (Figures 4-2 and Supporting information Figure C1)

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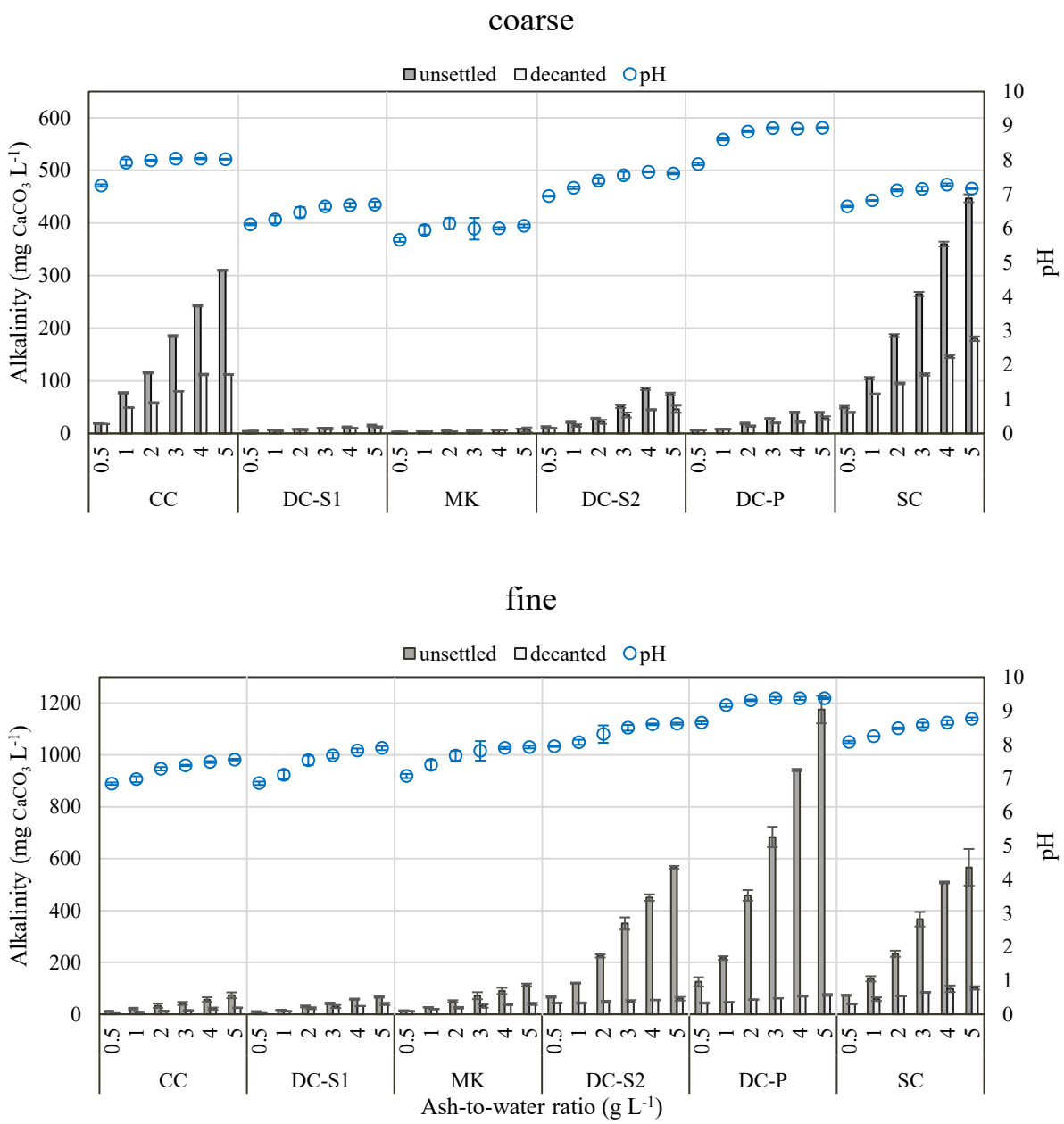


Figure 4-2 Changes in pH and alkalinity in unsettled and decanted WAIWs prepared using coarse and fine ash mixed in ultrapure water. Darker grey bars represent alkalinity in unsettled WAIWs, and adjacent lighter bars represent decanted WAIWs. pH values are shown with blue circles. Each bar/symbol represents the average value (n = 3) with error bars representing standard deviation.

Table 4-2 Carbonate proportions in coarse and fine fractions of different ash types.

	Carbonate (%)	
Ash type	Coarse	Fine
CC	< 0.04	4.09
DC-S1	< 0.04	0.91
MK	< 0.04	3.17
DC-S2	< 0.04	7.71
DC-P	< 0.04	13.8
SC	11.29	12.1

4.3.2 Settleable ash solids impact on coagulation

Figure 4-3 shows the changes in pH in conventionally coagulated WAIWs using different doses of alum. In all cases, pH decreased following the addition of coagulant to WAIWs, and this reduction increased at higher alum doses (Figure 4-3). Notably, decanted WAIWs showed a slightly more pronounced change in pH than their unsettled counterparts, highlighting the contribution of SAS to the buffering capacity of WAIW.

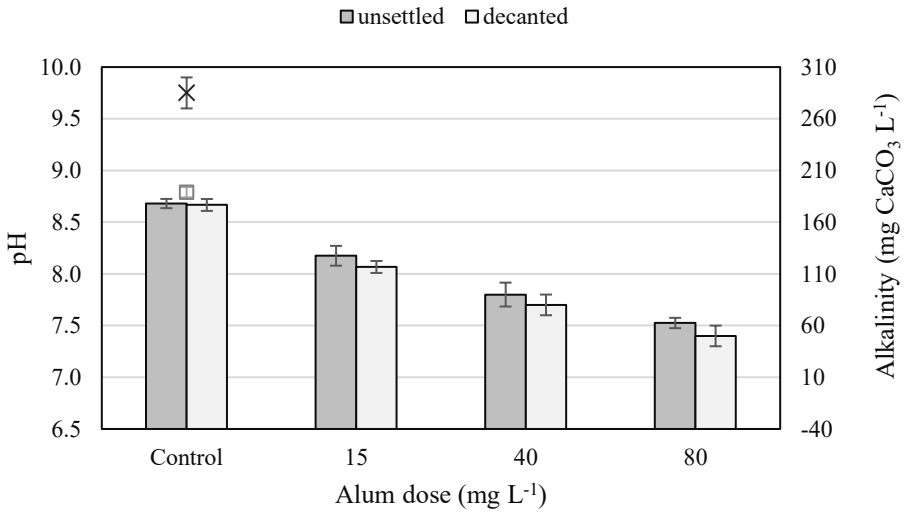


Figure 4-3 Changes in pH in unsettled and decanted WAIWs prepared using TC ash and Elbow River water following coagulation using different alum ($Al_2(SO_4)_3.16H_2O$) doses. Darker grey bars represent values in unsettled WAIWs, and adjacent lighter bars represent decanted WAIWs. Each bar/symbol represents the average value (n = 3) with error bars representing one standard deviation.

Although the ash concentration in WAIWs was moderate (1.2 g L^{-1}), it substantially increased the alkalinity of the already high-alkalinity source water—from 170 ± 3 to 258 ± 15 mg $CaCO_3$ L^{-1}. Following the removal of SAS through decanting, alkalinity was reduced to 189 ± 5 mg $CaCO_3$ L^{-1}. This reflected a substantial decrease in acid demand for pH adjustment: to achieve target pH values of 7 and 6.5 for enhanced coagulation, unsettled WAIWs required 1.6 and 2.8 mL L^{-1} of acid (HCl 1.0 N), respectively, whereas decanted WAIWs required only 0.6 and 0.8 mL L^{-1}—representing reductions of over 60% and 70% for pH 7 and 6.5, respectively. These results underscore the critical role of SAS in elevating water's buffering capacity and demonstrate that SAS removal can improve pH control and organic carbon removal during coagulation.

Figure 4-4 shows changes in turbidity, UV_{254}, and DOC concentration of WAIW following conventional and enhanced coagulation with varying alum doses in the presence and absence of SAS (i.e., unsettled and decanted WAIWs). Turbidity ranged from 35.8 to 93.6 NTU and from 28.9 to 39.7 NTU for control WAIWs with and without SAS, respectively. Across all WAIWs, coagulant addition—even at the lowest dose—led to substantial turbidity reductions, with on average 97% and 83% reductions in WAIWs with and without SAS, respectively.

Turbidity reduction was consistently higher in unsettled WAIWs compared to decanted ones, as would be expected (Figures 4-4a and Supporting information Figure C2). This is likely due to the greater particle collision opportunities provided by the higher concentration of SAS in unsettled WAIWs, which may lead to the formation of larger, denser flocs that settle more efficiently. In contrast, the removal of SAS from WAIWs lowered the potential for effective floc formation. These observations are consistent with previously reported studies (Boller & Blaser 1998; Yao et al., 2014).

Turbidity reduction did not change much even at higher alum doses in unsettled WAIWs (Supporting information Figure C2). However, in decanted WAIWs, turbidity reduction decreased as alum dose increased, particularly during enhanced coagulation. While similar trends in low-turbidity waters at alkaline pH (~8) have been previously reported (Sun et al., 2019), this effect at acidic pH has not been well documented. The observed turbidity increases in decanted WAIWs with higher coagulant doses may be attributed to the formation of fine and unstable metal hydroxides that remain unsettled (Crittenden et al., 2012).

Unlike turbidity, organic matter (OM) removal was minimal, particularly at lower alum doses, but increased with higher alum concentrations, with the greatest reductions observed at 80 mg L^{-1} (Figures 4-4 b & c). As expected, pH adjustment during enhanced coagulation improved OM removal (Bell-Ajy

et al., 2000; Hohner et al., 2017), likely because the pH was brought closer to the optimal range of alum for OM removal (Amirtharajah & Mills, 1982; Crittenden et al., 2012).

While UV_{254} reduction was greater in decanted WAIWs—up to 10%—the acid demand to reach optimal pH varied considerably. Specifically, samples containing SAS required significantly more acid for pH adjustment than those without (1.5 and 2.8 mL L^{-1} compared to 0.6 and 0.8 mL L^{-1} to achieve pH 7 and 6.5, respectively). Although enhanced coagulation has been recommended as a strategy to improve OM removal following wildfires (e.g., Hohner et al., 2017), these results suggest that, while it can improve OM removal, it may also lead to less favorable conditions for turbidity reduction. This highlights the role of wildfire SAS on coagulation and suggests the importance of solids management in improving treatment performance and reducing chemical costs in wildfire-impacted source waters.

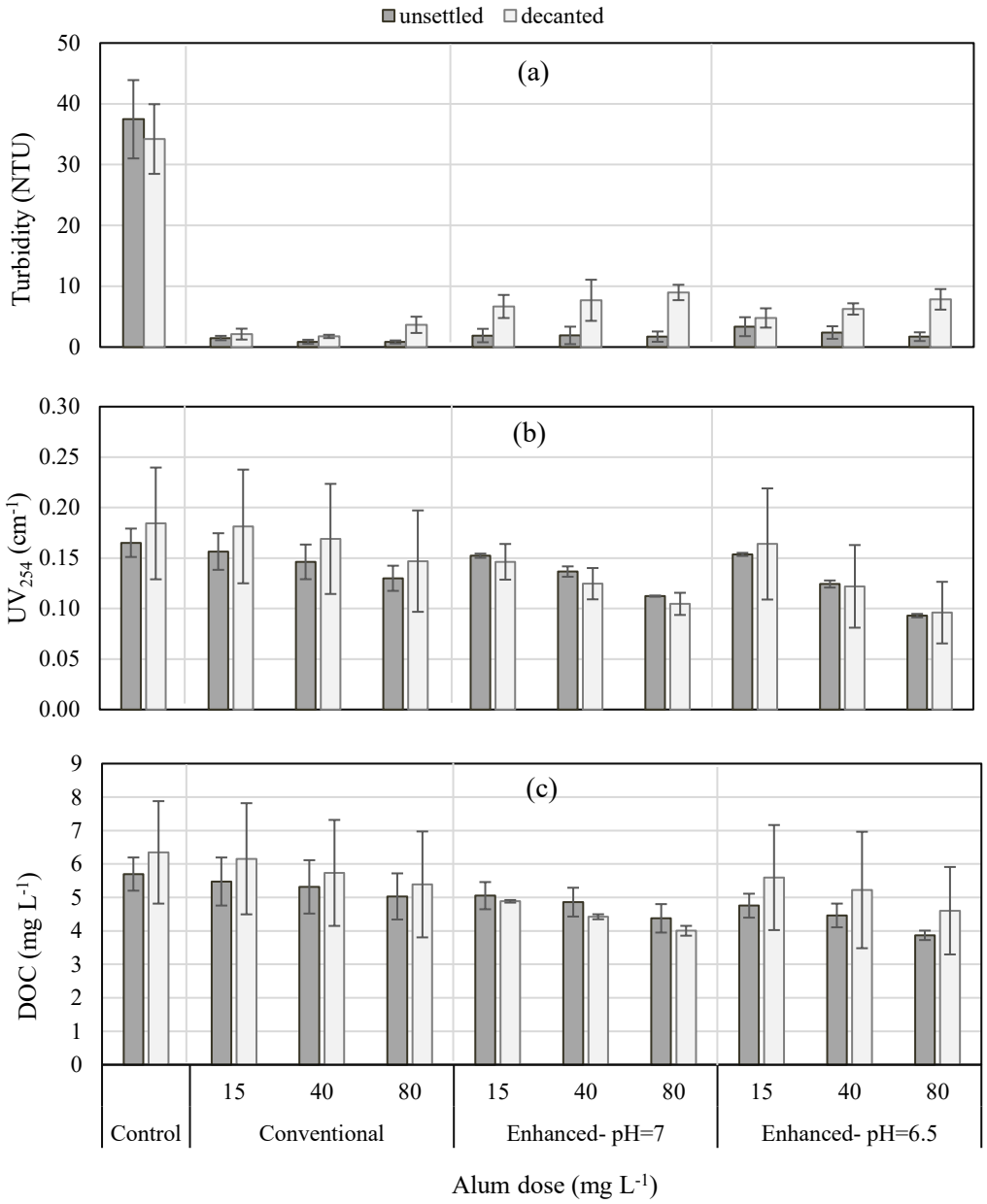


Figure 4-4 Changes in a) turbidity, b) UV_{254}, and c) DOC concentrations in unsettled and decanted WAIWs prepared using TC ash and Elbow River water following coagulation using different alum ($Al_2(SO_4)_3.16H_2O$) doses. Darker grey bars represent values in unsettled WAIWs, and adjacent lighter bars represent decanted WAIWs. Each bar/symbol represents the average value (n = 3) with error bars representing standard deviation.

Figure 4-5 presents the THM-UFC and -FP, and HAA-UFC and -FP yield in control and treated (i.e., coagulated at enhanced conditions) WAIWs, with and without SAS. The complete data set is available in Supporting information Table C5. Across all samples, THM-FP and HAA-FP concentrations were, on average, 1.6 and 4 times higher than their respective UFC counterparts, regardless of SAS concentration. Higher values for DBP-FP were expected, as DBP-FP represents the maximum formation potential.

In control WAIWs, DBP yields were consistently lower in decanted samples compared to unsettled suspensions. However, after coagulation, DBP-UFC and -FP yields were similar in both decanted and unsettled WAIWs. This may be attributed to comparable turbidity and DOC removal during coagulation in unsettled and decanted WAIWs, resulting in similar post-treatment DBPs precursors concentration.

These results suggest that while SAS removal may reduce acid demand and thus aid the coagulation process, it does not necessarily mitigate the impact of wildfire ash on DBP formation (Supporting information Table C5). While coagulation effectively reduced THM-UFC concentrations below Health Canada's maximum acceptable concentration (100 µg/L for THMs vs. 80 µg/L for HAAs; Health Canada, 2019), HAA-UFC remained above guideline values. Higher HAA concentrations relative to THMs have been previously observed in laboratory-produced WAIW and wildfire-affected streams (Shams, 2018; Skwaruk, 2020; Uzun et al., 2020), as well as in untreated and treated drinking waters (Williams et al., 1997; Golea et al., 2017). THM and HAA formation in water can be impacted by different factors including water pH organic carbon character, chlorine-to-DOC ratio, chlorine-water contact time, and inorganic compounds such as bromide and metal ions concentration (Goslan et al., 2009; Krasner, 2009; Zhao et al., 2023; Du et al., 2024). While wildfire ash can alter water pH (Ulery et al., 1993; Bodí et al., 2014; Bahramian et al., 2025- Chapter 2), the higher HAA levels relative to THMs observed in this experiment likely reflect changes in organic carbon character following wildfire ash addition to water (Wang et al., 2015; Cawley et al., 2017).

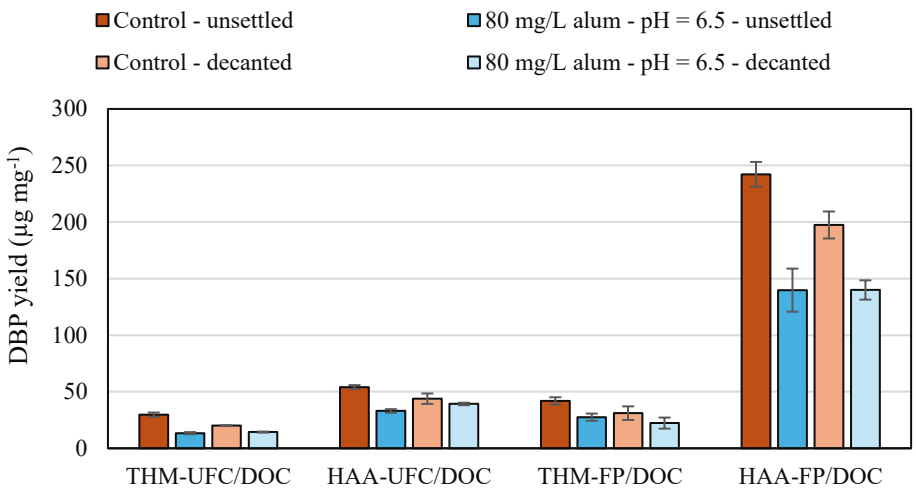


Figure 4-5 THM and HAA yields under UFC and FP conditions for unsettled and decanted WAIWs prepared using TC ash and Elbow River water. Dark and light orange bars represent control samples (no coagulant addition), while dark and light blue bars represent samples treated with 80 mg L^{-1} of alum following initial pH adjustment for enhanced OM removal. For each group, darker bars correspond to unsettled WAIWs and adjacent lighter bars correspond to decanted WAIWs. Each bar represents the average value (n = 3) with error bars representing standard deviation.

