

# **Assessing potential wildfire ash organic carbon threats to drinking water:**

## **Key considerations**

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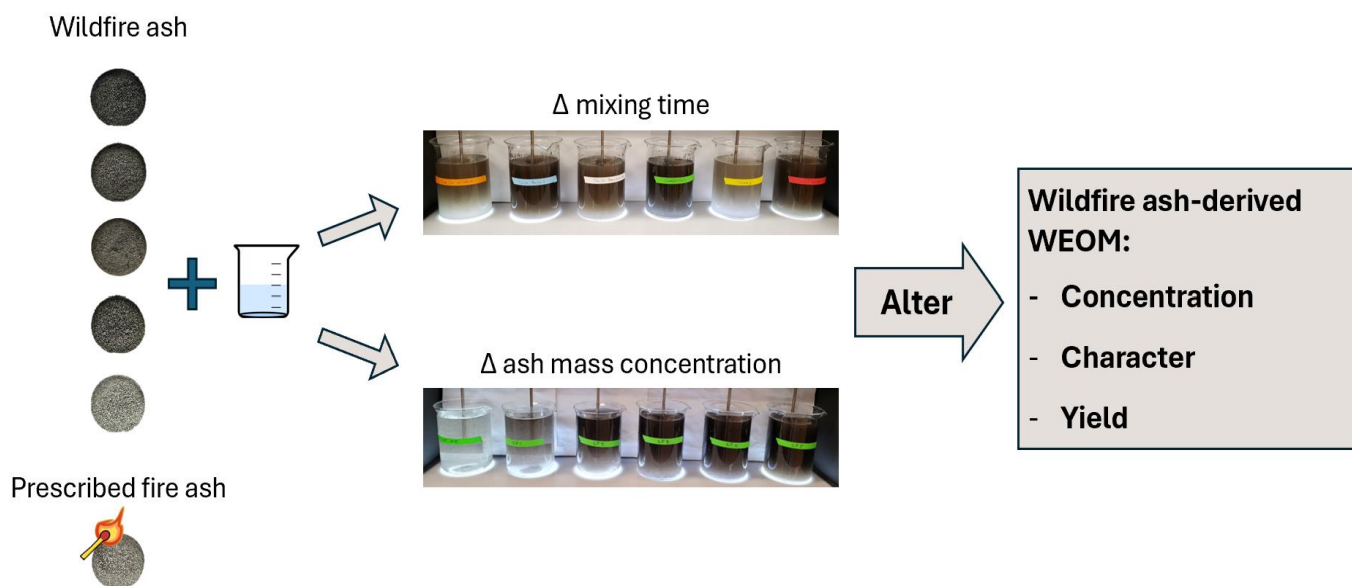
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## Abstract

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



# 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, increase stream temperature (Wagner et al., 2014; Williams et al., 2019), and change the structure of soils, decreasing infiltration capacity and increasing runoff (DeBano, 1991). Higher rates of runoff can increase the transport and delivery of sediments, nutrients, and other contaminants from hillslopes to receiving waters (Silins et al., 2009; Emelko et al., 2011; East et al., 2024). In some regions, these changes in water quality can fuel long-term (i.e., decade or longer) shifts in ecosystems (Martens et al., 2019) associated with chronic (not episodic) stress and changes in source water sediment and organic matter regimes that lead to higher turbidity, increased particulate and dissolved organic matter, and more frequent treatment challenges and upsets (e.g., higher coagulant demand, shorter filter runs, increased disinfectant demand and disinfection by-product formation potential). These impacts can be further exacerbated by wildfire suppression efforts, such as aerial application of wildfire retardants which can lead to longer-term availability of limiting nutrients such as phosphorus (Lux et al., 2025).

Warming temperatures, hydroclimatic changes, and disturbances such as wildfire can be of particular concern to drinking water treatment because they directly affect landscape processes that alter the mobility and delivery of organic carbon to water supplies (Emelko et al., 2024). Changes in concentration, character and flux of dissolved and particulate organic carbon in surface waters 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).

A wide range of changes in stream and lake organic carbon concentration and quality (e.g., aromaticity) have been reported after wildfire; impacts have ranged from long lasting and/or short-term (e.g., “first flush”) increases to no change and even to decreases in some cases (Carignan et al., 2000; Prepas et al., 2003; Mast & Clow, 2008; Betts & Jones, 2009; Emelko et al., 2011; Hohner et al., 2016; Davidson et al., 2019; Rhoads et al., 2019; Paul et al., 2022). Such variability makes it difficult to characterize the impacts of wildfire on downstream source water quality and limits the development of effective treatment operations responses and adaptation strategies. Nonetheless, the drinking water industry needs tools to support drinking water security decision-making by advancing wildfire resilience; this requires better understanding of (i) impacts of wildfire on source water quality and treatability, (ii) how long impacts may last, (iii) how far downstream impacts may propagate, and (iv) how resilient treatment processes are in responding to associated water source quality changes.

In absence of a wildfire impact that can be directly investigated, bench- and pilot-scale investigations of wildfire impacts on water quality and treatability have been widely used. They typically involve addition of either (a) ash from burned landscapes or (b) laboratory-heated materials to water to respectively produce wildfire ash-impacted water (WAIW) or a proxy that may contain materials that have been heated without combustion or burned at conditions that cannot be fully reflective of fire behavior (i.e., the variability and conditions of heating and combustion during a wildfire) (Campbell et al., 2024; Wang et al., 2025). Both types of water matrices are referred to as WAIW herein (for simplicity); a wide range of experimental (i.e., WAIW preparation and evaluation) conditions have been

reported for their preparation, including ash-to-water ratios and mixing conditions have been used (**Error! Reference source not found.**). 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 (with respect to points i to iii above), they are nonetheless important because they enable evaluation of water treatment responses to potential disturbance-associated source water quality changes (point iv above) when those changes can be sufficiently reflected in the production of WAIW. For example, recognizing that organic carbon is a key driver of drinking water treatability (Emelko et al., 2011), bench- and pilot-scale investigations that use WAIW may be designed to inform various treatment process responses to worst-case scenario water extractable organic matter (WEOM) (Skwaruk et al., 2020; Skwaruk, 2021), assess implications to specific processes such as increased coagulant demand during chemical pre-treatment or flux decline during membrane treatment (Emelko et al., 2011; Farooq et al., 2025), identify potential for disinfection by-product formation in absence of sufficient precursor removal (Chen et al. 2020; Lokesh et al., 2025), or enhance treatment operations resilience (Gifford et al., 2025).

