

Advancing characterization of spatiotemporal dynamics of
dissolved organic matter after landscape disturbance
to inform and protect drinking water treatability

by

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Author's Declaration

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

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Statement of Contributions

Carter Klanderud was the sole author for Chapters 1 and 4 which were written under the supervision of Professor Monica Emelko and were not written for publication.

This thesis consists in part of two manuscripts prepared as refereed papers for publication that have not yet been submitted. 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

Surface waters are critical sources of drinking water globally. The quality and availability of water from these sources is threatened by landscape disturbances (e.g., urbanization, agriculture, resource extraction) including climate shocks (e.g., wildfires, intense precipitation). To ensure reliable and consistent supply of drinking water, offline reservoirs are often used for raw water storage prior to treatment. While largely designed for managing water quantity and availability, reservoir storage can also affect water quality. In addition to providing bypass capacity during contamination events (e.g., accidental spills/releases), hydrodynamic factors such as dilution, physico-chemical and biological transformations occurring within reservoirs, including photodegradation, flocculation, and microbial primary production, can alter water quality relative to inflowing source water.

Drinking water treatment needs and performance are driven by many aspects of source water quality, one of the most critical being organic matter. Landscape disturbances can substantially change organic matter concentration and character in source water because they alter hydrologic connectivity, mobilizing organic matter from the landscape and affecting its delivery to and transport within receiving waters. Rapid shifts in source water quality can challenge water treatment plants (WTPs), potentially increasing operational costs or leading to service outages. Raw water reservoirs can help attenuate such source water quality change; however, this is not typically done by design. Here, ultraviolet absorbance at 254 nm (UV₂₅₄)—a real-time indicator of dissolved organic matter (DOM) concentration and aromaticity—was intensively monitored in a wildfire-impacted drinking water system with two off-line reservoirs in series to demonstrate how engineered storage can be leveraged to dampen landscape disturbance-associated changes in source water quality and increase treatment resilience. High-frequency sampling of UV₂₅₄ did not show meaningful differences across depth, lateral position within the reservoir cells, and time of day. Notably, UV₂₅₄ standard deviation was 1.6 and 2.2 times lower in the first and second reservoirs, respectively, than in the river source; respective peak UV₂₅₄ values were 1.45 and 1.6 times lower, indicating effective attenuation of DOM from the river by the reservoirs in series. This attenuation also reduced polyaluminum chloride coagulant dosing by approximately 70 mg/L during a period of particularly deteriorated source water in 2023, helping reduce aluminum residuals and the potential for exceeding regulatory maxima in treated water. Accordingly, this work demonstrates that raw water reservoirs can be intentionally and strategically designed to attenuate disturbance-driven fluctuations in source water quality, thereby enhancing drinking water system resilience and supporting climate change adaptation.

Watershed-scale source water quality monitoring is essential for assessing cumulative watershed effects to enable effective management of drinking water supplies and detection of threats to water treatability. However, it can pose substantial logistical challenges. Source water quality, including the concentration and character of organic matter, can change during the unavoidable period between sample collection and analysis, making effective sample preservation critical for maximizing return on monitoring effort. While a standard method is available for the preservation of dissolved organic carbon (DOC), a common surrogate for DOM, its implementation is not always feasible. Difficult access to remote or hydrologically-critical headwater locations for sample collection, limitations on *in situ* sample preservation, and associated challenges in transporting collected samples to analytical facilities within prescribed holding times can compromise data integrity and representativeness. Several alternative preservation (e.g., filtration, freezing) techniques for organic carbon concentration and character are often used when adherence to Standard Methods is impractical; however, their efficacy is highly variable and has not been systematically evaluated. Thus, the direct and combined effects of

temperature (e.g., refrigeration, freezing), filtration, and acidification were systematically investigated here using four natural water matrices of diverse quality. This analysis revealed that freezing effectively preserved DOC except when combined with acidification (which would be suggested by extension of Standard Methods); the combination of these methods caused significant shifts in DOC in some cases. Specific ultraviolet absorbance at 254 nm (SUVA) changed within 24 hours of sample collection in some water matrices; this was also reflected by change in the humic substances fraction of DOM, which was measured by size-exclusion chromatography using liquid chromatography-organic carbon detection (LC-OCD). DOC in unpreserved water samples remained stable (i.e., < 10% change) for up to seven days after collection. Accordingly, while Standard Methods remain the benchmark for preserving DOM in water samples, this work advances practical strategies to maximize the value and interpretability of monitoring data at conditions where adherence to these methods is not feasible.

Collectively, these findings highlight the value of offline raw water reservoirs and robust sample preservation strategies for enhancing WTP resilience to source water quality change. Reservoirs can effectively attenuate rapid shifts in DOM concentration and character following climate shocks such as wildfires and substantially reduce extremes in coagulant demand. Understanding the stability of DOM during the unavoidable period between sample collection and analysis further helps maximize the value of raw water monitoring to inform water quality and treatability change without compromising data integrity. By integrating high-frequency reservoir monitoring with matrix-specific preservation practices, drinking water utilities can better anticipate source water variability, prepare for disturbance, and improve overall treatment performance and resilience.

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List of Abbreviations

%	Percentage
>	Greater than; less than
≥	Greater than or equal to; less than or equal to
°C	Degrees Celsius
µm	microns
BL	Boat launch
C ₀	Inflow concentration
CSTR	Continuously stirred tank reactor
DBP	Disinfection By-product
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DWS	Drinking water system
e.g.	For example
E2:E3	UV absorbance at 250 nm divided by UV absorbance at 365 nm
E.C.C.C.	Environment and Climate Change Canada
ha	Hectares
HCl	Hydrochloric acid
HDPE	High-density polyethylene
i.e.	That is

LC-OCD	Liquid chromatography in combination with organic carbon detection
LMW	Low molecular weight
mg/L	Milligrams per liter
p	Probability value
PACl	Polyaluminum hydroxychloride
SEC	Size-exclusion chromatography
SUVA	Specific ultraviolet absorbance
TOC	Total organic carbon
U.S.EPA	United States Environmental Protection Agency
U.S.G.S.	United States Geological Survey
UV ₂₅₄	Ultraviolet absorbance at the wavelength of 254 nm
UV-Vis	Ultraviolet-visible wavelength spectrum from 200-800 nm
WTP	Water treatment plant
τ	Hydraulic retention time

Chapter 1

Introduction

1.1 Background

The provision of safe drinking water is a critical facet to the functioning of society that enables nearly all other pursuits. It is for this reason that a water-centric framing has been suggested for concurrent advancement of the United Nations Sustainable Development Goals (Makarigakis & Jimenez-Cisneros, 2019; Essex et al., 2020). North America contains approximately 20% of the world's freshwater within the Great Lakes alone; almost all drinking water treatment plants (WTPs) there rely on freshwater sources. Of these WTPs, approximately 60-70% rely on surface water sources, with the remainder supplied by groundwater (E.C.C.C., 2017; Steinman et al., 2018; U.S.G.S, 2018). Surface waters are particularly vulnerable to landscape disturbances (e.g., urbanization, agriculture, war) and climate shocks (e.g., wildfires, earthquakes, intense precipitation) that can adversely affect water availability, quality, and treatability (Hart et al., 2004; Busse et al., 2006; Emelko et al., 2011; 2024; Devane et al., 2014; Johnston et al., 2019; U.S. E.P.A., 2024).

Storage reservoirs are widely used in drinking water systems (DWSs)—the infrastructure used to collect, treat, store, and distribute drinking water (Ontario, 2003)—to ensure sufficient supply of raw (i.e., untreated) surface water for treatment (Granados et al., 2021; Zhang et al., 2022 & 2024). They are typically designed for ensuring sufficient quantity and availability of water (Kraus et al., 2011; Hur et al., 2014; Li et al., 2016; Wang et al., 2021; Imatazy et al. 2024; Jia et al., 2025) and are sometimes relied upon for operational flexibility during contamination events (e.g., accidental spills or releases) by providing bypass capacity during brief periods of deteriorated source water, thereby mitigating contaminant propagation through the system and preserving downstream treatment performance. Many biological and physico-chemical transformations, including microbial primary production, flocculation, and photodegradation, as well as hydrodynamic factors such as dilution, can impact reservoir water quality relative to inflowing source water. The form and intensity of these changes is based on external loadings, hydrodynamics, and the physico-chemical and biological processes that are modulated by basin morphology and climate (Kraus et al., 2011; Hur et al., 2014; Li et al., 2016; Wang et al., 2021; Imatazy et al. 2024; Jia et al., 2025). These mechanisms are generally understood; however, raw water storage reservoirs are not typically intentionally configured or operated to influence water quality prior to treatment.

Drinking water treatability—the capacity to treat water to a sufficient standard, in sufficient quantities, consistently, and at reasonable cost (Emelko et al., 2011)—is governed by a diverse array of source water quality parameters, including but not limited to pH, alkalinity, and turbidity, and organic matter concentration and character (Crittenden et al., 2012). Organic matter is a complex mixture of molecules that governs particle surface charge in natural waters (Ali et al., 1984; Edzwald, 1993). Specifically, it can drive the efficacy of coagulation and subsequent filtration and the formation of disinfection by-products

(Edzwald, 1985; Ratnaweera & Fettig, 2015; Beauchamp et al., 2020), as well as increase WTP operational costs (Emelko et al., 2011; 2024; Crittenden et al., 2012). Organic matter in treated drinking water can further promote biofilm growth in distribution systems, which may harbor pathogens, and contribute to taste and odor issues (Health Canada, 2019). In this thesis, organic matter—specifically dissolved organic matter (DOM)—includes both natural and anthropogenic sources and does not distinguish between them.

Landscape disturbances can substantially alter organic matter concentration and character, posing challenges for WTPs, including service outages (Hart et al., 2004; Busse et al., 2006; Emelko et al., 2011; 2024; Devane et al., 2014; Johnston et al., 2019; U.S. E.P.A., 2024). Such disturbances can mobilize organic matter and affect its delivery to and transport within receiving waters by substantially altering hydrologic connectivity. Wildfires can alter runoff processes by reducing vegetation and often increasing soil hydrophobicity (Doerr et al., 2005; Woods et al., 2006), mobilizing organic matter and altering its delivery to and transport within receiving waters; this can result in episodically-elevated organic matter and turbidity levels (Emelko et al., 2024).

Investigations of reservoir attenuation of disturbance-associated organic matter impacts within reservoirs are limited, and only available in large, online reservoirs and lakes with multi-year retention times and ecological characteristics (e.g., unstable littoral zones) not present in smaller, offline reservoirs (Alexander et al., 2004; Furey et al., 2004; Emmerton et al., 2019; Basso et al., 2021). Lake and reservoir attenuation of incoming pollutant loads is well-documented (Sprague, 2002; Sarmiento et al., 2009; Santisteban et al., 2016; Guo et al., 2022). Although not typically practiced, raw water storage reservoirs can be intentionally designed to improve WTP resilience to sudden water quality changes by diluting impacted inflowing source water and/or providing sufficient residence time for targeted physico-chemical and/or biologically-mediated water quality change. Offline raw water storage reservoirs hold potential to mitigate such source water quality fluctuations and associated threats to treatability through intentional design. Their hydraulic decoupling from continuous inflows enables control of residence time, withdrawal depth, and internal flow paths, enabling targeted attenuation of disturbance-driven water quality fluctuations prior to treatment. Investigations on the subject are scant, however.

Effective management of reservoirs and associated threats to source water quality and treatability requires an understanding of the natural spatial and temporal variability in reservoir water quality. Few studies have investigated the spatial distribution of organic matter within reservoir systems; of those, the focus has only been on natural, deep (> 20 m) reservoirs (Hur et al., 2007; Kraus et al., 2011; Nguyen et al., 2011), not engineered offline reservoirs. Furthermore, temporal shifts in organic matter concentration and character within engineered offline raw water storage reservoirs have not been systematically described. This understanding is essential to accurate characterization of in-reservoir changes in organic matter

concentration and character relative to natural variability and elucidation of the processes driving these changes; therefore, it is also foundational to informing design and operational strategies to maximize attenuation of source water quality fluctuations before treatment.

To describe changes within systems—whether sudden disturbances or gradual, prolonged shifts—it is necessary to first accurately characterize their current state. Watershed-scale water quality monitoring programs are essential for detecting changes in drinking water source quality and treatability, and therefore for supporting WTP decision-making (Behmel et al., 2016). Established monitoring programs are particularly important for providing operational resilience in (i) assessing threats from climate shocks and other landscape disturbances that can affect the timing, quantity, quality, and treatability of runoff-impacted receiving waters, informing effective management of drinking water sources, and (ii) informing the development and evaluation of source water protection strategies (Emelko et al., 2011; Behmel et al., 2016; Park & Hwang, 2016; Sudriani et al., 2024). Despite their value, watershed-scale monitoring programs are inherently constrained by the logistical realities of remote environments, with direct implications for sampling continuity and sample integrity. Many headwater catchments are characterized by limited accessibility, often requiring helicopter-supported access or similarly intensive field logistics, which constrains sampling frequency and increases both the cost and operational complexity of routine monitoring. To reduce the need for repeated field visits, automated samplers are frequently deployed to enable time-integrated collection and storage of samples over extended deployment periods. However, reliance on autonomous instrumentation in these settings introduces practical constraints associated with maintaining equipment functionality under prolonged exposure to harsh environmental conditions and limited opportunities for maintenance or repair. These constraints can compromise sampling continuity and increase the likelihood of partial data capture.

Even when sampling systems function successfully over long deployment periods, a fundamental challenge remains: samples cannot be analyzed in situ. Instead, there is an unavoidable and often extended lag between sample collection in remote headwaters, retrieval and transport under non-ideal conditions, and eventual laboratory analysis. During this interval, samples may be exposed to temperature fluctuations, variable holding times, and limited opportunities for immediate stabilization—conditions that can compromise the representativeness of measured water quality parameters. As a result, sample preservation in remote watershed monitoring is not simply a procedural step, but a critical and often limiting factor in the reliability of the resulting data.

Organic matter concentration is often quantified using organic carbon as a surrogate (Schwarzenbach et al., 2017). In this thesis, the term dissolved organic carbon (DOC) represents DOM concentration and will be mentioned only when referring to a specific measurement performed. A standard method exists for the

preservation of total organic carbon (i.e., acidification to $\text{pH} \leq 2$ and storage at 4°C ; APHA, AWWA, and WEF, 2022) which can further be classified as DOC when filtering through a $0.45\ \mu\text{m}$ filter prior to analysis. This method is only intended to preserve DOC, not to be extended to DOM character. Filtration through a 0.7 , 0.45 , or $0.2\ \mu\text{m}$ filter is commonly used to remove particulate matter and microorganisms that could alter DOC (Kaplan, 1994; Dean et al., 2018). The standard method prescribes acidification to $\text{pH} \leq 2$ using HCl or H_2SO_4 and refrigeration at 4°C to inhibit microbial activity and slow chemical reactions (APHA, AWWA, and WEF, 2022). Additionally, minimizing exposure to sunlight and air prevents photochemical reactions and oxidation that can change organic matter concentration and character. Even with preservation, samples should be analyzed within recommended holding times defined to maintain accuracy (APHA, AWWA, and WEF, 2022). Preservation following Standard Methods can be challenging, particularly in remote or logistically-constrained settings (e.g., headwater streams), as it requires the use of concentrated acids which impose significant safety and regulatory burdens, including the need for personal protective equipment and secondary containment to prevent acid spills. These constraints can limit the feasibility and effectiveness of standard preservation during watershed-scale sampling. For the same reason, preservation of DOC via the addition of biocides such as sodium azide or mercuric chloride will not be discussed in depth, as these can have high toxicity and are similarly limited in remote work (U.S. N.I.S.T, 2019; U.S. C.D.C., 2026). To circumvent these challenges, filtration and/or freezing may serve as alternative approaches for preserving organic matter concentration and character prior to analysis.

Several studies have utilized freezing for organic matter preservation, but its effects have not yet been systematically evaluated in a comprehensive manner. While unpredictable changes in DOC after freezing relative to non-frozen controls have been reported (Sugimara & Suzuki, 1988; Fellman et al., 2008; Spencer et al., 2007; Druffel et al., 2013; Norman & Thomas, 2014; Chen et al, 2015; Peacock et al., 2015; Cook et al., 2016; ; Pokrovsky et al., 2018; Jonker, 2020; Nachimuthu et al, 2020; Payandi-Rolland et al, 2021; Fonvielle et al., 2023), others have demonstrated effective preservation of DOC within a specific matrix (Tupas et al., 1993; Thieme et al., 2016; Walker et al, 2016; Heinz & Zak, 2017). This wide range of matrix-specific responses may indicate that freezing is an unreliable preservation technique without matrix-specific validation; however, it is also likely that these discrepancies reflect methodological differences in the freezing and thawing practices, prefiltration status, filter pore size, or storage duration. Notably, some investigations have involved freezing in isolation and others only after filtration; only one study examined freezing after acidification of freshwater samples and then performing analyses after long storage durations (1-2 years- Norman & Thomas, 2014). However, the individual and combined effects of shorter-term freezing, filtration, and acidification on the preservation of organic matter concentration and character in freshwater have not been evaluated.

1.2 Research Objectives

The overall goal of this research was to advance characterization of spatiotemporal dynamics of dissolved organic matter after landscape disturbance to inform and protect drinking water treatability. To address this goal, the specific objectives of the research were to:

- 1) Characterize the spatial and temporal variability of dissolved organic matter concentration and character within an offline raw water reservoir system;
- 2) Demonstrate the capacity and benefit of source water quality change attenuation in offline reservoirs; and
- 3) Evaluate the reliability of alternative dissolved organic matter preservation techniques (i.e., filtration, acidification, refrigeration, and freezing) and the effects of interactions between them.

Collectively, these objectives aim to advance characterization of organic matter to aid utilities, researchers, regulators, and others to better understand, prepare for, and recover from climate shocks and other landscape disturbance threats to drinking water source quality and treatability. This work may be of particular importance in small, remote, or rural systems that have different resources than larger, urban systems (e.g., more land availability, fewer personnel).

1.3 General Research Approach

To achieve the overall goal of advancing characterization of the spatiotemporal dynamics of dissolved organic matter (DOM) after landscape disturbance to inform and protect drinking water treatability by addressing the objectives identified in Section 1.2, much of this research was conducted in a DWS that was affected by landscape disturbance in Fort McMurray, Alberta, Canada. This system was impacted by the 2016 Horse River wildfire, which burned approximately 600,000 ha of northern Alberta's boreal forest, and was the costliest natural disaster in Canadian history (\$8.9 billion in direct costs- Emmerton et al., 2020). The impacted region is within the Boreal Plains ecozone, characterized by extensive upland coniferous forests and wetland coverage (Chanasyk et al., 2003; Devito et al., 2017). Within the final fire perimeter, 77% of the area was burned, half of which at high severity (Emmerton et al., 2020). Since the fire, the DWS in Fort McMurray has experienced elevated and more variable levels of organic matter and turbidity in its source water (Alam et al., 2018; Emmerton et al., 2020). This research was conducted in two phases.

The first experimental phase was designed to demonstrate the potential for offline, raw water reservoirs to provide a barrier to the impacts of climate shocks and other landscape disturbances by attenuating changes in source water quality, specifically DOM concentration and character. Targeted, extensive water sampling for analysis of water quality, including DOM concentration and character via ultraviolet

absorbance at 254 nm (UV_{254}), was performed in multiple locations within the Fort McMurray raw water reservoir system, and immediately outside in the Athabasca River for three consecutive years. Additionally, a high-frequency sampling program was conducted to investigate the effects of time of day on UV_{254} (Objective #1). Results were then compared between the river and each subsequent reservoir to assess the potential for offline, raw water reservoirs to attenuate rapid shifts of incoming DOM concentration and character, having direct implications to water treatment resilience against disturbance. Water quality, both entering the treatment plant and from the river source, was then compared to coagulant doses applied in treating the water to assess the practical value of enhanced stability of water quality to treatment (Objective #2).

The second phase of this thesis research was designed to evaluate the potential to stabilize organic matter concentration and character using preservation techniques alternative to what is recommended in Standard Methods (e.g., freezing). A preliminary literature review was performed to investigate previous applications of these preservation techniques, and conditions were selected to best represent practical field conditions (e.g., selecting high-density polyethylene bottles over glass). Water was collected from multiple diverse matrices across Canada, before preserving in a systematic evaluation of the compounding effects of water temperature (e.g., refrigeration), filtration, and acidification on the preservation of organic matter concentration and character over multiple storage durations (Objective #3).

1.4 Thesis Organization

This thesis consists of four chapters, with Chapters 2 and 3 formatted for submission to refereed journals (i.e., a paper-based thesis); thus, there is some repetition of introductory material in Chapters 2 and 3.

Chapter 2 provides the results of three years of river and offline reservoir monitoring, and the potential for reservoirs to act as attenuators to water quality changes after disturbance. Chapter 3 presents a systematic evaluation of the efficacy of commonly-practiced methods for the preservation of organic matter, as well as recommendations for the effective preservation of organic matter in different matrices. Chapter 4 provides a summary of the conclusions, implications, and recommendations of this work. Related references are shared at the end of Chapters 2 and 3, and a complete reference list is provided following Chapter 4. Finally, several appendices containing additional details associated with Chapters 2 and 3 are shared.

Chapter 2

Building Drinking Water Resilience to Climate Shocks: Post-Fire Dissolved Organic Matter Dynamics and Attenuation in an Offline Raw Water Reservoir System

2.1 Introduction

Surface waters (e.g., rivers and lakes) are critical sources of drinking water globally (Gil et al., 2019; Zhang et al., 2023). Landscape disturbances (e.g., urbanization, agriculture, resource extraction) and climate shocks (e.g., wildfires, intense precipitation) can have substantial impacts on surface water quality that challenge water treatment plants (WTPs- Hart et al., 2004; Busse et al., 2006; Emelko et al., 2011, 2024; Johnston et al., 2019; U.S. E.P.A., 2024). Drinking water systems (DWSs)—the infrastructure used to collect, treat, store, and distribute drinking water (Ontario, 2003), widely include storage reservoirs to maintain adequate supplies of raw surface water (Granados et al., 2021; Zhang et al., 2022 & 2024). Offline reservoirs are hydraulically separate from source water supplies and receive water only when it is intentionally diverted through controlled intake infrastructure. They can buffer short-term variability in source water quality and provide operational flexibility during sudden source water quality change or contamination events (e.g., accidental spills) by enabling temporary bypass of inflows, thereby limiting deteriorated water quality inflows and protecting downstream treatment processes.

Within these systems, water quality often differs from that of incoming source water due to the combined effects of hydrodynamic processes (e.g., dilution) and physico-chemical and biological transformations, such as microbial primary production, flocculation, and photodegradation (Dalzell et al., 2009; Hur et al., 2009; Nghiem et al., 2024). The nature and magnitude of water quality change are governed by the coupled effects of hydrodynamics, external loading, and internal physico-chemical and biological processes as modulated by basin morphology and climate (Goodman et al., 2011; Kraus et al., 2011; Hur et al., 2014; Li et al., 2016; Oliver et al., 2016; Wang et al., 2021; Imtiaz et al. 2024; Jia et al., 2025). While these processes are generally recognized, raw water storage reservoirs are not typically intentionally configured or operated to influence water quality prior to treatment.

Drinking water treatment performance is governed by a diverse array of source water quality parameters, including but not limited to pH, alkalinity, and turbidity (Crittenden et al., 2012). One of the most critical water quality parameters to treatment, however, is organic matter. Organic matter is a diverse mixture of molecules that drives particle surface charge in natural waters (Ali et al., 1984; Edzwald, 1993). Specifically, it can drive the efficacy of coagulation and subsequent filtration and the formation of disinfection by-products (Edzwald, 1985; Ratnaweera & Fetting, 2015; Beauchamp et al., 2020), as well as increase WTP operational costs (Emelko et al., 2011; 2024; Crittenden et al., 2012). Residual organic matter in treated drinking water may also pose health concerns by promoting biofilm growth in the distribution system—which can potentially harbor pathogens—and by contributing to taste and odor issues (Health Canada, 2019). Organic matter—specifically dissolved organic matter (DOM)—reported in this work includes both natural and anthropogenic sources and does not differentiate between them.