4.3.3 Implications for post-fire drinking water treatment

In this study, the addition of wildfire ash to water increased alkalinity, with effects intensifying at higher ash-to-water ratios. This is consistent with previously reported studies showing that ash inputs can raise pH and buffering capacity in aquatic systems (Ulery et al., 1993; Bodí et al., 2014). To mitigate such impacts, post-fire solids management strategies such as erosion control measures (e.g., mulching, silt fences, and contour wattles) and hydraulic interventions (e.g., sediment forebays and offline settling basins) have been recommended (Robichaud et al. 2000; Emelko et al., 2011; Bladon et al., 2014; Pierson et al., 2019; Paul et al., 2022).

The removal of SAS substantially reduced alkalinity and acid demand, therefore lowering the coagulant dose required for effective organic matter removal. These findings suggest that controlling particulate inputs can improve WAIW treatability and reduce chemical use at downstream treatment

plants. However, site-specific jar tests remain necessary to determine optimal coagulant dosing for OM and turbidity removal.

While solids management can improve source water quality, it may introduce new operational challenges at drinking water treatment plants (DWTP). For example, offline reservoirs are effective at reducing SAS through settling, thereby lowering turbidity and suspended solids in treatment plant inflows. However, the accumulation of sediments and ash in these systems can act as a longer-term internal source of nutrients and alkaline compounds, continuing to affect source water quality even after surface waters appear visually clear. This poses latent risks to treatment performance (McEachern et al., 2000; Silins et al., 2014; Emelko et al., 2016; Murphy et al., 2016; Martens et al., 2019; Rhoades et al., 2019a; Paul et al., 2022). Moreover, extended water retention times in these reservoirs can enhance microbial activity and promote algal growth, potentially altering the organic carbon concentration and character and further complicating drinking water treatability (Kraus et al., 2011; Du et al., 2022).

In addition to overland transport, wildfire ash can reach surface waters via atmospheric deposition. The size and quantity of particles carried by the atmosphere depend on several factors, including wind speed and direction as well as the distance from the fire to the water body (Adachi et al., 2022; Farruggia et al., 2024). Wildfire smoke and plumes often contain reactive elements such as potassium, phosphorus, sulfates, and nitrates (Silva et al., 2011; Boyer et al., 2022; Farruggia et al., 2024; Fernandez et al., 2024) that can potentially impact water pH and alkalinity.

While addressing atmospheric deposition was not directly measured in this study, the results suggest that ash-to-water ratios below 1 g L^{-1} have minimal impact on water alkalinity. To explore the potential impact of atmospheric ash deposition on drinking water quality and treatability, calculations were conducted to estimate potential ash concentrations in drinking water treatment plant (DWTP) reservoirs. For this purpose, reservoir dimensions from two DWTPs located in fire-prone regions—Fort McMurray and Rainbow Lake, Alberta, Canada—were used. While direct measurements of ash deposition into surface waters are lacking, several studies have reported wildfire ash production loads and surface layer thickness (e.g., Bodí et al., 2014; Santín et al., 2015; Quigley et al., 2019). Here, an average ash load of 6062 mg h^{-1} was calculated from these studies, with an assumed ash thickness of 50 mm (Bodí et al., 2014) and two deposition scenarios considered: (i) 50% of the ash being delivered to water and (ii) a worst-case scenario where the entire ash load deposits into the reservoirs.

Detailed calculations (Supporting information Table C6) indicate that under both ash delivery scenarios, and assuming typical operational water levels (~7.5 m), the resulting ash concentrations in

water remain below 1 g L^{-1}—suggesting negligible effects on pH and alkalinity. Under extremely low water level conditions (~4 m), complete delivery of ash could potentially affect water alkalinity. It should be noted that while the amount of atmospheric deposition of ash on a water body primarily depends on its exposed surface area, the extent to which the ash affects water alkalinity is largely determined by the depth of the water column. Therefore, the effects of atmospheric ash deposition on water alkalinity are most likely to be observed in shallow water bodies, where reduced depth increases the chemical influence of deposited ash.

To confirm these calculations, alkalinity data from the Regional Municipality of Wood Buffalo (RMWB) water treatment plant, collected from January 2010 till June 2025, are shown in Figure 4-6. Despite the wildfire in 2016 (indicated by the red vertical line), no notable immediate or sustained change in alkalinity levels was observed after the fire. Overall, Supporting information Table C6 and Figure 4-6 suggest that large volumes of atmospheric ash would be required to meaningfully alter the pH and alkalinity of large water bodies—such as reservoirs and lakes—particularly those with high initial buffering capacity.

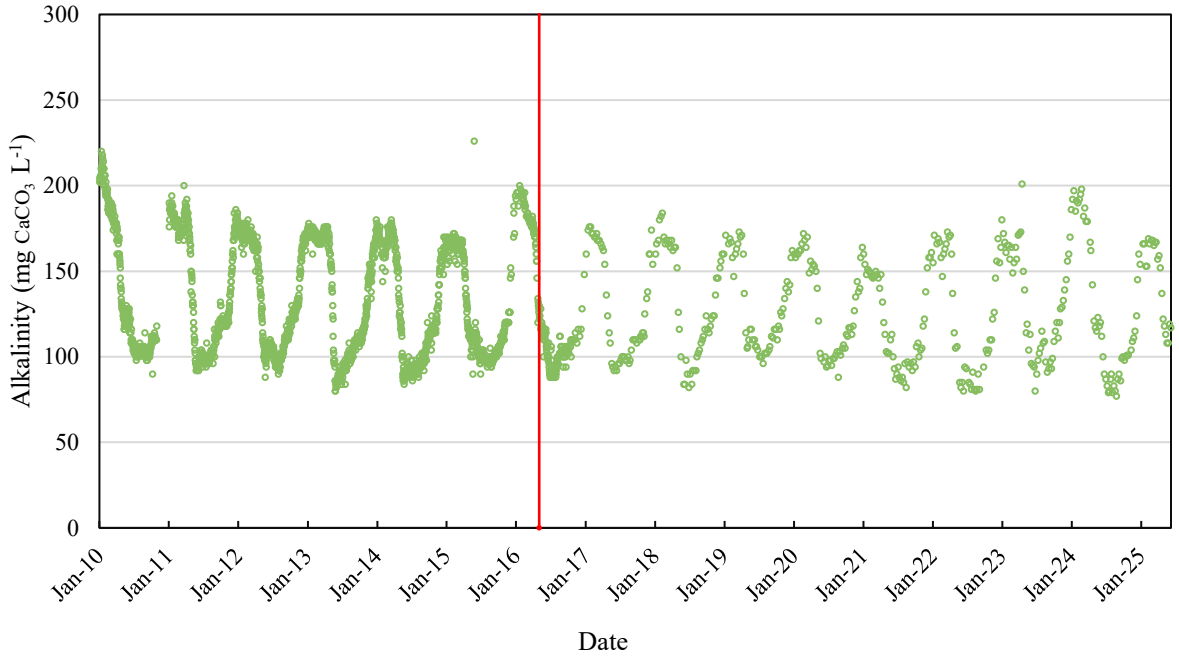


Figure 4-6 alkalinity data from the Regional Municipality of Wood Buffalo (RMWB) water treatment plant from January 2010 till June 2025. The red line indicates a wildfire during May 2016.

4.4 Conclusions

This study investigated the influence of settleable ash solids (SAS) on the alkalinity and treatability of wildfire ash-impacted water (WAIW). The results demonstrated that alkaline inorganic constituents in wildfire ash—both particulate and dissolved—can substantially alter water pH and alkalinity and increase the chemical demand of drinking water treatment processes. The key findings of this work are as follows:

- The addition of wildfire ash to water increases pH and alkalinity, particularly at higher ash-to-water ratios. Fine ash fractions, likely due to their greater surface area and higher concentrations of reactive alkaline compounds, have a more pronounced impact on alkalinity.

- Removal of SAS reduces alkalinity and acid demand, improving pH control and lowering the coagulant dose needed for effective organic matter removal. However, this also reduces turbidity removal efficiency due to fewer particle collisions and limited floc formation—highlighting a trade-off in solids management strategies.

- SAS removal had minimal impact on DBP-UFC and FP concentrations following coagulation, indicating that highly reactive dissolved organic matter—likely the primary precursor to DBP formation—was not effectively removed, regardless of the initial solids concentration in WAIWs.

- Atmospheric ash deposition following wildfires is unlikely to compromise the buffering capacity of large water bodies, as ash-to-water ratios below 1 g L^{-1} have minimal impact on alkalinity, and achieving such concentrations would require an unrealistically high deposition volume.

Solids management strategies, such as offline sedimentation basins, *may* help reduce SAS concentrations prior to treatment. However, their practicality and effectiveness remain uncertain and may be impacted by site-specific factors, including source water chemistry, ash composition, and solids loading. These considerations highlight the need for a more nuanced evaluation of both the prospective benefits and unintended consequences of implementing such strategies in dynamic aquatic systems.

Chapter 5

Coagulation under fire:

Wildfire ash alters magnitude, not the mechanisms of coagulation

Summary

Post-fire runoff can deteriorate drinking water source quality and challenge drinking water treatment processes by increasing coagulant demand and disinfection by-product formation potential. Coagulation is typically the primary treatment process in which turbidity and dissolved organic carbon (DOC) are managed. While field observations demonstrate that water quality responses to wildfire can vary considerably because of the interplay between ash delivery to receiving waters and hydrology, bench-scale investigations of ash delivery to water invariably demonstrate that wildfire ash increases all water quality drivers of coagulation: pH, alkalinity, turbidity, and DOC concentration and aromaticity. Although the magnitude of change varies, this consistency suggests that the worst-case scenario implications of wildfire for coagulation during drinking water treatment are universal. Accordingly, this work focused on mechanistically confirming that wildfire ash-induced changes in source water quality composition do not introduce fundamentally new challenges that affect coagulation performance. Turbidity and organic matter removals by coagulation of wildfire ash-impacted waters (WAIWs) were investigated at bench-scale using: 1) different ash types (from two wildfires and one prescribed fire), 2) different coagulation conditions (conventional and enhanced with pH adjustment to 7 and 6.5), and 3) different background water matrices (natural river and ultrapure water). Regardless of ash type, WAIWs had similar impacts on coagulation, with differences observed only in the magnitude of effects. Turbidity was reduced substantially even at low alum doses, indicating that (sa expected) it was not the primary driver of coagulant demand. In contrast, DOC removal was limited, reflecting lower removal efficiency of ash-derived organic matter dominated by low molecular weight, hydrophilic fractions. Enhanced coagulation improved DOC removal but reduced turbidity removal compared to WAIWs treated without pH adjustment. Background water conductivity, alkalinity, and DOC also affected coagulation performance. These relationships between water quality and coagulation performance were directly consistent with those observed in natural waters unaffected by wildfire. Collectively, these findings indicate wildfire ash does not alter water quality composition in a manner that presents new challenges to coagulation and thus emphasize that it is the magnitude and rate of these post-fire water quality changes that most threaten coagulation performance and consequently, the effectiveness of downstream treatment processes. In brief, they emphasize that "extreme" source water quality change requires "extreme" shifts in treatment response.

5.1 Introduction

Forested catchments are critical drinking water sources worldwide; however, water quality and quantity from these regions are increasingly threatened by climate change-driven disturbances, with large wildfires emerging as one of the most significant risks (Delpla et al., 2009; Flannigan et al., 2013; Dennison et al., 2014). Wildfires affect watershed hydrology and soil structure, which in turn increases overland flow and the delivery of sediments and burned material to receiving waters (DeBano, 1991; Bladon et al., 2008; Silins et al., 2009; Wagner et al., 2014; Williams et al., 2019). These post-fire pulses can increase turbidity and organic carbon concentrations and aromaticity, potentially overwhelming drinking water treatment processes. Operational challenges can include higher coagulant demand, reduced filter run times, impairment of disinfection processes, and increased formation of regulated disinfection byproducts (DBPs; Emelko et al., 2011; Hohner et al., 2016; 2019a; Fischer et al., 2023). Depending on fire severity, watershed characteristics, and subsequent storm events, these impacts can persist for months, years, and even decades in some cases.

Long-term effects of wildfire on surface waters have been documented at the watershed scale, with studies reporting a broad range of responses in streams and lakes (Paul et al., 2022). For example, some watersheds have experienced persistent increases in organic carbon concentration for years after a fire (Carignan et al., 2000; Betts & Jones, 2009; Rhoads et al., 2019a), while others reported no impact or even decreases in DOC concentrations following fire (Prepas et al., 2003; Mast & Clow, 2008; Betts & Jones, 2009; Davidson et al., 2019). These differences make it difficult to generalize watershed-scale water quality responses solely from field observations. The variability in these impacts can be attributed to the wide range biotic and abiotic factors that affect water quality at the watershed scale (Gomez Isaza et al., 2022; Paul et al., 2022; Chen & Change, 2023).

In contrast, bench-scale experiments, where ash inputs and background water quality are controlled, have invariably demonstrated that adding wildfire ash to water increases pH (depending on background water buffering capacity), alkalinity, turbidity, and DOC concentration and aromaticity (e.g., Revchuk & Suffet, 2014; Cerrato et al., 2016; Tsai et al., 2019; Skwaruk et al., 2020; Blackburn et al., 2023; Bahramian et al., 2025- Chapter 2). Such controlled studies eliminate the effects of hydrological variability, making it possible to quantify ash impact on key water quality metrics and the performance of drinking water treatment processes such as coagulation, which is used probably here to reflect particle destabilization (by coagulant addition), flocculation, and sedimentation processes (Crittenden et al., 2012).

Surface water coagulation efficiency for organic matter removal is typically governed by water chemistry; specifically, pH, alkalinity, turbidity, and DOC concentration and aromaticity (Edzwald, 1993; Crittenden et al., 2012; Bratby, 2016). Organic matter typically drives coagulant dosing and coagulation efficiency (Rebhun, M., & Lurie, 1993; O'Melia et al., 1999; Sharp et al., 2006). To improve organic matter removal efficiency and control DBP precursors, enhanced coagulation is widely recommended (U.S. EPA, 1999). This approach involves adjusting the water pH closer to the optimal range for the coagulant, based on the total organic carbon concentration and alkalinity of the water (U.S. EPA, 1999).

Wildfire ash-derived organic matter typically contains higher proportions of oxygenated, more aromatic, and smaller organic molecules, and it typically is enriched in nitrogenous compounds (Tshering et al., 2023). Compared to higher molecular weight and/or hydrophobic organic matter, these fractions are poorly removed by coagulation (Dennett et al., 1996; Chow et al., 2009; Hohner et al., 2019b; Chen et al., 2020; Skwaruk, 2021). Consequently, DOC removal in WAIWs is generally reported to be less efficient than turbidity reduction (Hohner et al., 2017; 2019b; Chen et al., 2020; Skwaruk et al., 2020).

The efficiency of WAIW coagulation is also impacted by pH, which affects both the surface charge of organic and inorganic colloids and the hydrolysis products of metal salt coagulants such as alum (Randtke, 1988; Ye et al., 2007). Highly alkaline conditions—commonly observed in WAIWs—reduce the positive charge of hydrolyzed aluminum species, weakening their electrostatic attraction to anionic organic matter and thereby lowering DOC removal efficiency (Ching et al., 1994). Although several studies have attempted to address the coagulation of drinking water sources following wildfires, few have systematically evaluated WAIW coagulation responses through the lens of coagulation mechanisms. Different ash types can vary in composition; however, existing laboratory evidence suggests their effects on water quality are similar, meaning they consistently increase pH (depending on the water's buffering capacity), alkalinity, turbidity, and DOC (e.g., Revchuk & Suffet, 2014; Cerrato et al., 2016; Tsai et al., 2019; Skwaruk et al., 2020; Blackburn et al., 2023; Chapters 2, 3, and 4). This strongly suggests that the impact of WAIW on coagulation is also consistent, with only the magnitude of the effects varying. However, this assumption has not been systematically evaluated across a range of ash types, water matrices, and coagulation strategies. Accordingly, the goal of this study was to demonstrate that coagulation of WAIWs follows the same fundamental mechanisms as other surface waters and that wildfire ash does not alter these mechanisms.

5.2 Materials and methods

5.2.1 Experimental approach

A series of bench scale experiments were conducted to substantiate that the factors impacting WAIW coagulation areflct established coagulation theory. In these experiments different (i) ash types, (ii) coagulation conditions, and (iii) background water quality (ultrapure and natural river water) were evaluated. Three ash samples were collected from two wildfires and a prescribed fire to enable investigation of ash with different characteristics. WAIW matrices were prepared using high-quality (i.e., low turbidity and DOC) source water collected from the Elbow River in Calgary, Alberta, Canada. WAIWs were also prepared using ultrapure water, allowing for benchmarking of organic matter leaching from wildfire ash between sites, in absence of water matrix effects.

5.2.2 Experimental design

The experimental approach is summarized in Figure 5-1. All WAIWs were prepared and treated using a jar test apparatus (Phipps & Bird, PB-900 Series Programmable 6-Paddle Jar Tester). All experiments were conducted at typical laboratory conditions. Elbow River (ER) water served as the source water for most experiments, which was stored in sealed pails at 4°C after collection until use, and its nominal quality during the study is summarized in Supporting information Table D1. Temperatures of all WAIW suspensions were maintained near 21°C.

A target of 6 mg L^{-1} of DOC was selected for WAIWs, based on previously reported post-fire DOC increases in receiving waters after wildfire (Uzun et al., 2020; Richardson et al., 2022; Hickenbottom et al., 2023). To ensure consistent leaching, ash-water suspensions were mixed for 24 h at 120 RPM before coagulation, following Bahramian et al. (2025)- Chapter 2.

The coagulation procedure was based on Skwaruk et al. (2020): Aluminum sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$) was added to WAIWs during rapid mixing at 120 RPM for 1 min, followed by 20 min of slow mixing at 40 RPM to promote flocculation. After mixing, samples were allowed to settle for 15 min before water quality analyses.

Experiment 1 investigated the impact of different ash types on coagulation performance (i.e., turbidity reduction and DOC removal). WAIWs were prepared in ER water using three ash types: Doctor Creek sampling site 2 (DC-S2), Thuya Creek (TC), and Doctor Creek prescribed fire (DC-P). The mass of ash added was adjusted to achieve a DOC concentration of 6 ± 0.5 mg L^{-1}: 0.9 g L^{-1} for

DC-P, 1.2 g L^{-1} for TC, and 1.5 g L^{-1} for DC-S2. Alum doses of 15, 25, 40, 60, and 80 mg L^{-1} (equivalent to 1.28, 2.14, 3.43, 5.14, and 6.85 mg L^{-1} Al^{3+}), along with control WAIW (where no coagulant was added), were used in jar tests. The resulting pH, alkalinity, turbidity, DOC, UV_{254}, specific ultraviolet absorbance (SUVA), and E2:E3 ratios were evaluated; DOC character was further analyzed by LC-OCD. For the TC ash type, an additional series of jar tests was performed across a wider alum dose range (15–300 mg L^{-1}) to investigate the potential for particle restabilization and to enable comparison with a previous study that used the same ash type and high doses of alum (Skwaruk et al., 2020).