Currently, no guidance for WAIW preparation exists and the use of diverse WAIW preparation methods can lead to inconsistent water quality results and even contradictory implications to treatment resilience, however. For example, Wang et al. (2015a) and Chen et al. (2020) used fresh ash collected from the same wildfire for WAIW preparation yet applied different preparation protocols. While Wang et al. (2015) mixed WAIWs for 2 h, Chen et al. (2020) used a 24 h mixing time. Also, the studies used different ash concentrations; Wang et al. (2015a) used a high concentration of 200 g L<sup>-1</sup>, whereas Chen et al. (2020) used a lower concentration of 1.9 g L<sup>-1</sup> on average. While the WAIW DOC concentrations from these studies were comparable (180 and 177 mg L<sup>-1</sup>, respectively), average SUVA differed substantially: Wang et al. (2015a) reported an average SUVA of 2.3 L mg<sup>-1</sup> m<sup>-1</sup>, while Chen et al. observed 4 L mg<sup>-1</sup> m<sup>-1</sup>. As a result, DBP yields (i.e., µg of DBP per mg of DOC) in the untreated WAIWs varied substantially, with Wang et al. (2015a) reporting an average of approximately 28 µg

mg<sup>-1</sup> while Chen et al. (2020) observed 72 µg mg<sup>-1</sup> (equivalent to 23 µg g ash<sup>-1</sup> and 130 µg g ash<sup>-1</sup>, respectively). Consequently, Wang et al. concluded that wildfire could reduce major DBP precursor levels, whereas Chen et al. emphasized the need for specific pretreatment strategies to mitigate DBP precursor concentrations in wildfire-impacted waters. 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 WAIW.

Table 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 <sup>-1</sup> )	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	Sánchez-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)
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 (2020)
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	Rodella 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	wildfire burned soil	stream water	1 year post-fire	5	Farooq et al. (2025)
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	-	Olefelt et al. (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 Materials and Methods

### 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 Experimental design

The overall design of the bench-scale experiments reported herein is presented in **Error! Reference source not found.**. 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 S1. 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 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 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<sup>-1</sup> 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 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 3.1.4.

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<sup>-1</sup> 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 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).

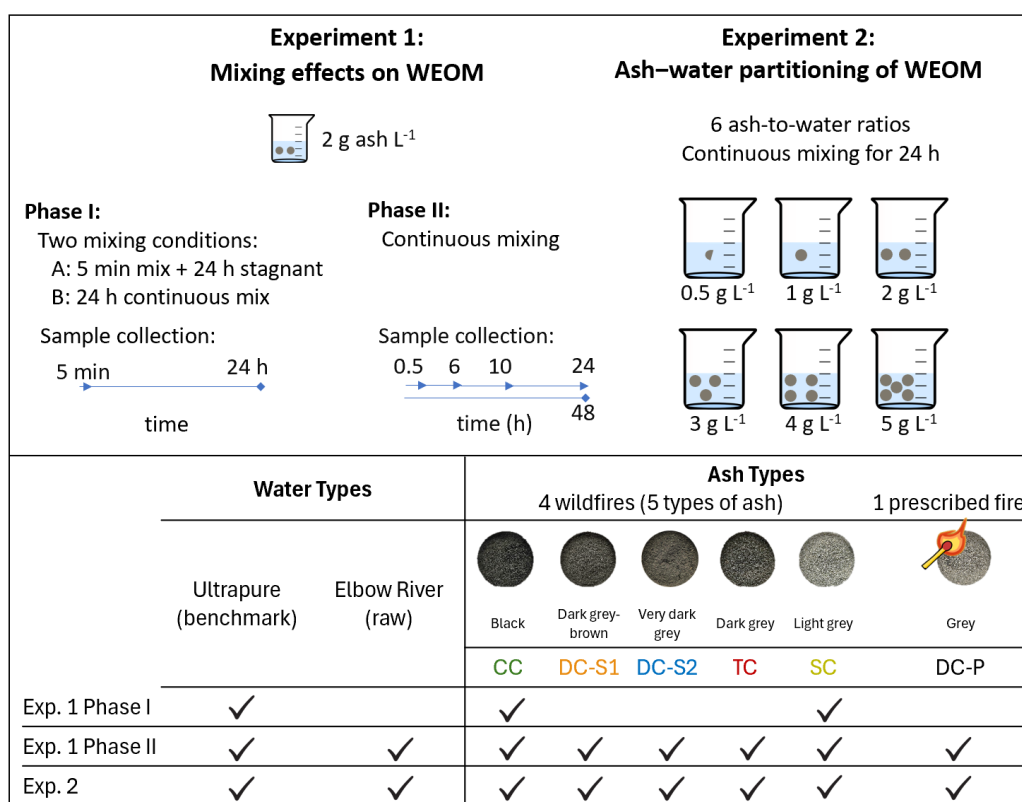


Figure 1 Experimental design for investigating effects of WAIW preparation methods on WEOM. The impact of mixing conditions and time (Experiment 1) and the effect of ash mass concentration (Experiment 2) on the concentration and characteristics of WEOM were investigated. Either ultrapure or natural untreated 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).