Landscape disturbances can substantially impact organic matter concentration and character, challenging WTPs (e.g., potential service outages- Hart et al., 2004; Busse et al., 2006; Emelko et al., 2011; 2024; Devane et al., 2014; Johnston et al., 2019; U.S. E.P.A., 2024). Such disturbances can mobilize organic matter and affect its delivery to and transport within receiving waters by substantially altering hydrologic connectivity. Wildfires can particularly alter runoff processes by reducing vegetation and affecting soil hydrophobicity (Doerr et al., 2005; Woods et al., 2006), mobilizing organic matter and impacting its delivery to and transport within receiving waters; this can result in episodically-elevated turbidity and organic matter levels (Emelko et al., 2024).

Investigations of reservoir attenuation of disturbance-associated dissolved organic matter (DOM) impacts within reservoirs are few and limited to large-scale, online reservoirs and lakes with years of retention time and ecological characteristics (e.g., unstable littoral zones) not present in smaller, offline reservoirs (Alexander et al., 2004; Furey et al., 2004; Basso et al., 2021). Although not typically practiced, raw water storage reservoirs can be intentionally designed to improve WTP resilience to sudden water quality changes by diluting impacted inflowing source water and/or providing sufficient residence time for targeted physico-chemical and/or biologically-mediated water quality change. While lake and reservoir buffering of external pollutant loads has been well-documented (Sprague, 2002; Sarmiento et al, 2009; Santisteban et al., 2016; Guo et al., 2022), offline raw water storage reservoirs hold particular promise for climate change adaptation via intentional design to mitigate such source water quality fluctuations and associated threats to treatability. Their hydraulic decoupling from continuous inflows enables control of residence time, withdrawal depth, and internal flow paths; thus, enabling targeted attenuation of disturbance-driven water quality fluctuations prior to treatment. Investigations demonstrating or characterizing these capacities at high temporal frequencies with parameters relevant to drinking water treatment process performance (e.g., organic matter) are scant, however.

To effectively manage reservoirs and their associated threats to source water quality and treatability requires an understanding of the natural spatial and temporal variability in reservoir water quality. Few studies have investigated the spatial distribution of DOM within reservoir systems; of those, the focus has been limited to natural, deep (>20 m) reservoirs (Hur et al., 2007; Kraus et al., 2011; Nguyen et al., 2011), with no studies examining engineered offline reservoirs. Temporal shifts in DOM concentration and character within such systems have not been systematically described. This limits accurate characterization of in-reservoir changes in DOM concentration and character relative to natural variability and hinders clarification of the processes driving these changes—both of which are foundational to informing reservoir design and operational strategies that maximize attenuation of source water quality fluctuations prior to treatment.

The goal of this study was to demonstrate the dynamics and attenuation of DOM within offline raw water reservoirs to evaluate the potential for reservoirs to enhance climate adaptation and resilience through intentional design to better protect drinking water source quality and treatability. Thus, the specific objectives of this study were to evaluate 1) the spatiotemporal distribution of DOM within offline reservoirs in series, and 2) the capacity of such reservoirs to mitigate water quality shifts after landscape disturbances.

2.2 Materials & Methods

2.2.1 Experimental approach

Here, ultraviolet absorbance at 254 nm (UV_{254})—a real-time indicator of DOM concentration and character (Edzwald, 1993)—was intensively, spatiotemporally monitored to observe its dynamics within a wildfire-impacted river and subsequent DWS with two raw water reservoirs in series. Water quality changes through the DWS were then assessed to demonstrate the associated water treatment implications of reservoir operation in series after water quality disturbance. While potential drivers of observed changes in these parameters were explored, mechanistic attribution was not a primary objective of this study.

2.2.2 Study site

Water was collected from multiple locations within and immediately outside the Regional Municipality of Wood Buffalo offline raw water reservoir system in Fort McMurray, Alberta ($56^{\circ} 43' N$, $111^{\circ} 24' W$). The region lies within an ecozone dominated by wetlands and coniferous forests (Chanasyk et al., 2003), which promotes *fill-and-spill* hydrological behavior, whereby water inputs are retained within landscape storage until a threshold is exceeded, triggering hydrologic connectivity and subsequent outflow (Spence & Woo, 2003; McDonnell et al., 2021). As shown in Figure 2.1, the sampling locations are hydrologically linked, with water flowing from the Athabasca River into the River Intake Structure, the East Reservoir, then into the West Reservoir, prior to entering the WTP. The reservoirs have a combined surface area of 0.11 km^2 and a maximum depth of 8 m. The reservoirs have a total storage capacity to allow for approximately 14 days between the water entering the East Reservoir and intake to the treatment plant. As Fort McMurray is located in a cold climate, water collection was restricted to the ice-free months of June to September, hereafter referred to as “ice-free period.” Collection was performed during this ice-free period for three consecutive years (2023-2025).

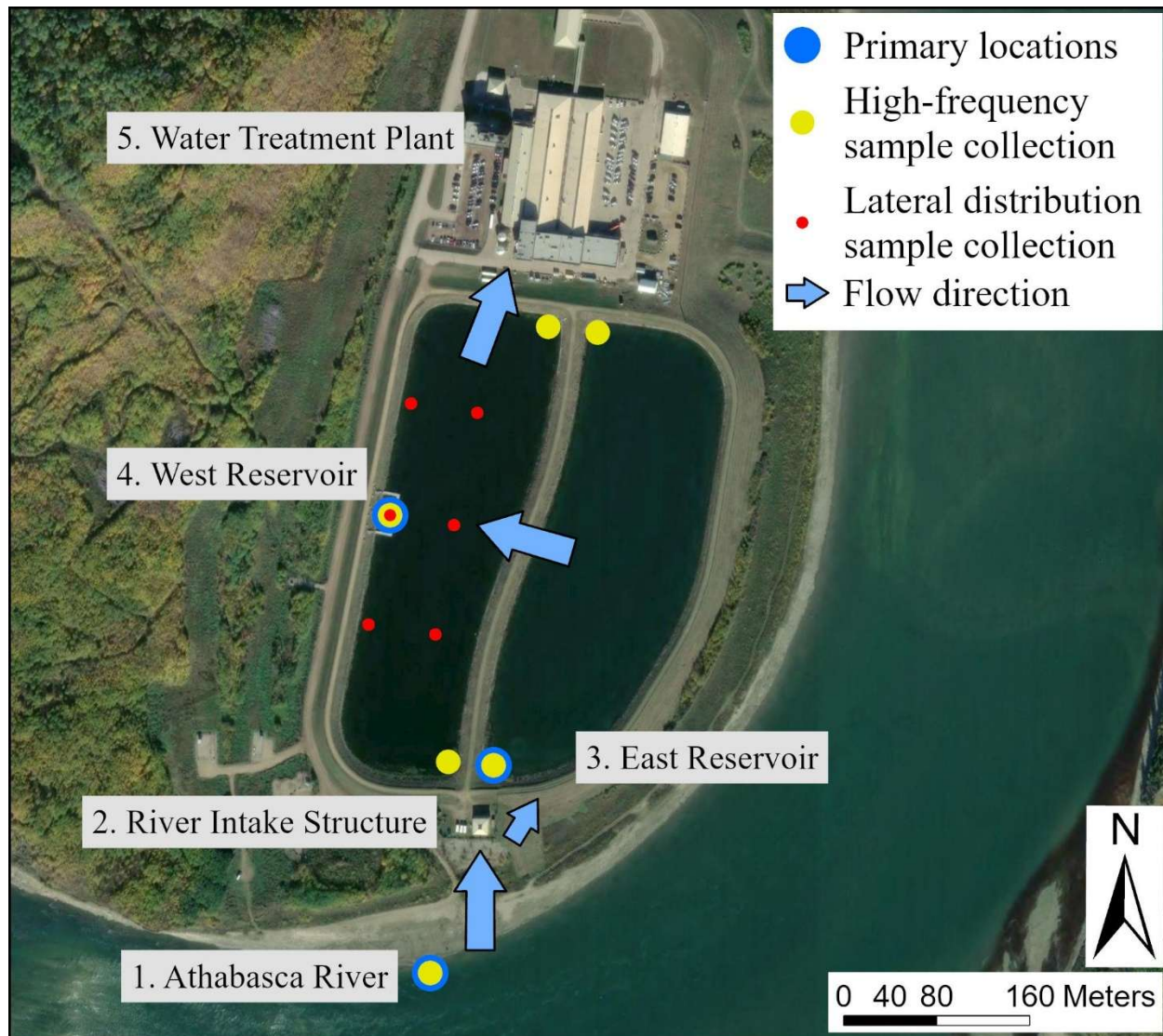


Figure 2-1 Sample collection locations in the Fort McMurray DWS. Locations are numbered according to flow path order. Water enters from the Athabasca River into the River Intake Structure before pumping into the East Reservoir, then flowing into the West Reservoir and entering the treatment plant from an intake within the West Reservoir. [Picture source: Esri, Vantor, Earthstar Geographics, and the GIS User Community].

The Fort McMurray DWS was impacted by the Horse River wildfire of 2016, which burned an estimated 600,000 ha and is currently the most expensive natural disaster in Canadian history (\$8.9 billion in direct costs- Emmerton et al., 2020). The effects of this disturbance have persisted since the fire and still challenge the Fort McMurray WTP with elevated and more variable levels of source water UV_{254} (Alam et al., 2018; Emmerton et al., 2020).

The Fort McMurray WTP uses a conventional water treatment approach (coagulation, flocculation, clarification, granular media filtration, and disinfection), similar to most WTPs treating surface water (Crittenden et al., 2012). As such, effective destabilization of particulates via coagulation to enable subsequent flocculation and physico-chemical filtration is an essential step for the provision of safe drinking water in Fort McMurray. The Fort McMurray WTP uses polyaluminum hydroxychloride (PACl; specific gravity 1.334-1.37 @ 20 °C; Isopac; Klearwater Equipment & Technologies) in their coagulation. Coagulant doses reported in the following sections were provided by the Fort McMurray WTP.

2.2.3 Sample collection and handling

All water samples were collected in triple-rinsed 1 L high-density polyethylene bottles. Surface water samples were obtained by grab sampling and, when relevant (i.e., benthic layer sampling) using a peristaltic pump and National Sanitation Foundation (NSF) 61-rated tubing. They were then transported to the on-site laboratory for preservation, storage, and shipping (on ice) or immediate analysis. Samples shipped to the University of Waterloo were analyzed as soon as possible upon receipt; hold times did not exceed 28 days, as recommended by Standard Methods (APHA, AWWA, and WEF, 2022).

Routine sampling for dissolved organic carbon (DOC) and liquid chromatography paired with organic carbon detection (LC-OCD), were conducted on an approximately weekly basis for the duration of the study. Ultraviolet absorbance at 254 nm (UV_{254}) was collected on an approximately weekly basis in 2023 and a daily basis in 2024 and 2025. To evaluate the effects of sampling depth on DOM concentration and character, samples were collected and evaluated for UV_{254} and DOC at the surface and benthic levels of the primary (Figure 2-1) West Reservoir location in 2025. Additionally, to investigate lateral position impacts on UV_{254} , samples were collected from six locations across the West Reservoir in 2023. A period of high-frequency UV_{254} sampling was conducted in September 2023, consisting of three samples per day (07:00, 12:00, 19:00) in multiple locations, to investigate the effects of sample collection timing on UV_{254} results. Further sampling was conducted at the Northeastern West Reservoir (Figure 2-1), to investigate any potential impacts on water quality by the microbial and macrophyte growth observed in that location.

2.2.4 Water quality analyses

Organic matter is often quantified by measurement of organic carbon because carbon typically comprises between 40 and 60% of natural organic molecules by mass (Schwarzenbach et al., 2017). DOC and UV_{254} were analyzed according to Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, and WEF, 2022). Samples for DOC analysis were preserved by filtration through 0.45 μm polyethersulfone filter, acidification to pH 2 by addition of 37% HCl, and subsequent refrigeration at 4 °C. DOC was analyzed via high-temperature combustion (Standard Method 5310C) using a Shimadzu TOC-L

analyzer with a detection limit of 0.1 mg/L (APHA, AWWA, and WEF, 2022). UV_{254} was measured using a portable UV spectrophotometer (Realtech, UV_{254} P200B). Specific ultraviolet absorbance at 254 nm (SUVA) was then calculated by dividing UV_{254} by DOC and multiplying by 100 (Edzwald & Van Benschoten, 1990). UV_{254} data from the River Intake Structure were recorded by the Fort McMurray WTP using spectrophotometry (Hach DR 6000 Benchtop Spectrophotometer). Temperature measurements were obtained from the surface of the reservoirs and the Athabasca River using a handheld thermometer. DOM fractions were analyzed by size exclusion chromatography using liquid chromatography paired with organic carbon detection (LC-OCD) using a Model 8 LC-OCD analyzer (DOC-Labor GmbH, Karlsruhe, Germany). This subdivides DOM into five fractions: biopolymers, humic substances, building blocks, low molecular weight (LMW) acids, and LMW neutrals based on molecular size (Huber et al., 2011). The samples for LC-OCD analysis were preserved by filling 40 mL glass vials completely, removing any headspace, before refrigeration at 4 °C.

2.2.5 Statistical analyses

Linear mixed-effects models were employed to assess the significance of changes in water quality. Linear mixed-effects were selected over multiple linear regression models to account for nested data, treating location as a random effect rather than a fixed effect. Model assumptions such as homoscedasticity and normality of residuals were evaluated through diagnostic plots and Shapiro-Wilk tests. Statistical analyses were conducted in R (version 4.5.2) using the *lmer()* function and associated diagnostic packages. Two-tailed t-tests were used to assess the significance of differences between sample locations. Any p-values less than 0.05 were considered significant in this work.

2.3 Results & Discussion

2.3.1 DOM: Spatiotemporal variability

Figure 2-2 shows the benthic and surface UV_{254} and DOC data in the primary (Figure 2-1) West Reservoir location. Differences in DOC between the surface and benthic levels of the reservoir were statistically significant ($p = 0.03$); however, DOC trended similarly in both levels over time (Figure 2-2), and the means in the surface and benthic levels were comparable (4.74 and 4.83 mg/L for the surface and benthic levels, respectively). This suggests that DOM concentration is relatively homogenous throughout the water column despite statistically significant differences between depths.

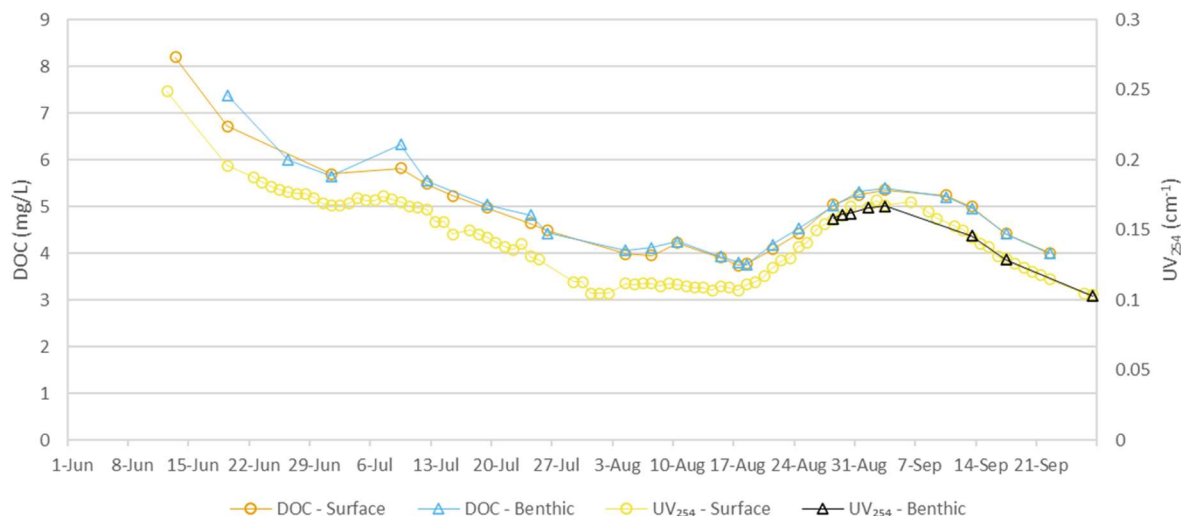


Figure 2-2 Surface and benthic DOC and UV₂₅₄ in the West Reservoir. Samples were collected at the surface and benthic levels by peristaltic pump.

During investigation of lateral position impacts on DOM (Figure 2-1) standard deviation and relative standard deviation (i.e., coefficient of variation) in the West Reservoir were 0.002 cm⁻¹ and 0.48%, demonstrating that DOM concentration and character are laterally homogenous throughout the reservoir. Similarly, UV₂₅₄ was measured at two locations in the East Reservoir (Figures 2-1 & 2-3) during a separate high-frequency sampling period. Differences in UV₂₅₄ were not significant between the East Reservoir locations ($p = 0.32$). The UV₂₅₄ in the Northeastern West Reservoir (Figure 2-1), often aligned with that of the primary West Reservoir location (Figure A-1). However, it occasionally yielded substantially (> 10%) different UV₂₅₄ results (Figure A-1), likely due to occasional, accidental sampling of algal or macrophyte biomass (Table A-1). Kraus et al. (2011) also reported that DOM can be spatially variable during an algal bloom event; however, attributing causation to differences observed was outside the scope of this study. Pictures of the Northeastern West Reservoir are shared in Figure A-2. Taken together, these results indicate that DOM concentration and character are spatially homogenous throughout each reservoir cell; however, care should be taken to avoid collecting biomass when attempting to represent the larger water body.

Figure 2-3 shows the results of high-frequency sampling of reservoir UV₂₅₄ performed from September 18, 2023 to September 29, 2023 in the Athabasca River and multiple locations within the reservoirs. Gradual (< 0.05 cm⁻¹) day-to-day changes in UV₂₅₄ were observed, but within each day, despite the hours of difference between samples, little variation in UV₂₅₄ (relative standard deviation < 5%) was noted with the exception of three days (Figure 2-3). UV₂₅₄ decreased in all locations with time, likely associated with a seasonal shift in water quality in the river and decreasing water temperatures (Figure A-2- Lewandowska et al., 2012; Parr et al., 2019). These results suggest that strict timing of sample collection may be less

critical for DOM concentration or character (e.g., DOC or SUVA), as reservoir-scale changes in DOM occur over days to weeks rather than hours, reducing logistical pressure on sample collection. This should not be generalized to all water quality metrics as some parameters (e.g., biological community composition) may alter more rapidly with changes in factors such as light and/or temperature (Shahraki et al., 2020).

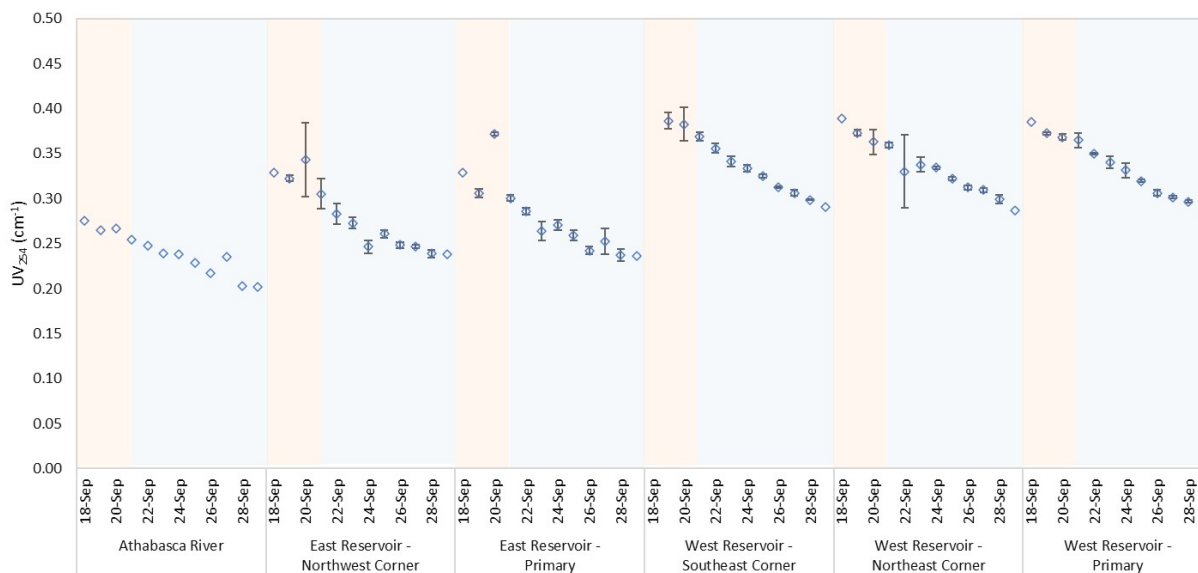


Figure 2-3 High-frequency UV₂₅₄ monitoring in six locations in the Fort McMurray DWS in 2023. The Athabasca River measurements were performed singularly at 07:00, all other locations were measured three times per day (07:00, 12:00, 19:00). Markers show the mean of the three daily measurements and error bars indicate the standard deviation from the mean (n = 3). Red and blue areas on the graph indicate the periods when the intake pumps to the reservoirs were off and on, respectively.

2.3.1.1 DOM character

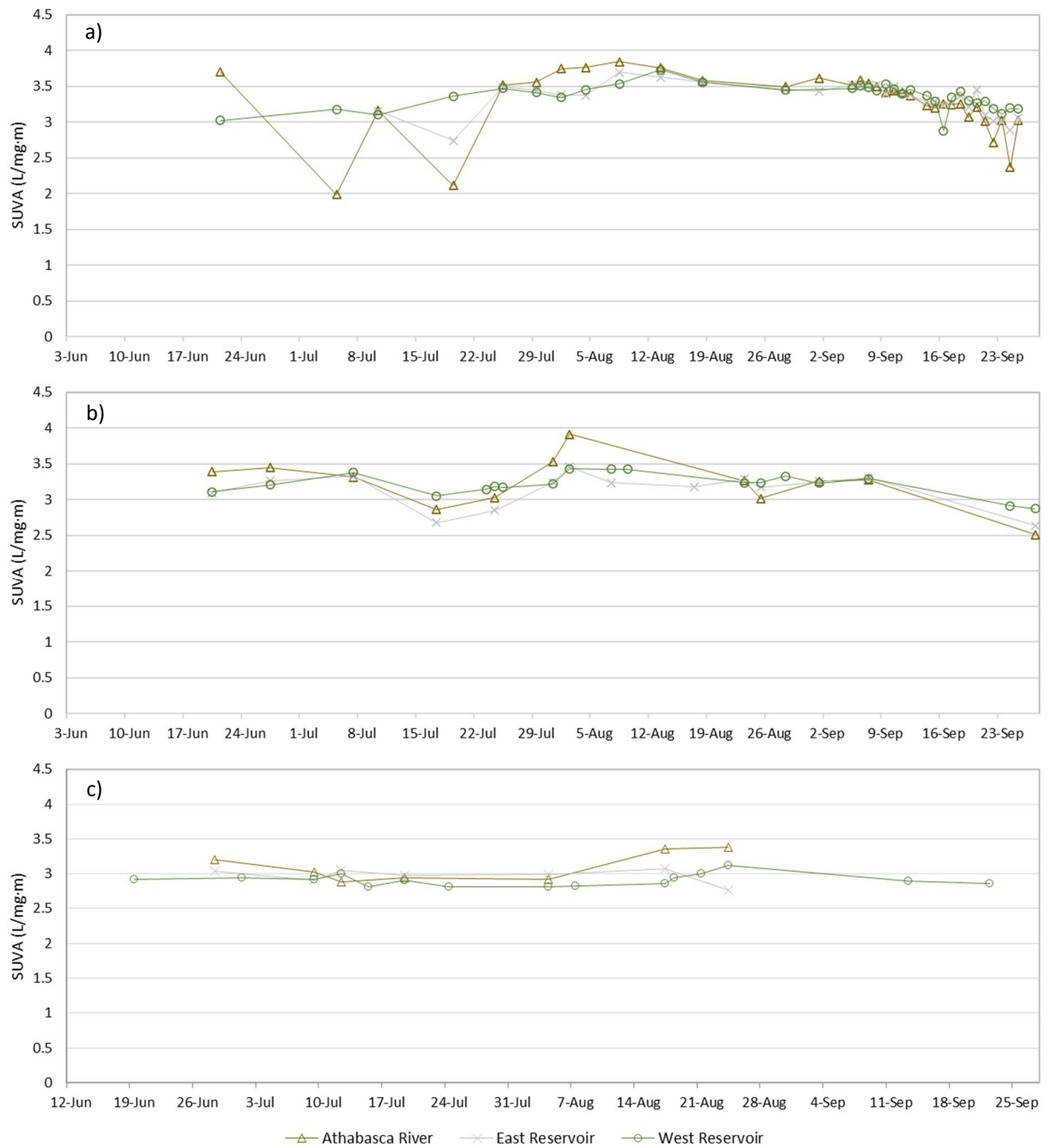


Figure 2-4 SUVA in the three primary sampling locations (i.e., Athabasca River, East Reservoir, and West Reservoir) during the ice-free periods of a) 2023, b) 2024, and c) 2025.