Experiment 2 involved an assessment of enhanced coagulation (i.e., lowering pH) on turbidity and organic matter removal. In this series of experiments, WAIWs were prepared by adding 1.2 g L^{-1} of TC ash to ER water. Three alum doses, 15, 40, and 80 mg L^{-1} (equivalent to 1.28, 3.43, and 6.85 mg L^{-1} Al^{3+}), were tested under three pH conditions: no adjustment (conventional coagulation); adjustment to pH 7, as recommended by the EPA for waters with similar DOC concentrations and alkalinity (U.S. EPA, 1999); and adjustment to pH 6.5, which is within the optimal range of alum for organic matter removal (Amirtharajah & Mills, 1982). Similar to Experiment 1, this experiment also had a control WAIW where no coagulant was added to the suspension. HCl (1.0 N) was used to adjust the pH in WAIW before alum addition. Due to the high alkalinity of the WAIWs, 1.5 mL L^{-1} of acid was required to reach pH 7-, and 2.8-mL L^{-1} to reach pH 6.5, after which samples were mixed for 30 minutes to stabilize pH. For comparison, ER water without ash was also treated at both conventional conditions and with pH adjustment to 6.5 using 40 mg L^{-1} of alum. Following coagulation, pH, alkalinity, turbidity, DOC, UV_{254}, and SUVA were measured, and organic matter was further characterized using LC-OCD.

Experiment 3 evaluated the impact of the background water matrix on coagulation of WAIW. Here 1.2 g L^{-1} of TC ash was added to both ER and ultrapure (UP) water. The responses of WAIWs prepared with different water matrices to conventional coagulation were evaluated using 40 mg L^{-1} of alum. Following coagulation, pH, alkalinity, turbidity, DOC, UV_{254}, and SUVA were measured to evaluate treatment performance. Consistent with previous experiments, each coagulation set also included a control WAIW without coagulant addition.

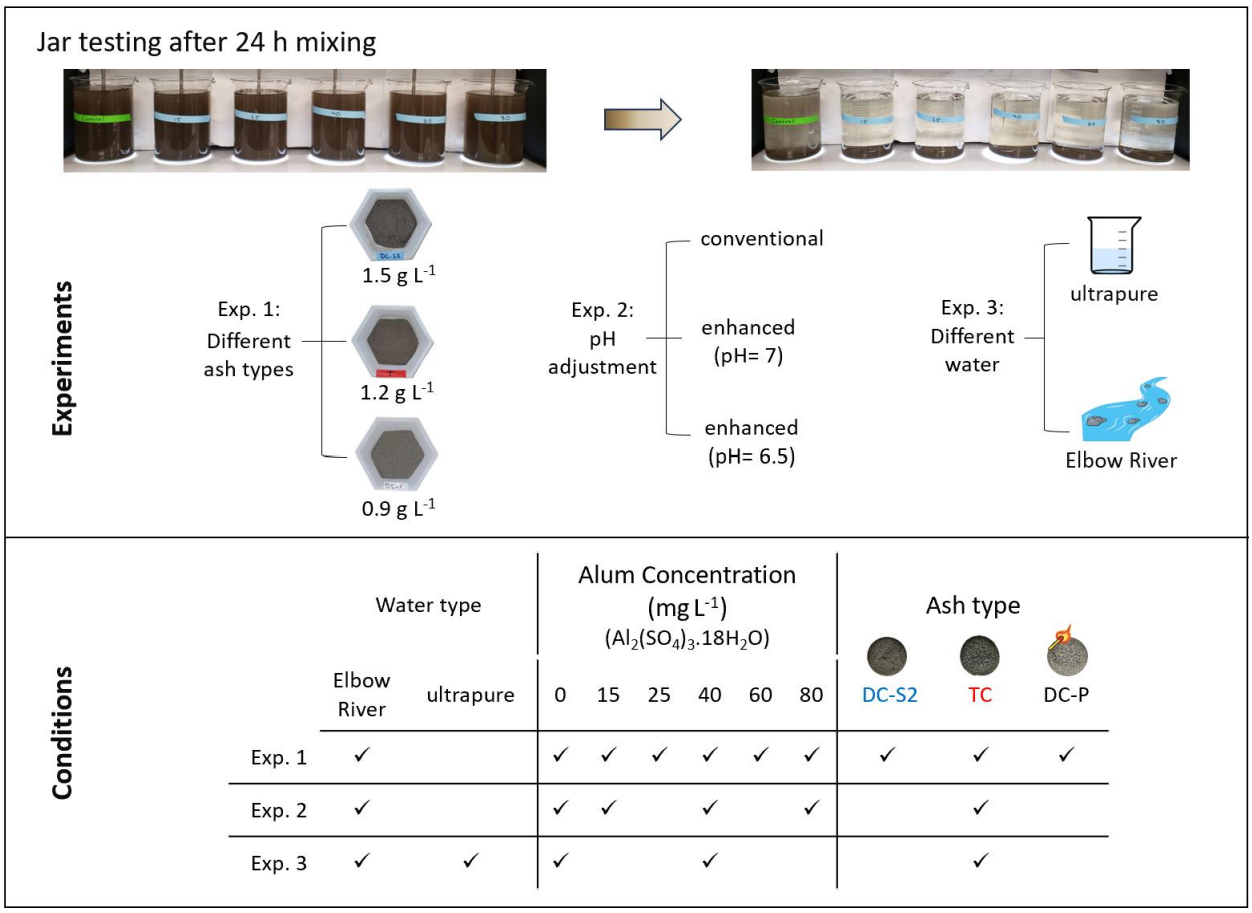


Figure 5-1 Experimental design to evaluate WAIW coagulation. This was evaluated through three experimental series, each addressing different impacting factors: (1) ash type: Doctor Creek sampling site 2 (DC-S2), Thuya Creek (TC), and Doctor Creek prescribed fire site (DC-P) mixed in ER water, (2) coagulation condition: conventional (no pH adjustment) and enhanced (pH adjusted to 7 or 6.5); and (3) background water matrix: ER and UP water. In this experiment different ash doses were used to maintain a DOC concentration of approximately 6±0.5 mg L^{-1} across all WAIWs. All tests were performed in triplicate.

5.2.3 Wildfire ash collection

Ash samples collected from two wildfires and one prescribed fire reflect a range of pyrogenic materials produced by different burn severities (Table 5-1). To homogenize the samples and remove large debris and conifer needles, all ash types were air-dried and sieved through a 1 mm screen, consistent with previously reported methods (Chapters 2, 3, and 4; Cawley et al., 2018; Harper et al., 2019; Skwaruk et al., 2020). The color of different ash types was identified visually using a Munsell color chart (Pantone). Processed samples were stored in closed containers at a controlled temperature of 21°C. Organic matter content of each ash type was measured using loss on ignition according to the ASTM D7348 method.

Table 5-1 Ash collection location, date and fire information.

Ash type	Fire	Location (Canada)	Burn area (ha)	Fire start date (mm/yyyy)	Vegetation type	Burn severity	Ash collection date (mm/yyyy)
Doctor Creek sampling site 2 (DC-S2)	Doctor Creek Wildfire[a]	Canal Flats, BC[a]	7645[a]	08/2020[c]	Lodgepole Pine[1a] Douglas Fir[2a], Ponderosa Pine[3a], Western Larch[4c]	Medium[c]	09/2020
Doctor Creek prescribed fire site (DC-P)	Doctor Creek Prescribed Fire[a]					Medium[c]	
Thuya Creek (TC)	Little Fort Fire Complex[b]	Little Fort, BC[b]	556[b]	07/2017[b]	Lodgepole Pine[1c], Douglas Fir[2c], Spruce Hybrids[5c], Paper Birch[6c]	High[c]	08/2017[c]

1- *Pinus contorta var. latifolia*
2- *Pseudotsuga menziesii var. glauca*
3- *Pinus ponderosa*
4- *Larix occidentalis*
5- *Picea* spp.
6- *Betula papyrifera*

a- BC Wildfire Service Information Section (2020)

b- Skwaruk (2021)

5.2.4 Water quality analyses

Water quality was analyzed according to Standard Methods for the Examination of Water and Wastewater, 24th edition (APHA, 2022) whenever possible. The pH was measured according to Method 4500H, using an Accumet AB250 benchtop meter (Fisher Scientific, Toronto, Canada). Turbidity was quantified following Method 2310, using a HACH 2100Q Portable Turbidimeter (HACH, Loveland, Colorado, USA). Dissolved and total organic carbon (DOC/TOC) were analyzed via the combustion method (Method 5310C) on a Shimadzu TOC-VCHP analyzer with a detection limit of 0.1 mg L^{-1}. UV absorbance at 254 nm (UV_{254}) was measured according to Method 5910 using a RealTech P200B analyzer, and specific ultraviolet absorbance (SUVA) was calculated as the ratio of UV_{254} to DOC concentration (Edzwald et al., 1985). E2:E3 was calculated as the ratio of UV absorbance at 250 nm to that at 365 nm, serving as a proxy for organic matter molecular size (Peuravuori & Pihlaja, 1997).

Size-exclusion chromatography with organic carbon detection (LC-OCD) was performed following Huber et al. (2011) using a DOC-Labor Model 8 analyzer equipped with Toyopearl HW 50S columns. The system was calibrated with potassium hydrogen phthalate, and data were processed using ChromCALC software. In this method, dissolved organic carbon is divided into five size-based fractions: biopolymers, humic substances, building blocks, low molecular weight (LMW) acids, and LMW neutrals (Huber et al., 2011). Biopolymers are the largest molecular fraction of DOC, with molecular weights above 20,000 g mol^{-1} (>10 kDa), and include polysaccharides, proteins, polypeptides, and amino sugars; they do not absorb UV light at 254 nm. Humic substances, including humic and fulvic acids, have molecular weights of approximately 400 to 1,100 g mol^{-1}. Building blocks are lower molecular weight (300 to 500 g mol^{-1}) breakdown products of humic substances. LMW acids consist of small aliphatic organic acids with molecular weights below 350 g mol^{-1}, while LMW neutrals include weakly charged or slightly hydrophobic organics such as alcohols, aldehydes, ketones, sugars, and amino acids. For DOC, UV_{254}, and LC-OCD analyses, all WAIW samples were filtered through pre-rinsed 0.45 µm polyethersulfone (PES) filters (Millipore Express® PLUS; Merck Millipore, Burlington, MA). PES filters were prerinsed first with ultrapure water and then with WAIW before sample collection. Minimum reporting limits for the water quality metrics analyzed here are presented in Supporting information Table D2.

5.2.5 Statistical Analysis

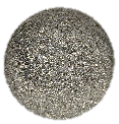
Statistical analyses were conducted to determine whether enhanced coagulation improved turbidity reduction and organic matter removal. Due to samples small size and violation of normal distribution a non-parametric test (Kruskal-Wallis) was used (n = 9).

5.3 Results and discussion

5.3.1 WAIW coagulation: different ash impacts

Table 5-2 summarizes DOC concentration and ash properties for the three ash types (DC-S2, TC, DC-P) used. The organic matter content of the ash types ranged from 14.2% to 20.8%, with the lowest for TC and the highest for DC-P. While lighter-colored ash is typically considered more completely combusted and less likely to leach organic matter (Bodí et al., 2014; Rodela et al., 2022), DC-P, the lightest-colored ash in this study, produced the highest DOC yield. This suggests that ash color does not directly reflect leachable WEOM concentration, which is in agreement with what has been reported previously (Wang et al., 2016; Bahramian et al., 2025- Chapter 2).

Table 5-2 DOC concentration, yield, and alkalinity in WAIWs prepared by mixing different ash types with ER water, alongside the organic matter content and color of the ash.

Ash type	DOC (mg L^{-1})	DOC yield (mg g^{-1})	Organic matter content (wt%)	Alkalinity (mg $CaCO_3$ L^{-1})	Ash color	Ash photo
DC- S2 (1.5 g L^{-1})	6.0 ± 0.3	3.3 ± 0.2	16.07 ± 1.2	297	very dark grey	
TC (1.2 g L^{-1})	5.9 ± 0.5	4.2 ± 0.5	14.7 ± 0.7	215	dark grey	
DC-P (0.9 g L^{-1})	6.5 ± 0.5	6.0 ± 0.6	19.2 ± 2.0	279	grey	

5.3.1.1 Turbidity reduction

Table 5-3 presents turbidity values for control WAIWs (i.e., without coagulant addition) during rapid mixing and after sedimentation. After the 36-minute jar test (1 min rapid mix, 20 min slow mix, 15 min settling), turbidity in all control WAIWs decreased by over 90% compared to initial mixed values, indicating that a high portion of ash particles were readily settleable.

Table 5-3 Turbidity in control WAIW (without coagulant) during fast mixing and after settling (n = 3).

Ash type	Turbidity (NTU)	
	During fast mixing	After settling
DC-S2	470 ± 186	26 ± 8.2
TC	391 ± 28	38 ± 6.4
DC-P	338 ± 47	33 ± 12

Figure 5-2 shows changes in turbidity for WAIWs following coagulation with varying alum concentrations. Turbidity values in Figure 5-2a represent post-sedimentation measurements for all WAIWs, including the controls. Even the lowest alum dose resulted in over 88% turbidity removal across all WAIWs. These results are consistent with previous studies that observed substantial turbidity reductions in WAIWs treated with conventional alum coagulation (Hohner et al., 2017; 2019b; Skwaruk et al., 2020), suggesting that turbidity does not dictate coagulant dose in WAIWs, similar to other surface waters (Yao & O'Melia 1989; Edzwald & Van Benschoten, 1990).

The maximum turbidity removal was achieved at an alum concentration of 60 mg L^{-1} (equivalent to approximately 5.1 mg L^{-1} of Al^{3+}), which aligns with what was reported by Hohner et al. (2019b) for WAIWs with similar DOC levels (~5 mg L^{-1}) and initial turbidity of ~17 NTU. Figure 5-2b shows turbidity responses in WAIWs prepared with 1.2 g L^{-1} of TC ash across a broader alum dose range (15 to 300 mg L^{-1}). As anticipated, turbidity began to increase at alum doses around 80 mg L^{-1} (6.9 mg L^{-1} Al^{3+}), likely due to restabilization of readily destabilized particles (Crittenden et al., 2012; Bratby, 2016). While this observation is in agreement with Hohner et al. (2019b), it differs from Skwaruk et al. (2020), where a slight increase in turbidity was only noted at substantially higher Al^{3+} concentrations—above 36.4 mg L^{-1}. This difference is likely attributed to variations in initial water quality and the alum dose ranges tested in each study. While the present study and Hohner et al. (2019b) had comparable

WAIW quality and alum doses, Skwaruk et al. (2020) tested substantially more deteriorated WAIW (prepared by adding 5 g L^{-1} of TC ash to Elbow River water) and applied substantially higher alum doses (100–400 mg L^{-1}). As a result, WAIW in Skwaruk et al. (2020) had different ionic strength, alkalinity, and suspended solids concentration, which potentially contributed to delaying particle restabilization.

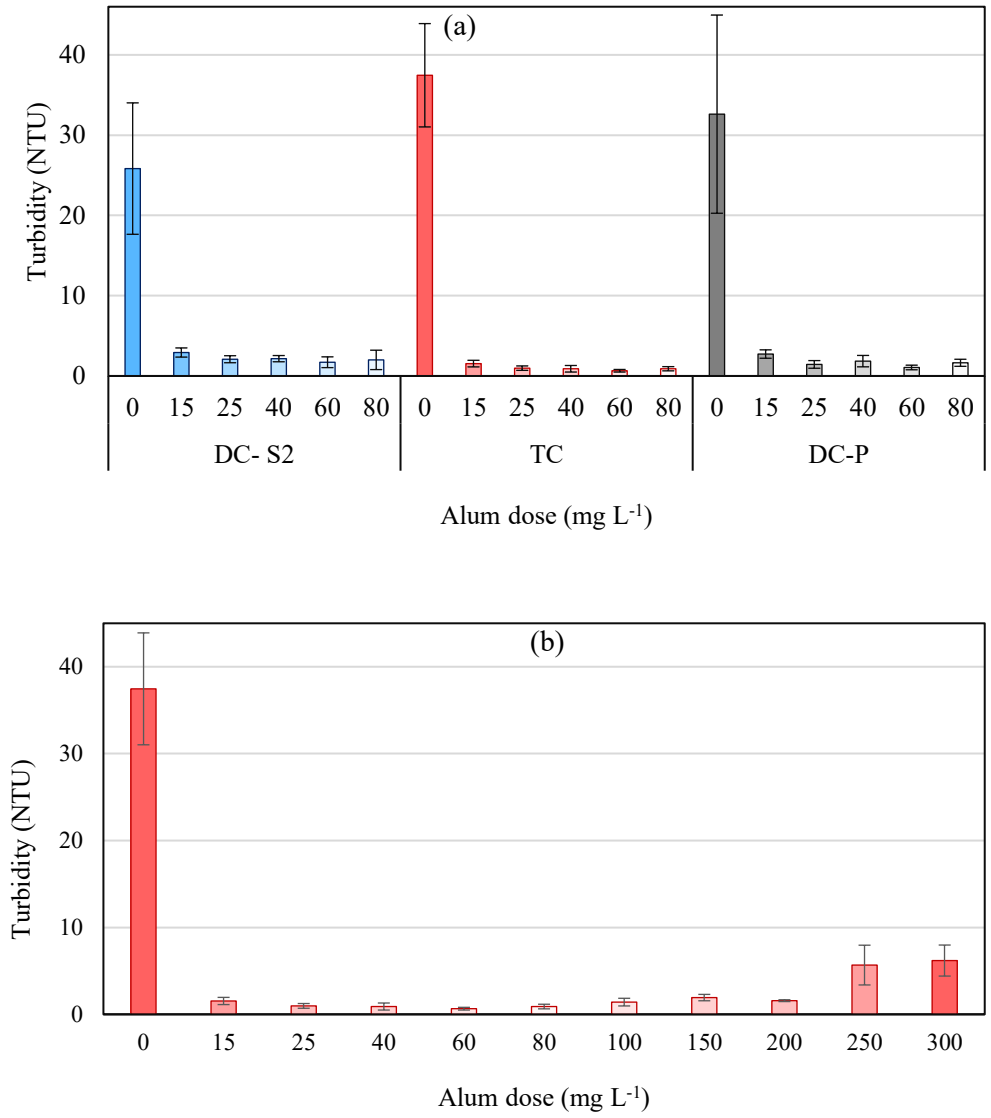


Figure 5-2 Turbidity reduction in (a) WAIWs prepared with different ash types (DC-S2, TC, and DC-P) coagulated with 15–80 mg L^{-1} alum, and (b) TC suspensions coagulated with a wider alum dose range (15–300 mg L^{-1}). Each bar represents the average value (n = 3) with error bars representing standard deviation.