### **2.3 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). 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). 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 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 <sup>a</sup>	Waterton, AB <sup>a</sup>	35,000 <sup>a</sup>	09/2017 <sup>a</sup>	Lodgepole Pine <sup>1a</sup> , Subalpine Fir <sup>2a</sup>	High to extreme <sup>b</sup>	06/2018 <sup>b</sup>
Doctor Creek sampling site 1 (DC-S1)	Doctor Creek Wildfire <sup>c</sup>					High <sup>c</sup>	
Doctor Creek sampling site 2 (DC-S2)	Doctor Creek Wildfire <sup>c</sup>	Canal Flats, BC <sup>c</sup>	7645 <sup>c</sup>	08/2020 <sup>c</sup>	Lodgepole Pine <sup>1c</sup> Douglas Fir <sup>3c</sup> , Ponderosa Pine <sup>4c</sup> , Western Larch <sup>5c</sup>	Medium <sup>c</sup>	09/2020
Doctor Creek prescribed fire site (DC-P)	Doctor Creek Prescribed Fire <sup>c</sup>					Medium <sup>c</sup>	
Thuya Creek (TC)	Little Fort Fire Complex <sup>d</sup>	Little Fort, BC <sup>d</sup>	556 <sup>d</sup>	07/2017 <sup>d</sup>	Lodgepole Pine <sup>1d</sup> , Douglas Fir <sup>3d</sup> , Spruce Hybrids <sup>6d</sup> , Paper Birch <sup>7d</sup>	High <sup>d</sup>	08/2017 <sup>d</sup>
Scottie Creek (SC)	Elephant Hill Fire Complex <sup>e</sup>	Ashcroft, BC <sup>e</sup>	191,865 <sup>e</sup>	07/2017 <sup>e</sup>	Douglas Fir <sup>1d</sup> , Spruce Hybrids <sup>6d</sup> , Yellow Pine <sup>8d</sup> , Trembling Aspen <sup>9d</sup>	High <sup>d</sup>	08/2017 <sup>d</sup>

- 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)

## 2.4 Water quality analyses

Most water quality analyses were conducted according to Standard Methods 24<sup>th</sup> 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<sup>-1</sup>). 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<sup>-1</sup>. UV absorbance at 254 nm was measured using a UV<sub>254</sub> analyzer (RealTech P200B) following Standard Method 5910B. Specific ultraviolet absorbance at 254 nm (SUVA) was calculated by dividing UV<sub>254</sub> 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<sup>-1</sup> (>10 kDa) that do not 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<sup>-1</sup>. Building blocks are defined as humic substance-like material of lower molecular weight (300-500 g mol<sup>-1</sup>). LMW acids consist of small aliphatic organic acids with molecular weights lower than 350 g mol<sup>-1</sup>. 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  $\mu\text{m}$  polyethersulfone (PES), Millipore Express<sup>®</sup> PLUS; Merck Millipore, Burlington, MA, for DOC, UV<sub>254</sub> 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 S2.



## 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, a non-parametric test (Wilcoxon signed rank test) with  $\alpha = 0.05$  was used ( $n = 18$ ).

## 3 Results and Discussion

### 3.1 Mixing effects on WEOM

#### 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 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 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 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.

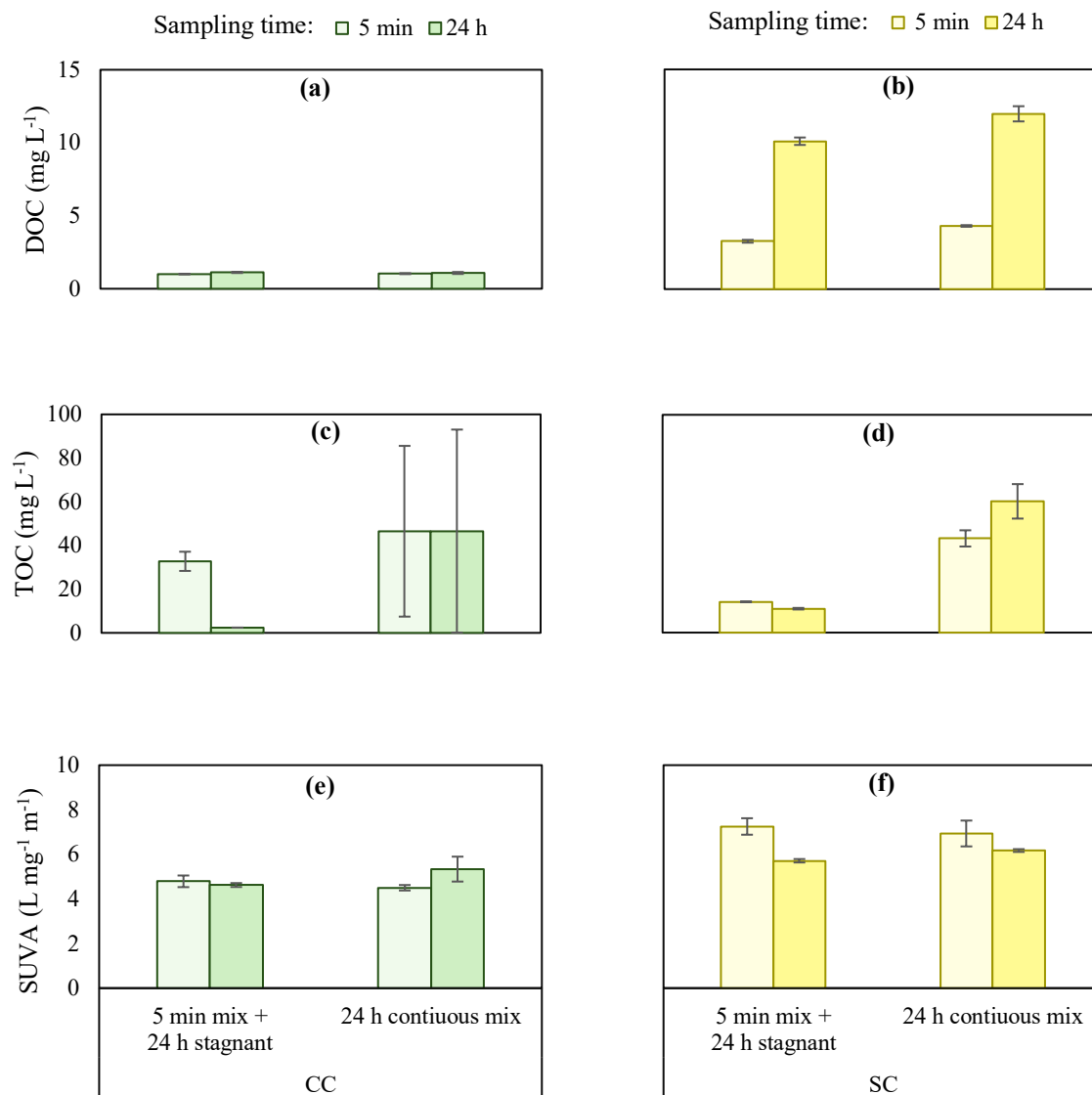


Figure 2 Change in (a & b) DOC concentration, (c & d) TOC concentration, and (e & f) SUVA for WAIW prepared using CC (Cameron Creek) and SC (Scottie Creek) ash mixed in ultrapure water at two different leaching conditions. Each bar represents average values ( $n = 3$ ) with error bars representing standard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