Figure 2-4 shows the SUVA values across the three primary study locations for each reported year. No notable intra-seasonal variation in SUVA is visually apparent across each ice-free period. Consistent with this visual trend, linear mixed-effects modeling indicated that intra-ice-free period temporal trends in

SUVA were not statistically significant ($p = 0.17$) across all three study years, in each location, while inter-annual differences in SUVA were significant (both $p < 0.01$), indicating that DOM aromaticity was relatively stable within a given ice-free period but differed across years (Figure A-4). Consistent SUVA in source water allows for more reliable coagulation results and stable DBP formation potential (Edzwald, 1993; Hua et al., 2015). Similarly, SUVA did not appear to shift within the reservoirs (Figure 2-5), contrasting with previous studies (Kraus et al., 2011; Hur et al., 2014; Imtiaz et al., 2024) and suggesting negligible microbial or abiotic impacts on DOM character within the reservoirs. These differences may be related to variations in study length and timing, ecological characteristics, hydrological differences, or background water quality, highlighting the need for further investigation into the impact of offline raw water reservoirs on DOM character.

Figure 2-5 presents the relative proportions of biodegradable (including biopolymers, LMW acids, and LMW neutrals) and refractory (humic substances, building blocks) fractions in the three primary (Figure 2-1) locations for each year studied. The fractions were individually quantified using LC-OCD and grouped for clarity of interpretation, shared in Figures A-5 through A-8. Concordant with SUVA results, almost no substantial ($> 10\%$) shifts in biodegradable or refractory fractions occurred within each ice-free period; however, notable differences were observed between years. Refractory compounds reached their highest relative proportion in 2024 and their lowest in 2025 (Figure 2-5) but were dominant for the entire study duration. This consistency in DOM character likely reflects the inputs of organic matter with similar quality from the surrounding landscape, and/or consistent transformation of organic matter within the Athabasca River. The root causes of these dynamics are outside the scope of this study; however, the relative stability of biodegradable and refractory fractions suggests that the system has reached a biogeochemical steady state, wherein organic matter inputs are balanced by consumption, degradation, and burial (i.e., sedimentation and subsequent coverage by accumulating sediment- Mendonca et al., 2017). This stability implies that the ecological processing and nutrient cycling is largely consistent throughout the system, rather than changing as water moves through it.

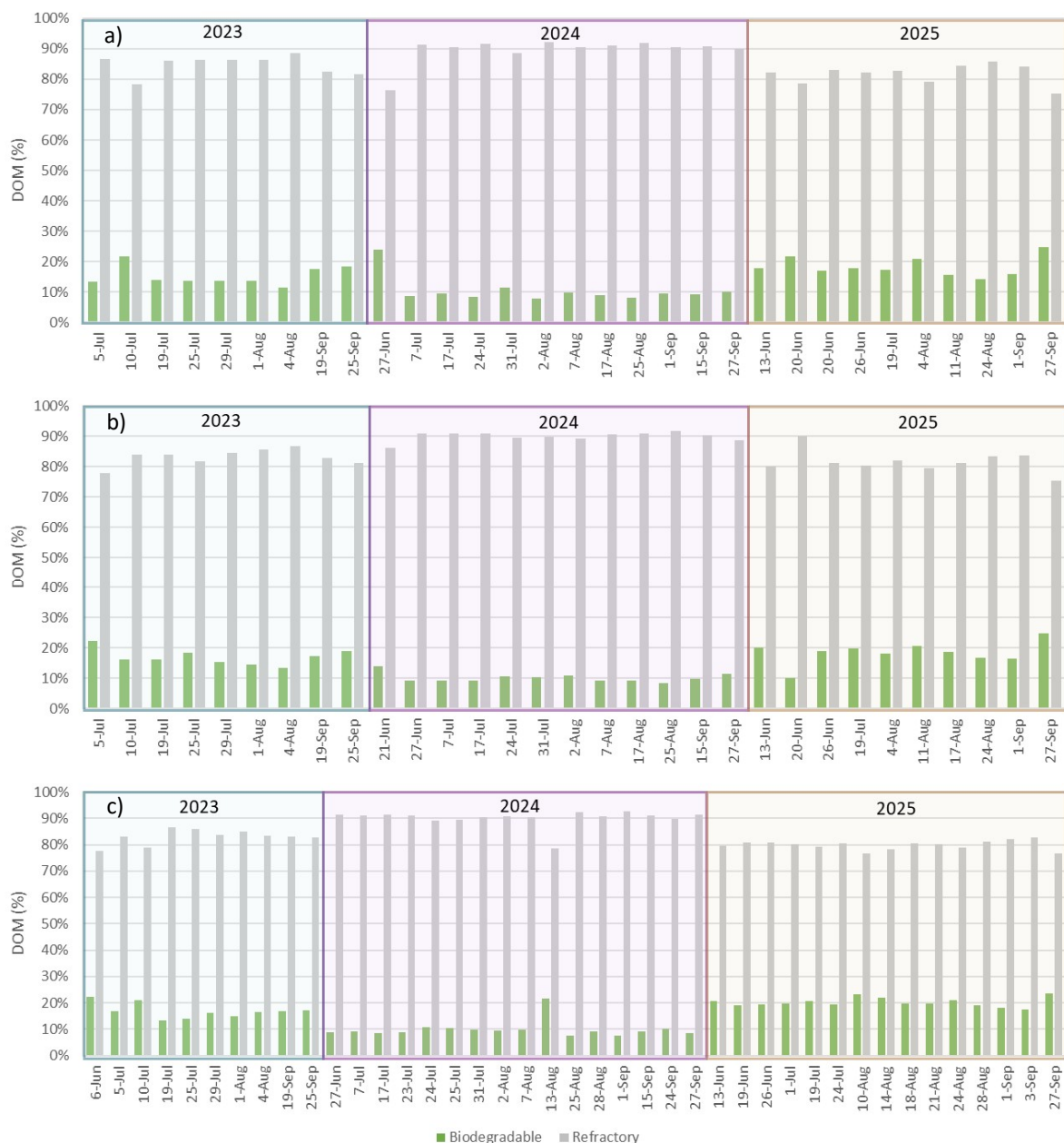


Figure 2-5 Biodegradable and refractory DOM fractions in the three primary sample collection locations (i.e., Athabasca River [a], East Reservoir [b], and West Reservoir [c]) during the study period. Biodegradable fractions include biopolymers, LMW acids, and LMW neutrals. Refractory fractions include humic substances and building blocks (broken down humic substances).

2.3.2 Reservoir impacts on river DOM

To illustrate spatial and temporal differences in source water DOM during the ice-free period, UV_{254} levels measured at the three primary sample collection locations (i.e., Athabasca River [AR]; East Reservoir [ER]; West Reservoir [WR]; Figure 2-1) are presented in Figure 2-6, which differentiates between the ice-free period in 2023 (a), 2024 (b), and 2025 (c). DOC concentrations generally followed the same trends; and are provided in Figure 2-7.

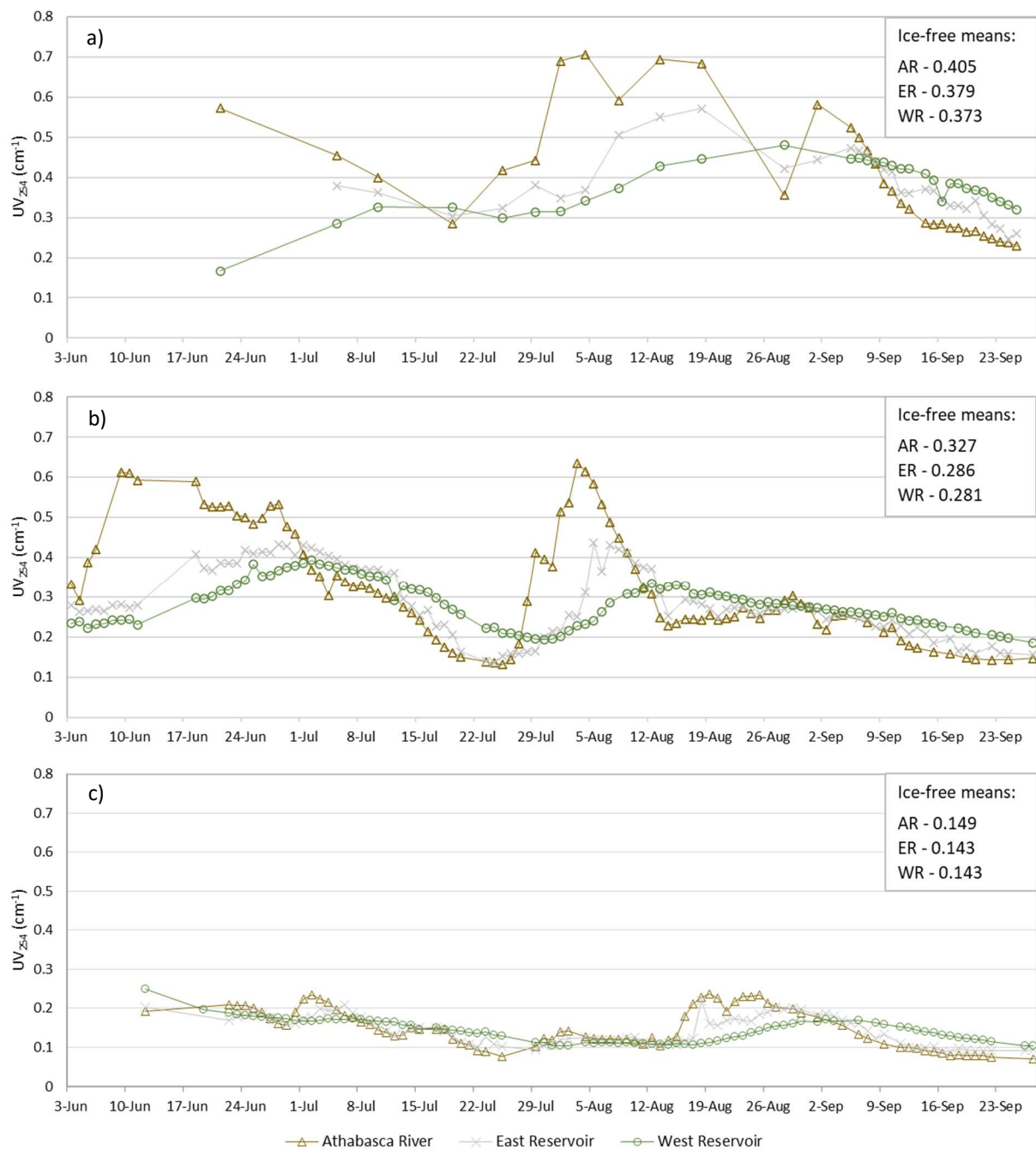


Figure 2-6 UV_{254} at the three primary sample collection locations (i.e., Athabasca River [AR]; East Reservoir [ER]; West Reservoir [WR]) during the ice-free periods of a) 2023, b) 2024, and c) 2025.

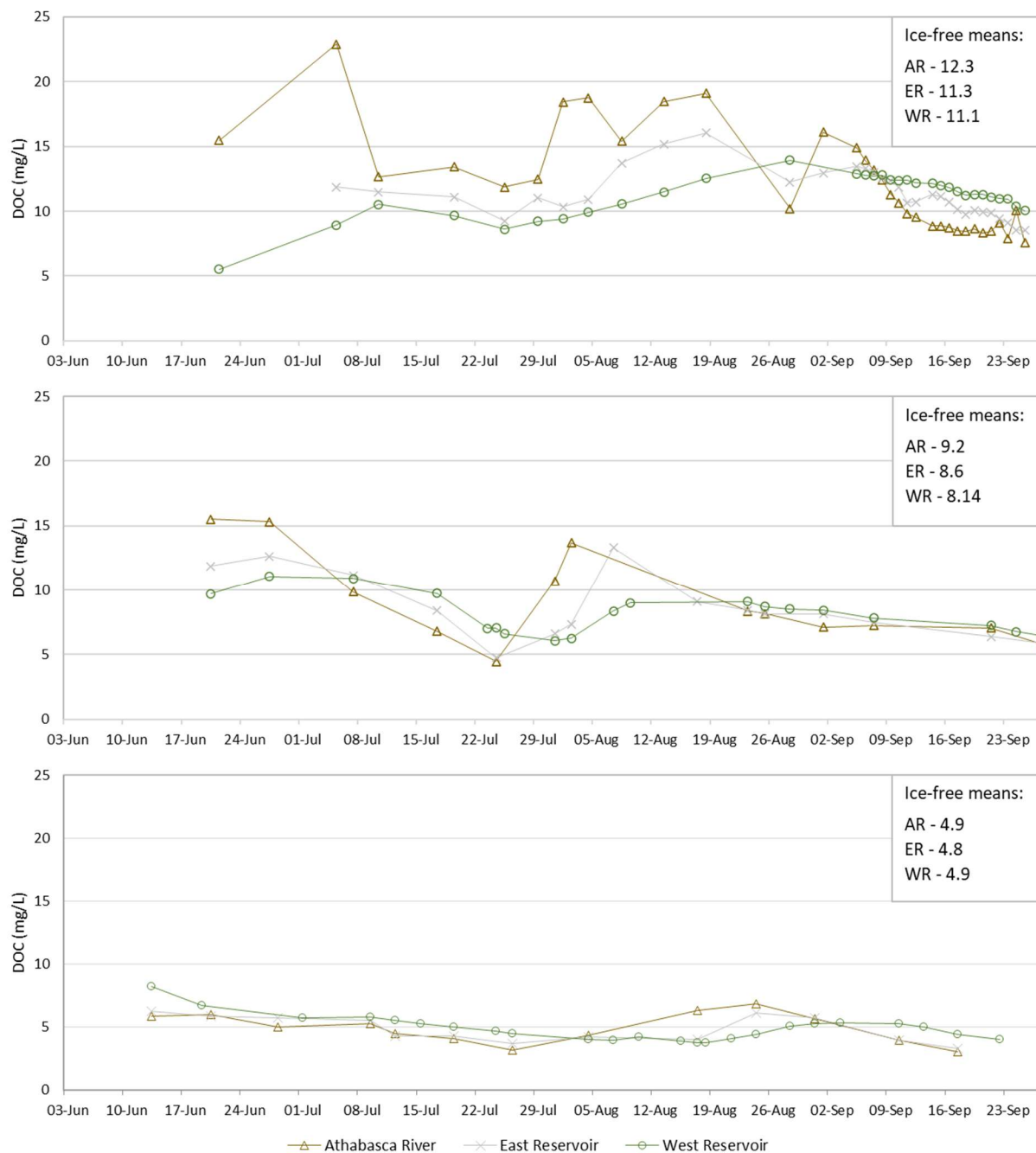


Figure 2-7 DOC at the three primary collection locations (i.e., Athabasca River [AR]; East Reservoir [ER]; West Reservoir [WR]) during the ice-free periods of a) 2023, b) 2024, and c) 2025.

Changes in the Athabasca River UV_{254} and DOC are reflected in the East Reservoir and subsequently the West Reservoir (Figures 2-6 & 2-7). This dependence on the river source without notable intra-reservoir changes in DOM concentration or character is unique compared to what has been reported for larger, online reservoirs (Goodman et al., 2011; Kraus et al., 2011; Hur et al., 2014; Oliver et al., 2016; Imtiaz et al.

2024). The dependence was further supported by the comparable UV_{254} and DOC means across all sites (Figures 2-6 & 2-7). The slightly higher mean UV_{254} and DOC in the Athabasca River during 2023 and 2024 is associated with relatively elevated UV_{254} and DOC early in the ice-free period. Notably, despite the spatial homogeneity of DOM concentration and character observed across each reservoir (Figure 2-3), UV_{254} and DOC values still differed consistently and meaningfully between the Athabasca River, East Reservoir, and West Reservoir at any given point in time (Figures 2-6 & 2-7).

Notably, while UV_{254} and DOC changed throughout each ice-free period (Figures 2-6 & 2-7), SUVA remained constant (Figure 2-4). UV_{254} reflects both DOM concentration and its aromaticity (Edzwald, 1993). In this case, the observed changes in UV_{254} were primarily driven by changes in DOC, rather than aromaticity. Although some studies reported changes in DOC without a proportional change in UV_{254} (Archer & Singer, 2006; Raudina et al., 2022; Andersson et al., 2024; Chapter 3), others have shown a strong correlation between the two (Peacock et al., 2014; Yates et al., 2023). The results here demonstrated UV_{254} as a reliable proxy for DOC, potentially reducing the need for direct DOC analysis.

As would be expected, the offline raw water reservoirs attenuated fluctuations in water quality from the Athabasca River. Standard deviation comparisons across all primary sampling locations indicate that the Athabasca River showed the highest intra-annual UV_{254} variability during the study duration (i.e., ice-free periods of 2023, 2024, and 2025), averaging 1.6 and 2.2 times higher than that of the East Reservoir and West Reservoir, respectively. This attenuation can be explained by considering the reservoirs as ideal continuously stirred tank reactors (CSTRs) in series, where mixing and dilution reduce variability in incoming water quality. In such systems, multiple reactors in series introduce both damping and lag in the system response, leading to greater attenuation of short-term fluctuations compared to a single reactor with the same total volume. Detailed explanation of reactor theory as applied to this system is provided in Appendix A. While observation of attenuation of shifts by the reservoirs was anticipated, modeling and prediction of specific responses was not an objective of this study. With an estimated combined hydraulic retention time of ~14 days, the reservoirs provide substantial attenuation capacity even without the extended hydraulic retention times previously reported on, the smallest of which was more than seven times longer than that of the Fort McMurray reservoir system (Goodman et al., 2011; Kraus et al., 2011; Hur et al., 2014; Li et al., 2016; Oliver et al., 2016; Wang et al., 2021; Imtiaz et al. 2024; Jia et al., 2025).

Given the dependence of the reservoirs on river water quality, and the observed attenuation through the system, coordinated monitoring of the river and the reservoirs can serve as an early indicator of subsequent changes in treatment plant intake water quality. Modeling reservoir attenuation could help utilities to anticipate future WTP intake water quality based on river data, which would allow treatment plants to proactively adjust coagulant dosing, rather than responding reactively. Additionally, monitoring of the river

allows for anticipation and bypassing of contaminated inflows, protecting downstream treatment processes. These operational strategies can improve treatment efficiency and optimize chemical use during events that can cause elevated levels of DOM (e.g., snowmelt- Emelko et al., 2011; Tiwari et al., 2018). Overall, these findings underscore the value of integrated watershed monitoring, predictive modeling of water quality changes through the DWS, and strategic operation of offline reservoirs for enhancing climate resilience and preparedness for disturbance events.

2.3.3 Sand pump impacts on reservoir DOM

Submersible “sand pumps” designed to remove particulate matter from intake water are used by the Fort McMurray WTP within the River Intake Structure; however, they were not consistently operational during the study duration. Figure 2-8 shows the UV_{254} of Athabasca River and River Intake Structure within the Fort McMurray WTP, as well as the operating time of the sand pumps. The Athabasca River UV_{254} measurements visually coincided with those in the River Intake Structure, barring the beginning of the ice-free period of 2024 when the sand pumps were in operation. This period corresponded with lower UV_{254} in the River Intake Structure, suggesting sand pump operation may improve water quality; however, a similar effect was not observed during the brief period of operation in 2025. The effects of submersible sand pumps on water quality parameters like UV_{254} have not yet been reported.

Water samples were filtered through 0.45 μm PES filters prior to UV_{254} analysis, as was mentioned in Section 2.2.4; therefore, the impact of turbidity on such measurements is not immediately apparent. One likely explanation is that DOM does not consist solely of truly dissolved molecules and may also include colloidal or nano-scale aggregates that pass through the 0.45 μm filter pores (Christl et al., 2008; Huber et al., 2011). Consequently, the processes that remove suspended sediments—such as sand pump operation—may also remove some of these smaller organic aggregates leading to lower UV_{254} . Accordingly, the effects of sand pumps on drinking water source quality merit further investigation.

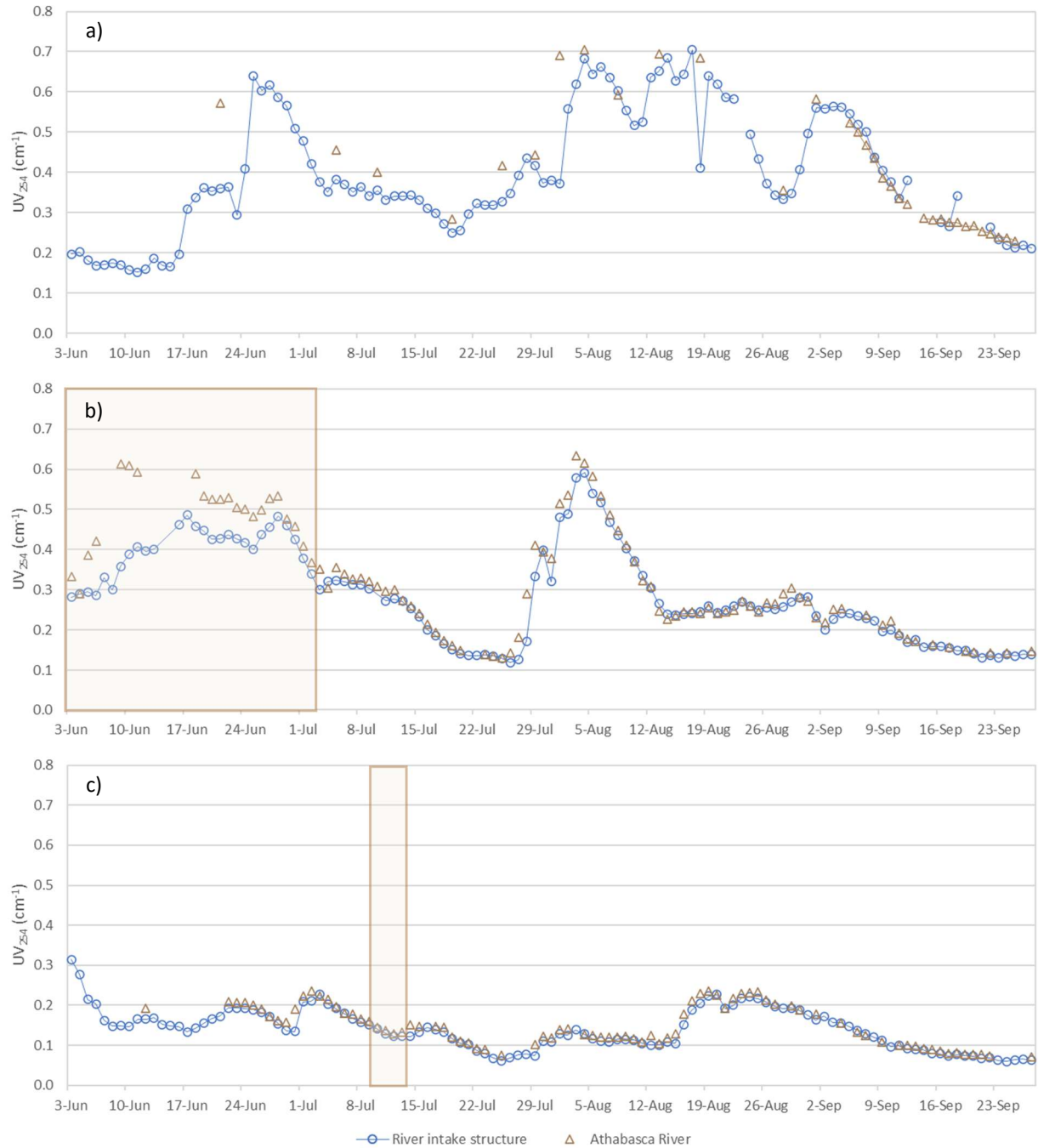


Figure 2-8 Comparison of UV₂₅₄ in the River Intake Structure and Athabasca River during the ice-free periods of a) 2023, b) 2024, and c) 2025. The highlighted regions show the durations of sand pump operation in the River Intake Structure.