5.3.1.2 Organic carbon removal

Figure 5-3 shows changes in pH, DOC concentration, SUVA, and E2:E3 values for WAIWs prepared using DC-S2, TC, and DC-P ash types after conventional coagulation with different alum concentrations. As expected, alum addition to WAIWs consumed buffering capacity and lowered the pH, which in turn facilitated DOC removal from suspensions (MWH, 2012; Bratby, 2016). Accordingly, an increase in DOC removal with higher alum doses was anticipated. The highest DOC concentration removal was equal to 26, 10, and 15% for DC-S2, TC, and DC-P, respectively, at the highest coagulation dose (80 mg L^{-1}). Although DOC removal in DC-S2 met the minimum EPA requirements for waters with high alkalinity (25%), in WAIW prepared using TC and DC-P ash types, the EPA requirement was not met, suggesting further treatment processes and/or enhanced coagulation is needed to lower DOC concentration and control disinfection by-products formation (U.S. EPA, 1999).

The addition of ash to natural river water increased SUVA from 1.3 to 2.8, 2.8, and 3.8 L mg^{-1} m^{-1} for DR-S2, TC, and DC-P ash, respectively (Figure 5-3c). These SUVA values (below 4 L mg^{-1} m^{-1}) suggest organic carbon is partially composed of hydrophilic, less aromatic, and low molecular wight (LMW) compounds (Edzwald, 1993), which are less amenable to removal by conventional alum coagulation (Bratby, 2016; Hohner et al., 2019a; Chen et al., 2020; ; Skwaruk, 2021; Cao et al., 2024 Notably, the low DOC removal per unit alum (~0.01 mg DOC per mg alum) further supports the presence of high proportions of LMW compounds in WAIW. This is aligns with previous r3eports (Hohner et al., 2017; 2019b).

Coagulation reduced SUVA slightly, indicating preferential removal of larger, more aromatic molecules and leaving behind smaller, more hydrophilic fractions. This shift in organic matter character was also reflected in E2:E3 values (Figure 5-3d); such an increase typically signals a reduction in the average molecular size and aromaticity of dissolved organic compounds (De Haan & De Boer, 1987; Peuravuori & Pihlaja, 1997; Wang et al., 2015b). These optical findings are corroborated by LC-OCD data (Figure 5-4), which show that humic substances concentrations consistently declined with increasing alum dose, regardless of ash type. In contrast, fractions consisting of smaller and more hydrophilic compounds, including building blocks, LMW neutrals, and LMW acids, remained largely unaffected, indicating their resistance to removal by alum coagulation. Collectively, these findings demonstrate that alum preferentially removed larger molecules from WAIWs, as has been reported previously for natural waters unaffected by wildfire (Dennett et al., 1996) and was thus expected.

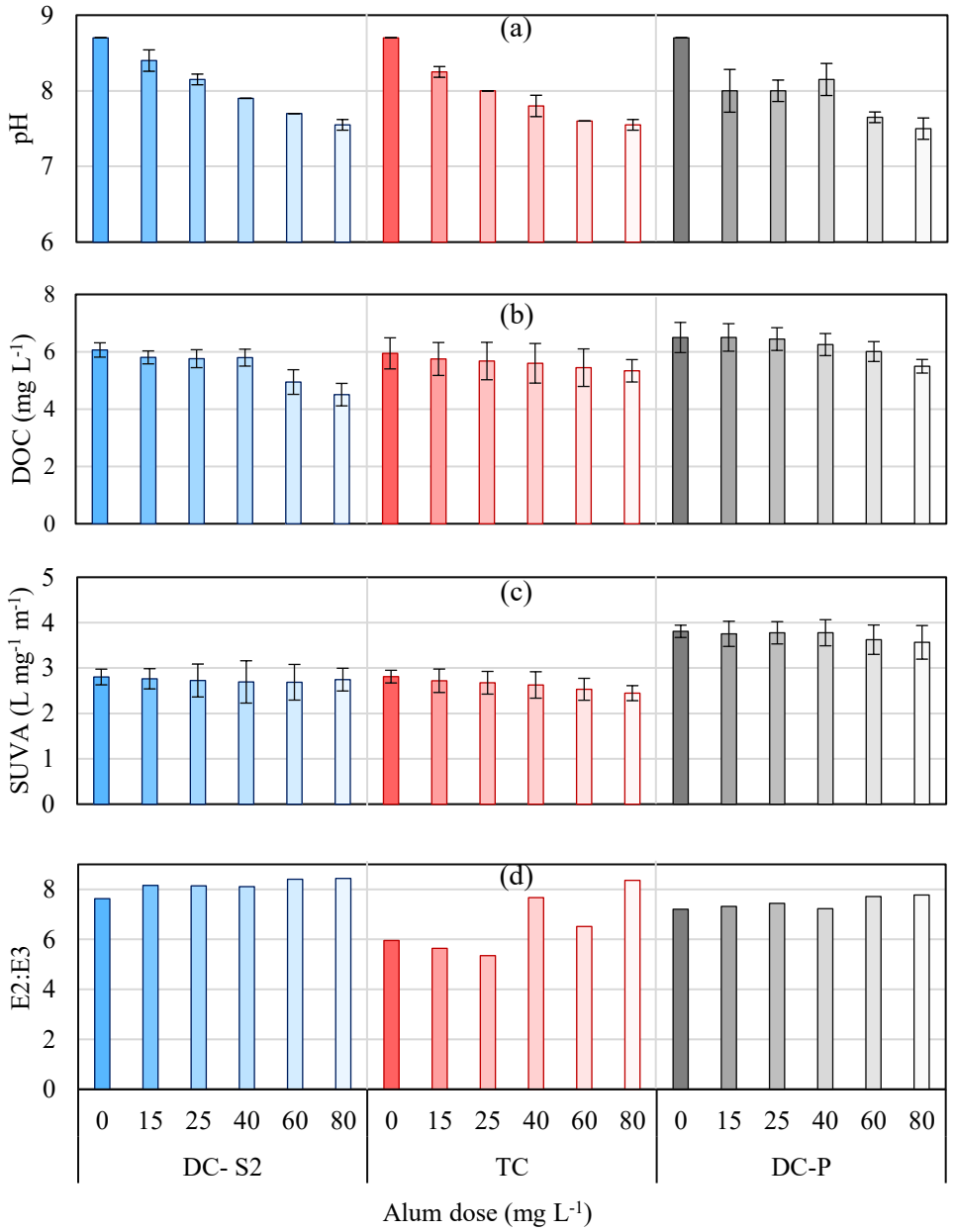


Figure 5-3 Changes in a) pH, b) DOC concentration, c) SUVA values, and d) E2:E3 ratio following coagulation of WAIW prepared in Elbow River water using different ash types (DC-S2, TC, and DC-P; Doctor Creek sampling site 2, Thuya Creek, and Doctor Creek after prescribed burn) with 15, 25, 40, 60 and 80 mg L^{-1} of alum. Each bar represents the average value (n = 3) with error bars representing standard deviation.

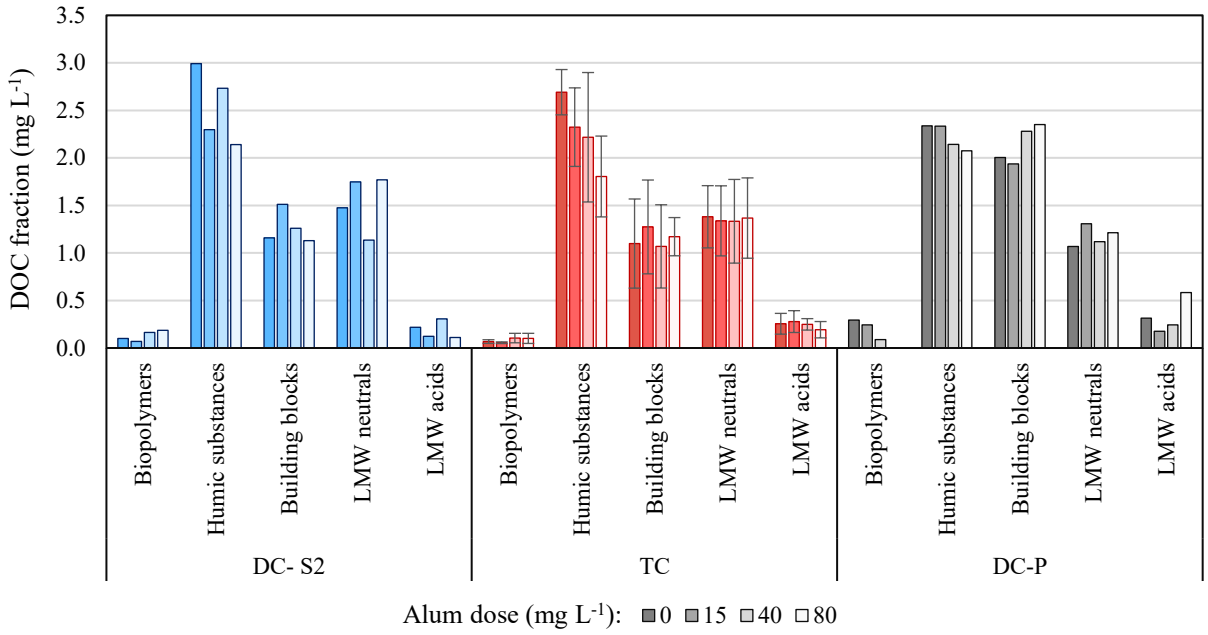


Figure 5-4 Changes in the concentration of different DOC fractions following coagulation of WAIW prepared in Elbow River water using different ash types (DC-S2, TC, and DC-P; Doctor Creek sampling site 2, Thuya Creek, and Doctor Creek after prescribed burn) with 15, 40, and 80 mg L^{-1} of alum. Bars for TC ash represent mean values, with error bars for TC showing standard deviation (n = 3; no replication is available for DC-S2 and DC-P)

5.3.2 WAIW enhanced coagulation

5.3.2.1 Turbidity reduction

Figure 5-5 presents turbidity for TC ash-impacted water (TC+ER WAIW) following coagulation at varying alum doses, with and without pH adjustment. Turbidity removal in WAIWs coagulated without pH adjustment, and with pH adjusted to 7 and 6.5 averaged 97%, 95%, and 93%, respectively, across a range of alum doses. Although the alum solubility diagram (Supporting information Figure D1) suggests higher turbidity reduction at lower pH values (around 6 to 7 for alum; Amirtharajah & Mills, 1982) primarily due to (i) enhanced aluminum hydrolysis and the formation of aluminum hydroxide precipitates and flocs, and (ii) increased H^+ concentration that compresses the electrical double layer and reduces particle surface charge, therefore reducing repulsive forces between particles and particle stability in the suspension (Packham, 1962; Amirtharajah & Mills, 1982; Crittenden et al., 2012), this trend was not observed in the current study.

As shown in Figure 5-5, residual turbidity was consistently higher in WAIWs with pH adjustment to 7 or 6.5 compared to those coagulated without pH adjustment. Although this difference was not statistically significant (p-value = 0.051, n = 9), the closeness of p-value to α (0.05) suggests that a statistically significant difference might be detected with a larger sample size or increased analytical power. The increased turbidity residual in pH adjusted WAIWs following coagulation may be attributed to the combined effects of mixed particle types (hydrophobic and hydrophilic), high organic matter concentrations, and the presence of reactive compounds such as phosphate in WAIW (Edzwald et al., 1990; Edzwald, 1993; Crittenden et al., 2012; Bratby, 2016). These factors can shift the operational boundaries of the alum coagulation diagram, altering the density and stability of formed flocs (Bratby, 2016; Alansari, 2021). Additionally, at lower pH values, a portion of alum may be consumed in reactions with dissolved organic matter (Edzwald, 1993; Crittenden et al., 2012; Bratby, 2016) and through complexation with phosphate (Stumm & Morgan, 1962), reducing the aluminum available for particle destabilization and turbidity reduction.

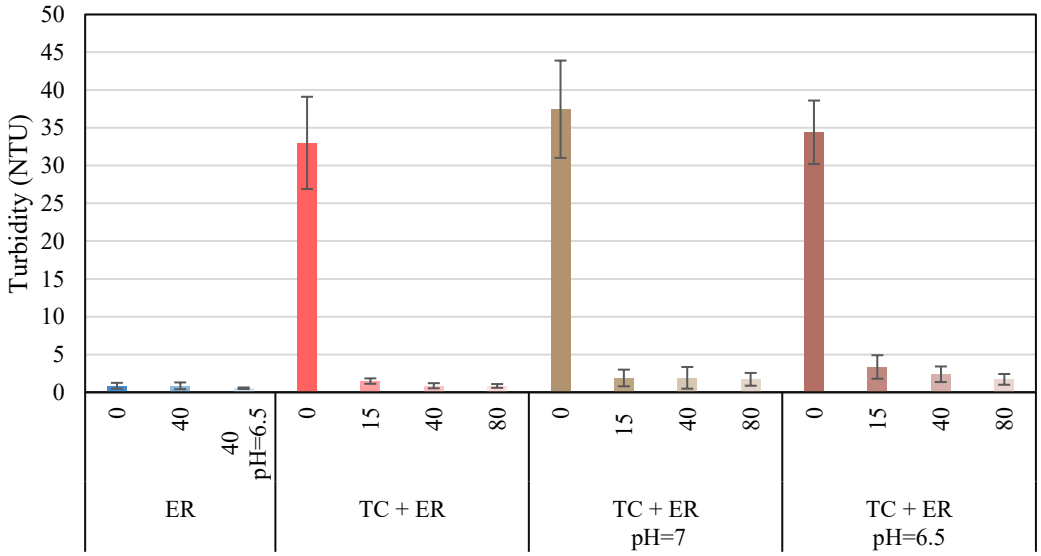


Figure 5-5 Changes in turbidity reduction in WAIW prepared using TC (Thuya Creek) ash and Elbow River water (TC+ER) following coagulation with and without pH adjustment. Each bar represents the average value (n = 3) with error bars representing standard deviation.

5.3.2.2 Organic carbon removal

Figure 5-6 presents DOC concentration and SUVA values in Elbow River (ER) water and TC ash-impacted water (TC+ER WAIW) following coagulation at varying alum doses, with and without pH adjustment. As expected, pH adjustment improved DOC removal in both Elbow River water (ER) and WAIW (TC+ER). Although DOC removal in WAIWs treated with enhanced coagulation was not significantly different from that observed at conventional conditions (p-value = 0.08, n = 9), enhanced coagulation was more efficient on mg DOC removal per mg alum. On average, 0.05 and 0.08 mg of DOC were removed per mg of alum in WAIWs adjusted to pH 7 and 6.5, respectively, which was an improvement compared to WAIWs without pH adjustment (0.01 mg mg^{-1}). These removal efficiencies are consistent with values previously reported for enhanced coagulation of WAIWs (Chen et al., 2020).

DOC removal improved in WAIWs with lower pH, suggesting an increase in complexation and adsorption of organic matter onto aluminum (Figure 5a; Edzwald, 1993; Bratby, 2016). Notably, pH adjustment resulted in much higher removal in WAIW (TC+ER) compared to Elbow River (ER) water: in ER water treated with 40 mg L^{-1} of alum, DOC removal increased slightly from 15% to 16% when pH was adjusted to 6.5; however, in WAIW (TC+ER), removal increased from 13% to 20% when pH was adjusted. The highest DOC removal achieved in WAIWs with a pH adjustment of 6.5 and an alum dose of 80 mg L^{-1} (i.e., 30%). This percentage removal is higher than the required removal value recommended in U.S. EPA (1999) for waters with similar organic carbon concentrations and alkalinities.

Reduction in SUVA in waters treated at enhanced coagulation conditions shows improvement in the removal of aromatic and larger molecules with controlling pH, regardless of the presence of ash in water (Figure 5-6b). However, this improvement was more noticeable in natural river water compared to WAIW, suggesting ash addition to water increases the concentration of some organic molecules in water that are poorly removed by alum, even under optimized pH conditions, as discussed in Section 3.1.2.

LC-OCD results (Figures 5-7), further suggest a change in dissolved organic carbon character in WAIW. In untreated ER samples, humic substances accounted for approximately 64% of the total DOC. Upon addition of TC ash, this proportion dropped to 49%, while building blocks and LMW compounds increased by 8% and 9%, respectively (Figure 5-7). This compositional shift toward smaller, more hydrophilic molecules reduced the effectiveness of conventional coagulation. The limited ability of alum to remove low molecular weight organic matter has also been previously documented in natural

waters (Dannett et al., 1996). These results highlight the importance of DOC character, not just concentration, in determining treatability.

Following coagulation, humic substances with high molecular weight and aromatic compounds were preferentially removed, especially under enhanced conditions (pH adjustment to 6.5 and alum doses of 40–80 mg L^{-1}). As humic substances were removed, the relative fractions of LMW neutrals and building blocks increased proportionally. Biopolymers and LMW acids showed minimal changes across all coagulation treatments, indicating limited interaction with alum. These results suggest that while humic substances are effectively removed by alum, smaller, less aromatic organic matter fractions persist and may require alternative or complementary treatment approaches. These results highlight the importance of considering DOC character, not just concentration, in assessing water treatability.

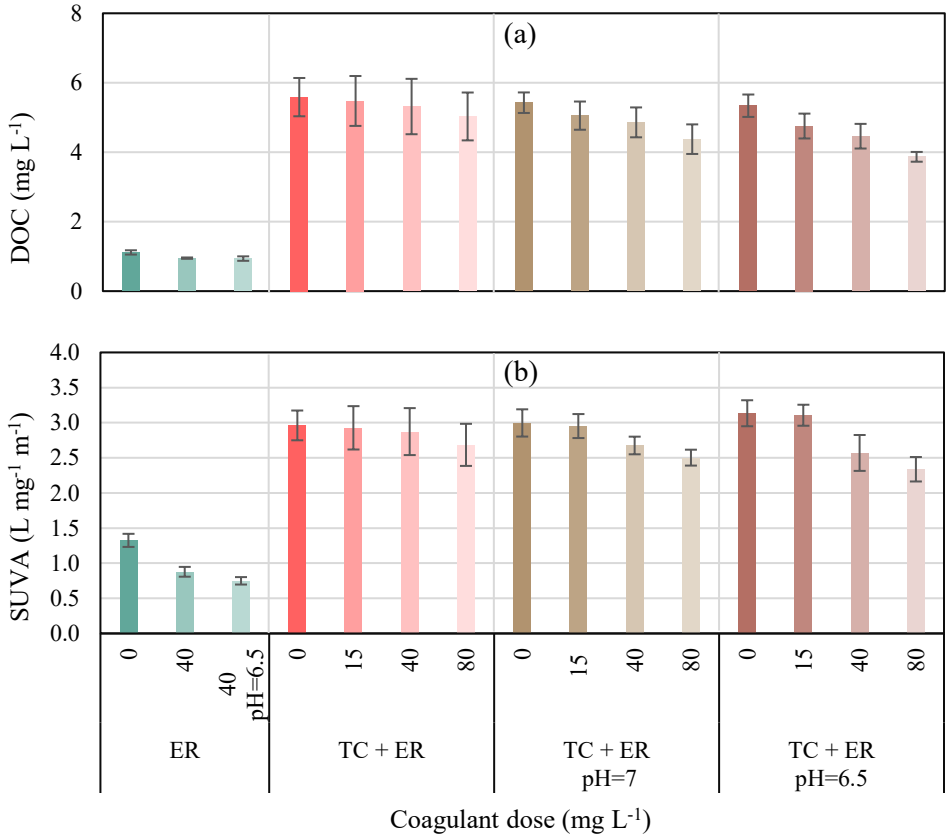


Figure 5-6 Changes in a) DOC concentration and b) SUVA values before (zero coagulant dose) and after coagulation of Elbow River (ER) water and TC ash-impacted water (TC+ER; Thuya Creek + Elbow River water) with and without pH adjustment. Each bar represents the average value (n = 3), with error bars representing standard deviation.