DOC concentrations of WAIWs in Phase II are shown in Figure 3a. These concentrations ranged from  $0.85 \pm 0.07 \text{ mg L}^{-1}$  to  $14.0 \pm 1.02 \text{ mg L}^{-1}$ . 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  $\ll 0.05$ ,  $n = 18$ , Supporting information Table S3).

The changes in DOC concentration decreased during the second half (i.e., 24 to 48 h) of the experiment for all WAIWs (Table 3). This reduction continued for all ash types during the one-week experiment (Supporting information Figure S1). 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).

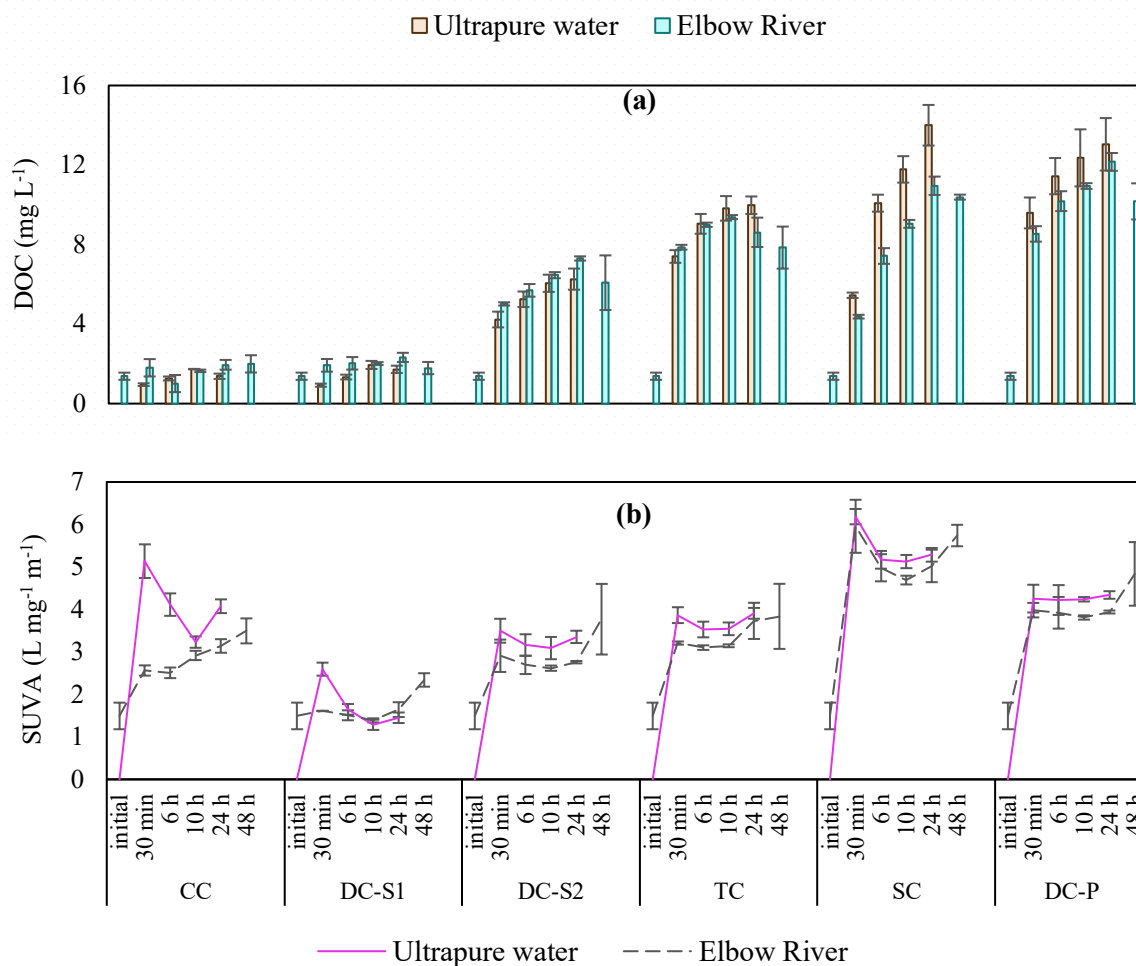








Figure 3 (a) Change in DOC concentration, and (b) SUVA during 48-hour experiment. Light brown and turquoise bars show the changes in DOC concentrations for WAIWs prepared using ultrapure and Elbow River water, respectively. Solid purple and dashed grey lines show SUVA in WAIWs prepared using ultrapure 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 (**Error! Reference source not found.a**) with SC and CC ash demonstrating the highest and lowest rates (12.1 and 8.3 mg L<sup>-1</sup> DOC for SC ash and 0.5 and 0.2 mg L<sup>-1</sup> 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 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 3).

Table 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 $\Delta\text{DOC}_{0.5}$ (mg L <sup>-1</sup> )	Change in DOC between 30 min to 24 h of experiment $\Delta\text{DOC}_{0.5-24}$ (mg L <sup>-1</sup> )	Change in DOC within the second 24 h of experiment $\Delta\text{DOC}_{24-48}$ (mg L <sup>-1</sup> )	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	

### 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 e & f. Ash addition to water resulted in an increase in SUVA regardless of ash type and mixing condition (Figure 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 3b).

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

Differential leaching dynamics associated with the molecular size and character indicated by the LC-OCD analysis are presented in Figure 4 and Supporting information Figure S2. 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 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 S2). 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 S2).