2.3.4 Reservoir implications for drinking water treatment

DOM concentration and character are well understood to drive coagulant demand in water treatment processes, with more aromatic DOM (e.g., humic substances) typically exerting greater coagulant demand than less aromatic DOM (e.g., LMW acids- Edzwald, 1993; Pernitsky and Edzwald, 2006; Edzwald & Kaminski, 2009). Accordingly, the consistency of aromatic, humic substance-dominated DOM character in this system indicates that coagulant dose was driven by DOM (Figures 2-5 & 2-6). UV_{254} is recognized as an efficient and effective proxy for DOM in water (Edzwald, 1985; Albrektienė et al., 2012). As such, it has also been recommended that coagulant dosing be proportional to UV_{254} of the raw water (Ratnaweera & Fetting, 2015; Beauchamp et al., 2020), and the relative UV_{254} stability offered by the reservoirs has practical value for operational decision-making. The relationship between UV_{254} in the West Reservoir and the PACl dose applied in the WTP is presented below in Figure 2-9.

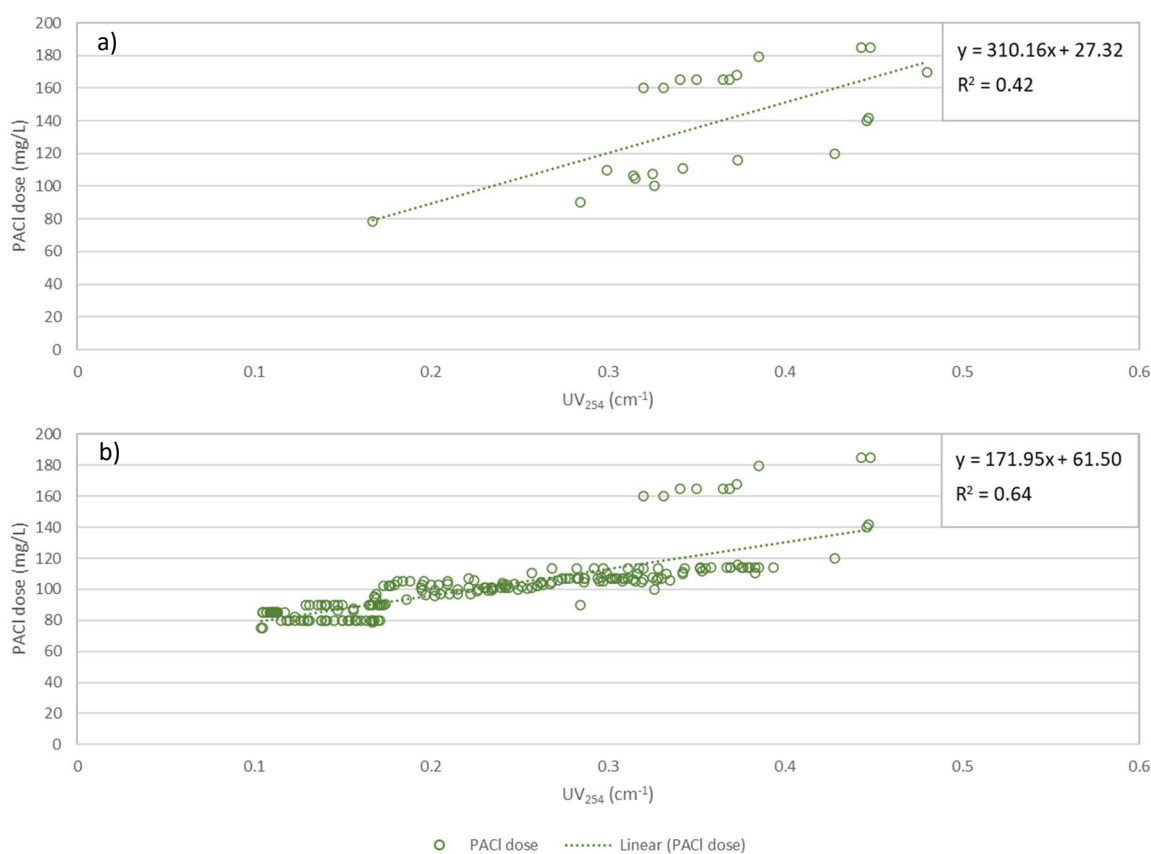


Figure 2-9 Relationship between UV_{254} in the West Reservoir and PACl dose for a) 2023, and b) 2023, 2024, 2025 combined. UV_{254} was measured in the West Reservoir and PACl dose was provided by the Fort McMurray WTP. Both regressions were significant ($p < 0.05$ - Table A-1). UV_{254} and PACl dose data from 2019-2025 were provided by the Fort McMurray WTP and are provided in Figure A-2.

Notably, highly-variable water quality during certain events lead to additional challenges in selecting PACl dose (Figures 2-6, 2-7 & 2-9 [a]). Occasionally, utilities may increase and potentially over-dose coagulant in order to ensure finished water quality and protect consumers during periods of deteriorated source water quality. For example, in 2023, PACl doses approached 200 mg/L, a threshold beyond which residual aluminum in finished water becomes a concern with direct implications for consumer health (Figure 2-9 [a]). The peak UV_{254} in the Athabasca River was higher than the East and West Reservoirs in 2023 by approximately 1.2 and 1.5 times, respectively (Figure 2-6). In the absence of reservoir attenuation, the WTP would have been required to treat Athabasca River water directly at these elevated DOM concentrations, driving coagulant demand higher (Edzwald, 1993; Pernitsky and Edzwald, 2006; Edzwald & Kaminski, 2009), modeled at 246 mg/L using 2023 data (Figure 2-9 a). This represents a savings of 70 mg/L of PACl due to attenuation by two reservoirs in series; with only one reservoir online, a modeled decrease of 42 mg/L would still be provided. Without this attenuation, operators would be confronted with an acute risk-management trade-off between residual aluminum exceedances and decreased treated water quality. This observation underscores the value of the reservoirs to attenuate DOM variability prior to intake to the WTP, even with limited hydrological capacity.

Shifting water quality, among other challenges, can make it so that optimal coagulant dose is not always achieved in treatment. Consistent raw water quality, supported by reservoir attenuation, requires fewer coagulant dose adjustments (Edzwald, 1985), minimizing the risk of overdosing—thereby reducing unnecessary chemical expenditures—while also preventing underdosing, which can compromise coagulation efficacy, potentially resulting in higher levels of organic matter in treated water (Yao et al., 2015). It should be noted, however, that the reservoirs attenuated both increases and decreases in DOM (Figures 2-6 & 2-7), and systems with reservoirs may therefore retain elevated DOM concentrations longer than those without.

Although a relationship between raw water UV_{254} and recommended coagulant dose has been reported (Ratnaweera & Fetting, 2015; Beauchamp et al., 2020), coagulant dose determination can also be impacted by operational factors (Crittenden et al., 2012; Bratby, 2016; Sheng et al., 2022; AWWA, 2025). For example, WTPs may choose not to adjust coagulant dose during night shifts to reduce operational workloads during periods of limited personnel. Such operational factors may explain the low R^2 values reported in Figure 2-9. The results presented here show WTP decision-making is informed by water quality metrics but ultimately driven by practical factors such as operational stability and risk management.

2.4 Conclusions

1. Open-water DOM concentration and character were consistent across depth and lateral position within each reservoir.

Differences in sample collection depth within the West Reservoir proved to be statistically significant ($p = 0.03$) but practically inconsequential. The West Reservoir maintained a UV_{254} distribution that was near-uniform across lateral position (relative standard deviation of 0.48%), and the East Reservoir collection locations were not statistically significant ($p = 0.32$). This suggests that offline raw water reservoirs may exhibit limited primary production and organic matter transformation relative to natural systems (e.g., lakes). These observations have potential to simplify sample collection logistics for utilities monitoring source water; however, a preliminary assessment of UV_{254} is nevertheless recommended before assuming spatial uniformity.

2. UV_{254} changes in the reservoirs were not substantial ($> 5\%$) within a single day but became substantial over multiple days.

Time of day was not a critical factor when evaluating UV_{254} in the reservoirs. Combined with the observed spatial consistency of UV_{254} , this observation further simplifies sample collection logistics for utilities monitoring source water. Multiple days of measurements are recommended to better understand DOM changes within a given water body.

3. Inter-annual variability in DOM character (as measured by SUVA and LC-OCD) was statistically significant (both $p < 0.01$) but intra-annual variability was not ($p = 0.17$).

The Athabasca River consistently delivered DOM of a similar character through each ice-free period of each year. This observation likely indicates either a consistent source of DOM from the surrounding landscape, or consistent transformation within the Athabasca River prior to delivery to the reservoirs. DOM was predominantly comprised of humic substances, driving the coagulant demand during water treatment. Understanding a SUVA profile and its consistency can help a drinking water utility to anticipate the effectiveness of its coagulation processes and potential for DBP formation.

4. Utilizing a “sand pump” to reduce incoming particulate matter to a raw water reservoir may offer a reduction of source water DOM concentration.

A disparity in water quality (as measured by UV_{254}) between the Athabasca River and the River Intake Structure was observed only during periods when the sand pumps were active, suggesting that pump operation may contribute to the observed improvement in water quality. Further study is required to

investigate the effects of particulate removal via pumping on reservoir organic matter concentration and character.

5. Reservoir water quality exhibited a lagged, attenuated response to DOC and UV₂₅₄ loading from the river.

Inputs from the Athabasca River drove changes in water quality (as measured by DOC & UV₂₅₄) within the East Reservoir, which in turn drove changes in water quality in the West Reservoir. Consistent with expectations for dilution-driven attenuation, the reservoirs were effective in stabilizing water quality from the river, providing a more consistent intake water quality to the WTP. This stabilization has helped the Fort McMurray WTP to reduce peak coagulant demands, maintain effective coagulation, and protect consumer health, highlighting the value of reservoirs in protecting against disturbances and mitigating the associated water quality fluctuations. Operation of the reservoirs in series allowed for the observation of these water quality changes through the DWS and likely served to provide a more consistent attenuation of DOM shifts from the river by reducing short-circuiting. Further work is needed in order to investigate the impacts of other aspects of reservoir design (e.g., reservoir depth, flow patterns) on the stabilization of source water quality. Additionally, the observed temporal lag and consistent attenuation and trending of water quality in downstream locations based on upstream water quality may offer the potential of bypassing inflows during extreme events, and anticipation of future West Reservoir water quality based on Athabasca River measurements, highlighting the value of monitoring for the efficient production of safe drinking water.

6. Attenuation of water quality shifts by the reservoirs had practical implications to consumer health and treatment costs.

The established relationship between UV₂₅₄ in the incoming source water and PACl dose within the treatment plant underscores additional consumer health protection and additional treatment resilience in the face of disturbance provided by the reservoirs, especially when considering the challenging water quality and elevated coagulant doses in 2023. The observed attenuation of water quality shifts has helped the Fort McMurray WTP to reduce peak coagulant demands (up to 70 mg/L), maintain effective coagulation, and protect consumer health, highlighting the value of reservoirs in protecting against disturbances and mitigating the associated water quality fluctuations.

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Chapter 3

Alternative Preservation Approaches for Remote or Field- Constrained Monitoring of Dissolved Organic Matter Concentration and Character

3.1 Introduction

Rivers and lakes are critical sources of drinking water globally, and their protection is fundamental to the multi-barrier approach for ensuring the provision of safe drinking water (Health Canada, 2017; U.S. E.P.A., 2024). Water quality from these sources can be impacted by anthropogenic and natural landscape disturbances (Emelko et al., 2011; Ji et al., 2021). Monitoring water quality changes at the watershed scale is therefore essential for assessing incremental impacts on water quality from headwaters (e.g., cumulative watershed effects) and supporting effective management (Park & Hwang, 2016; Sudriani et al., 2023). Implementation of watershed-scale water quality monitoring programs enables the evaluation of variability across hydrologic pathways and the identification of impacts from different landscape disturbances that can affect the timing, quantity, and quality of runoff entering receiving waters (Behmel et al., 2016). Such programs are also critical for detecting changes in drinking water source quality, supporting operational decision-making at drinking water treatment plants, and informing the development and evaluation of source water protection strategies (Emelko et al., 2011; Behmel et al., 2016).

Despite their value, the implementation of watershed-scale monitoring programs is limited by the logistical realities of remote environments, with direct implications for sampling continuity and sample integrity. Many headwater catchments are difficult to access, often requiring helicopter-supported access or similarly intensive field logistics, which constrains sampling frequency and increases both the cost and operational complexity of routine monitoring. To reduce the need for repeated site access, automated samplers are frequently deployed to enable time-integrated collection and storage of samples over extended deployment periods. However, reliance on autonomous instrumentation in these settings presents additional challenges related to sustaining equipment performance under prolonged exposure to harsh environmental conditions and limited opportunities for maintenance or repair. These constraints can compromise sampling continuity and increase the likelihood of partial data capture.

Even when sampling systems function successfully over extended deployment periods, a fundamental limitation persists: samples cannot be analyzed *in situ*. Consequently, there is an unavoidable and often extended lag between sample collection in remote headwaters, retrieval and transport under non-ideal conditions, and eventual laboratory analysis. During this period, samples may be exposed to fluctuating temperatures, extended holding times, and limited opportunities for immediate stabilization—conditions that can compromise the representativeness of measured water quality parameters, resulting in data that do not reflect source water quality at the time of sample collection. As a result, sample preservation in remote watershed monitoring is not simply a procedural step, but a critical and often limiting factor in the reliability of the resulting data. Consequently, a field-applicable, effective preservation technique is required to stabilize sample composition and ensure data reliability.

Organic matter, often quantified by organic carbon surrogates (Schwarzenbach et al., 2017), is a complex mixture of molecules that governs particle surface charge in natural waters (Ali et al., 1984). Organic matter—specifically dissolved organic matter (DOM)—reported in this work encompasses both natural and anthropogenic sources and does not differentiate between them. DOM is a critical consideration in the design of drinking water treatment plants (Edzwald, 1993). It drives the efficiency of coagulation and filtration processes and can react with chlorine to form disinfection by-products (Edzwald, 1985; Ratnaweera & Fettig, 2015; Beauchamp et al., 2020), and increase WTP operational costs (Emelko et al., 2011; 2024; Crittenden et al., 2012). Organic matter concentration and character are susceptible to physico-chemical and microbial transformations, including photodegradation and biodegradation (Rutledge et al., 2010; Dalzell et al., 2009; Hur et al., 2009). Effective preservation of organic matter within samples therefore becomes essential to extract benefit from monitoring efforts.

Dissolved organic carbon (DOC) is the fraction of total organic carbon (TOC) that passes through a 0.45 μm filter (APHA, AWWA, and WEF, 2022). There is an established standard method (i.e., Method 5310) for TOC and DOC preservation which includes acidification to pH 2 (using HCl or H₂SO₄) and storage at 4 °C (APHA, AWWA, and WEF, 2022). This method is only intended to preserve organic carbon concentration, not prevent DOM character changes. Acidification suppresses microbial processes by lowering pH, as most microorganisms function within a narrow range near neutral pH (i.e., ≈ 6.5 -7.5- Lewis et al., 1983; Rao et al., 1989; Ahern et al., 2025); however, it may also alter organic matter character through the protonation of functional groups, potentially impacting molecular structure and reactivity (Harshad et al., 2018). Filtration limits biologically mediated degradation by removing microorganisms via size exclusion (Kaplan, 1994; Dean et al., 2018). Temperature reduction, particularly freezing, decreases both microbial metabolism (Gao et al., 2006) and abiotic chemical reactions within the sample (Crittenden et al., 2012). Minimizing exposure to sunlight and air limits photochemical reactions and oxidation that can change organic matter concentration or character. Even with preservation, samples should be analyzed within recommended holding times to ensure analytical accuracy (APHA, AWWA, and WEF, 2022). When immediate transportation of samples to the laboratory for preservation is infeasible, the use of concentrated acids, as required by the standard method, introduces significant safety and regulatory burdens, including the need for secondary containment and extensive personal protective equipment. These constraints can substantially limit the feasibility of standard preservation approaches during remote, watershed-scale, and logistically-constrained sampling efforts (e.g., headwater streams). For the same reason, preservation of DOM through addition of biocides such as sodium azide or mercuric chloride will not be explored here, as these can have high toxicity and are similarly limited in remote work (U.S. N.I.S.T, 2019; U.S. C.D.C., 2026). Nevertheless, robust and representative DOC datasets remain essential for describing cumulative watershed effects, supporting water management decisions, and informing a wide range of scientific and

operational applications. In scenarios where standard preservation is infeasible, alternative preservation approaches (e.g., filtration, freezing) are often employed to stabilize organic matter concentration and character prior to analysis. However, the efficacy of these techniques remains contested in literature.

Table 3-1 summarizes investigations that have discussed freezing as a preservation technique for dissolved organic matter (DOM) concentration (e.g., DOC) and character (e.g., SUVA). While some studies report unpredictable changes in DOC after freezing relative to non-frozen controls, others suggested that freezing was an effective preservation technique for DOC concentration (Table 3-1). These disparate results may be due to methodological differences in freezing and thawing methods, prefiltration, pore size of filters, and storage time used in the different studies. While some aspects of aquatic DOM preservation by freezing and other preservation techniques (e.g., refrigeration, acidification, and filtration) have been reported, a comprehensive, systematic investigation of these techniques, as well as the interactions between them, has not been reported (Table 3-1).

Given the lack of a systematic evaluation on the preservative effects of these techniques, and the associated lack of consensus as to their efficacy, the overall goal of this work was to clarify impacts of different preservation techniques on DOM concentration and character during storage. Specific objectives were to evaluate the effects of (i) temperature control, filtration, and acidification, (ii) interactive effects of these preservation techniques, and (iii) assess the viability of freezing as a preservation technique when performed in isolation on DOM concentration and character.

Table 3-1 Summary of reported methods used when freezing to preserve freshwater DOM concentration and character.

Freezing temp. (°C)	Thawing temp. (°C)	Pre-filtered	Pore size (µm)	Storage time (days)	DOM concentration change (≥ 10%)	DOM character change (≥ 10%)	Investigation
-50 & -7	-	yes	0.2, 0.7	1	yes	yes	Fellman et al., 2008
-50, -24, -20, & -15	5	yes	0.45	1, 30	yes	-	Chen et al., 2015
Liquid nitrogen → -20*	-	no	-	-	no	yes	Tupas et al., 1993
Liquid nitrogen → -18*	-	yes	0.7	42	no	yes	Thieme et al., 2016
-20	11	no	-	-	-	yes	Hudson et al., 2009
-20	-	no	-	-	yes	yes	Druffel et al., 2013
-20	-	yes	0.45	365, 730	yes	yes	Norman & Thomas, 2014
-20	-	yes	0.7	89–269	no	yes	Walker et al., 2016
-20	ambient	yes	0.45	2	yes	-	Cook et al., 2016
-20	-	yes	0.45	7	no	yes	Heinz & Zak, 2017
-20	-	no	-	2	yes	no	Jonker, 2020
-20	4	yes	0.22, 0.45	1 x 9 cycles**	yes	yes	Payandi-Rolland et al., 2021
-20	4	yes	0.2	21, 95	yes	-	Fonvielle et al., 2023
-18	-	yes	0.15	5	-	-	Giesy & Briesse, 1978
-18	-	yes	0.22, 0.45	1 x 10 cycles**	yes	-	Pokrovsky et al., 2018
-18	-	yes	0.45	21, 44	yes	-	Nachimuthu et al., 2020
-	4	yes	-	< 365	yes	-	Spencer et al., 2007
-	refrigerated	yes	0.45	> 2	yes	-	Peacock et al., 2015

*Samples were flash-frozen with liquid nitrogen before being transferred to a freezer at the designated temperature

**Samples were repeatedly frozen and thawed equivalent to the number of cycles indicated

3.2 Materials and Methods

3.2.1 Experimental approach

The effects of acidification, filtration, and temperature control on DOM concentration and character were systematically evaluated across multiple water matrices and storage durations. Storage durations were limited to a maximum of 28 days, in accordance with Standard Method 5310 (APHA, AWWA, and WEF, 2022), to enable effective and focused comparison between preservation techniques. Water matrices were purposefully selected from a range of sites across Canada, including high-quality, wildfire-impacted, and municipally-impacted sources to provide greater insight (i.e., matrix-specific responses) into the effects of the aforementioned preservation techniques across diverse water types.

3.2.2 Experimental design

The experimental design is summarized in Figure 3-1 below. This design enabled effective differentiation between the preservative impacts of each treatment and evaluation of their interactive effects when used in combination. Four water types (i.e., Athabasca River, Fort McMurray reservoir, Grand River, Lake Ontario) were preserved using four treatment types (i.e., untreated, filtered, acidified, and filtered and acidified), four storage durations (i.e., 1, 3, 7, and 28 days) including a baseline measurement, and three temperatures (i.e., 21, 4, and -24 °C). Storage durations were limited to 28 days in order to represent the maximum holding time recommended by Standard Methods. Temperatures were selected to represent ambient (21 °C), refrigerated (4 °C), and frozen (-24 °C) storage conditions. Waters were tested in triplicate where feasible; however, only limited water volumes were available for samples from Alberta (i.e., Athabasca River and Fort McMurray reservoir). Each water sample was divided, and each aliquot was preserved with one of four distinct preservation strategies: 1) untreated, 2) acidified to pH 2 using 37% HCl, 3) filtered through 0.45 µm polyethersulfone filters, and 4) filtered and then acidified. Filtration followed by acidification to pH 2 is the current recommendation in Standard Method 5310 (APHA, AWWA, and WEF, 2022). To minimize carbon leaching (Khan et al., 2006) each filter was pre-rinsed with 10 mL of ultrapure water and 10 mL of sample. After treatment, 200 mL of each water type was collected in high-density polyethylene (HDPE) bottles. They were stored at three different temperatures (ambient storage at 21 °C, refrigerated storage at 4 °C, and frozen storage at -24 °C) for four storage periods (1, 3, 7, 28 days). Baseline (i.e., prior to preservation) water quality was also evaluated in triplicate. To allow for

complete thawing, frozen samples were placed at ambient temperature for 12 hours prior to analysis. Twelve hours allowed the samples to thaw completely, with their temperature remaining below 4 °C before analysis. Refrigerated samples were removed from cold storage immediately prior to analysis.

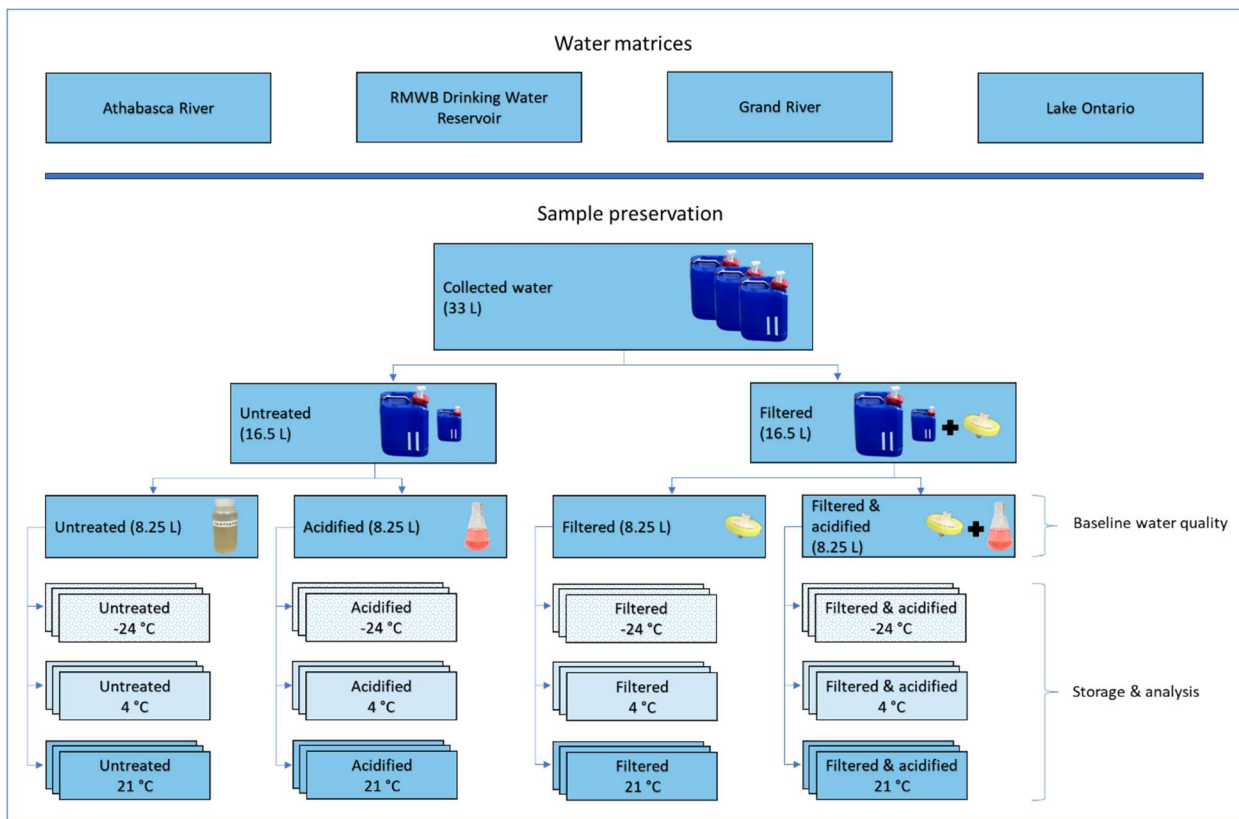


Figure 3-1 Experimental design for DOM preservation within collected samples. The arrows show the progression of experimental treatments, beginning by filtering half of the collected water. Half of both the untreated and filtered water was then acidified to prepare the four treatments used in the study. Baseline water quality was then established prior to sample storage at frozen, refrigerated, and ambient conditions. Athabasca River and Fort McMurray reservoir samples were analyzed singularly due to logistical challenges, while Grand River and Lake Ontario waters were analyzed in triplicate.