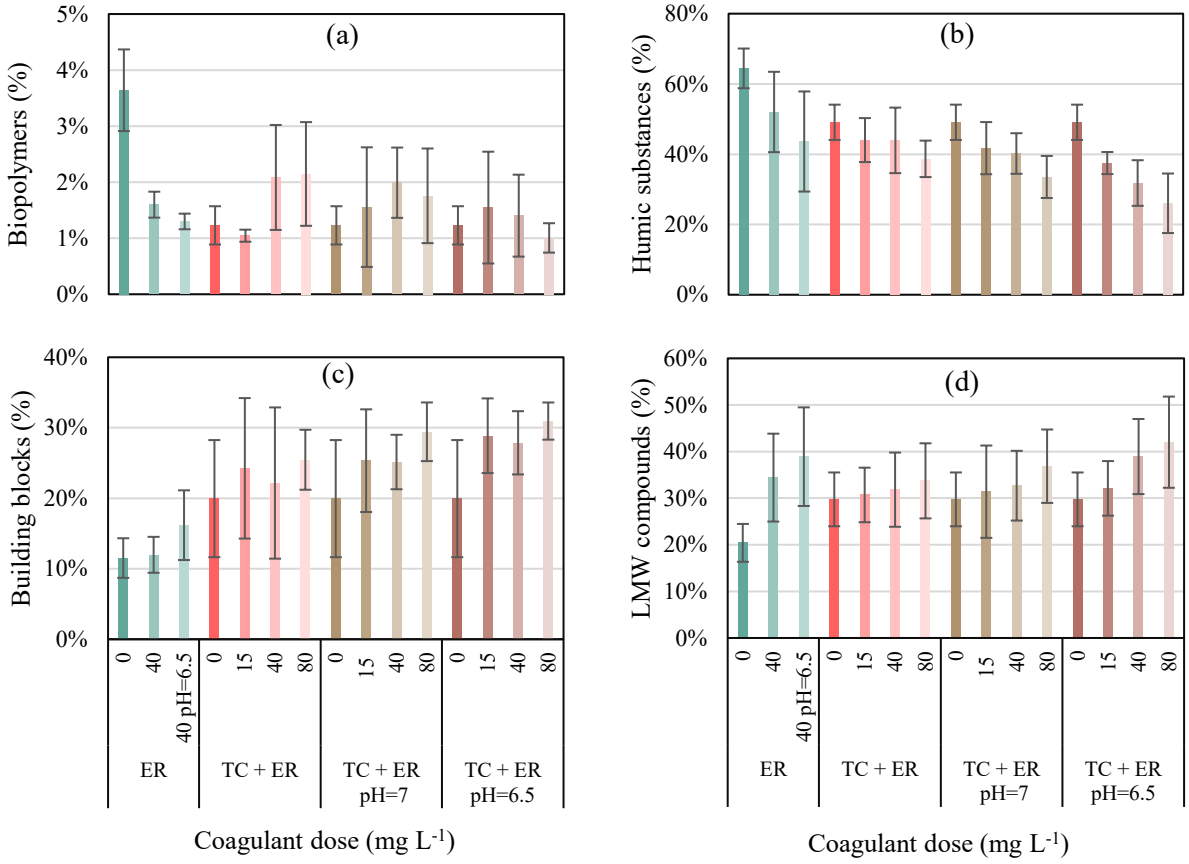


Figure 5-7 Changes in the proportions of (a) biopolymers, (b) humic substances, (c) building blocks, and (d) LMW compounds following coagulation of Elbow River (ER) water and TC ash-impacted water (TC+ER; Thuya Creek + Elbow River water) with and without pH adjustment, using 15, 40, and 80 mg L^{-1} alum. Each bar represents the average value (n = 3), with error bars representing standard deviation.

5.3.3 Water matrix impact on WAIW coagulation

The addition of 1.2 g L^{-1} of TC ash to ultrapure water increased the alkalinity to 75 mg $CaCO_3$ L^{-1}. Although this increase was comparable in magnitude to the increase observed in Elbow River water following ash addition—from 193 mg L^{-1} to 258 mg $CaCO_3$ L^{-1} (a 65 mg $CaCO_3$ L^{-1} increase)—it represents a greater shift in ultrapure water. This aligns with what has been reported (Hohner et al. 2017). In ultrapure water, the lack of alkalinity enhances the extraction of alkaline compounds from ash, leading to a more pronounced increase in alkalinity. In contrast, river water contains alkaline

species (e.g., bicarbonate, carbonate), which buffer the system, limit the leaching of alkaline compounds, and moderate shifts in alkalinity. This highlights the critical role of background water quality in moderating ash-induced changes in alkalinity.

The responses of WAIW prepared using Elbow River (TC+ER) and ultrapure (TC+UP) water to coagulation using 40 mg L^{-1} of alum is shown in Figure 5-8. While coagulation effectively reduced turbidity in all cases, relative removal was slightly greater in WAIWs prepared with ultrapure water (97%) than in those prepared with Elbow River water (93%; Figure 5-8a). However, residual turbidity remained significantly higher in the former (4.6 NTU vs. 0.9 NTU, respectively). This difference is likely attributable to the absence of ionic strength in ultrapure water, which can increase the extent of the particle double layer, impair floc formation, and hinder effective particle aggregation during coagulation (Crittenden et al., 2012).

DOC removal was similar across WAIWs prepared with Elbow River and ultrapure water, with reductions of approximately 9% and 10%, respectively (Figure 5-8b). While these removal percentages are lower than previously reported values (Hohner et al., 2017), both studies found comparable removal efficiency in water with and without background organic matter, suggesting coagulation response is largely governed by the concentration and character of wildfire ash-derived organic matter, rather than the background water quality itself.

The highest SUVA reduction, following coagulation was observed in Elbow River water without ash, while the lowest occurred in WAIWs prepared with Elbow River water (Figure 5-8c). This suggests a shift in organic matter character following wildfire ash addition, with increased proportions of compounds that are less reactive with alum, as discussed previously. Notably, SUVA reduction was greater in WAIWs prepared with ultrapure water than in those with Elbow River water. This highlights the impact of the background water matrix on coagulation. In ultrapure water, ash-derived WEOM is the only source of organic matter. In contrast, WEOM from ash interacts with Elbow River water natural organic matter, yielding a more complex and diverse organic matter mixture with broader molecular size distribution and inherently lower SUVA. Consequently, identical alum doses produce smaller SUVA reduction in the mixed Elbow River system compared to ultrapure water. These results collectively show the impact background water chemistry and organic matter concentration and character in influencing coagulant dose and suggest the potential need for higher coagulant doses or alternative treatment strategies to effectively manage organic matter in wildfire ash-impacted source waters.

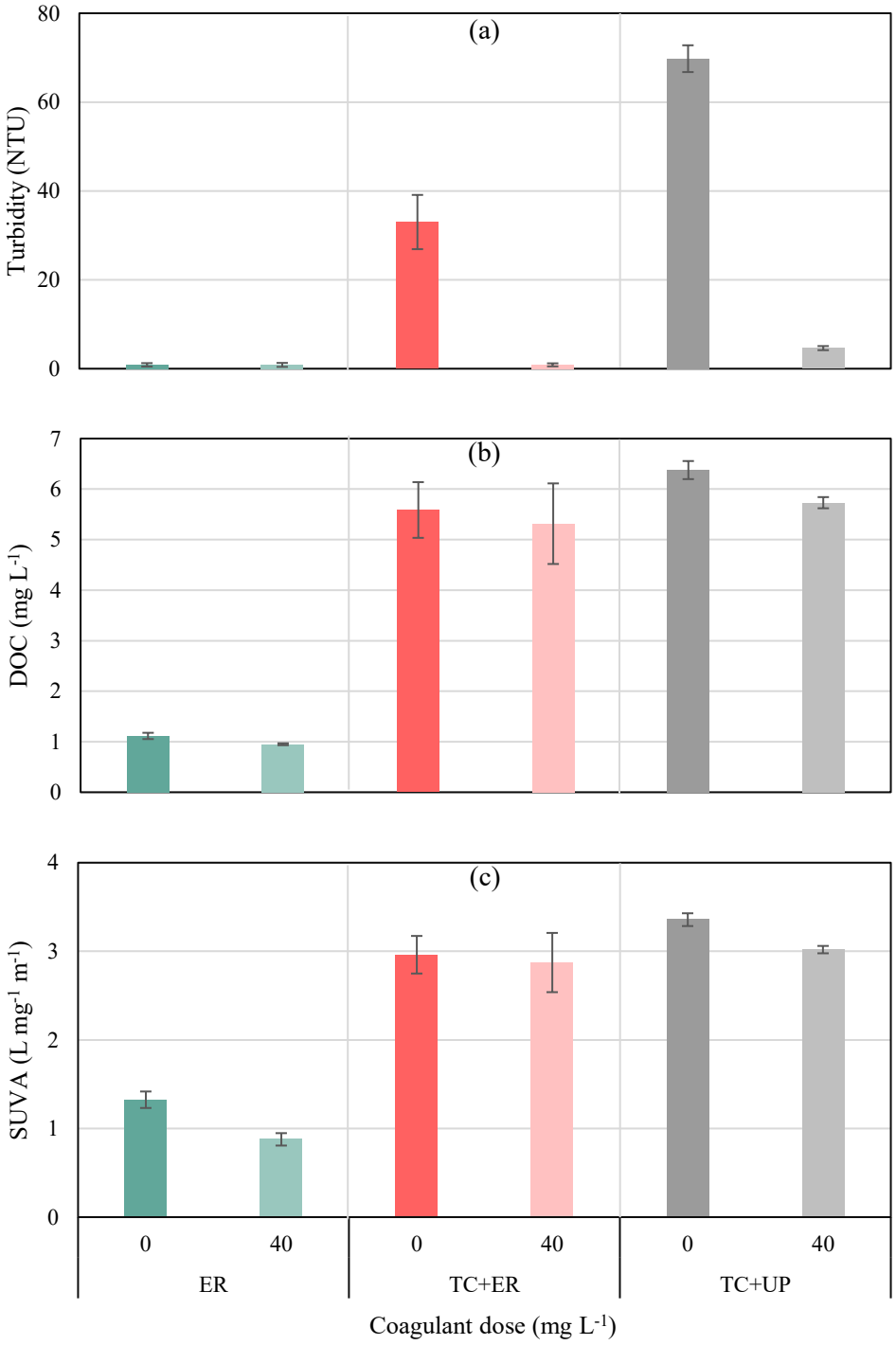


Figure 5-8 Changes in a) turbidity, b) DOC concentration, and c) SUVA values before and after coagulation of Elbow River water (ER), TC ash-impacted water using Elbow River (TC+ER), and ultrapure water (TC+UP). Each bar represents the average value (n = 3), with error bars representing standard deviation.

5.4 Conclusions and implications

This study systematically confirmed that WAIW coagulation does not introduce fundamentally new challenges by assessing coagulation performance measures (i.e., turbidity reduction and DOC removal). In all experimental scenarios, wildfire ash consistently altered source water quality by increasing turbidity, alkalinity, and DOC concentrations, and shifting organic matter character. Key findings are:

- The deterioration in water quality following ash addition reduced the effectiveness of conventional alum coagulation, resulting in lower organic matter removal compared to unimpacted waters. This suggests that enhanced coagulation and/or increased coagulant doses may be necessary for effective organic matter removal in WAIW.

- Even the lowest alum concentrations reduced turbidity substantially across all experiments; thus, minimal coagulant inputs can achieve some turbidity reduction. This indicates that post-fire treatment challenges are not primarily associated with particle removal but are instead dominated by the presence of dissolved organic matter and associated coagulant demand required for destabilizing solids so that they can be sufficiently removed.

- Enhanced coagulation improved DOC removal in WAIW, likely by facilitating greater adsorption and complexation of organic matter onto aluminum species. The extent of improvement was insufficient to meet the targets established by the U.S. EPA (1999) for some ash types. This limitation may be attributed to the presence of high concentrations of hydrophilic and/or low molecular weight organic fractions introduced by wildfire ash. Enhanced coagulation led to reduced turbidity removal in some cases, potentially due to changes in floc structure as well as competition of organic matter and other reactive compounds for aluminum binding under lower pH conditions. This suggests that while enhanced coagulation can provide incremental DOC removal benefits, it may also introduce trade-offs in particle removal efficiency.

- The chemistry of the background water matrix, including metrics such as alkalinity, ionic strength, and initial organic matter concentration, can substantially affect both turbidity reduction and organic matter removal in WAIW coagulation. Higher alkalinity can buffer pH changes during coagulation, limiting the formation of optimal coagulant hydrolysis products, while higher DOC concentration can increase coagulant demand.

All these observations align with what has been widely observed in natural waters unaffected by wildfire. Collectively, these findings demonstrate that while wildfire ash can deteriorate source water quality to varying degrees, its effects on coagulation performance are consistent with those observed in other natural surface waters. In WAIW, background water chemistry and the concentration and character of organic matter are the primary factors governing coagulation outcomes. These results also suggest that the magnitude and rapid fluctuations of post-fire water quality present the greatest risks to coagulation effectiveness.

Chapter 6

Summary of findings and future work

6.1 Summary and key contributions

Wildfire ash can deteriorate drinking water source water quality by inducing a range of physical and chemical changes, including elevated alkalinity, turbidity, and dissolved organic carbon (DOC), along with alterations in organic matter composition. These changes can disrupt drinking water treatment by reducing coagulation efficiency, shortening filter run times, and increasing disinfectant demand, leading to complex operational, regulatory, and public health challenges. Operationally, they may require more advanced and costly process adjustments. From a regulatory standpoint, they can increase the risk of non-compliance with drinking water standards. Public health concerns may also arise, as these impacts may compromise the delivery of safe drinking water.

Research into wildfire impacts on drinking water treatability has grown substantially in recent years. However, comparison and synthesis of findings have been constrained by differences in experimental design, especially in the preparation of wildfire ash-impacted waters (WAIWs) for bench-scale testing. Variations in ash pretreatment methods, mixing durations and procedures, ash-to-water ratios, and the chemistry of the background water matrix have produced results that are not only inconsistent but, in some cases, contradictory, as discussed in Chapters 2 and 3. Thus, uncertainties remain regarding the robustness and applicability of research findings, which limit their use in guiding real-world emergency preparedness, post-fire water management, and the development of broadly applicable risk management strategies for utilities.

This research was undertaken to help provide insights that could inform the design of future investigations and the implementation of effective operational responses to wildfire impacts on drinking water treatment. Achieving this required a structured, sequential approach that systematically addressed major sources of uncertainty in existing WAIW quality and treatability research.

In Chapter 2, the impacts of WAIW preparation methods that can substantially impact the concentration and character of water-extractable organic matter (WEOM) were evaluated. Across six ash types originating from multiple wildfires and a prescribed burn, dissolved organic carbon (DOC) concentrations increased most rapidly within the first 24 hours of mixing, after which values either plateaued or declined. This temporal pattern suggests that shorter mixing durations, common to many bench-scale assessments of wildfire threats to drinking water treatability, risk underestimating DOC release, while extended mixing periods may alter organic matter concentration and character, likely due to biodegradation, particle settling, or other secondary processes. Based on these findings, a 24-hour mixing period is recommended for worst-case treatability testing, as it maximizes WEOM yield while

providing a reproducible benchmark for comparative studies and minimizing methodological bias. Ash type also affected DOC yield; however, neither ash color nor bulk organic content served as reliable predictors of leaching potential. This finding challenges the common assumption that darker ash, typically associated with lower combustion completeness, will always release more DOC. In several cases, lighter-colored ash, presumed to result from more complete combustion, produced the highest DOC concentrations. Such results highlight the shortcomings of visual proxies when characterizing ash. The chemistry of the source water was equally important in determining WEOM release. Ultrapure water with almost no ionic strength, buffering capacity, and organic matter concentration consistently facilitated higher DOC concentrations than natural river water, underscoring the importance of water matrix in impacting extraction dynamics. At higher ash-to-water ratios, the normalized DOC yield (expressed as mg DOC per g ash) declined, indicating that solubility gets limited, and electrostatic interactions constrain DOC release in more concentrated suspensions.

In Chapter 3, the evaluation of how different ash pretreatment techniques affect WEOM leaching was conducted to address a key methodological gap. Three common pretreatment techniques (manual separation, sieving, and pulverization) were applied to two ash fractions to assess their effect on sample consistency and WEOM characteristics. Sieving consistently resulted in more reproducible replicates by removing large, non-representative debris such as rocks, unburned vegetation, and pyrogenic material. Both sieving and pulverization homogenized ash and reduced within-sample variability; however, pulverization impacted the character of leached WEOM, likely due to increased surface reactivity and exposure of organic matter that was previously encapsulated within larger particles. Additionally, pulverization presents practical drawbacks, including the risk of ash particles becoming airborne during handling, which raises safety and contamination concerns. For these reasons, its use should be reserved for situations where such processing is clearly necessary to meet specific research objectives. The results also showed that WAIWs prepared using coarse ash fractions showed greater variability in dissolved organic carbon (DOC) and specific ultraviolet absorbance (SUVA) than fine fractions, reflecting the heterogeneous nature of those wildfire ash fractions. In most cases, large particles and/or the presence of compacted soil or rock in the coarse fractions limited the leachability of WEOM. In contrast, fine fractions typically contained higher proportions of pyrogenic material and yielded higher DOC concentrations. In the absence of system-specific preparation protocols, sieving offers a practical compromise between replicates reproducibility and representativeness. This approach reduces unwanted sample heterogeneity while avoiding the chemical alterations that more aggressive processing can introduce, providing a more reliable basis for comparing results across wildfire ash treatability studies.