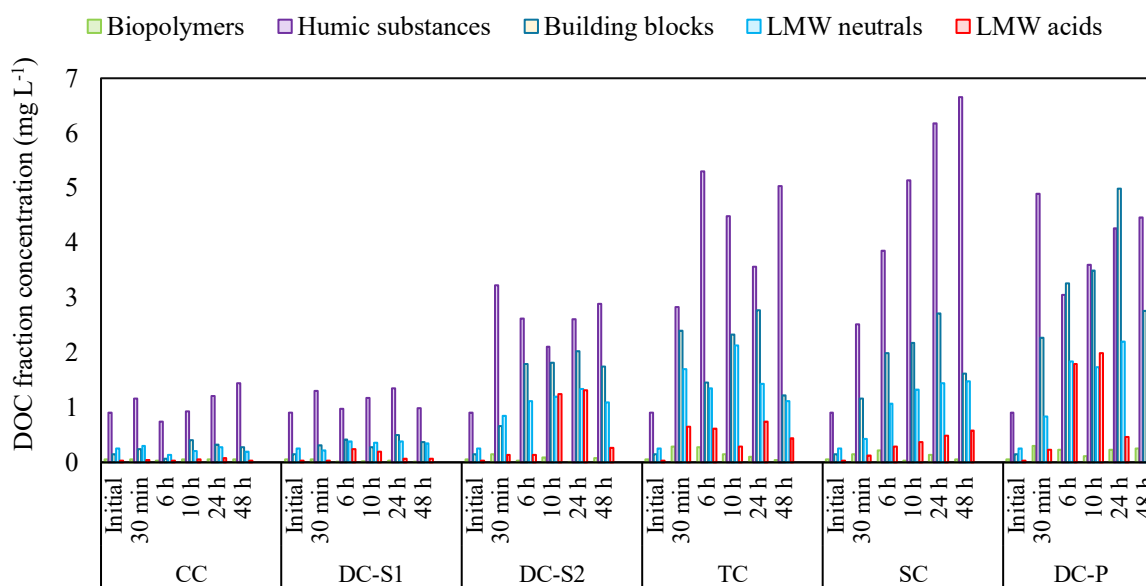


Figure 4 Change in different fractions of dissolved organic matter over time for WAIWs prepared in Elbow River water. These fractions are presented in descending order of molecular weight: biopolymers, humic substances, building blocks, LMW acids and LMW neutrals.

### 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 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 S2 and Figure 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<sub>2</sub> into the WAIWs (Figure 5).

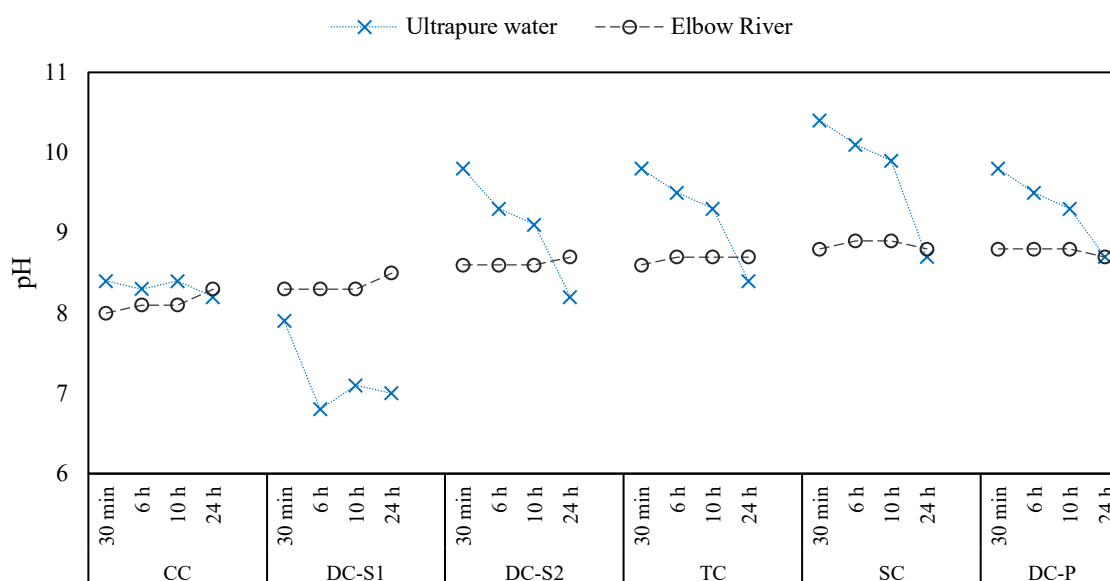


Figure 5 pH for all WAIWs prepared in ultrapure and Elbow River water during the first 24 h of the experiment. Blue crosses and grey circles indicate the pH of the WAIWs prepared in ultrapure and Elbow River water, respectively. The initial pH of Elbow River water was  $8.3 \pm 0.1$  ( $n = 3$ ).

Table 4 presents conductivities of WAIWs prepared with 2 g L<sup>-1</sup> 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; Saurich 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 6).

Table 4 Conductivity (mean  $\pm$  SD,  $n = 3$ ) of the WAIWs made with 2 g L<sup>-1</sup> 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)		(b)		
WAIW in ultrapure water	Conductivity ( $\mu\text{S cm}^{-1}$ )	WAIW in Elbow River water	Conductivity ( $\mu\text{S cm}^{-1}$ )	$\Delta$ Conductivity ( $\mu\text{S cm}^{-1}$ )
Ultrapure	$0.00 \pm 0.005$	Elbow River	$0.50 \pm 0.03$	-
CC	$0.05 \pm 0.002$	CC	$0.51 \pm 0.08$	0.01
DC-S1	$0.03 \pm 0.001$	DC-S1	$0.51 \pm 0.04$	0.01
DC-S2	$0.14 \pm 0.03$	DC-S2	$0.61 \pm 0.03$	0.11
TC	$0.13 \pm 0.05$	TC	$0.55 \pm 0.04$	0.05
SC	$0.23 \pm 0.06$	SC	$0.66 \pm 0.03$	0.16
DC-P	$0.21 \pm 0.02$	DC-P	$0.69 \pm 0.05$	0.19