3.2.3 Water quality analyses

DOC, ultraviolet-visible spectrophotometry (UV-Vis), pH, and alkalinity were analyzed according to Standard Methods for the Examination of Water and Wastewater (APHA, 2022). DOC was analyzed

via high-temperature combustion (Standard Method 5310C) using a Shimadzu TOC-L analyzer (Shimadzu Corporation, Jiangsu, China) with a detection limit of 0.1 mg/L (APHA, AWWA, and WEF, 2022). Water samples were allowed to warm to room temperature before filtration and UV_{254} analysis using a UV-vis analyzer (Agilent Cary 3500 UV-Vis Spectrophotometer, Santa Carla, United States) following Standard Method 5910B. Specific ultraviolet absorbance at 254 nm (SUVA) was then calculated by dividing UV_{254} by DOC and multiplying by 100 (Edzwald & Van Benschoten, 1990). In addition, absorbance at 250 and 365 nm (E_2 and E_3 , respectively) was measured to further characterize DOM, and the $E_2:E_3$ ratio was calculated from these values, as described in Peuravuori & Pihlaja, 1997. pH was measured following Method 4500H using a Fisher Scientific Accumet AB250 (Thermo Fisher Scientific, Seoul, Korea) benchtop pH/ISE meter and alkalinity (Method 2320B) via titration with 0.1 N HCl. DOM fractionation by size exclusion chromatography was performed using liquid chromatography – organic carbon detection (LC-OCD) with a Model 8 LC-OCD analyzer (DOC-Labor GmbH, Karlsruhe, Germany). This subdivides dissolved DOM into five fractions—biopolymers, humic substances, building blocks, low molecular weight (LMW) acids, and LMW neutrals—based on molecular size (Huber et al., 2011). These DOM fractions can be grouped into refractory (humic substances and building blocks) and biodegradable (biopolymers, LMW acids, and LMW neutrals) categories for clarity of interpretation. Zeta potential was evaluated using a Malvern Zetasizer Nano Z, to enable comparison of particle stability across samples and support interpretation of observed changes.

3.2.4 Water matrices

Source waters were collected from four sites across Canada, encompassing low to high levels of DOC concentrations (< 2.5 to > 7.5 mg/L): the Fort McMurray western raw water reservoir, the Athabasca River, the Grand River, and Lake Ontario. The Fort McMurray reservoir and the Athabasca River are located in Fort McMurray, AB (56° 43' N, 111° 24' W) and are hydrologically linked. The off-line reservoir receives water from the Athabasca River and holds it for approximately 7–10 days before intake into a drinking water treatment plant. Both the Fort McMurray and Athabasca River sources are anticipated to have high DOC concentrations (> 5 mg/L- Chapter 2), and both were impacted by the 2016 Horse River wildfire. The Grand River, which is influenced by agricultural and municipal activity, was collected near Waterloo, ON (43° 28' N, 80° 28' W) downstream of a municipal wastewater outfall and is also expected to have high DOC concentrations (> 5 mg/L- Venkiteswaran et al., 2019). Lake Ontario water was collected from a deep-water intake in partnership with the R.C. Harris Water

Treatment Plant in Toronto, Ontario (43° 40' N, 79° 16' W), and is understood to be a “high-quality” water source with respect to DOC (< 2.5 mg/L- Hiriart-Baer et al., 2012). Pictures of each water matrix are shared in Appendix B – Figure B-1.

3.2.5 Sample collection and handling

The Fort McMurray, Athabasca River, and Grand River waters were collected via grab sample directly from the source and stored in 11 L HDPE carboys. Lake Ontario water was obtained via a tap within the R.C. Harris Water Treatment Plant and stored in 11 L HDPE carboys. Triplicate samples were collected at the Grand River and Lake Ontario sites; logistical constraints precluded triplicate sample collection from the Fort McMurray and Athabasca River sites. All water samples were stored at 4°C during transportation and preserved within 48 hours of collection in accordance with Standard Method 5310 (APHA, 2022).

3.2.6 Statistical analyses

Multiple linear regression analysis was used to investigate the significance of any water quality changes observed. All independent variables were treated as categorical, comprising two levels for each of acidification and filtration (e.g., filtered or unfiltered), three levels for water temperature (21, 4, and -24 °C), four levels for water matrix (Athabasca River, Fort McMurray, Grand River, Lake Ontario), and four levels for storage duration (1, 3, 7, 28 days). Dependent variables were the change in DOC and SUVA mean values relative to baseline (i.e., prior to preservation) measurements. Model assumptions such as homoscedasticity and normality of residuals were evaluated through diagnostic plots and Shapiro-Wilk tests. Interaction terms were included unless theoretically unjustified (e.g., acidified vs. filtered & acidified). Statistical analyses were conducted in R (version 4.3.2) using the *lm()* function and associated diagnostic packages.

3.3 Results & discussion

The initial (i.e., day zero of the experiment, prior to any preservation) DOC and UV₂₅₄ respectively ranged from 1.93 to 7.73 mg/L and 0.01 to 0.25 cm⁻¹ for the different water matrices. This corresponds to approximately a fourfold difference in DOC and a 25-fold difference in UV₂₅₄, spanning a range of low to high DOC (Health Canada, 2020) and underscoring the heterogeneity in source water quality across the study sites. The DOC and UV₂₅₄ of the investigated water matrices for each preservation technique (i.e., untreated, acidified, filtered, filtered and acidified) at each temperature (21, 4, and -24

°C) for each storage time (1, 3, 7, and 28 days) are presented in Figure 3-2. DOM fractionation results using LC-OCD for the Grand River and Lake Ontario are presented in Figure 3-3 below.

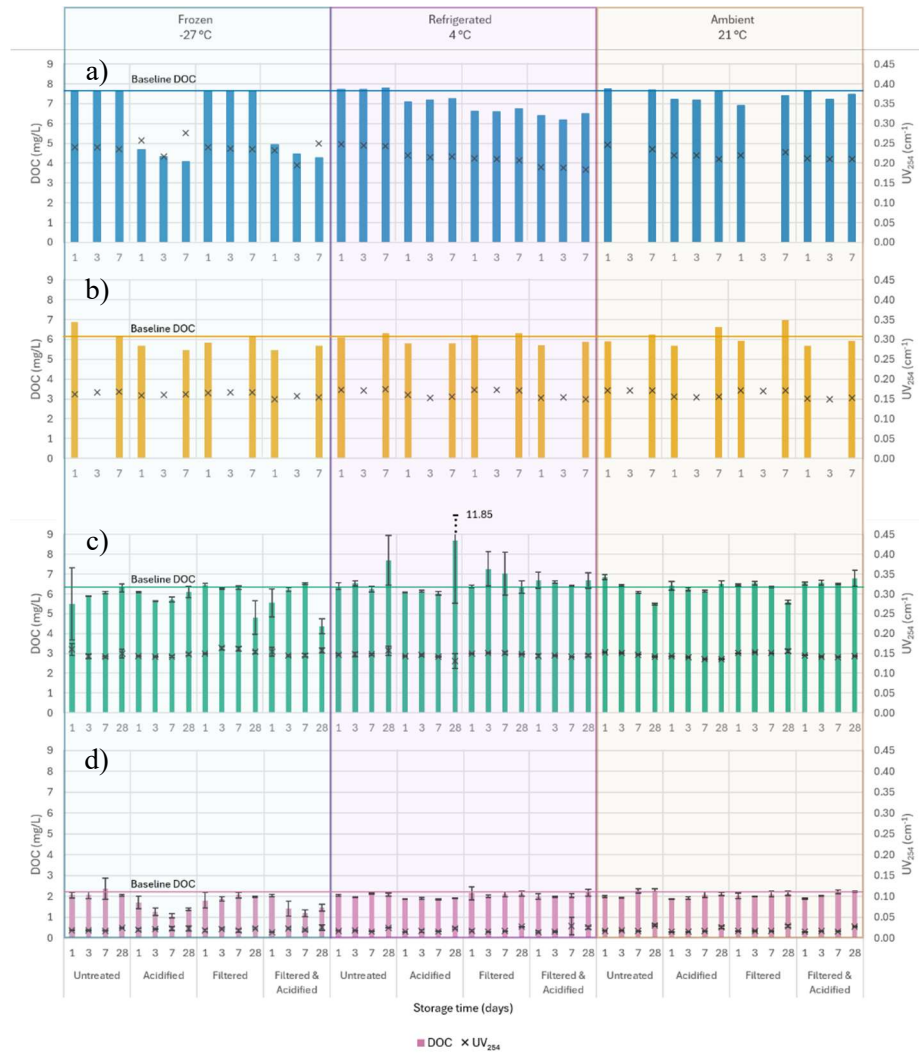


Figure 3-2 DOC & UV₂₅₄ for each preservation technique (i.e., untreated, acidified, filtered, filtered and acidified) at each temperature (21, 4, and -24 °C) for each storage time (1, 3, 7, and 28 days) in each water matrix (Athabasca River [a], Fort McMurray reservoir [b], Grand River [c], and Lake Ontario [d]). Bars indicate DOC means, and cross markers indicate UV₂₅₄ means. Error bars indicate one standard deviation from the mean. Samples from the Grand River and Lake Ontario were analyzed in triplicate, while those from the Athabasca River and Fort McMurray were analyzed once. Due to water transport limitations, three-day storage samples were not available for the Fort McMurray water.

3.3.1 DOM concentration

Figure 3-2 shows the changes in DOC and UV₂₅₄ for all investigated water types and preservation techniques during the experimental period. Water quality responses to each preservation technique were inconsistent between water matrices. For example, acidification followed by refrigeration stabilized DOC in Lake Ontario waters for the duration of the study but resulted in a 37% DOC increase in Grand River waters (Figure 3-2).

DOC in the Athabasca River samples preserved according to Standard Methods' recommendations (i.e., filtration, acidification, and refrigeration; APHA, AWWA, and WEF, 2022) decreased by 1.23 mg/L (16%) after seven days. This loss might be due to adsorption of organic matter to the walls of the container. HDPE bottles are often used in field studies (Tupas et al., 1993; Peacock et al., 2015; Thieme et al., 2016) due to their hardness, and as such were selected for this study to best replicate field conditions. Despite this, glass containers are recommended for water storage for DOC as they are the most inert material that is readily available (APHA, AWWA, and WEF, 2022; Tisserand et al., 2024) and are preferable to HDPE where possible to prevent adsorption to the container.

The most pronounced post-preservation reductions in DOC, 47% and 46%, were respectively observed in Athabasca River and Lake Ontario waters subjected to acidification and freezing, after seven days of storage. These substantial losses may have been due to sorption to the bottle as discussed above or may have been the result of DOM flocculation and sedimentation within the sample bottle. DOM may exhibit reduced electrostatic repulsion at low pH through the protonation of certain functional groups (e.g., carboxylates- Tombacz & Meleg, 1990; Singh & Song, 2007). This promotes aggregation, especially when combined with elevated ionic strength that may result after freezing (Yang et al, 2022).

Freezing has also been noted to promote natural flocculation within water, and samples that are frozen and then thawed may contain more particulate matter (Giesy & Briese, 1978). This may in part be due to the physical concentration of solutes produced by freezing and in part due to freezing-induced shift in the zero-point of charge towards higher pH (Halde, 1980; Drzymala et al., 1999). Full zeta potential measurement data is provided in Figures B-2 to B-5. Zeta potentials near zero can destabilize solutes and allow for flocculation to occur more easily (Eilers & Kroff, 1940; Ofir et al., 2006). It is possible that nanomolecules of DOM (e.g., biopolymers and large humic substances) flocculated and

formed particles larger than 0.45 μm that would not be included in DOC analysis and thus might explain some of these losses.

Nachimuthu et al. (2020) recommended filtration prior to freezing to minimize potential changes in DOC. However, filtration before acidification of Athabasca River and Lake Ontario waters did not prevent pronounced losses in DOC after freezing, with DOC decreasing by 45% and 38% in Athabasca River and Lake Ontario waters, respectively. Similarly, a DOC reduction for Grand River samples that were filtered or filtered & acidified before freezing was recorded (24% and 31% respectively). These observations are consistent with biopolymers and humic substances passing through 0.45 μm filters while remaining susceptible to freezing-induced aggregation. These results contrast with those of Norman & Thomas (2014), who suggested sample acidification before freezing may prevent DOC reduction over one- to two-year storage periods. This discrepancy may be due to differences in source water quality, as there was no reduction in DOC in Fort McMurray and Grand River waters that were acidified or filtered and acidified prior to freezing in this study.

Freezing did not produce a statistically significant ($p > 0.05$) effect on DOC when used in absence of other preservation techniques. This result aligns with several prior studies that have reported minimal DOC alteration following freezing (Tupas et al., 1993; Thieme et al., 2016; Heinz & Zak, 2017; Nachimuthu et al., 2020; Fonvielle et al., 2023). In contrast, other studies advise against freezing due to observed DOC shifts (Fellman et al., 2008; Spencer et al., 2007; Druffel et al., 2013; Xue et al., 2014; Chen et al., 2015; Peacock et al., 2015; Pokrovsky, 2018). Such discrepancies may reflect matrix-specific responses; however, they could also arise from substantial methodological inconsistency between studies (Table 3-1). Additionally, it has been suggested that waters with high DOC ($> 5 \text{ mg/L}$) may undergo greater changes after freezing and thawing (Fellman et al., 2008; Heinz & Zak, 2017). This was not observed in this study for waters with DOC higher than this threshold (i.e., Athabasca River, Fort McMurray, and Grand River), but accordingly, such changes might be observed in waters with substantially higher DOC (e.g., $> 10 \text{ mg/L}$), however investigation of additional water matrices was outside the scope of this work.

In contrast to preserved samples, changes in DOC and UV_{254} for unpreserved (i.e., untreated and stored at ambient temperature [21°C]) waters remained minimal during the first seven days, ranging from -0.28 to $+0.16 \text{ mg/L}$ and -0.010 to $+0.007 \text{ cm}^{-1}$, respectively. Samples storage for 28 days resulted in a decrease in DOC (0.86 mg/L , 14%) in the unpreserved Grand River water. Although there are no

available studies on unpreserved freshwater, Ogura (1972) reported no changes in DOC in seawater stored at 25 °C for up to 15 days, aligning with the results of this experiment. Notably, the average UV_{254} in the unpreserved Grand River water remained unchanged throughout the study period (Figure 3-2). As UV_{254} reflects both DOM concentration and aromaticity, a decrease in DOC without a corresponding change in UV_{254} suggests that prolonged storage may alter both DOM concentration and character in some freshwaters. Collectively, these results demonstrate that a deferral in sample preservation of up to seven days, if necessary, may be defensible in similar contexts to those examined here, as opposed to the 48-hour limit prescribed by Standard Method 5310 (APHA, AWWA, and WEF, 2022).

After 28 days of storage, substantial increases in Grand River waters DOC were observed in samples that were either left untreated or acidified without filtration before refrigeration (21 & 37%; Figure 3-2). Such observations may be associated with larger particulate organic matter—previously retained by a 0.45 μm filter—fragmenting during storage into smaller colloids and becoming available for analysis, leading to the observed increases in DOC. This fragmentation is consistent with hydrolytic cleavage of organic polymers, involving the breaking of covalent bonds by water, promoted by residual enzymatic activity, oxidation reactions, pH-driven reactions, instability of functional groups, and in acidified samples, acid-catalyzed hydrolysis (Filella & Buffle, 1992; Tebes-Stevens et al., 2017).

3.3.2 DOM character

Figure 3-3 shows changes in DOM character via SUVA and E2:E3 ratios. The trends in DOM aromaticity, as indicated by SUVA, varied across preservation methods and water types. In Lake Ontario water, at least a 40% increase in SUVA values was observed after 28 days, regardless of preservation method. In contrast, Athabasca River water showed a notable twofold increase in SUVA only in acidified and frozen samples, while aromaticity did not change substantially over time for other preservation methods. SUVA increased by 39% after 24 hours in the Grand River sample that was untreated before freezing, indicating potential for rapid shifts in DOM character. Increases in SUVA can either indicate a shift toward aromatic fractions of DOM or a preferential loss in non-aromatic DOM fractions. SUVA is commonly noted to change after acidification (Zhang et al., 2023) or freezing (Table 3-1); however, in contrast with these findings, no systematic relationship between SUVA and preservation technique was observed in this study. This discrepancy is unsurprising as SUVA response to preservation has differed between studies (Table 3-1), likely in part due to diverse source waters

investigated. For example, sample pH may impact SUVA response to freezing, due to the protonation of carboxylic and phenolic functional groups, leading to reduced electrostatic repulsive forces and subsequent potential for aggregation and exclusion from analysis as described in Section 3.3.1.

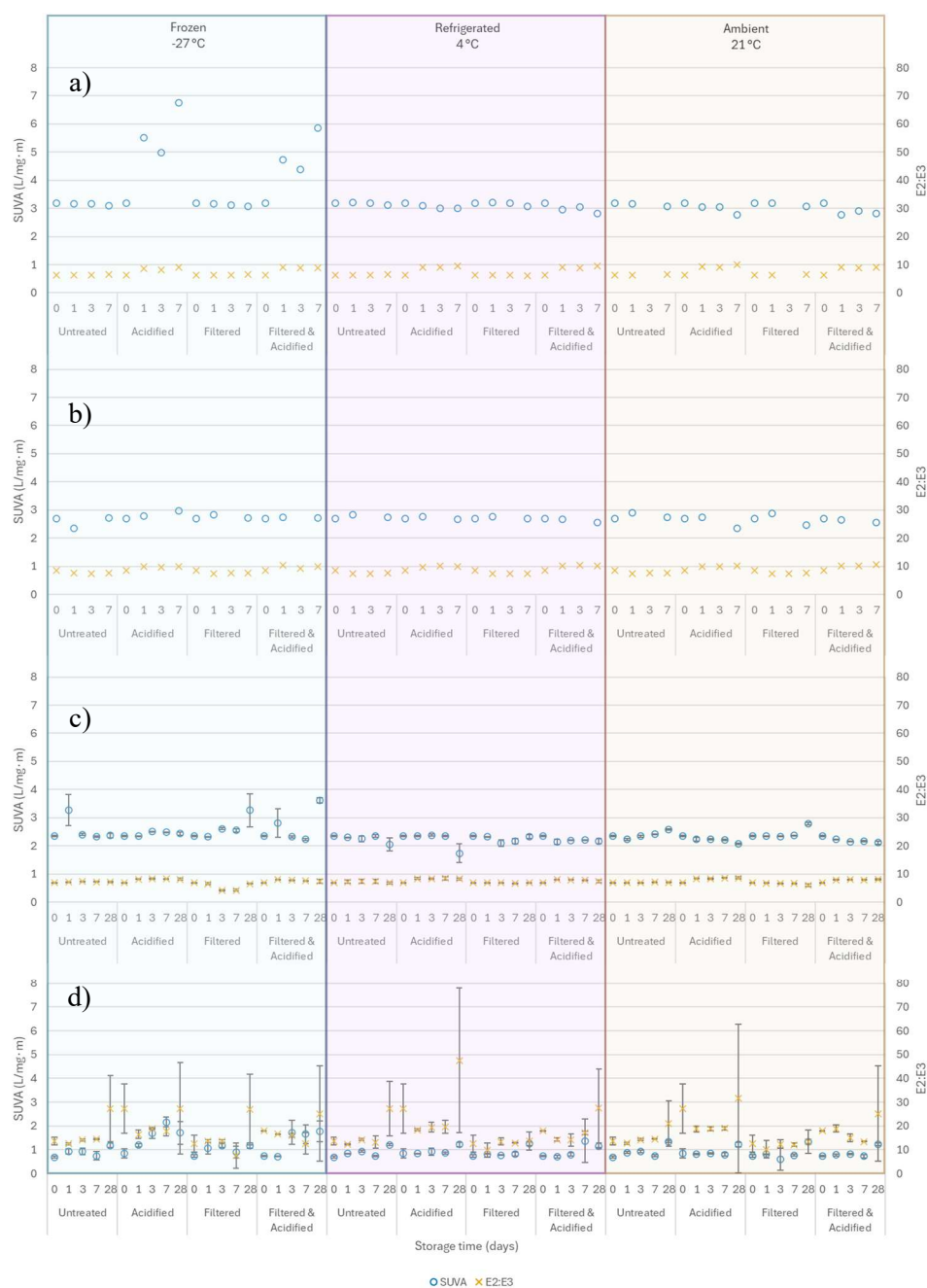


Figure 3-3 SUVA & E2:E3 for each preservation technique in a) Athabasca River, b) Fort McMurray reservoir, c) Grand River, and d) Lake Ontario. Markers represent mean values and error bars indicate one standard deviation from the mean ($n = 3$). Baseline values are presented as Day 0 to reduce visual clutter. Frozen, refrigerated, and ambient temperatures are separated by light blue, purple, and orange boxes, respectively.

Freezing has been reported to have a wide range of impacts on aromaticity (Fellman et al., 2008; Chen et al., 2015; Peacock et al., 2015; Thieme et al., 2016; Heinz & Zak, 2017; Pokrovsky, 2018); however, no impact on aromaticity was observed in this study. While several significant ($p < 0.05$) shifts in SUVA were observed after freezing (Figure 3-5), they were all inversely correlated with DOC changes, indicating losses of less-aromatic fractions of DOM.

E2:E3, a ratio with an inverse relationship to the molecular weight and aromaticity of DOM (Peuravuori & Pihlaja, 1997; Weishaar et al., 2003; Korak & McKay, 2024), responded differently to treatments in each matrix. However, acidification consistently showed higher E2:E3 values compared to other treatments across all matrices, consistent with existing theory (Haan et al., 1983). In unacidified Athabasca River and Grand River waters, as well as in filtered and filtered & refrigerated Lake Ontario samples, the E2:E3 ratio remained stable throughout the storage period. In contrast, the E2:E3 ratio substantially increased in the remaining Lake Ontario samples after 28 days (i.e., 46–115%), and the variability of results increased substantially (Figure 3-3). The E2:E3 ratio decreased consistently (-11% to -14%) in unacidified Fort McMurray water over the seven-day storage period.

Figure 3-4 presents the concentration of biodegradable (including biopolymers, LMW acids, and LMW neutrals) and refractory (humic substances, building blocks) compounds in the unpreserved Grand River and Lake Ontario waters, grouping the LC-OCD data for clarity of interpretation (full LC-OCD results are presented in Figure B-6). Storage of unpreserved samples for 28 days resulted in a 29% reduction in the concentration of biodegradable compounds in Grand River water, in contrast to a minimal change of approximately 0.3% in Lake Ontario water.

