EXPLORING DECADAL INCREASES IN THE CONCENTRATION OF NATURAL ORGANIC MATTER AND THE IMPACT ON SURFACE DRINKING WATER TREATMENT PROCESSES

BY

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Natural organic matter (NOM) is prevalent in surface waters and impacts all aspects of drinking water treatment. In recent decades, there have been reports of increasing NOM concentration (often referred to as brownification) in the northern hemisphere and reduced atmospheric deposition has been identified as a potential driver. The objectives of this thesis were to 1) provide a comprehensive review of surface water quality responses to decreased acid deposition with a focus on NOM dynamics, and identify the potential impacts of these responses on water treatment infrastructure, 2) quantify the impact of decreased deposition and its effect on NOM concentration and subsequent surface water treatment practices in Atlantic Canada, 3) investigate the relationship between NOM and metal colloids (Fe, Al, Mn) in lakes representing a range of DOC levels in a region where surface waters are browning significantly, and 4) evaluate the use of granular activated carbon (GAC) adsorption as a robust adaptation strategy for enhancing NOM removal.

This work identified the primary drivers of brownification to be a combination of reductions in atmospheric deposition and climate change, where climate impacts will have a more pronounced impact as acid deposition stabilizes. This work also showed that in Atlantic Canada, reductions in atmospheric sulfate deposition was a primary driver of brownification and was responsible for up to 3.8-fold increases in lake color and corresponding alum dosing at the treatment facilities drawing from browning lakes. This resulted in compromised filter performance at a direct filtration facility and revealed that treatment facilities may be under designed as a result. This work highlighted the importance of colloid characterization in drinking water supplies challenged with brownification, as opposed to the convention of quantifying dissolved material via separation through a 0.45 μm filter adopted by industry. Finally, this work determined that GAC is a robust adaptation strategy, however it can release significant quantities of dissolved Mn when potassium permanganate is used. The source water complexities that are anticipated through brownification and the need for considering robust adaptation water treatment solutions that consider many factors in addition to NOM, including Mn and Fe, were highlighted.

LIST OF ABBREVIATIONS USED

AOP	Advanced oxidation process
ANC	Acid neutralization capacity
ANT	Anthracite
APHA	American Public Health Association
BC	Base cation
BV	Bed volume
BIX	Biological index
CAPMoN	Canadian Air and Precipitation Monitoring Network
CDOM	Colored dissolved organic matter
DOM	Dissolved organic matter
DOC	Dissolved organic carbon
DBP	Disinfection by product
EBCT	Empty bed contact time
EEM	Excitation emission matrix
ES	Effective size
FEEM	Fluorescence excitation emission matrix
FFF	Field flow fractionation
FRT	Filter run time
FSP	Full scale plant
GAC	Granular activated carbon
HAA	Haloacetic acid

HAAfp	Haloacetic acid formation potential
HIX	Humification index
IQR	Interquartile range
JDKWSP	J.D. Kline Water Supply Plant
kDa	Kilodalton
$KMnO_4$	Potassium permanganate
LED	Light emitting diode
LMWSP	Lake Major Water Supply Plant
MIEX	Magnetic ion exchange
MKT	Mann-Kendall Test
MLD	Millions of litre per day
NF	Nanofiltration
NTU	Nephelometric turbidity unit
PAC	Powdered activated carbon
PARAFAC	Parallel factor analysis
PtCo	Platinum cobalt unit
SDG	Sustainable development goal
SMKT	Seasonal Mann0Kendall test
SO_4	Sulfate
SO_2	Sulfur dioxide
THM	Trihalomethane
THMfp	Trihalomethane formation potential
TOC	Total organic carbon

TCU	True color unit
UF	Ultrafiltration
UFRV	Unit filter run volume
UV	Ultraviolet
UV254	UV absorbance at 254 nm
WHO	World Health Organization
WSP	Water safety plan