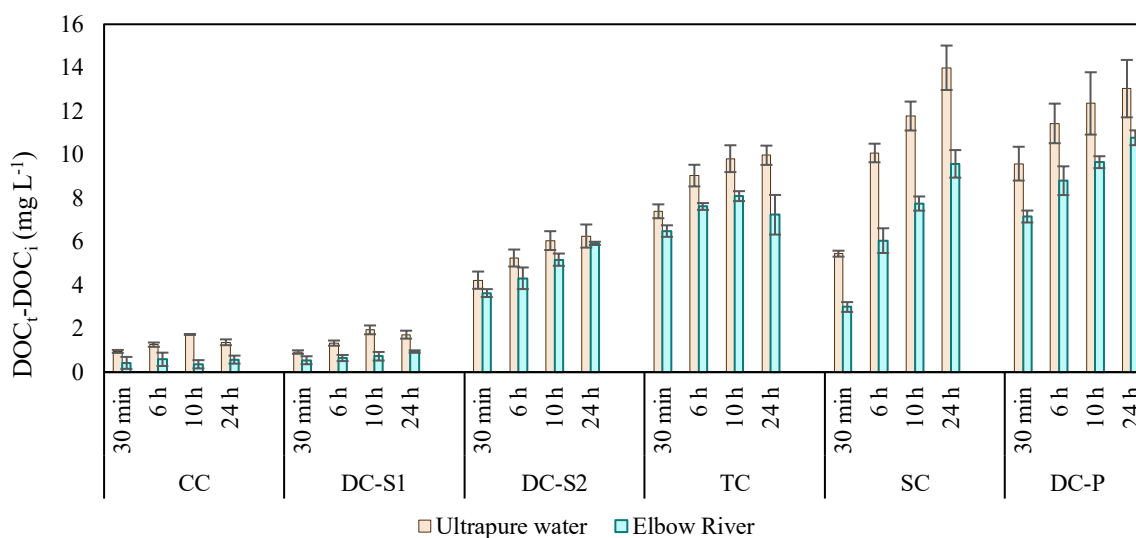


Figure 6 Change in DOC concentration (DOC at time t - source water initial DOC) and pH for all WAIWs during the first 24 h of the experiment. Light brown and turquoise bars show the changes in DOC concentrations for WAIWs prepared with ultrapure and Elbow River water, respectively. Changes in DOC concentrations 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  $1.47 \pm 0.08$  (mean  $\pm$  SD,  $n = 6$ ), respectively.

### 3.1.4 Changes in disinfection by-product precursors

DBP formation of WAIWs prepared using  $2 \text{ g L}^{-1}$  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  $3.99 \pm 0.12 \text{ mg L}^{-1}$  to  $10.9 \pm 0.40 \text{ mg L}^{-1}$ ; Figure 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 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 (**Error! Reference source not found.**). 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.

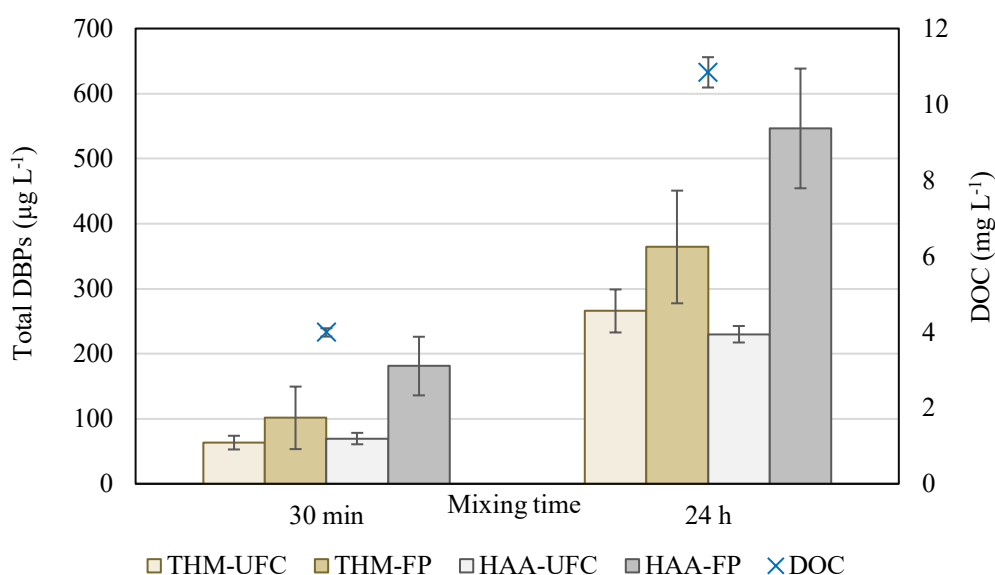


Figure 7 Change in DOC and DBP concentration in WAIWs prepared using SC (Scottie Creek) ash after 30 minutes and 24 hours of mixing in Elbow River water. Brown and grey bars represent concentrations of THMs and HAAs, respectively, and blue crosses indicate DOC concentration at each mixing time. Each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

## 3.2 Ash–water partitioning of WEOM

### 3.2.1 Changes in WEOM concentration

Figures 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<sup>-1</sup>. Notably, the lowest ash mass concentration (i.e., 0.5 g L<sup>-1</sup>) resulted in a considerable increase in DOC concentration for some ash types such as SC and DC-P; Figure 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 3.1).

Ash organic matter content and WEOM concentration for the investigated ash types are presented in Table 5. Organic matter content ranged from  $3.7 \pm 0.1\%$  to  $21 \pm 1.9\%$  for DC-S1 and CC, respectively (Table 5). 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<sup>-1</sup>, 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 8 c & d). For ash-to-water ratios exceeding 2 g L<sup>-1</sup>, 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.