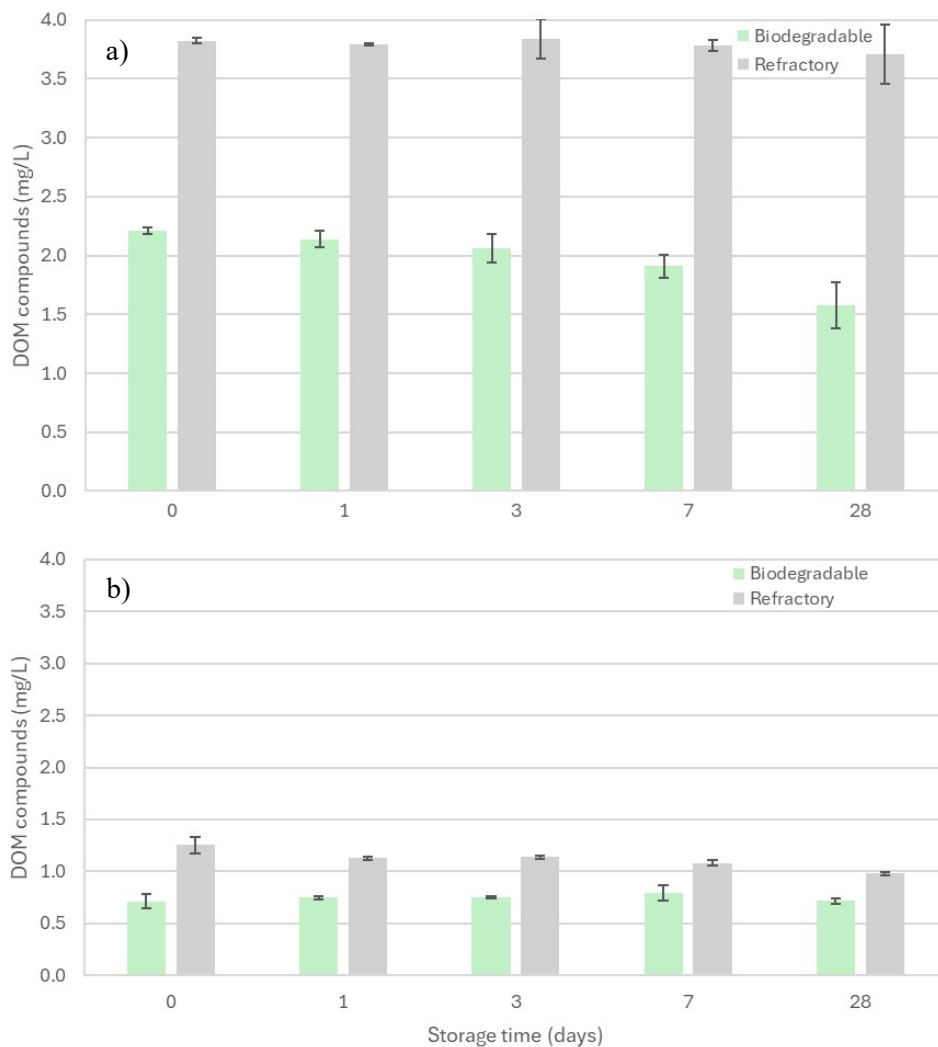


Figure 3-4 Biodegradable and refractory DOM fractions for Grand River (a) and Lake Ontario (b) samples. Bars indicate mean values, and error bars indicate one standard deviation from the mean (n = 3). Biodegradable fractions include biopolymers, LMW acids, and LMW neutrals. Refractory fractions include humic substances and building blocks.

The substantial changes in the concentration of biodegradable compounds within the unpreserved Grand River water align with the observed decline in DOC (Figure 3-2 & 3-4). In contrast, the changes in DOC in unpreserved Lake Ontario samples are attributable to a decrease in the fraction of DOM that successfully passed through the instrument for analysis rather than to a shift in the balance between biodegradable and refractory compounds (Figures 3-4 & B-6). While no studies on DOM character

within unpreserved freshwaters are available for comparison, the results of this study collectively suggest that the DOC decline in the unpreserved Grand River water may be driven by microbial breakdown and mineralization of biodegradable material within the bottles (Brailsford et al., 2019).

3.4 Conclusions

1. DOC & UV₂₅₄ in unpreserved waters remained stable during the first seven days after sample collection, regardless of water matrix.

Although immediate DOC preservation as recommended by Standard Methods is strongly preferred, meaningful analytical insights can still be obtained when preservation is deferred. Previous investigations on DOM samples left fully unpreserved (i.e., no treatments or temperature control) are scant if available at all, and this work is the first to say that DOC & UV₂₅₄ may remain stable for up to seven days without substantial loss of interpretive value, despite recommendations by Standard Methods to preserve within 48 hours. This was demonstrated in a wide range of raw water qualities, and has implications for challenging, remote sample collection, potentially allowing samples to be held until return to the laboratory, where they can then be preserved in accordance with Standard Methods' recommendations prior to analysis.

2. DOM character in collected waters can change within 24 hours and Standard Methods preservation techniques (i.e., Method 5310- APHA, AWWA, and WEF, 2022) or alternatives (i.e., filtration, acidification, and freezing) do not improve character stability.

DOM character metrics (i.e., SUVA, E2:E3, LC-OCD) were not stable regardless of preservation technique. Standard Methods preservation recommendations are designed for concentration and should not be extended to character. Additionally, substantial UV₂₅₄ changes (>10%) were observed within 24 hours even when preserved according to Standard Method 5910 (UV₂₅₄ preservation recommendations- APHA, AWWA, and WEF, 2022) and accordingly should be analyzed as soon as possible. In contrast, minimal (< 10%) changes in aromaticity (SUVA and E2:E3) were frequently observed after seven days of storage, indicating potential for deferred analysis of these parameters in certain water matrices.

3. Freezing alone did not compromise DOC or SUVA stability; however, its combination with acidification led to pronounced reductions in DOC in some water matrices.

Freezing as a sole preservation technique was not a detriment to data reliability in this study, for either DOM concentration or character. With baseline water quality characteristics similar to those examined

here (i.e., $\text{DOC} < 10 \text{ mg/L}$), freezing may be an effective preservation technique for DOC when Standard Methods' protocols are infeasible. It is not recommended to freeze low-pH samples due to the associated risk of losses via flocculation and precipitation or adsorption. Further work is needed to clarify the processes driving DOC change within frozen samples.

4. Preservation protocols outside Standard Methods' recommendations, while necessary in certain scenarios, should not be expected to stabilize DOM concentration and character for a 28-day holding period.

While preservation approaches alternative to Standard Methods, such as freezing or filtration, were largely effective in the short-term, instances of substantial ($> 10\%$) DOC change were observed after 28 days of storage under these treatments. Despite this, they may prove effective techniques for stabilizing DOC until Standard Methods' recommended preservation can be applied. Further study would be useful to clarify the timing of DOC change under these conditions. Accordingly, Standard Methods remain the benchmark for preservation of DOC; however, this work advances necessary strategies for maximizing the value of sampling when adherence to these methods is infeasible.

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Chapter 4

Conclusions and contributions

The overall goal of this research was to advance characterization of the spatiotemporal dynamics of dissolved organic matter (DOM), with the aim of informing source water monitoring—both at the drinking water system and watershed scale—and associated water management decision-making to support utilities in preparing for and recovering from landscape disturbances. The key findings of this work are:

1. Open-water DOM concentration and character were consistent across depth and lateral position in each reservoir.

Differences in sample collection depth within the West Reservoir proved to be statistically significant ($p = 0.03$) but practically inconsequential. The West Reservoir maintained a UV_{254} distribution that was near-uniform across lateral position (relative standard deviation of 0.48%), and the East Reservoir collection locations were not statistically significant ($p = 0.32$). This suggests that offline raw water reservoirs may exhibit limited primary production and organic matter transformation relative to natural systems such as lakes. Observations of spatial heterogeneity can simplify sample collection logistics for utilities monitoring source water; however, a preliminary assessment of UV_{254} is nevertheless recommended before assuming spatial uniformity.

2. DOM concentration and character (as measured by UV_{254}) in the raw water reservoirs did not change substantially ($> 5\%$) within a single day.

UV_{254} values in the raw water reservoirs were not substantially temporally varied. When considered alongside the aforementioned spatial consistency of UV_{254} , these observations together have the potential to simplify collection logistics for utilities monitoring raw water reservoirs. A preliminary assessment of UV_{254} is nonetheless recommended before assuming spatiotemporal uniformity of DOM. Multiple days of measurements are recommended to better understand DOM changes within a given water body.

3. Inter-annual variability in DOM character (as measured by SUVA and LC-OCD) was statistically significant (both $p < 0.01$) but intra-annual variability was not ($p = 0.17$).

The raw water within the Fort McMurray DWS maintained a consistent character through each ice-free period of each year. This observation indicates either homogeneous sourcing of organic matter from the surrounding landscape, or uniform transformation within the Athabasca River prior to delivery to the reservoirs. DOM was predominantly comprised of humic substances, driving the coagulant demand

during water treatment. The consistent SUVA profile likely helped the Fort McMurray WTP to optimize its coagulation processes and better understand its potential for DBP formation.

4. “Sand pumps” designed to remove incoming particulate matter from raw water reservoirs may offer improvements to source water organic matter concentration or character.

A notable disparity in water quality (as measured by UV_{254}) between the Athabasca River and the River Intake Structure was observed only when the sand pumps were active. This finding suggests that sand pump operation may have potential to improve water quality beyond the turbidity that they are designed to remove. Further study is required to investigate the effects of particulate matter removal via pumping on reservoir organic matter concentration and character.

5. Reservoir water quality exhibited a lagged, attenuated response to DOC and UV_{254} loading from the river.

The Athabasca River drove changes in water quality (as measured by DOC and UV_{254}) in the reservoirs, which responded sequentially and maintained distinct water quality profiles from one another. The series configuration of the reservoirs allowed for clear observation of the gradual changes in water quality as it passed through the DWS. Furthermore, the consistent water quality trends observed in downstream locations based on upstream water quality may offer the potential for bypassing contaminated water during extreme events, and anticipation of future WTP intake water quality, underscoring the value of monitoring for the efficient production of safe drinking water. Peak UV_{254} values in the Athabasca River were on average 25% higher than those in the East Reservoir, and 34% higher than those in the West Reservoir. These observations are consistent with theoretical expectations for dilution-driven attenuation, which accordingly helped to provide a more consistent intake water quality to the WTP. Furthermore, operation of the reservoirs in series is advantageous in that it provides a more consistent attenuation of water quality shifts by reducing short-circuiting, even when only two cells are available.

6. Attenuation of water quality shifts by the reservoirs had practical implications to consumer health and treatment costs.

The established relationship between UV_{254} in the incoming source water and PACl dose within the treatment plant underscores additional consumer health protection and treatment resilience in the face of disturbance provided by the reservoirs, especially when considering the challenging water quality

and elevated coagulant doses in 2023. The observed attenuation of water quality shifts has helped the Fort McMurray WTP to reduce peak coagulant demands (up to 70 mg/L), maintain effective coagulation, and protect consumer health, highlighting the value of reservoirs in protecting against disturbances and mitigating the associated water quality fluctuations.

7. DOM concentration metrics such as DOC & UV₂₅₄ can remain stable without preservation for the first seven days after sample collection.

While immediate DOC preservation as recommended by Standard Methods is strongly preferred, this work shows that preservation may be deferred for up to seven days without compromising reliability. Previous investigations on DOM samples left fully unpreserved (i.e., no treatments or temperature control) are scant if available at all, and this work is the first to say that DOC & UV₂₅₄ may remain stable for up to seven days without substantial loss of interpretive value, despite recommendations by Standard Methods to preserve within 48 hours. This was demonstrated in a wide range of raw water qualities, and may enable remote sample collection, potentially allowing samples to be held until return to the laboratory, where they can then be preserved in accordance with Standard Methods' recommendations prior to analysis.

8. DOM character within collected waters can change within 24 hours and Standard Methods preservation techniques (i.e., Method 5310- APHA, AWWA, and WEF, 2022) or alternatives (i.e., filtration, acidification, and freezing) do not improve character stability.

DOM character metrics (i.e., SUVA, E2:E3, LC-OCD) were not stable regardless of preservation technique. Standard Methods preservation recommendations are designed for concentration and should not be extended to character. Additionally, substantial UV₂₅₄ changes (>10%) were observed within 24 hours even when preserved according to Standard Method 5910 (UV₂₅₄ preservation recommendations) and accordingly should be analyzed as soon as possible. In contrast, minimal (< 10%) changes in aromaticity (SUVA and E2:E3) were frequently observed after seven days of storage, indicating potential for deferred analysis of these parameters in certain matrices, similar to what was observed for DOC.

9. Freezing did not alter DOC or SUVA stability, except when combined with acidification; the combination of these can cause significant changes in DOC and associated increases in SUVA.

Although freezing has been reported to increase variability of DOC data and to substantially alter SUVA values in thawed samples, this was not observed in the present study. When compared to refrigerated and ambient samples, freezing yielded similar standard deviations, except when combined with acidification. Marked decreases in DOC (up to 47%) were observed when acidified samples were subsequently frozen, regardless of storage duration. Accordingly, it is not recommended to freeze low-pH samples to avoid potential losses in DOC via flocculation and precipitation or adsorption; further work is necessary to clarify the mechanisms driving DOC change within frozen samples.

10. Preservation protocols outside Standard Methods recommendations, while necessary in certain scenarios, should not be expected to stabilize DOM concentration and character for a 28-day holding period.

Freezing and filtration were both effective preservatives over the first seven days of storage, but there were instances of substantial DOC change ($> 10\%$) after 28 days and should not be relied on to stabilize DOC for a 28-day period without prior method verification. Despite this, they may prove effective techniques for stabilizing DOC until Standard Methods' recommended preservation can be applied. Further study would be useful to clarify the timing of DOC change under these conditions. Accordingly, Standard Methods remain the benchmark for preservation of DOC; however, this work advances necessary strategies for maximizing the value of sampling when adherence to these methods is infeasible.

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Appendices

Appendix A

Supporting information for

Chapter 2

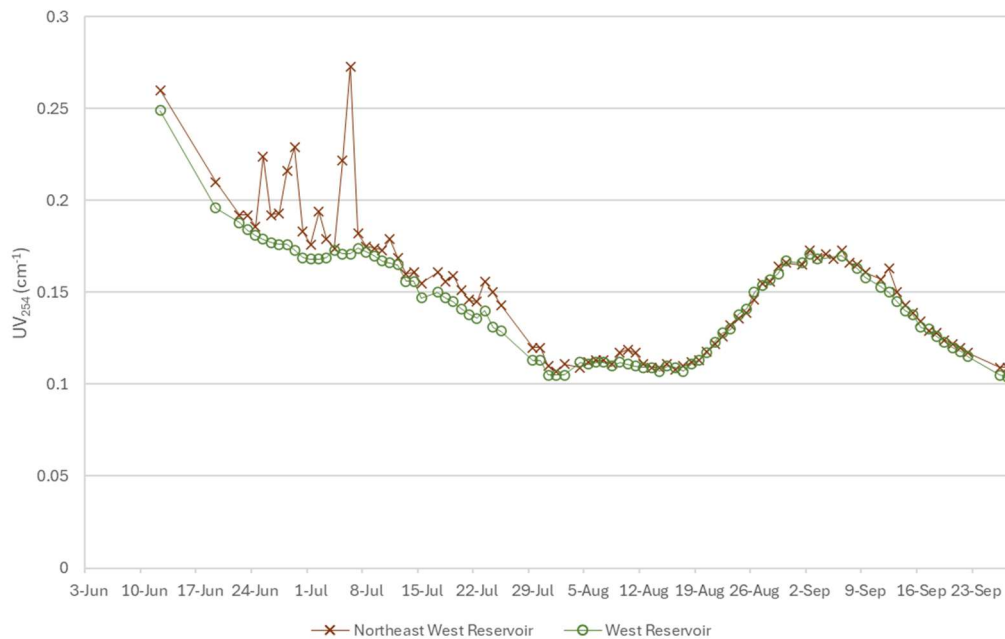


Figure A-1 UV₂₅₄ values in the Northeastern West Reservoir compared to the typical monitoring location in the central-western section of the West Reservoir in 2025. Northeast West Reservoir samples were collected from the shore while typical sample collection was performed off a dock. See Figure A-2 for site pictures.

Table A-1 Comparison of UV_{254} of samples collected with dense microbial and macrophyte growth against its adjacent water. Results indicate that care should be taken not to collect growth when attempting to represent the larger water body.

	UV_{254}							Average	Standard deviation
Control water	0.258	0.258	0.254	0.251	0.258	0.256		0.256	0.003
Concentrated growth	0.403	0.375	0.35	0.284	0.387	0.507	0.305	0.373	0.073



Figure A-2 Pictures of the Northeastern West Reservoir. Discrepancies in UV_{254} noted between the West Reservoir and Northeastern West Reservoir locations may have been due to accidental collection of the microbial and macrophyte growth frequently noted in this location.

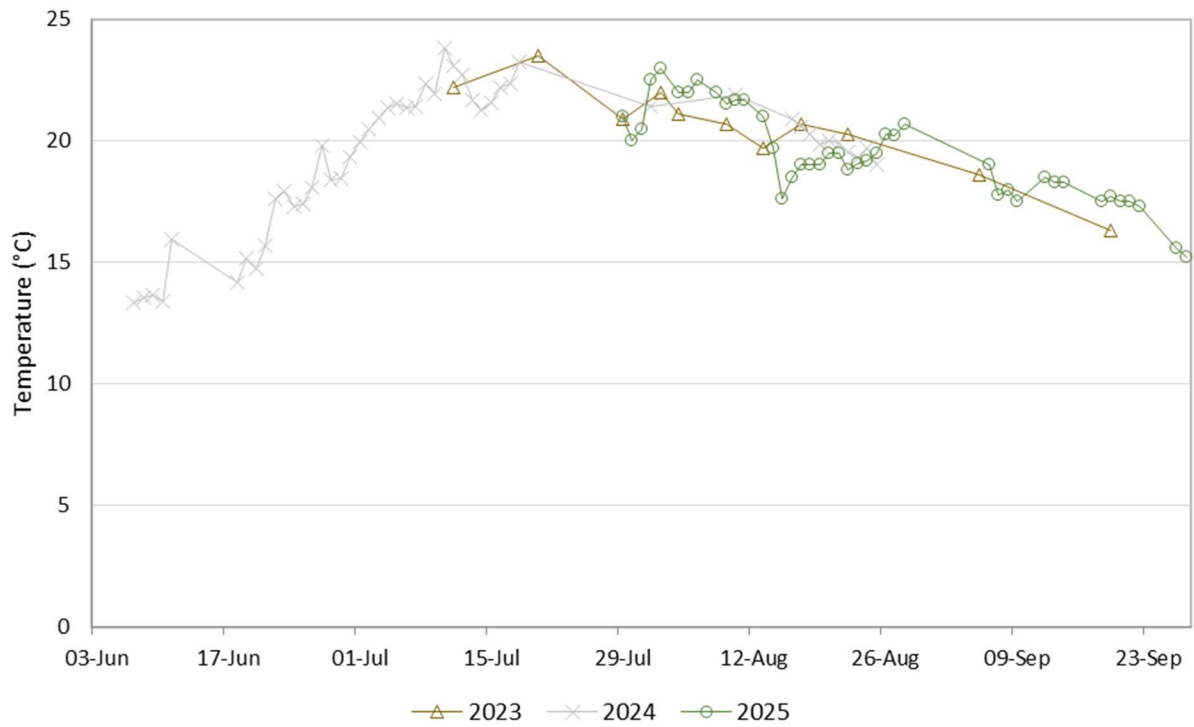


Figure A-3 Water temperature within the West Reservoir during the ice-free period in 2023, 2024, and 2025.

```

boundary (singular) fit: see help('issingular')
> mSUVA <- lmer(
+   SUVA ~ factor(Year) + jday + (1 | Location),
+   data = mcp
+ )
boundary (singular) fit: see help('issingular')
> summary(mSUVA)
Linear mixed model fit by REML. t-tests use Satterthwaite's method ['lmerModLmerTest']
Formula: SUVA ~ factor(Year) + jday + (1 | Location)
Data: mcp

REML criterion at convergence: 59.2

Scaled residuals:
    Min       1Q   Median       3Q      Max
-5.1628 -0.3772  0.1327  0.5636  2.6506

Random effects:
 Groups Name      Variance Std.Dev.
Location (Intercept) 0.00000  0.0000
Residual              0.07276  0.2697
Number of obs: 169, groups: Location, 3

Fixed effects:
              Estimate Std. Error      df t value Pr(>|t|)
(Intercept)   3.584e+00  1.963e-01  1.650e+02  18.260 < 2e-16 ***
factor(Year)2024 -1.457e-01  5.211e-02  1.650e+02  -2.796  0.0058 **
factor(Year)2025 -3.797e-01  6.223e-02  1.650e+02  -6.102  7.21e-09 ***
jday          -1.107e-03  8.061e-04  1.650e+02  -1.373  0.1717
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Correlation of Fixed Effects:
      (Intr) f(Y)2024 f(Y)2025
fctr(Y)2024 -0.406
fctr(Y)2025 -0.454  0.366
jday        -0.990  0.335  0.395
optimizer (nloptwrap) convergence code: 0 (OK)
boundary (singular) fit: see help('issingular')

```

Predictors	SUVA		
	Estimates	CI	p
(Intercept)	3.58	3.20 – 3.97	<0.001
Year [2024]	-0.15	-0.25 – -0.04	0.006
Year [2025]	-0.38	-0.50 – -0.26	<0.001
jday	-0.00	-0.00 – 0.00	0.172
Random Effects			
σ^2	0.07		
τ_{00} Location	0.00		
N Location	3		
Observations	169		
Marginal R ² / Conditional R ²	0.190 / NA		

Figure A-4 t-test results to compare SUVA from 2023-2025.

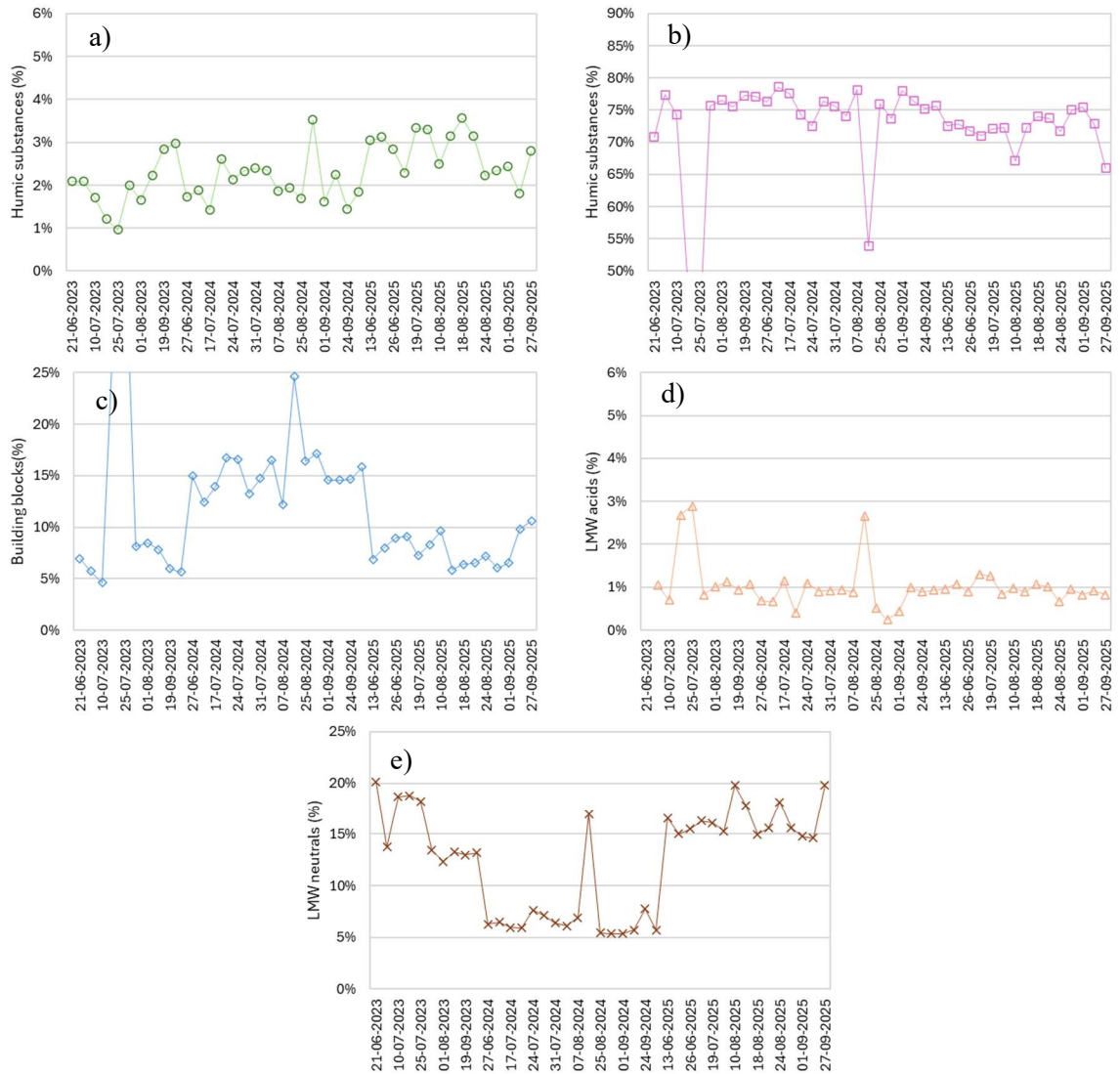


Figure A-5 DOM fraction percentages at the surface level of the West Reservoir during each year of the study period, as measured by LC-OCD. Graphs show a) Biopolymers, b) Humic substances, c) Building blocks, d) LMW acids, and e) LMW neutrals.