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1. CHAPTER 1: INTRODUCTION

1.1. Research rationale

Natural organic matter (NOM) is ubiquitous in surface water supplies and is comprised of a heterogeneous mixture of organic compounds originating from allochthonous (terrestrially derived) or autochthonous (generated in the water column through biological activity) input (Croue et al., 2000; Zularisam et al., 2006). NOM is known to be very complex in nature with a wide range of molecular weight (MW) and functional groups (phenolic, hydroxyl, carbonyl, carboxylic acid) (Zularisam et al., 2006) and generally is classified in terms of humic acids (HA) and fulvic acids (FA), as well as non-humic fractions including carbohydrates, amino acids, and proteins (Sillanpää, 2014). Despite the complexity of NOM, humic acids are the largest constituent in freshwater and account for 50 to 90% (Artinger et al., 2000) of the organic carbon content.

For several decades, there have been increases in NOM concentration measured as dissolved organic carbon (DOC) or colour in surface waters, a phenomenon commonly referred to as brownification (Evans & Monteith, 2001; Stoddard et al., 2002; Monteith et al., 2007; Skjelkvåle et al., 2001; Skjelkvåle et al., 2005; Garmo et al., 2020; Redden et al., 2021). Brownification has been widespread throughout the northern hemisphere with one of the most reported drivers of browning being anthropogenic pressures such as the reversal of atmospheric acid (e.g., SO4) deposition. For example, Monteith et al. (2007) evaluated the spatial distribution of DOC trends in six North European and North American countries between 1990 and 2004 and found widespread significant upward (up to 0.15 mg/L/year) trends in DOC in the northeastern portion of the United States (US), southern Nordic regions, and in the United Kingdom (UK), which were related to reductions in atmospheric acid (e.g., SO_4) deposition. Garmo et al. (2014) analyzed trends in surface water chemistry for 12 sites in Europe and North America and found that declining acid deposition at the majority of study sites corresponded with increasing DOC concentrations.

More recently, the importance of climate change (Finstad et al., 2016; Riise et al., 2018; Kopáček et al., 2019; Imtiazy et al., 2020; Meyer-Jacob et al., 2020; Marty et al., 2021; Nelson et al., 2021; Lepistö et al., 2021) and changing land use (e.g., Skerlep et al., 2020; Garmo et al., 2020; Kritzberg et al., 2020) have been highlighted as other drivers of brownification, particularly as atmospheric acid deposition stabilizes. According to Meyer-Jacob et al. (2019), climate change is forcing lakes to new ecological states, with lake water DOC concentrations exceeding pre-industrial levels. Skerlep et al. (2020) noted that 75% of the long-term variation in NOM can be explained by a combination of precipitation, temperature, reduced acid deposition, and land-use change, but disentangling the contributions of these factors to rising DOC will be challenging due a lack of long-term datasets. Weyhenmeyer et al. (2016) predicted increases in lake color, which is controlled by water flushing through the landscape, in a worst-case climate scenario (32% increase in precipitation) and showed that color would increase by a factor of between 1.1 and 7.6, noting that it would impact the preparation of drinking water.

NOM plays a critical role in the cycling and mobility of metals in aquatic environments (Aiken et al., 2011), and many surface waters with increasing DOC have also had changes in metals cycling, particularly with respect to iron (Fe) (Neal et al., 2008; Kritzberg and Ekstron, 2012; Weyhenmeyer et al., 2014; Brezonik et al., 2019) and aluminum (Al) (Sterling et al., 2020; Lawrence et al., 2021; Redden et al., 2021). NOM can also interact with Manganese (Mn) in Mn rich environments (Trainer et al., 2021). For example, Fe concentrations have been increasing in many browning lakes in regions with reduced acid deposition. Neal et al. (2008) examined temporal trends in the concentration of Fe in UK surface waters and found that Fe correlated with