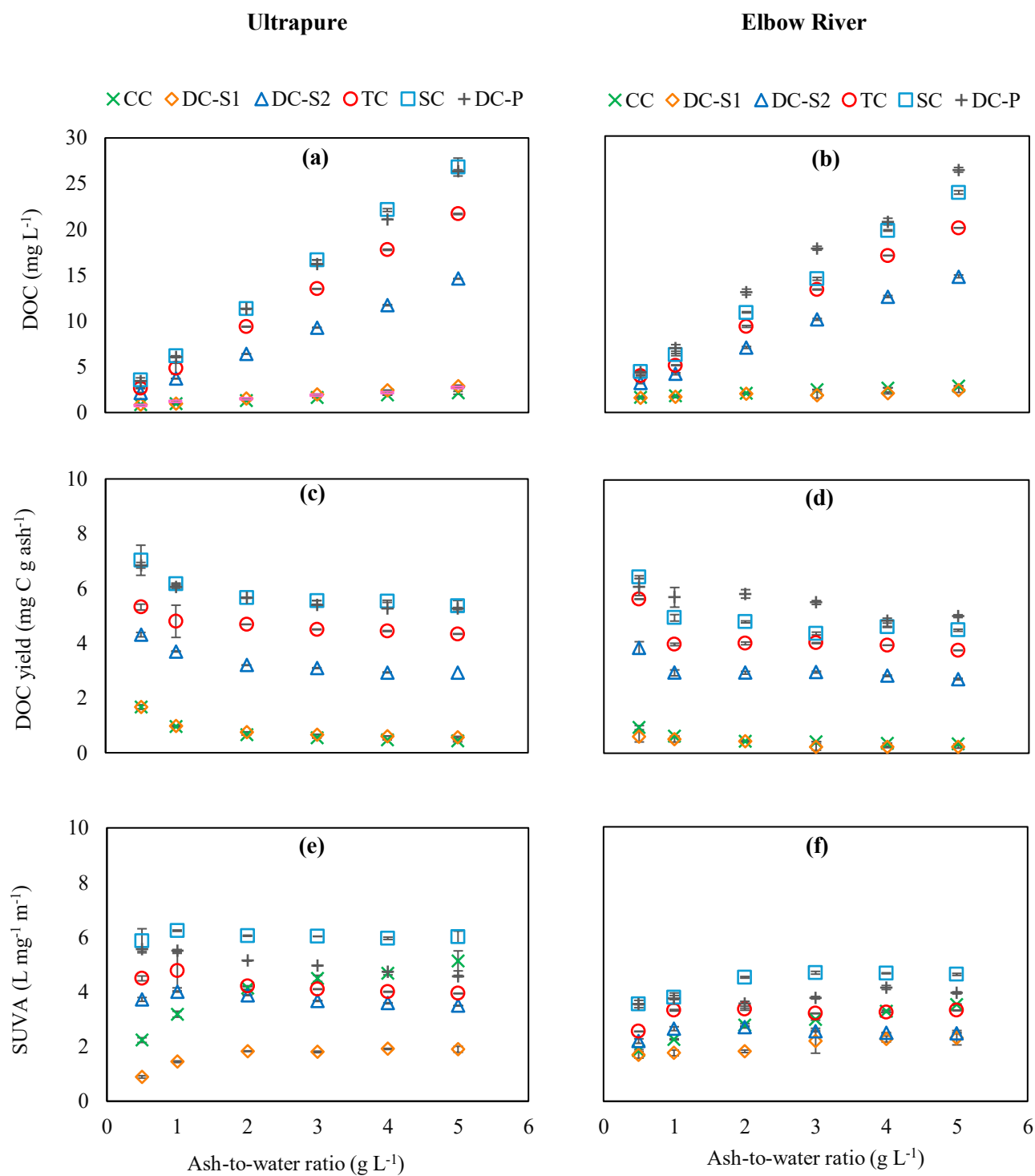


Figure 8 Change in (a & b) DOC concentration, (c & d) DOC yield, and (e & f) SUVA for different WAIWs prepared using ultrapure and Elbow River water across a range of ash-to-water ratios. Each symbol represents the average values ( $n = 3$ ) with error bars representing standard deviation.

Table 5 Organic matter content, DOC concentration in WAIW containing 2 g L<sup>-1</sup> 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 <sup>-1</sup> )
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

### 3.2.2 Changes in WEOM character: SUVA and LC-OCD

Figure 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<sup>-1</sup>). However, at ash-to-water ratios greater than 2 g L<sup>-1</sup>, SUVA stabilized for almost all ash types, except for CC (Figure 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 9 and Supporting information Figure S3. 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 3.1) 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 9). In contrast to SUVA, refractory fractions yield generally remained stable in all WAIWs across different ash-to-water ratios (Supporting information Figure S3). 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.

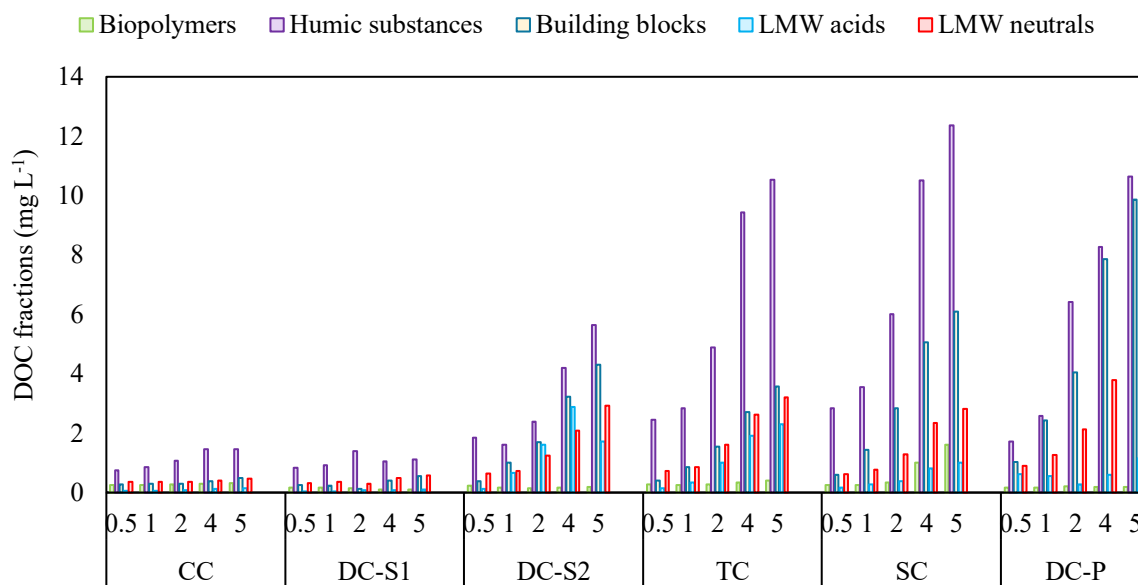


Figure 9 Organic matter character over time as indicated by LC-OCD for different ash types across a range of ash-to-water ratios mixed in Elbow River water. a) DOC fractions are presented in descending order of molecular weight: biopolymers, humic substances, building blocks, LMW neutrals and LMW acids;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

### 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 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<sup>-1</sup>; Supporting information Table S1).