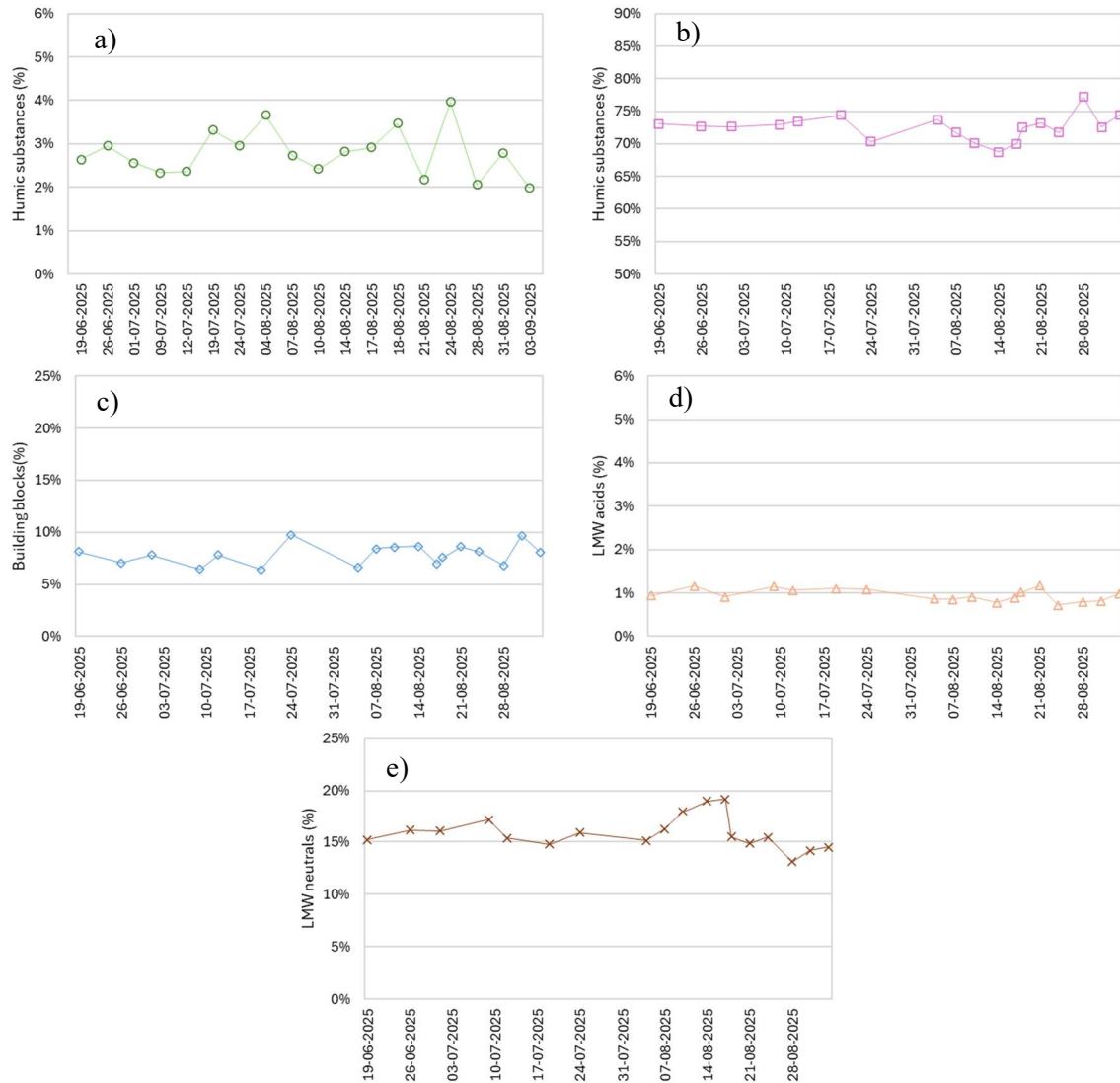


Figure A-6 DOM fraction percentages at the benthic level of the West Reservoir in the ice-free period of 2025, as measured by LC-OCD. Graphs show a) Biopolymers, b) Humic substances, c) Building blocks, d) LMW acids, and e) LMW neutrals.

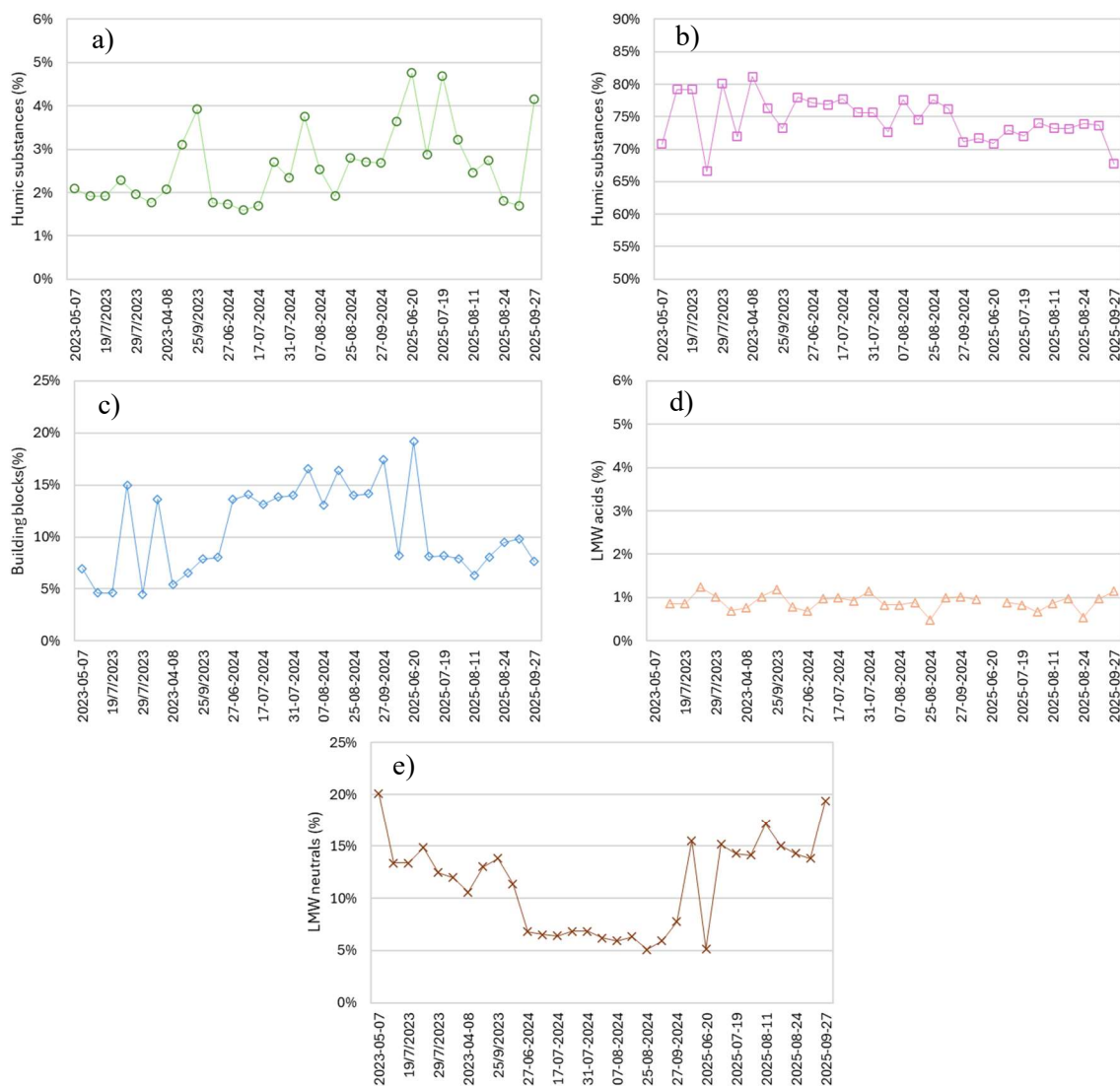


Figure A-7 DOM fraction percentages at the surface level of the East Reservoir during each year of the study period, as measured by LC-OCD. Graphs show a) Biopolymers, b) Humic substances, c) Building blocks, d) LMW acids, and e) LMW neutrals.

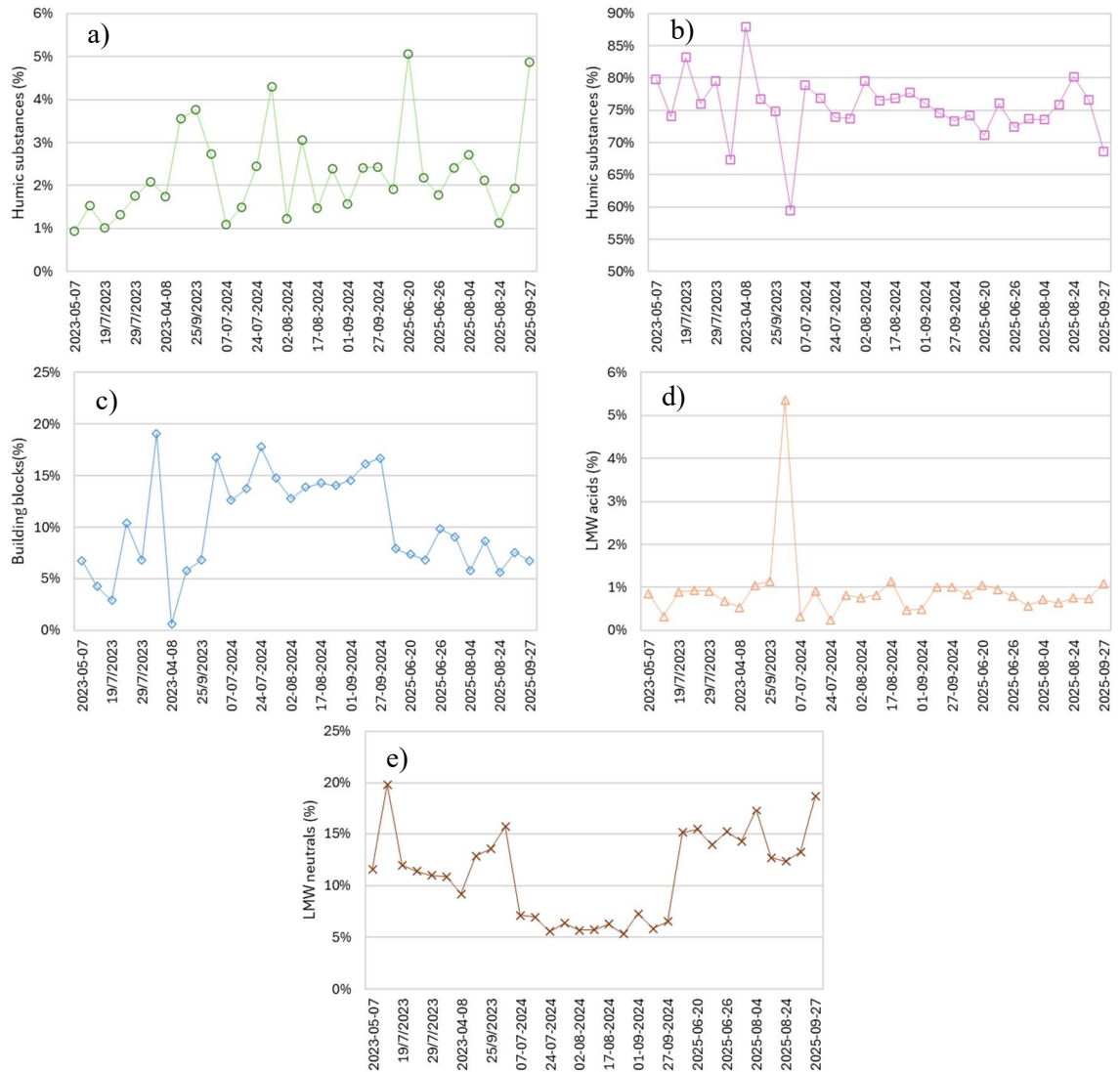


Figure A-8 DOM fraction percentages at the surface level of the Athabasca River during each year of the study period, as measured by LC-OCD. Graphs show a) Biopolymers, b) Humic substances, c) Building blocks, d) LMW acids, and e) LMW neutrals.

Reactor theory for reservoirs in series modeled as continuously-stirred tank reactors (CSTRs)

For a single, ideally mixed CSTR with no internal reactions, the change in concentration can be modeled according to Equation 2-1. τ represents hydraulic retention time, equal to flow divided by total reservoir volume. C_0 is the inflow concentration of a desired parameter (e.g. UV_{254}), and C_1 is the outflow concentration of that same parameter.

$$\frac{dC_1}{dt} = \tau(C_0 - C_1) \quad [2-1]$$

Extending this framework to two equal-volume CSTRs in series, the outlet concentration of the downstream reservoir is governed by a second-order response function, as expressed in Equations 2-2 and 2-3, with the compounded attenuation of the two-stage system exceeding that predicted by a single equivalent-volume reactor.

$$\frac{dC_1}{dt} = \frac{\tau}{2}(C_0 - C_1) \quad [2-2]$$

$$\frac{dC_2}{dt} = \frac{\tau}{2}(C_1 - C_2) \quad [2-3]$$

In the event of a water quality disturbance, with an inflow of concentration $C_0 + \Delta C_0$, the outflow concentration can be modeled for one CSTR in Equation 2-4 or two CSTRs in series with equivalent total volume in Equation 2-5.

$$C_1(t) = (C_0 + \Delta C_0)(1 - e^{-\frac{t}{\tau}}) \quad [2-4]$$

$$C_2(t) = (C_0 + \Delta C_0)(1 - \left(1 + \frac{t}{\tau}\right) e^{-\frac{t}{\tau}}) \quad [2-5]$$

The additional term $\frac{t}{\tau}$ in Equation 2-5 reflects the additional lag introduced by the second reactor, causing the system to respond more slowly to the incoming disturbance signal and therefore achieve greater attenuation of influent variability.

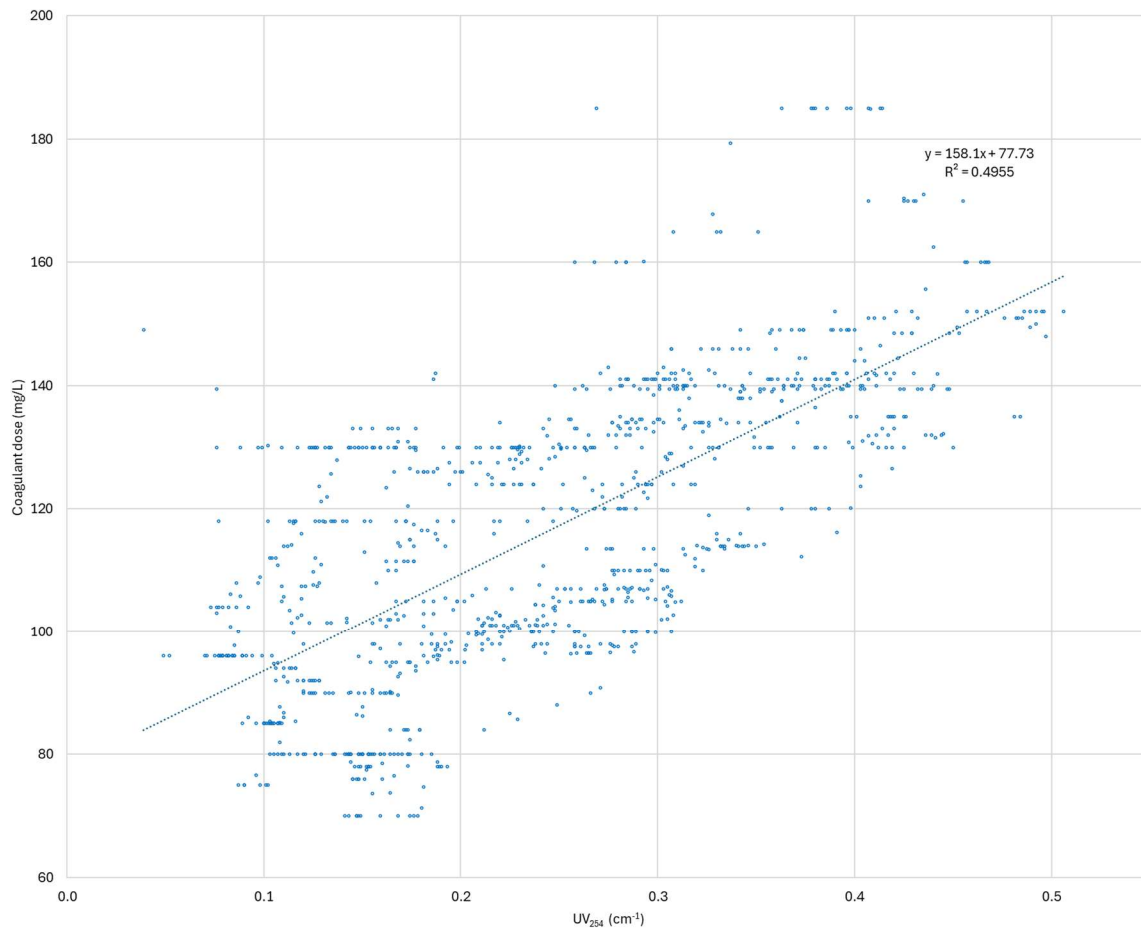


Figure A-9 PACl dose applied in the WTP vs. UV_{254} in the raw water intake during the ice-free periods of 2019-2025. The regression is significant ($p < 0.001$ - Table A-2).

Table A-2 Summary of linear regressions relating PACl doses to UV_{254} of plant intake water. Performed with Excel Data Analysis add-in. All regressions performed were significant ($p < 0.001$).

Regression	R^2	p-value	Slope	Intercept	n
2023 PACl vs. UV_{254}	0.42	< 0.001	310.16	27.32	23
2023-2025 PACl vs. UV_{254}	0.65	< 0.001	175.51	60.79	214
2019-2025 PACl vs. UV_{254}	0.50	< 0.001	158.1	77.73	1071

Appendix B

Supporting information for

Chapter 3



Figure B-1 Pictures of sampling locations a) Athabasca River, b) Fort McMurray raw water reservoir, c) Grand River, and d) Lake Ontario. [Photo credit: c) Kelvin Vianini, d) Kalani de Silva]

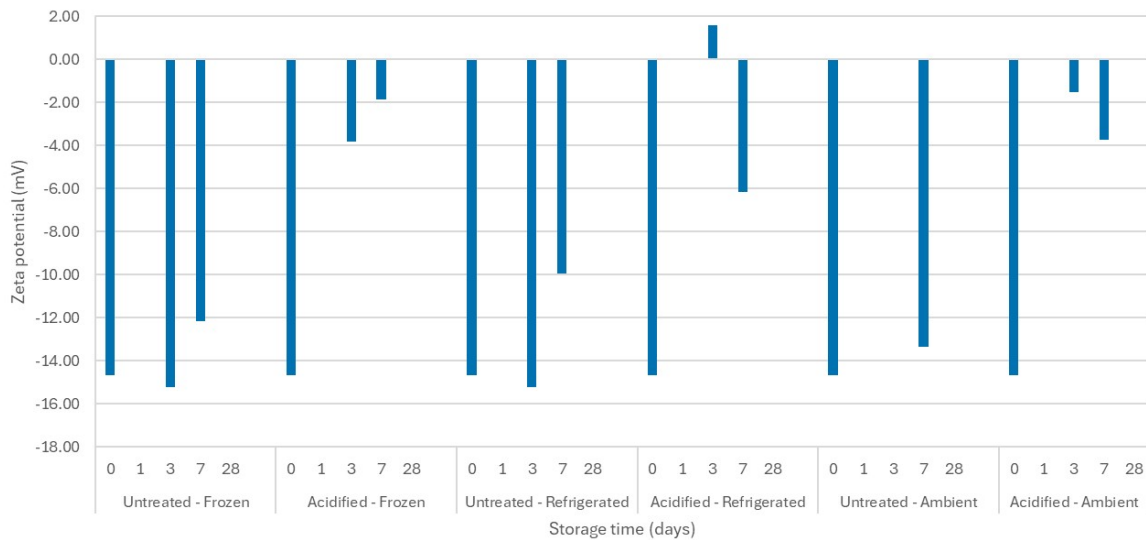


Figure B-2 Zeta potential in Athabasca River samples. Filtered treatments were not analyzed for zeta potential as filtration interferes with measurement accuracy. Determinations were performed singularly.

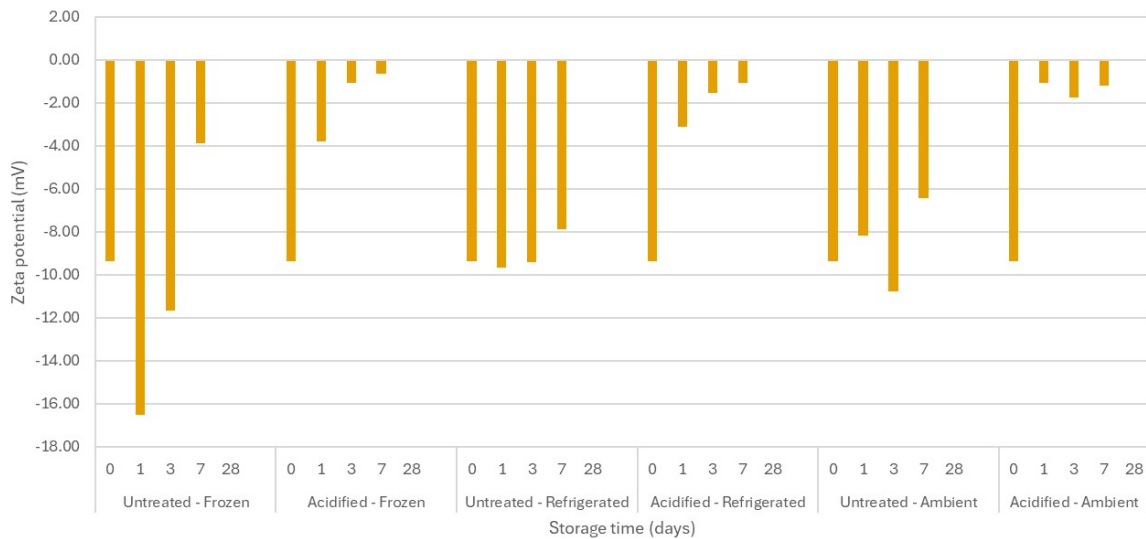


Figure B-3 Zeta potential in Fort McMurray samples. Filtered treatments were not analyzed for zeta potential as filtration interferes with measurement accuracy. Determinations were performed singularly.