Chapter 4 assessed the role of settleable ash solids (SAS) in altering alkalinity and pH of WAIW and evaluated their implications on coagulation performance. Wildfire ash, rich in carbonates and other alkaline minerals, substantially increased alkalinity in WAIW. While dissolved, colloidal, and settleable particles impacted alkalinity to different degrees, SAS acted as a long-term source of alkalinity. This persistent buffering effect poses a challenge for coagulation and required pH adjustment for enhanced DOC removal. Bench-scale experiments demonstrated that removing SAS reduced this persistent source of alkalinity (thereby lowering coagulant demand) and further improved coagulation performance in removing DOC. However, it also hindered floc formation and reduced turbidity removal. The initial dissolution of alkaline compounds increased alkalinity in all WAIWs, indicating that while managing SAS through physical removal may reduce coagulant and/or acid demand, it does not fully address the alkalinity and pH-related challenges associated with post-fire water treatment. Effective adaptation strategies must also address the residual dissolved alkalinity, which may require operational adjustments such as pH correction, increased coagulant dosing, or the use of alternative treatment methods.

Chapter 5 mechanistically confirmed that wildfire ash does not fundamentally alter the coagulation mechanisms of WAIW. In all cases, the impacts of wildfire ash on water quality and coagulation were consistent with established understanding of coagulation processes. DOC removal was limited at conventional coagulation. While enhanced coagulation improved DOC removal minimally, its effectiveness was limited by the character of the organic matter, particularly the high concentrations of LMW compounds that cannot readily adsorb onto metal salt coagulants and form precipitates. Overall, the findings of this chapter demonstrate that the coagulation performance of WAIW is governed by multiple interacting factors, including the concentration and composition of organic matter and the background water quality.

The results of this study offer novel and fundamental insights that contribute to the advancement of understanding of how wildfire impacts on drinking water treatability can be assessed. The results provide practical considerations for designing bench-scale drinking water treatability studies to address the intended research objectives. They also highlight the importance of clearly defining study objectives and providing explicit justification for the chosen experimental approach, as these decisions directly affect the relevance, comparability, and applicability of the results.

6.2 Future work

While this study provided novel insights into the bench-scale preparation and coagulation of WAIWs, it has also identified several avenues for further investigation. The identified knowledge gaps for further investigation are required to deepen understanding of wildfire ash effects on drinking water treatability, refine experimental approaches, and strengthen the preparedness of water utilities facing post-fire conditions. Future research recommendations are as follows:

- Assessing light exposure and water temperature effects on the release, biodegradation, and transformation of WEOM from wildfire ash. In nutrient-enriched systems, such as WAIWs, sunlight exposure with warmer water temperatures can stimulate microbial growth. This may alter WEOM concentration and character over time, shift the balance between particulate and dissolved fractions, and impact WAIW treatability. Experiments should simulate realistic light/dark exposure at different temperatures to reflect seasonal and climatic variability. They should also track not only chemical changes in WEOM but also shifts in microbial community activity, providing an understanding of the microbial community impact on organic matter transformation following wildfires.
- Determining how varying source water qualities, particularly from deteriorated sources such as urban-impacted areas, impact the release of WEOM from wildfire ash. Such waters frequently contain high concentrations of organic matter, nutrients, and a wide array of chemical constituents, all of which can alter the leaching dynamics of wildfire ash and impact the treatability of affected water. As severe and large-scale wildfires increasingly burn through regions not historically classified as fire-prone, already deteriorated water sources may now face additional stress from ash deposition. Understanding how these complex water quality conditions affect WEOM leaching is critical for enhancing the applicability of laboratory findings and guiding the development of region-specific water treatment and management strategies.

- Assessing process trade-offs when applying mitigation strategies aimed at improving DOC removal. For example, removing SAS or adjusting pH can improve DOC removal efficiency but may also reduce turbidity removal performance. Understanding the conditions under which such trade-offs occur, and quantifying their magnitude, would allow utilities to choose treatment adjustments that balance particle and organic matter removal.

- Bridging the gap between bench-scale findings and pilot- or full-scale treatment performance. Laboratory experiments offer controlled conditions that are essential for isolating variables, but they do not capture the full complexity of operational systems. Larger-scale systems experience fluctuating flows, variations in hydraulic retention times, changing environmental conditions, and process interactions that can modify treatment outcomes. Future research should therefore evaluate how processes identified as effective at the bench scale perform under real-world constraints. This work should include side-by-side comparisons of bench, pilot, and full-scale results to identify scale-dependent differences and help with operational decision-making.
- Investigating long-term, full-scale monitoring of source water quality and treatment performance after wildfires. Such studies can provide essential data on immediate and delayed consequences of ash inputs. These monitoring programs should span multiple years to capture seasonal cycles and hydroclimatic variability.
- Evaluating the duration over which wildfire ash continues to release WEOM in dynamic systems such as rivers and reservoirs. Ash that settles in water may exert prolonged impacts by gradually leaching nutrients, metals, and organic matter into the overlying water column. Simulating reservoir and river systems under conditions that maintain a continuous flow of water over deposited ash would be especially valuable for assessing these dynamics. Such studies could help determine whether the release of various compounds is predominantly an acute, short-term event or a protracted process extending over weeks or even months, thus contributing to long-term water quality concerns. Investigating the rates, mechanisms, and environmental conditions governing these releases, along with their ecological implications for reservoirs and downstream treatment challenges, is essential for anticipating delayed water quality impacts and guiding sediment management strategies.

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Appendices

Appendix A

Supporting information for

Chapter 2

Table A1 Nominal Elbow River water quality during the study.

Metric	Value
Turbidity (NTU)	1.0-5.0
pH	8.0-8.5
Alkalinity (mg L^{-1} as $CaCO_3$)	140-170
SUVA (L mg^{-1} m^{-1})	1.0-3.0
DOC (mg L^{-1})	1.0-2.0

Table A2 Minimum reporting limits for the water quality metrics analyzed in this study.

Metric	**Compound/fraction**	**Minimum Reporting Level**
UV_{254}	-	0.005 cm^{-1}
DOC	-	0.1 mg L^{-1}
THMs	TCM	0.6 µg L^{-1}
	BDCM	0.6 µg L^{-1}
	DBCM	0.7 µg L^{-1}
	TBM	0.9 µg L^{-1}
HAAs	MCAA	6.4 µg L^{-1}
	MBAA	5.9 µg L^{-1}
	DCAA	4.0 µg L^{-1}
	TCAA	4.6 µg L^{-1}
	DBAA	5.2 µg L^{-1}
LC-OCD	Biopolymers	26 µg L^{-1}
	Humic Substances	26 µg L^{-1}
	Building Blocks	77 µg L^{-1}
	Low Molecular Weight Acids	-
	Low Molecular Weight Neutrals	131 µg L^{-1}

Table A3 *p*-values resulting from Wilcoxon Signed rank test (n = 18).

	30 min	*6 h*	*24 h*
30 min		0.000	0.000
6 h	0.000		0.000
24 h	0.000	0.000	

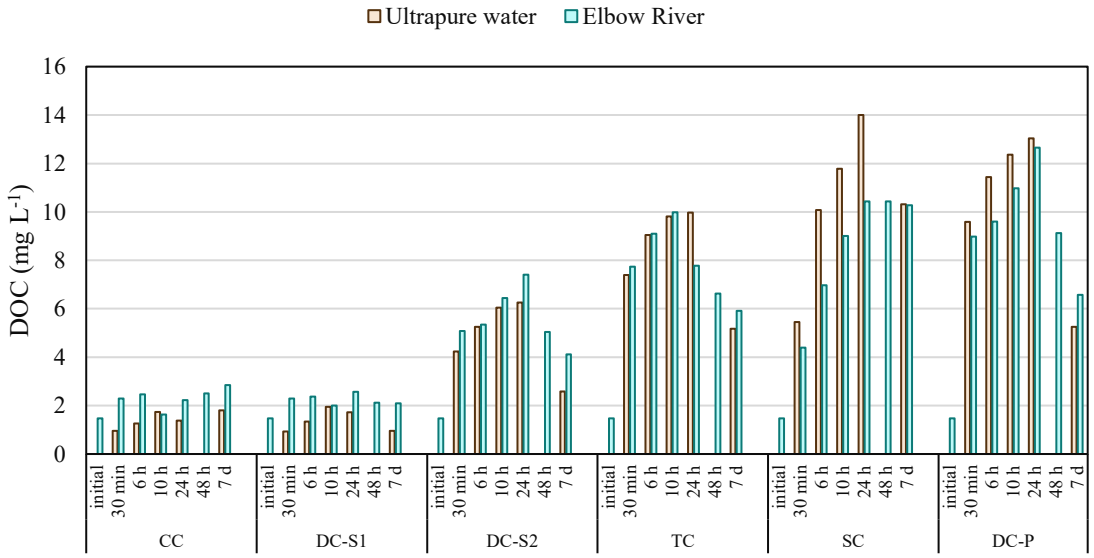


Figure A1 Change in DOC concentration in WAIWs prepared using ultrapure and Elbow River water at different sampling times during 7 days of experiment. Light brown and turquoise bars represent DOC concentrations for WAIW prepareed in ultrapure and Elbow River water, respectively. Initial sampling points represent values for ultrapure/raw water with no ash.

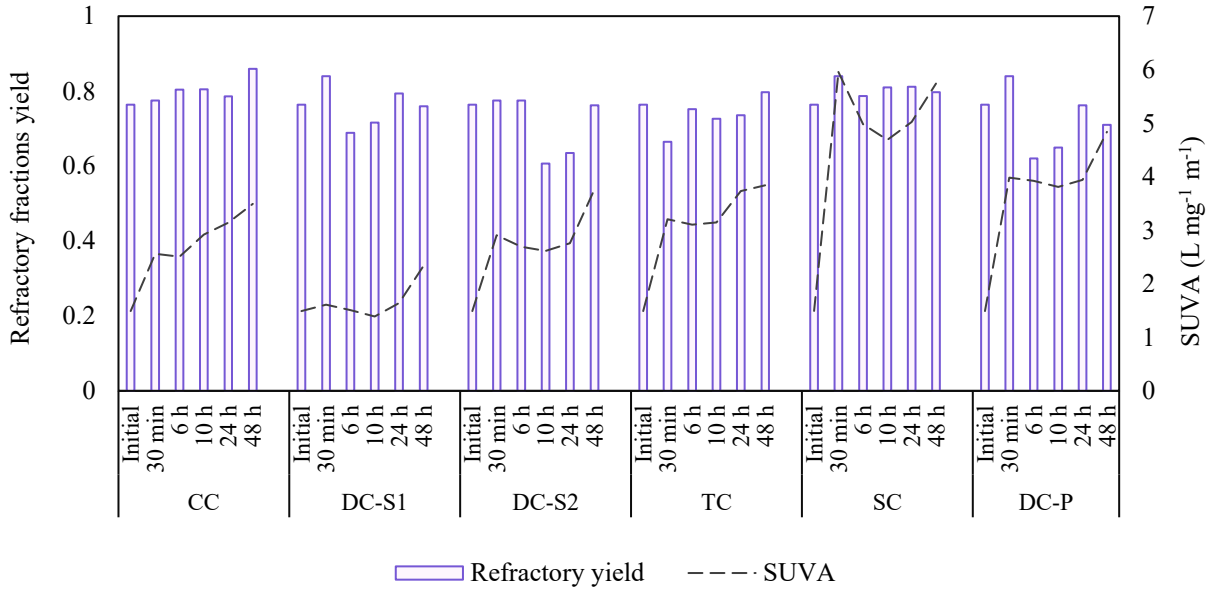


Figure A2 Comparison between refractory fraction of dissolved organic matter yield (including humic substances and building blocks) and SUVA over time for WAIWs prepared in Elbow River water.

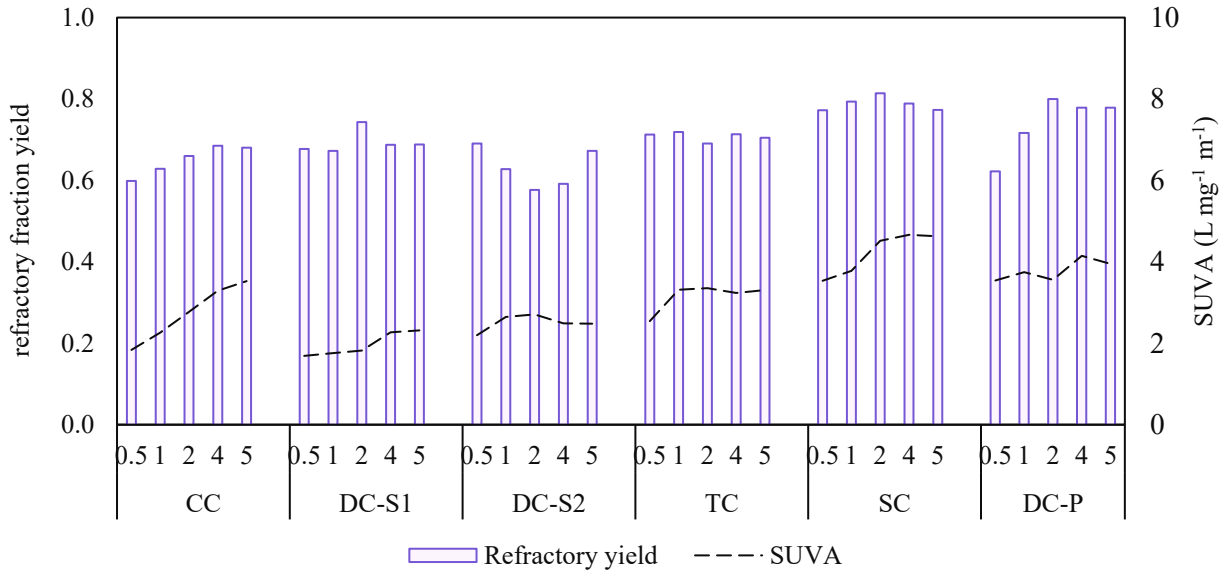


Figure A3 Comparison between refractory fraction of dissolved organic matter yield (including humic substances and building blocks) and SUVA for WAIWs with different ash mass concentrations prepared in Elbow River water.

Appendix B

Supporting information for

Chapter 3

Table B1 Minimum reporting limits for the water quality metrics analyzed in this study.

Metric	Compound/fraction	Minimum Reporting Level
UV_{254}	-	0.005 cm^{-1}
DOC	-	0.1 mg L^{-1}
LC-OCD	Biopolymers	26 µg L^{-1}
	Humic Substances	26 µg L^{-1}
	Building Blocks	77 µg L^{-1}
	Low Molecular Weight Acids	-
	Low Molecular Weight Neutrals	131 µg L^{-1}

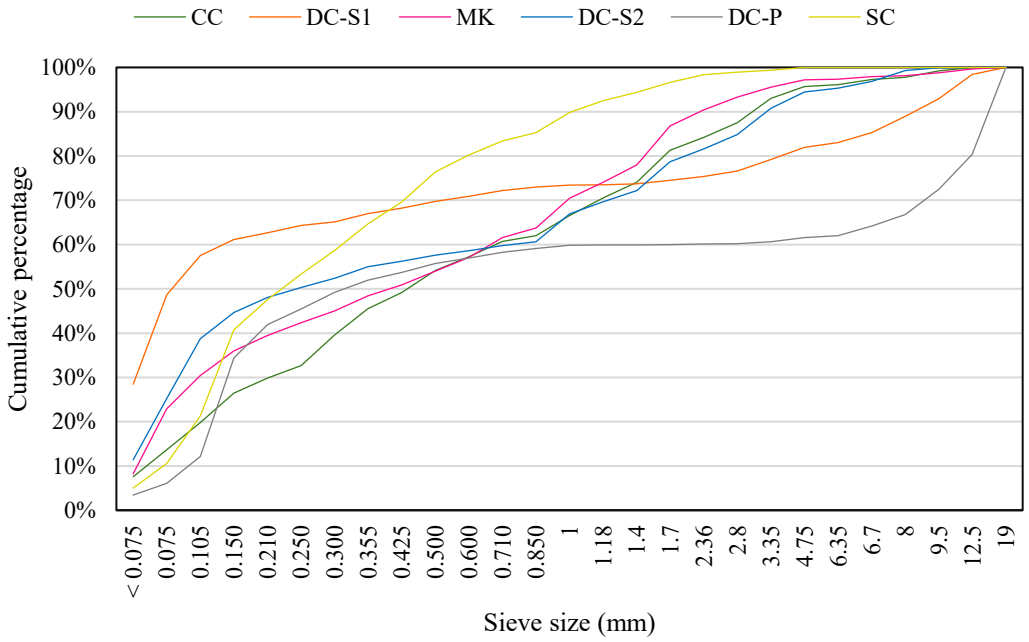


Figure B1 Cumulative particle size distribution of different ash types.

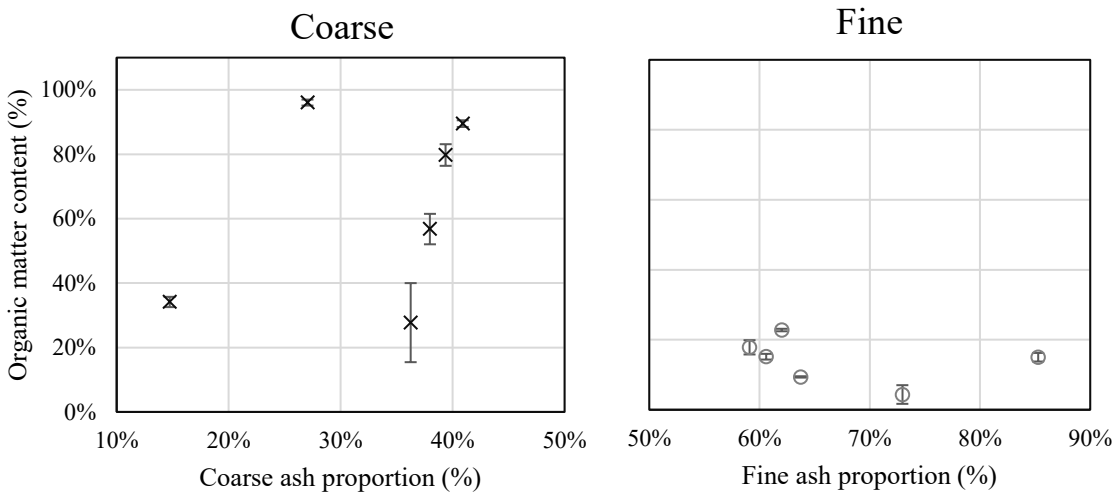


Figure B2 The proportion of coarse and fine ash and their associated organic matter content obtained by LOI.