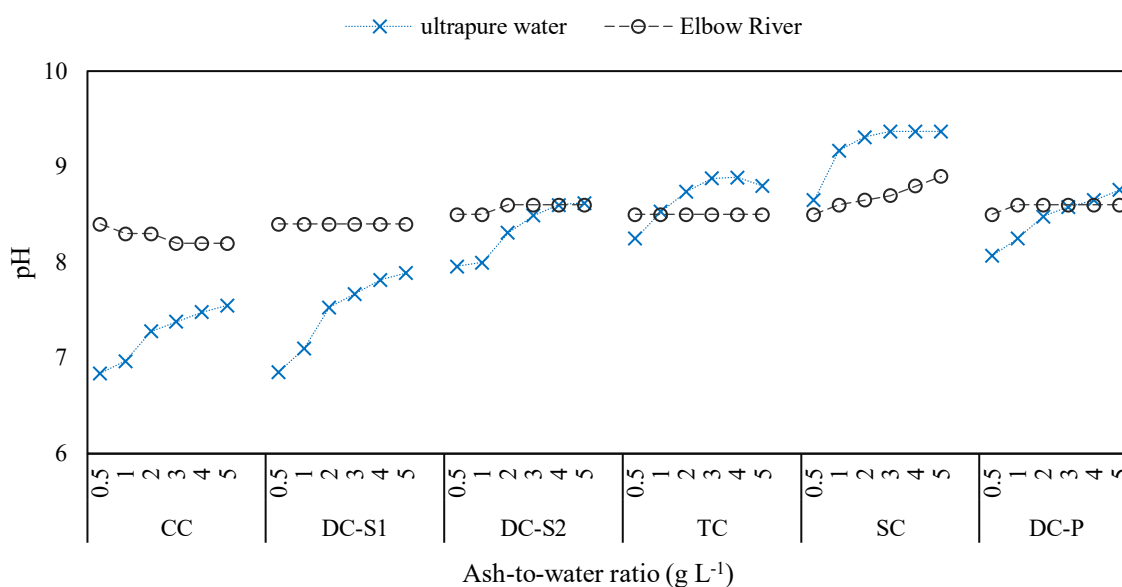


Figure 10 Change in pH for all ash types mixed in ultrapure and Elbow River water across a range of ash-to-water ratios. Blue crosses and grey circles indicate pH of WAIWs prepared in ultrapure and Elbow River water, respectively. The initial pH of Elbow River water was  $8.3 \pm 0.1$  (mean  $\pm$ 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

## 4 Conclusions & Implications


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 ash on WEOM characteristics were generally consistent across different ash types (i.e., from wildfires with a range of severities and a prescribed fire): 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. This is consistent with reviews of available data that have indicated wildfire ash addition to water increases DOC concentration and aromaticity, predominantly because of the significant fraction of humic substances composing WEOM (Bahramian, 2025).
- WEOM concentrations in ash leachates and ash organic content do not necessarily correlate with the ash color classification scheme.
- Source water quality and ash concentration used to prepare WAIW impact WEOM solubility and can therefore also impact inferred implications of wildfire ash on drinking water quality and treatability. This is one of the reasons it is impossible to reasonably predict wildfire impacts on water quality and treatability by adding wildfire ash to water during bench- and pilot-scale investigations.
- 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). After 24 h of mixing, decreases in WEOM concentration accompanied by changes in WEOM character were observed in almost all WAIWs, potentially reflecting the impact of biotic processes.
- 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. While such studies simplify the watershed-scale biogeochemical processes involved and are not intended to be predictive, they provide a controlled framework for assessing key water quality changes and treatment responses to disturbance-related inputs. Most notably, the conclusions 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.

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## Author Contributions

The manuscript was written through contributions of all authors and all authors have given approval to the final version of the manuscript. CRediT: **Soosan Bahramian** conceptualization (equal), formal analysis (equal), investigation (lead), methodology (lead), visualization (equal), writing-original draft (lead), writing-review & editing (equal); **Fariba Amiri** conceptualization (equal), formal analysis (equal), methodology (supporting), supervision (equal), visualization (equal), writing-review & editing (equal); **Uldis Silins** methodology (supporting), visualization (equal), writing-review & editing (equal); **William B Anderson** formal analysis (equal), methodology (supporting), visualization (equal), writing-review & editing (equal); **Mike Stone** formal analysis (equal), methodology (supporting), visualization (equal), writing-review & editing (equal); **Monica B. Emelko** conceptualization (equal), formal analysis (equal), funding acquisition (lead), methodology (supporting), resources (lead), supervision (equal), visualization (equal), writing-review & editing (equal).

## Acknowledgments

This research was undertaken, in part, thanks to funding from the Canada Research Chairs (CRC) Program. This research was undertaken, in part, thanks to funding from NSERC (Natural Sciences and Engineering Research Council of Canada), specifically through the *forWater* NSERC Network for Forested Drinking

Water Source Protection Technologies (NETGP-494312-16). It was also supported by Alberta Innovates (3360-E086), the Regional Municipality of Wood Buffalo, Alberta, Canada [Agreement #101978].

The assistance of the British Columbia Ministry of Forests with the collection of wildfire ash is appreciated.

The laboratory assistance of Steven Ngo from the Water Science, Technology and Policy group at the University of Waterloo is also appreciated.

## **Declaration of Competing Interest**

The authors declare no competing financial interest.

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