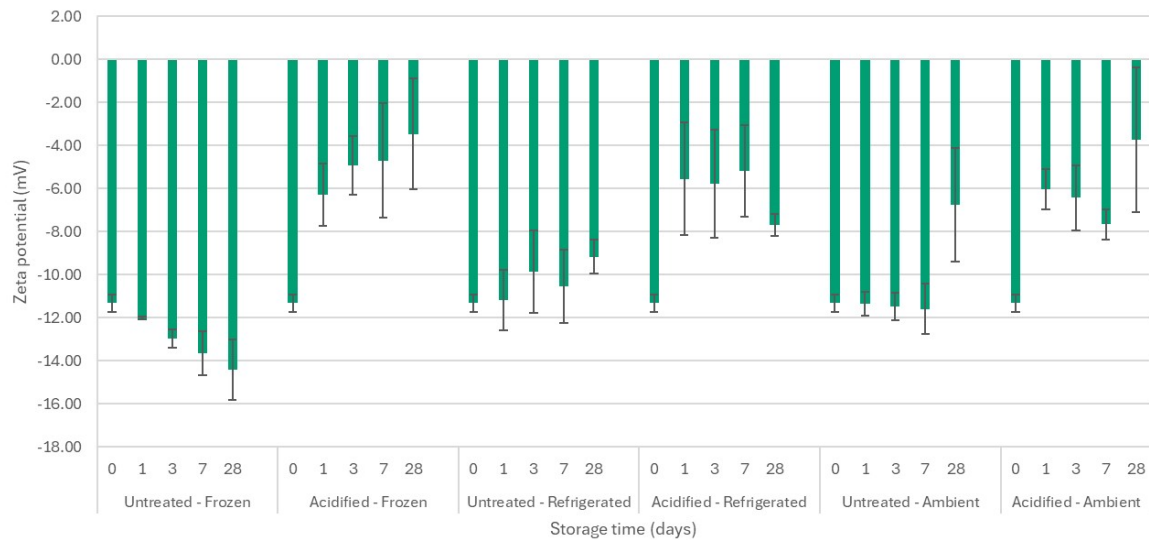


Figure B-4 Zeta potential in Grand River samples. Filtered treatments were not analyzed for zeta potential as filtration interferes with measurement accuracy. Determinations were performed in triplicate and error bars represent one standard deviation from the mean.

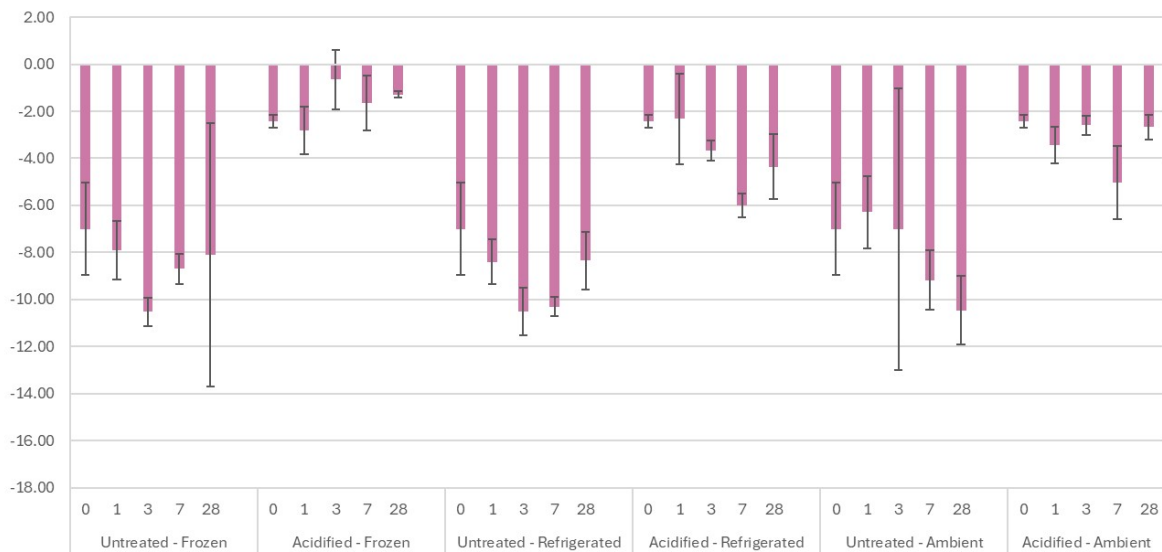


Figure B-5 Zeta potential in Lake Ontario samples. Filtered treatments were not analyzed for zeta potential as filtration interferes with measurement accuracy. Determinations were performed in triplicate and error bars represent one standard deviation from the mean.

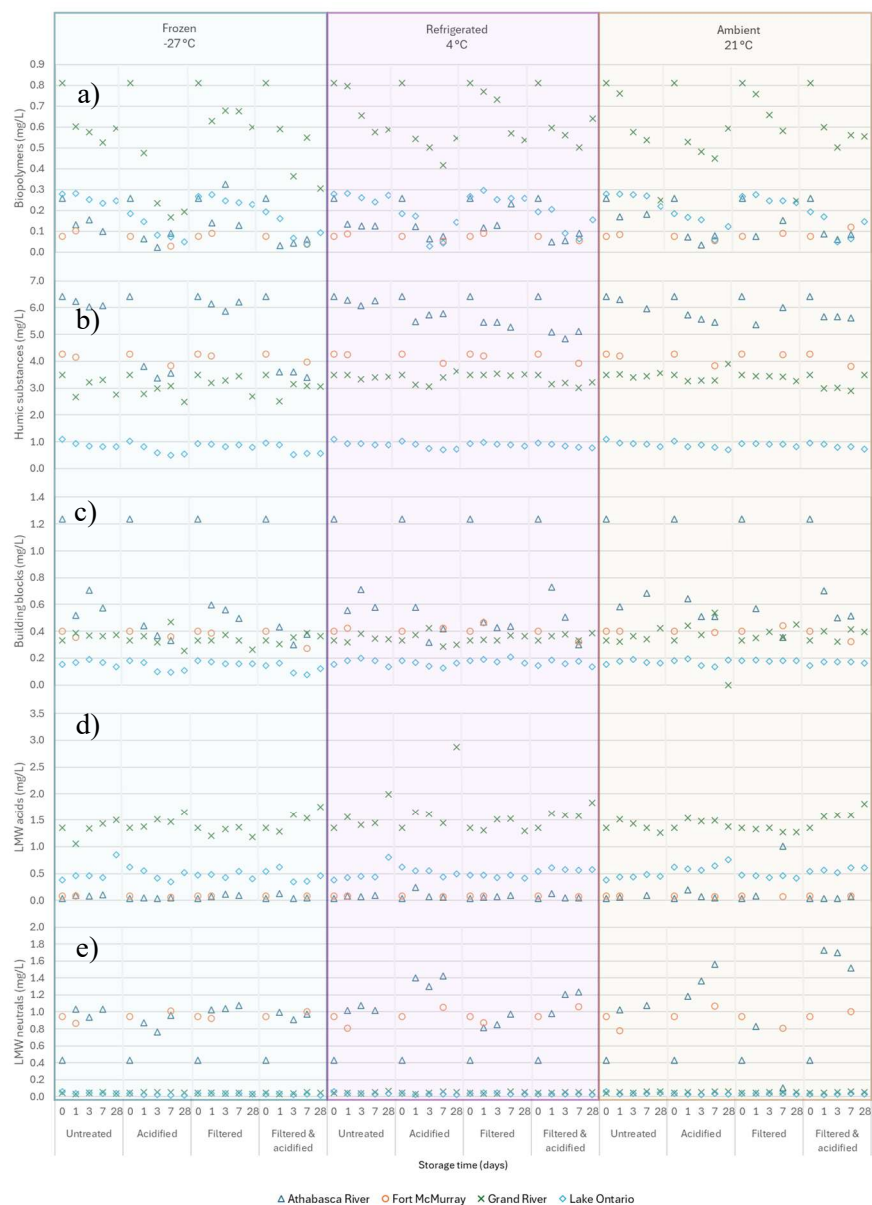


Figure B-6 DOM fractions for each preservation technique from LC-OCD analysis. Each graph shows a) Biopolymers, b) Humic substances, c) Building blocks, d) LMW acids, and e) LMW neutrals. Markers indicate means ($n = 3$), but error bars are not shown to improve visual clarity. Baseline values are presented as Day 0 to reduce visual clutter. Frozen, refrigerated, and ambient temperatures are separated by light blue, purple, and orange boxes, respectively. Note that the DOC axis scale differs between source waters to facilitate clearer comparison.

Table B-1 Detailed DOC data for each water matrix (Athabasca River, Fort McMurray, Grand River, and Lake Ontario), each treatment (Untreated, Acidified, Filtered, and Filtered & acidified), storage temperature (21, 4, -24 °C), and storage time (0, 1, 3, 7, 28 days).

		DOC (mg/L)							
	Storage time (days)	Athabasca River	Fort McMurray	Grand River-1	Grand River-2	Grand River-3	Lake Ontario-1	Lake Ontario-2	Lake Ontario-3
Untreated - Frozen	0	7.73	6.10	6.31	6.31	6.43	2.14	2.32	1.95
	1	7.60	6.89	3.41	6.75	6.31	2.13	2.13	1.91
	3	7.59		5.90	5.92	5.91	1.88	2.13	2.18
	7	7.59	6.17	6.10	5.98	6.09	2.17	1.98	2.95
	28			6.50	6.10	6.32	2.03	2.05	2.12
Acidified - Frozen	0	7.73	6.10	6.31	6.31	6.43	2.15	1.94	1.89
	1	4.68	5.69	6.09	6.13	6.08	2.04	1.47	1.60
	3	4.34		5.62	5.61	5.65	1.33	1.08	1.42
	7	4.08	5.46	5.83	5.77	5.58	1.05	1.19	0.97
	28			6.42	5.92	5.95	1.36	1.46	1.32
Filtered - Frozen	0	7.73	6.10	6.31	6.31	6.43	2.04	1.99	1.97
	1	7.60	5.83	6.53	6.37	6.43	2.02	1.38	2.02
	3	7.63		6.27	6.27	6.22	1.94	1.77	1.94
	7	7.62	6.16	6.37	6.39	6.21	1.91	2.16	2.13
	28			5.03	5.52	3.86	1.94	2.01	1.98
Filtered & Acidified - Frozen	0	7.73	6.10	6.31	6.31	6.43	1.95	1.94	1.90
	1	4.93	5.47	5.18	6.37	5.11	2.10	2.04	1.98
	3	4.44		6.32	6.14	6.17	1.28	1.83	1.17
	7	4.26	5.69	6.48	6.53	6.55	1.12	1.39	1.08
	28			4.03	4.77	4.30	1.43	1.33	1.64
Untreated - Cooled	0	7.73	6.10	6.31	6.31	6.43	2.14	2.32	1.95
	1	7.71	6.08	6.21	6.53	6.43	2.04	2.02	2.11
	3	7.71		6.44	6.46	6.67	1.97	1.95	1.94
	7	7.78	6.32	6.13	6.18	6.40	2.11	2.17	2.14
	28			8.76	6.31	8.05	2.17	2.05	2.05
Acidified - Cooled	0	7.73	6.10	6.31	6.31	6.43	2.15	1.94	1.89
	1	7.10	5.80	6.08	6.09	6.10	1.89	1.86	1.87
	3	7.20		6.08	6.15	6.17	1.88	1.95	1.88
	7	7.24	5.82	6.09	6.10	5.91	1.88	1.87	1.84
	28			10.92	6.45		1.92	1.93	1.93
Filtered - Cooled	0	7.73	6.10	6.31	6.31	6.43	2.04	1.99	1.97
	1	6.61	6.22	6.31	6.41	6.40	2.37	1.92	
	3	6.59		8.23	6.59	7.00	2.05	1.96	
	7	6.74	6.31	8.27	6.35	6.45	2.01	2.18	
	28			6.70	6.09	6.25	2.05	2.22	
Filtered & Acidified - Cooled	0	7.73	6.10	6.31	6.31	6.43	1.95	1.94	1.90
	1	6.39	5.73	6.81	7.05	6.25	2.15	1.96	1.88
	3	6.18		6.54	6.56	6.67	1.96	1.97	2.00
	7	6.50	5.86	6.41	6.42	6.44	2.16	1.99	2.00
	28			6.77	6.24	7.02	1.99	2.27	2.27
Untreated - Ambient	0	7.73	6.10	6.31	6.31	6.43	2.14	2.32	1.95
	1	7.76	5.91	6.70	6.87	6.95	2.01	1.93	2.02
	3			6.43	6.40	6.49	1.94	1.93	1.91
	7	7.70	6.26	6.01	6.09	6.11	2.16	2.29	2.36
	28			5.49	5.45	5.54	2.30	2.21	2.35
Acidified - Ambient	0	7.73	6.10	6.31	6.31	6.43	2.15	1.94	1.89
	1	7.22	5.67	6.46	6.60	6.16	1.87	1.88	1.85
	3	7.19		6.34	6.19	6.21	1.85	1.91	1.97
	7	7.59	6.62	6.09	6.13	6.18	1.98	2.24	2.03
	28			6.68	6.41	6.40	2.17	2.14	2.02
Filtered - Ambient	0	7.73	6.10	6.31	6.31	6.43	2.04	1.99	1.97
	1	7.22	5.93	6.52	6.42	6.44	2.17	1.94	1.98
	3			6.65	6.53	6.45	23.51*	1.98	2.02
	7	7.42	6.97	6.36	6.37	6.31	2.11	1.98	2.24
	28			5.54	5.53	5.69	2.22	2.07	
Filtered & Acidified - Ambient	0	7.73	6.10	6.31	6.31	6.43	1.95	1.94	1.90
	1	7.63	5.69	6.59	6.43	6.54	1.90	1.92	1.85
	3	7.22		6.59	6.67	6.42	2.03	2.05	2.05
	7	7.46	5.95	6.49	6.48	6.53	2.29	2.25	2.11
	28			7.16	6.82	6.36	2.24	2.21	2.21

Table B-2 Detailed UV₂₅₄ data for each water matrix (i.e., Athabasca River, Fort McMurray, Grand River, and Lake Ontario), each treatment (Untreated, Acidified, Filtered, and Filtered & acidified), storage temperature (21, 4, -24 °C), and storage time (0, 1, 3, 7, 28 days).

		UV ₂₅₄ (cm ⁻¹)							
	Storage time (days)	Athabasca River	Fort McMurray	Grand River-1	Grand River-2	Grand River-3	Lake Ontario-1	Lake Ontario-2	Lake Ontario-3
Untreated - Frozen	0	0.246	0.165	0.150	0.149	0.149	0.015	0.015	0.014
	1	0.240	0.161	0.176	0.157	0.145	0.018	0.019	0.020
	3	0.240	0.167	0.148	0.140	0.138	0.020	0.018	0.019
	7	0.235	0.168	0.139	0.142	0.143	0.018	0.017	0.016
	28			0.157	0.138	0.153	0.022	0.026	0.024
Acidified - Frozen	0	0.246	0.165	0.150	0.149	0.149	0.023	0.014	0.015
	1	0.258	0.158	0.144	0.142	0.142	0.024	0.019	0.018
	3	0.216	0.161	0.140	0.142	0.142	0.023	0.020	0.021
	7	0.276	0.162	0.145	0.142	0.139	0.023	0.028	0.019
	28			0.148	0.145	0.152	0.017	0.025	0.029
Filtered - Frozen	0	0.246	0.165	0.150	0.149	0.149	0.016	0.014	0.014
	1	0.240	0.165	0.149	0.148	0.151	0.022	0.018	0.016
	3	0.237	0.167	0.159	0.168	0.162	0.021	0.021	0.024
	7	0.235	0.167	0.161	0.167	0.156	0.023	0.015	0.017
	28			0.157	0.151	0.152	0.023	0.026	0.021
Filtered & Acidified - Frozen	0	0.246	0.165	0.150	0.149	0.149	0.014	0.014	0.014
	1	0.233	0.150	0.151	0.144	0.167	0.015	0.015	0.014
	3	0.195	0.157	0.143	0.147	0.143	0.021	0.023	0.026
	7	0.250	0.154	0.142	0.149	0.145	0.019	0.017	0.022
	28			0.158	0.163	0.151	0.032	0.019	0.026
Untreated - Cooled	0	0.246	0.165	0.150	0.149	0.149	0.015	0.015	0.014
	1	0.248	0.173	0.144	0.149	0.147	0.017	0.017	0.018
	3	0.245	0.171	0.150	0.150	0.141	0.019	0.019	0.017
	7	0.243	0.174	0.144	0.149	0.148	0.015	0.017	0.016
	28			0.170	0.152	0.148	0.025	0.026	0.024
Acidified - Cooled	0	0.246	0.165	0.150	0.149	0.149	0.023	0.014	0.015
	1	0.219	0.160	0.141	0.143	0.145	0.016	0.015	0.015
	3	0.216	0.152	0.148	0.146	0.143	0.020	0.017	0.015
	7	0.217	0.156	0.139	0.144	0.141	0.017	0.015	0.016
	28			0.140	0.142	0.109	0.022	0.025	0.023
Filtered - Cooled	0	0.246	0.165	0.150	0.149	0.149	0.016	0.014	0.014
	1	0.212	0.172	0.147	0.150	0.149	0.019	0.016	
	3	0.210	0.173	0.151	0.153	0.150	0.016	0.015	
	7	0.207	0.171	0.155	0.149	0.149	0.017	0.017	
	28			0.146	0.149	0.147	0.027	0.027	
Filtered & Acidified - Cooled	0	0.246	0.165	0.150	0.149	0.149	0.014	0.014	0.014
	1	0.189	0.153	0.146	0.145	0.140	0.017	0.014	0.013
	3	0.189	0.153	0.144	0.144	0.147	0.015	0.017	0.015
	7	0.183	0.150	0.141	0.142	0.141	0.053	0.016	0.018
	28			0.143	0.143	0.148	0.022	0.024	0.030
Untreated - Ambient	0	0.246	0.165	0.150	0.149	0.149	0.015	0.015	0.014
	1	0.246	0.171	0.153	0.153	0.151	0.018	0.017	0.017
	3		0.171	0.150	0.152	0.150	0.019	0.017	0.017
	7	0.236	0.172	0.145	0.147	0.148	0.017	0.017	0.016
	28			0.143	0.141	0.141	0.032	0.029	0.032
Acidified - Ambient	0	0.246	0.165	0.150	0.149	0.149	0.023	0.014	0.015
	1	0.220	0.155	0.144	0.142	0.142	0.015	0.016	0.014
	3	0.219	0.154	0.138	0.141	0.140	0.016	0.016	0.016
	7	0.211	0.156	0.135	0.137	0.135	0.017	0.017	0.016
	28			0.135	0.136	0.133	0.029	0.025	0.024
Filtered - Ambient	0	0.246	0.165	0.150	0.149	0.149	0.016	0.014	0.014
	1	0.220	0.171	0.152	0.151	0.151	0.017	0.016	0.016
	3		0.169	0.155	0.152	0.152	0.016	0.017	0.018
	7	0.227	0.172	0.152	0.151	0.150	0.017	0.016	0.016
	28			0.154	0.151	0.161	0.031	0.026	
Filtered & Acidified - Ambient	0	0.246	0.165	0.150	0.149	0.149	0.014	0.014	0.014
	1	0.211	0.151	0.147	0.144	0.145	0.015	0.014	0.015
	3	0.211	0.149	0.140	0.143	0.140	0.017	0.017	0.016
	7	0.210	0.152	0.140	0.141	0.140	0.015	0.016	0.017
	28			0.144	0.144	0.141	0.028	0.026	0.028

Table B-3 Detailed E2:E3 ratio for each water matrix (Athabasca River, Fort McMurray, Grand River, and Lake Ontario), each treatment (Untreated, Acidified, Filtered, and Filtered & acidified), storage temperature (21, 4, -24 °C), and storage time (0, 1, 3, 7, 28 days).

		E2:E3							
	Storage time (days)	Athabasca River	Fort McMurray	Grand River-1	Grand River-2	Grand River-3	Lake Ontario-1	Lake Ontario-2	Lake Ontario-3
Untreated - Frozen	0	6.26	8.57	6.89	6.91	6.94	12.26	13.30	15.28
	1	6.41	7.49	7.12	7.01	7.08	12.18	12.31	12.99
	3	6.38	7.38	7.24	7.36	7.37	14.45	13.84	14.00
	7	6.64	7.49	7.15	7.31	7.31	14.64	14.26	14.59
	28			6.93	7.30	7.10	39.55	12.00	30.33
Acidified - Frozen	0	6.26	8.57	6.89	6.91	6.94	19.65	39.12	23.35
	1	8.51	9.89	8.10	8.06	8.40	14.83	16.48	18.19
	3	8.19	9.71	8.39	8.18	8.44	18.56	19.09	19.24
	7	9.18	9.81	8.40	8.32	8.39	18.94	15.60	18.72
	28			8.40	7.77	8.46	16.41	49.55	16.06
Filtered - Frozen	0	6.26	8.57	6.89	6.91	6.94	8.37	14.58	14.52
	1	6.37	7.48	6.71	6.82	6.24	14.20	13.59	13.18
	3	6.35	7.59	4.26	3.98	4.43	13.20	14.10	13.49
	7	6.60	7.61	4.56	3.79	4.53	3.38	13.46	5.74
	28			6.41	6.51	6.62	30.01	10.78	39.86
Filtered & Acidified - Frozen	0	6.26	8.57	6.89	6.91	6.94	17.87	17.84	18.12
	1	9.12	10.48	8.06	8.04	8.03	16.73	16.74	16.66
	3	8.87	9.16	7.79	7.81	7.83	16.64	16.49	15.25
	7	8.89	9.93	7.43	7.72	7.45	14.55	15.88	7.60
	28			8.13	6.89	7.12	12.43	48.37	14.72
Untreated - Cooled	0	6.26	8.57	6.89	6.91	6.94	12.26	13.30	15.28
	1	6.34	7.46	7.98	6.89	6.98	12.46	11.94	12.07
	3	6.31	7.38	7.07	7.05	8.29	14.68	14.31	13.89
	7	6.54	7.60	8.08	6.80	7.03	10.16	14.66	14.82
	28			6.50	6.91	7.14	33.57	13.95	34.10
Acidified - Cooled	0	6.26	8.57	6.89	6.91	6.94	19.65	39.12	23.35
	1	9.09	9.73	8.28	8.10	8.73	17.99	18.26	18.81
	3	9.14	10.08	8.68	8.26	8.28	18.10	18.56	21.75
	7	9.49	9.89	8.33	8.01	8.99	17.81	22.84	18.38
	28			7.94	8.35	8.62	77.25	16.50	48.73
Filtered - Cooled	0	6.26	8.57	6.89	6.91	6.94	8.37	14.58	14.52
	1	6.38	7.35	6.99	6.71	6.85	12.00	7.78	
	3	6.31	7.47	6.88	6.85	6.81	12.44	14.53	
	7	6.09	7.43	6.58	6.79	6.73	13.01	12.87	
	28			6.76	6.75	7.01	11.01	16.37	
Filtered & Acidified - Cooled	0	6.26	8.57	6.89	6.91	6.94	17.87	17.84	18.12
	1	8.96	10.13	7.96	8.14	7.97	15.09	13.86	13.96
	3	8.81	10.32	7.99	7.96	7.84	15.62	11.14	15.49
	7	9.54	10.23	7.93	7.89	7.63	16.37	17.79	17.04
	28			7.60	7.87	6.87	46.14	14.99	21.32
Untreated - Ambient	0	6.26	8.57	6.89	6.91	6.94	12.26	13.30	15.28
	1	6.34	7.46	6.94	6.91	6.94	12.21	12.64	13.24
	3		7.56	7.00	6.96	7.06	14.70	14.09	13.95
	7	6.56	7.63	7.06	7.19	7.23	14.52	14.52	14.74
	28			6.91	7.20	6.97	15.00	32.14	16.20
Acidified - Ambient	0	6.26	8.57	6.89	6.91	6.94	19.65	39.12	23.35
	1	9.28	9.87	8.40	8.47	8.41	18.07	17.90	20.17
	3	9.15	9.88	8.50	8.14	8.54	18.16	19.75	18.58
	7	10.00	10.24	8.66	8.50	8.77	18.30	18.74	19.86
	28			8.77	8.21	8.89	11.26	67.37	15.95
Filtered - Ambient	0	6.26	8.57	6.89	6.91	6.94	8.37	14.58	14.52
	1	6.33	7.41	6.67	6.88	6.84	6.02	12.07	12.51
	3		7.34	6.72	6.77	6.67	13.44	13.35	10.36
	7	6.43	7.55	6.68	6.71	6.67	11.56	12.78	11.95
	28			6.03	5.61	6.47	9.89	16.90	
Filtered & Acidified - Ambient	0	6.26	8.57	6.89	6.91	6.94	17.87	17.84	18.12
	1	9.05	10.10	7.86	8.00	7.96	18.63	20.51	17.73
	3	8.77	10.11	8.02	7.97	7.98	13.19	15.48	16.24
	7	9.17	10.50	7.97	7.98	7.98	13.23	13.74	13.54
	28			8.18	7.80	8.30	16.10	37.86	15.01