Table B2 Particle size distribution for different ash types.

Ash type	D10 (mm)	D50 (mm)	D90 (mm)
CC	0.074	0.44	3.02
DC-S1	0.074	0.078	8.38
MK	0.074	0.40	2.36
DC-S2	0.074	0.25	3.26
DC-P	0.095	0.32	15.8
SC	0.075	0.23	1

Table B3 ANOVA and Mann-Whitney test results for comparisons between coarse and fine fractions of different ash types (n = 18).

	p-value	F	z
CC	0.07	3.45	
DC-S1	0.006	8.78	
MK	0.03	4.86	
DC-S2	0.82	0.05	
DC-P	0.02		2.40
SC	0.002		3.10

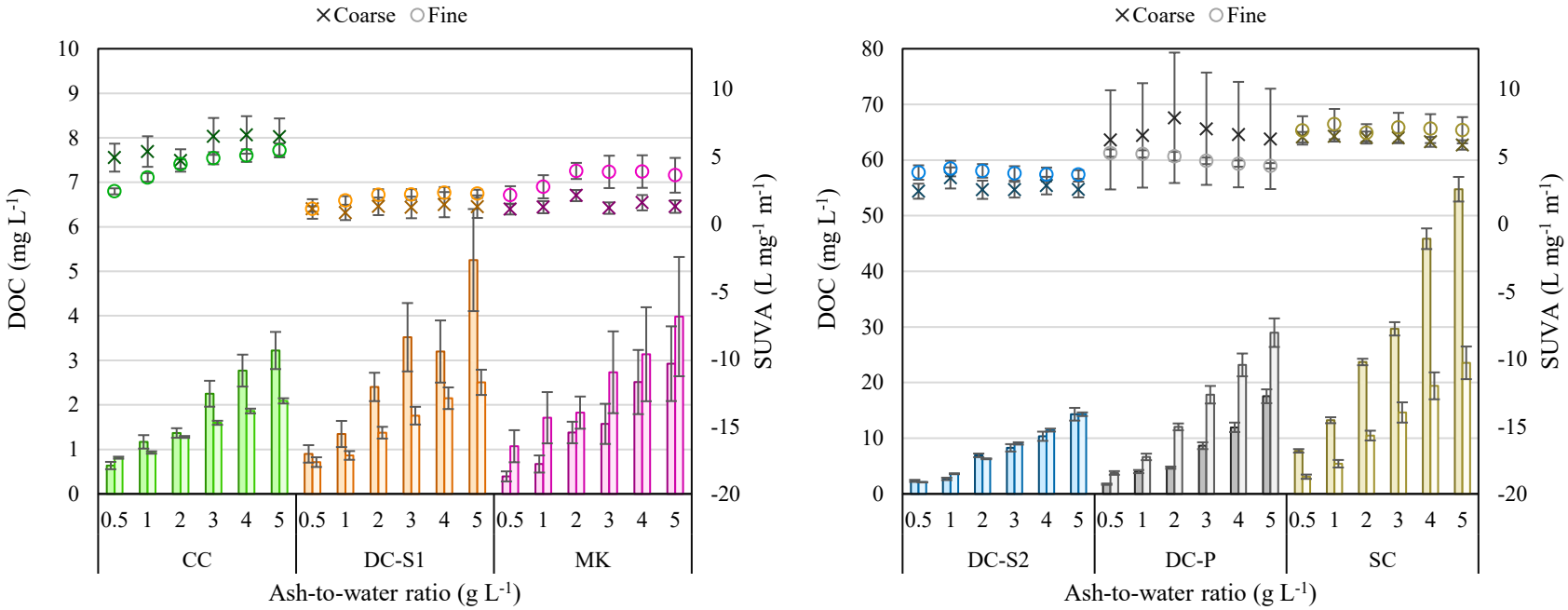


Figure B3 Changes in WEOM concentration and character (i.e., DOC and SUVA) for coarse and fine WAIWs across a range of ash-to-water ratios. For each concentration, darker and lighter bars show DOC concentrations for coarse and fine WAIWs, respectively, and crosses and circles show SUVA for coarse and fine WAIWs, respectively. Each bar/symbol represents the average values (n = 3) with error bars representing standard deviation.

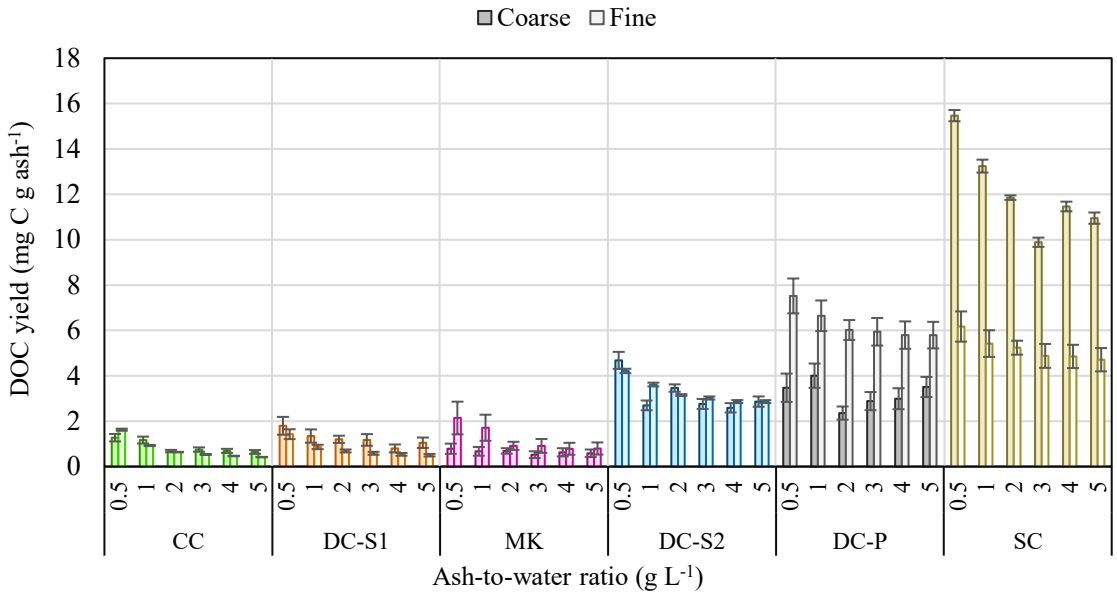


Figure B4 DOC yield, calculated as DOC per gram of ash, for coarse and fine WAIW samples across a range of ash-to-water ratios. Ash types are color-coded as follows: green (CC), orange (DC-S1), purple (MK), blue (DC-S2), grey (DC-P), and yellow (SC). For each sampling time, darker and lighter bars show DOC concentrations for coarse and fine WAIWs, respectively. Each bar represents the average values (n = 3) with error bars representing standard deviation.

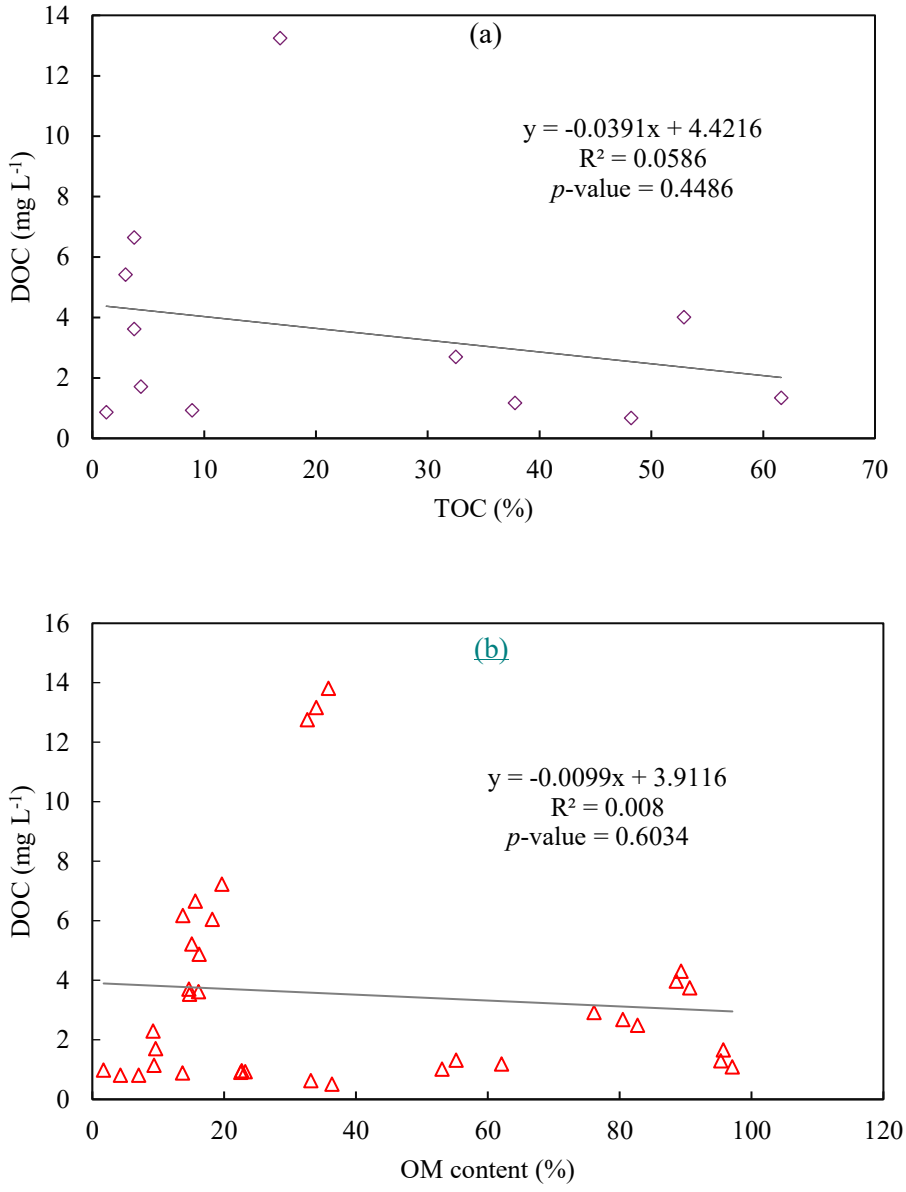


Figure B5 Least squares linear regression relationship between aqueous DOC concentration a) TOC and b) OM content in coarse and fine fractions of different ash types.

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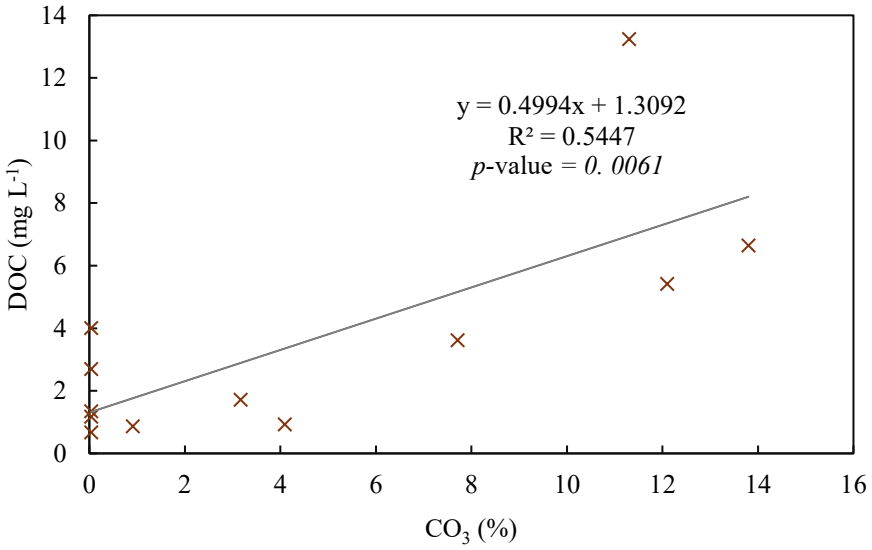


Figure B6 Least squares linear regression relationship between DOC concentration and carbonate content in coarse and fine fractions of different ash types.

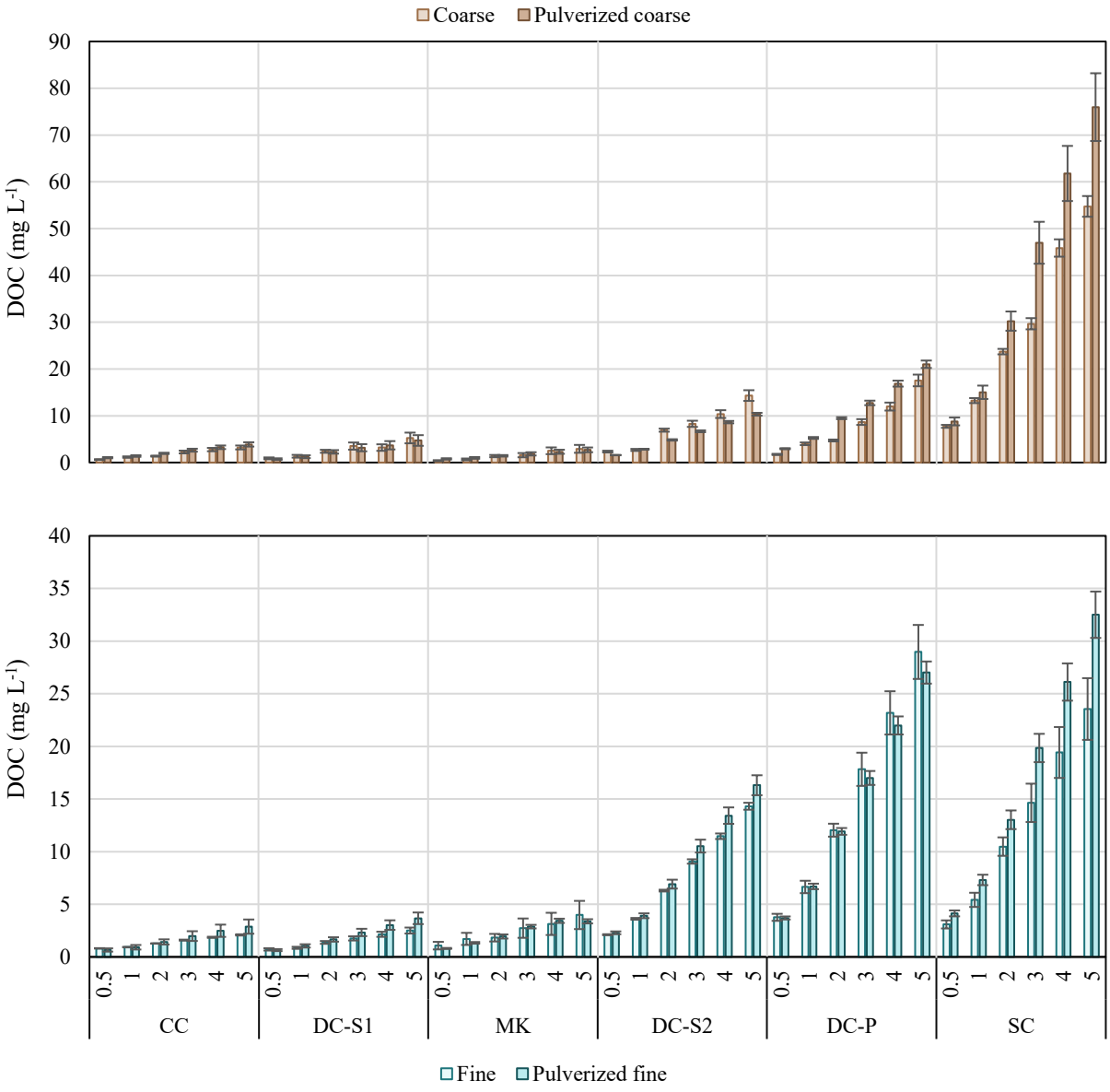


Figure B7 Changes in DOC concentrations for coarse, pulverized coarse, fine and pulverized fine WAIWs across a range of ash-to-water ratios. The graph on top represents coarse and pulverized coarse WAIWs, while the one on the bottom corresponds to fine and pulverized fine WAIWs. The experiments were run in triplicate, and the average values with standard deviations (error bars) are shown. Lighter bars on the left indicate DOC concentrations for coarse and fine ash, while darker bars on the right represent pulverized WAIWs.

Table B4 ANOVA and Mann-Whitney test results for comparisons between coarse and pulverized coarse and fine and pulverized fine ash (n = 18).

	Fine vs. pulverized fine		Coarse vs. pulverized corase		
	p-value	F	*p*-value	F	z
CC	0.009	4.26	0.000	4.26	
DC-S1	0.000	4.26	0.56	4.26	
MK	0.12	0.32	0.47	4.26	
DC-S2	0.000	4.26	0.000	4.26	
DC-P	0.09	4.26	0.09		1.71
SC	0.000	4.26	0.16		1.39

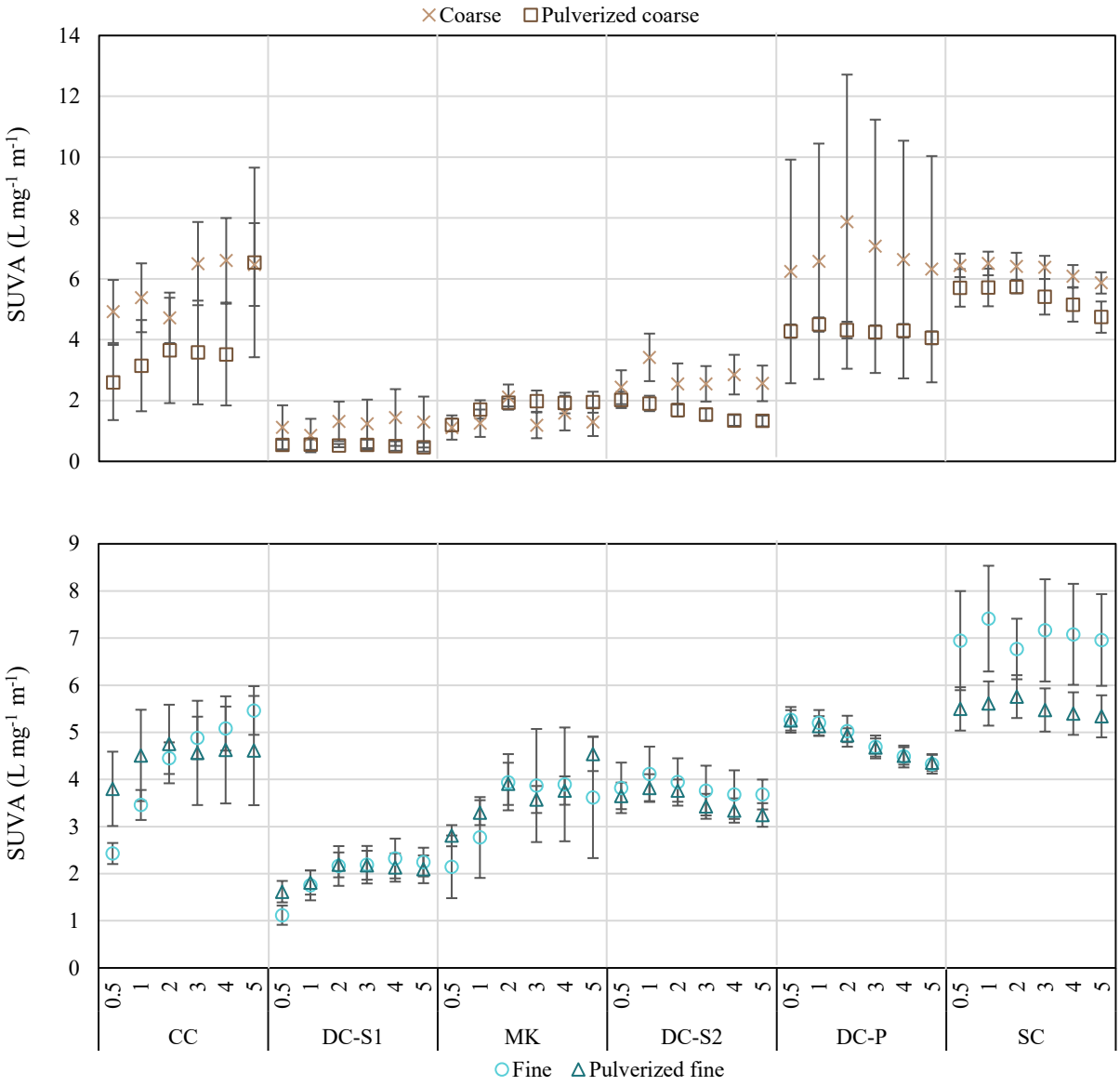


Figure B8 Changes in SUVA values for coarse, pulverized coarse, fine and pulverized fine WAIWs across a range of ash-to-water ratios. The graph on top represents coarse and pulverized coarse WAIWs, while the one on the bottom corresponds to fine and pulverized fine WAIWs. The experiments were run in triplicate, and the average values with standard deviations are shown. Crosses and circles show SUVA values for coarse and fine ash, while squares and triangles indicate values for pulverized coarse and pulverized fine ash, respectively.