DOC concentration— the greatest rates of Fe increase coincided with those for DOC. Kritzberg and Ekstrom (2012) noted that Fe-NOM complexes are responsible for maintaining Fe in solution. Lawrence et al. (2021) recently evaluated the status of Al chemistry in Adirondack streams and noted that inorganic levels of Al continue to decline and that increases in DOC are shifting speciation to non-toxic organically complexed Al. Redden et al. (2021) evaluated browning of Nova Scotia surface waters (and found apparent color increased in 54 of 64 lakes, while Al increased in 36 lakes, noting that Al was often bound to organic colloids. Lyvén et al. (2003) attributed 70% of Mn in freshwater to carbon-based colloids and Baalousha et al. (2011) found that Mn was bound to NOM colloids. Thus, the brownification of surface waters may increase the binding capacity for metals, causing a shift towards metal-NOM colloids as opposed to soluble or dissolved species.

NOM impacts virtually all aspects of drinking water treatment. For example, NOM is responsible for most of the chemical demand (e.g., coagulant, oxidant) during drinking water treatment. More specifically, humic-like NOM fractions with higher MW, aromaticity and hydrophobicity are most amenable to removal via enhanced coagulation, which is the major NOM removal process used in drinking water treatment (Edzwald, 1993; Sharp et al., 2006). The removal of NOM is typically driven by minimizing the formation of regulated DBPs, which are formed during chlorination when NOM is present. To date, there have been over 600 DBPs identified, although trihalomethanes (THMs) and haloacetic acids (HAAs) are the most commonly regulated (Richardson et al., 2007). Health Canada has established guidelines of 100 and 80 μg/L for THMs and HAAs (Health Canada, 2006; Health Canada, 2008), respectively, while the USEPA has lower permissible levels for THMS and HAAs at 80 and 60 μg/L, respectively (Richardson et al., 2007). Insufficient NOM removal can contribute to undesirable colour, taste, and odour problems, can impact the biological stability of distributed water (Hammes et al., 2010) and can act as a carrier of trace metals (e.g., Pb) in distribution systems (Trueman et al., 2017), if poorly removed during treatment. NOM can also impact the removal of other contaminants such as metals – unit processes for the removal of metals including Fe and Mn typically include pre-oxidation, which is designed for dissolved species (e.g., Fe^{2+} and Mn^{2+}) and are not effective for the removal of NOM-stabilized colloidal metals (Carlson et al. 1997). Thus, the aforementioned changes in the speciation of metals through brownification may impact the effectiveness their removal through pre-oxidation processes.

The synergistic effects of climate change, reductions in atmospheric acid deposition, and other anthropogenic pressures on source water quality and subsequent brownification processes is an important consideration for the design and operation of water treatment facilities. Most water treatment infrastructure was designed based on historical water quality conditions, and there is a need to better understand the drinking water treatment vulnerabilities and the transition towards robust treatment technologies and solutions that can adapt to climate change and other drivers of changing water quality.

1.2. Research questions

This research was guided by the following research questions:

1. How is water quality in drinking water reservoirs and surface waters in Nova Scotia responding to anthropogenic pressures such as atmospheric deposition and climate change?
2. What are the vulnerabilities to surface drinking water treatment systems in Nova Scotia in response to changing source water quality, including brownification?

1.3. Research objectives

Research was addressed through a series of objectives that focused on the concept of brownification of surface drinking water supplies because of reduced atmospheric acid deposition and climate change pressures, and the subsequent impacts on drinking water treatment. As part of this work, there was a need to address a knowledge gap surrounding robust adaptation processes for water facilities challenged with source water brownification. These objectives were as follows:

1. Provide a comprehensive review of surface water quality responses to decreased sulfate deposition and other brownification drivers (e.g., changing climate) in the northern hemisphere with a focus on NOM dynamics, and identify the potential impacts of these responses on water treatment infrastructure.

2. Quantify the impact of decreased atmospheric acid deposition and its effect on lake water quality (with a focus on NOM) and the impact on subsequent surface water treatment practices in Atlantic Canada.

3. Investigate the relationship between NOM and metal colloids in lakes representing a range of DOC levels in a region where surface waters are browning significantly and understand the implications for drinking water sources.