Appendix C

Supporting information for

Chapter 4

Table C1 Nominal Elbow River water quality during the study.

Metric	Value
Turbidity (NTU)	1.00-2.00
pH	8.0-8.1
Alkalinity (mg L^{-1} as $CaCO_3$)	165-175
SUVA (L mg^{-1} m^{-1})	1.2-1.5
DOC (mg L^{-1})	0.9-1.2

Table C2 Minimum reporting limits for the water quality metrics analyzed in this study.

Metric	**Compound/fraction**	**Minimum Reporting Level**
UV_{254}	-	0.005 cm^{-1}
DOC	-	0.1 mg L^{-1}
Turbidity	-	0.05 NTU
THMs	TCM	0.6 µg L^{-1}
	BDCM	0.6 µg L^{-1}
	DBCM	0.7 µg L^{-1}
	TBM	0.9 µg L^{-1}
HAAs	MCAA	6.4 µg L^{-1}
	MBAA	5.9 µg L^{-1}
	DCAA	4.0 µg L^{-1}
	TCAA	4.6 µg L^{-1}
	DBAA	5.2 µg L^{-1}

Table C3 pH of WAIWs prepared using coarse and fine ash across a range of ash-to-water ratios.

Ash type	Ash-to-water ratio (g L^{-1})	Coarse	Fine
CC	0.5	7.3	6.8
	1	7.9	7.0
	2	8.0	7.3
	3	8.0	7.4
	4	8.0	7.5
	5	8.0	7.6
DC-S1	0.5	6.1	6.9
	1	6.3	7.1
	2	6.5	7.5
	3	6.6	7.7
	4	6.7	7.8
	5	6.7	7.9
MK	0.5	5.7	7.1
	1	6.0	7.4
	2	6.1	7.7
	3	5.8	7.8
	4	5.7	8.9
	5	6.1	7.9
DC-S2	0.5	6.9	8.0
	1	7.2	8.1
	2	7.4	8.3
	3	7.6	8.5
	4	7.7	8.6
	5	7.6	8.6
T	0.5	-	8.3
	1	-	8.5
	2	-	8.7
	3	-	8.9
	4	-	8.9
	5	-	8.8
DC-P	0.5	7.9	8.6
	1	8.6	9.2
	2	8.8	9.3
	3	8.9	9.4
	4	8.9	9.4
	5	8.9	9.4
SC	0.5	6.6	8.1
	1	6.8	8.2
	2	7.1	8.5
	3	7.2	8.6
	4	7.3	8.7
	5	7.2	8.8

Table C4 Alkalinity of WAIWs prepared using coarse and fine ash across a range of ash-to-water ratios.

Ash type	Ash-to-water ratio (g L^{-1})	Coarse		Fine	
		unsettled	decanted	unsettled	decanted
CC	0.5	19	18	12	7
	1	77	49	22	8
	2	115	58	33	12
	3	185	80	42	15
	4	243	112	57	22
	5	310	112	73	25
DC-S1	0.5	4	4	8	5
	1	6	5	17	12
	2	8	7	30	23
	3	10	9	42	30
	4	12	10	58	32
	5	15	12	67	40
MK	0.5	3	3	13	12
	1	4	4	27	20
	2	5	4	50	25
	3	5	5	72	32
	4	7	6	90	37
	5	9	7	113	40
DC-S2	0.5	12	10	67	43
	1	21	15	120	43
	2	28	22	225	48
	3	51	35	350	50
	4	85	45	450	55
	5	75	46	567	60
T	0.5	-		58	35
	1	-		113	40
	2	-		227	43
	3	-		300	47
	4	-		417	57
	5	-		500	57
DC-P	0.5	6	6	125	43
	1	8	8	217	47
	2	19	14	458	57
	3	28	20	683	62
	4	40	22	942	70
	5	40	29	1175	75
SC	0.5	50	40	73	40
	1	105	75	137	58
	2	186	95	233	70
	3	265	112	367	85
	4	360	146	508	98
	5	447	180	567	102

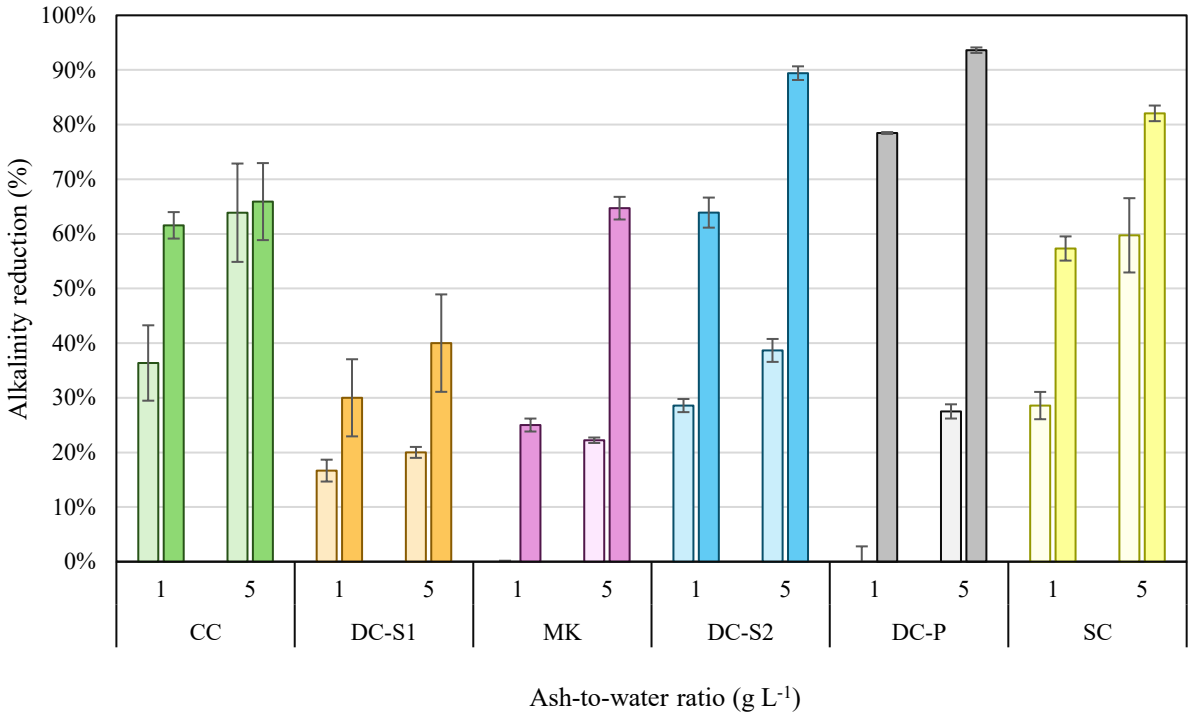


Figure C1 Alkalinity in WAIWs prepared using 1 g L^{-1} and 5 g L^{-1} of coarse and fine fractions of different ash types. For each ash type, lighter and darker bars respectively indicate coarse and fine WAIW alkalinity. Each bar represents the average values (n = 3) with error bars representing standard deviation.

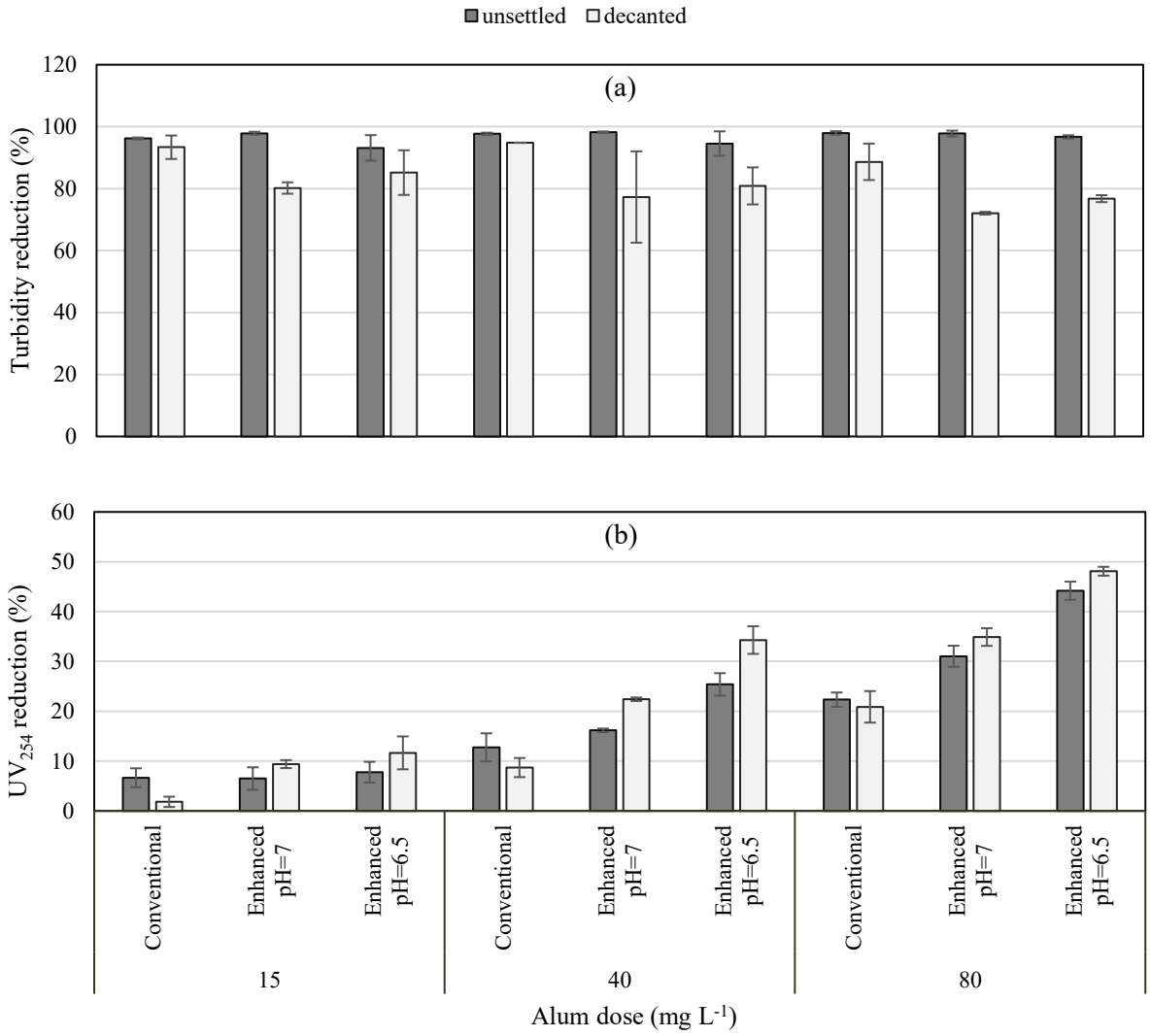


Figure C2 (a) turbidity, and (b) UV_{254} reduction in unsettled and decanted WAIWs. Darker grey bars represent values in unsettled WAIWs, and adjacent lighter bars represent decanted WAIWs. Each data point represents mean values with error bars indicating standard deviation (n = 3).

Table C5 DBP-UFC and -FP for control and coagulated WAIW, with and without SAS.

Sample	THM-UFC ($\mu g\ L^{-1}$)	HAA-UFC ($\mu g\ L^{-1}$)	THM-FP ($\mu g\ L^{-1}$)	HAA-FP ($\mu g\ L^{-1}$)	DOC ($mg\ L^{-1}$)
Control - unsettled	193 ± 15	353 ± 15	273 ± 21	1580 ± 108	6.5 ± 0.2
80 mg L^{-1} alum - pH=6.5 - unsettled	68 ± 7	166 ± 3	139 ± 22	706 ± 108	5.0 ± 0.2
Control - decanted	122 ± 2	267 ± 26	189 ± 39	1201 ± 78	6.1 ± 0.1
80 mg L^{-1} alum - pH=6.5 - decanted	62 ± 1	171 ± 4	97 ± 20	611 ± 30	4.4 ± 0.1

Table C6 Calculation of potential impact of ash atmospheric deposition on reservoir water quality.

Assumption: 50% of produced ash load deposits in reservoir									
Reservoir	Reservoir Dimension			Ash load (kg m^{-2})	Water volume (m^3)	Ash depth (m)	Reservoir surface area (m^2)	Ash mass (kg)	Ash concentration (g L^{-1})
	Length (m)	Width (m)	Depth (m)						
Rainbow Lake	390	380	4	3.031	592,800	0.05	148,200	449,194	0.76
	390	380	7.5	3.031	1,111,500	0.05	148,200	449,194	0.40
Fort McMurray	500	320	4	3.031	640,000	0.05	160,000	484,960	0.76
	500	320	7.5	3.031	1,200,000	0.05	160,000	484,960	0.40

Assumption: 100% of produced ash load deposits in reservoir									
Reservoir	Reservoir Dimension			Ash load (kg m^{-2})	Water volume (m^3)	Ash depth (m)	Reservoir surface area (m^2)	Ash mass (kg)	Ash concentration (g L^{-1})
	Length (m)	Width (m)	Depth (m)						
Rainbow Lake	390	380	4	6.062	592,800	0.05	148,200	898,388	1.52
	390	380	7.5	6.062	1,111,500	0.05	148,200	898,388	0.81
Fort McMurray	500	320	4	6.062	640,000	0.05	160,000	969,920	1.52
	500	320	7.5	6.062	1,200,000	0.05	160,000	969,920	0.81

Appendix D

Supporting information for

Chapter 5

Table D1 Nominal Elbow River water quality during the study.

Metric	Value
Turbidity (NTU)	1.00-2.00
pH	8.0-8.1
Alkalinity (mg L^{-1} as $CaCO_3$)	165-175
SUVA (L mg^{-1} m^{-1})	1.2-1.5
DOC (mg L^{-1})	0.9-1.2

Table D2 Minimum reporting limits for the water quality metrics analyzed in this study.

Metric	**Compound/fraction**	**Minimum Reporting Level**
UV_{254}	-	0.005 cm^{-1}
DOC	-	0.1 mg L^{-1}
Turbidity	-	0.05 NTU
LC-OCD	Biopolymers	26 µg L^{-1}
	Humic Substances	26 µg L^{-1}
	Building Blocks	77 µg L^{-1}
	Low Molecular Weight Acids	-
	Low Molecular Weight Neutrals	131 µg L^{-1}

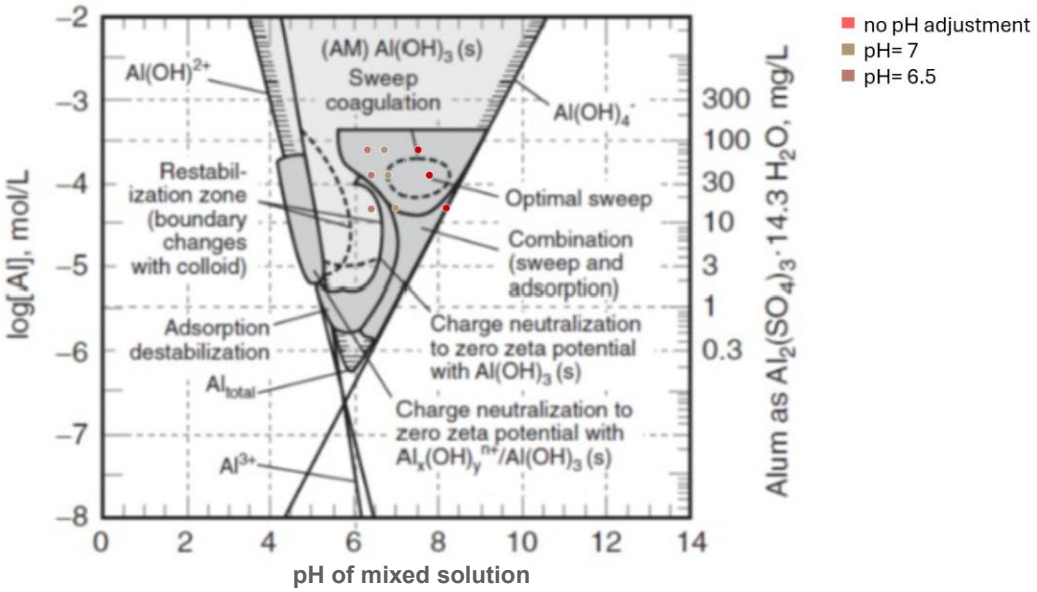


Figure D1 Alum solubility diagram (adapted from Amirtharajah & Mills, 1982) and the approximation of WAIW placement on the graph at different pH and alum concentrations.