4. Evaluate the use of granular activated carbon (GAC) filter configurations as a robust adaptation strategy for enhancing NOM removal, and assess the effectiveness for Fe and Mn removal, at a facility challenged with brownification of raw water.

1.4. Organization of thesis

Chapter 1 outlines the research rationale, research questions and research objectives. **Chapters 2 to 5** are arranged in the style of a series of journal articles for publication in peer-reviewed journals. These chapters contain individual abstracts, introduction, materials and methods, results and discussion, and conclusions. Supplementary information for each chapter is included as a series of appendices.

Chapter 2 addresses Objective 1 and provides a comprehensive review of surface water quality responses to decreased sulfate deposition and other brownification drivers including climate change in the northern hemisphere with a focus on natural organic matter NOM dynamics. It also identifies the potential impacts of these responses on water treatment infrastructure.

Chapter 3 addresses Objective 2 and studied atmospheric acid deposition in Nova Scotia and its association with changing source water quality, including brownification, in two drinking water supplies (Pockwock Lake and Lake Major). It also quantified the subsequent impacts on drinking water treatment processes.

Chapter 4 addresses Objective 3 and used field-flow fractionation coupled with UV and ICP-MS detection to measure the size distribution of colloidal iron, aluminum, manganese, and NOM in six lakes that have browned to some degree in the past three decades. This analysis was discussed in relation to the treatment of browning surface water supplies.

Chapter 5 addresses Objective 4 and includes a pilot-scale assessment of various adaptation strategies (e.g., implementation of clarification, use of alternative filter media such as GAC) for direct filtration facilities under the stress of increasing NOM through brownification of surface water supplies.

Chapter 6 contains concluding remarks and recommendations of the thesis.

2. CHAPTER 2: A REVIEW OF LONG-TERM CHANGE IN SURFACE WATER NATURAL ORGANIC MATTER CONCENTRATION IN THE NORTHERN HEMISPHERE AND THE IMPLICATIONS FOR DRINKING WATER TREATMENT

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L.E.A was responsible for article conceptualization, original draft preparation, writing-reviewing and editing.

2.1. Abstract

Reduced atmospheric acid deposition has given rise to recovery from acidification – defined as increasing pH, acid neutralization capacity (ANC), or alkalinity in surface waters. Strong evidence of recovery has been reported across North America and Europe, driving chemical responses. The primary chemical responses identified in this review were increasing concentration and changing character of natural organic matter (NOM) toward predominantly hydrophobic nature. The concentration of NOM also influenced trace metal cycling as many browning surface waters also reported increases in Fe and Al. Further, climate change and other factors (e.g., changing land use) act in concert with reductions in atmospheric deposition to contribute to widespread browning and will have a more pronounced effect as deposition stabilizes. The observed water quality trends have presented challenges for drinking water treatment (e.g., increased chemical dosing, poor filter operations, formation of disinfection by-products) and many facilities may be under designed as a result. This comprehensive review has identified key research areas to be addressed, including 1) a need for comprehensive monitoring programs (e.g., larger

timescales; consistency in measurements) to assess climate change impacts on recovery responses and NOM dynamics, and 2) a better understanding of drinking water treatment vulnerabilities and the transition towards robust treatment technologies and solutions that can adapt to climate change and other drivers of changing water quality.

2.2. Introduction

In response to concern over atmospheric acid deposition in the 1980s and 1990s, both national (the Eastern Canada Acid Rain Control Program, the United States Clean Air Act) and international (the United Nations Economic Commission for Europe [UN ECE] Convention on Long-Range Transboundary Air Pollution [LRTAP], the Canada-United States Air Quality Agreement) regulations have been implemented to reduce air emissions such as sulphur and nitrogen oxides. As a result, regions in both North America and Europe have shown massive reductions in SO_x emissions followed by decreased sulfate deposition (Driscoll et al., 2016; Garmo et al., 2020; Stoddard et al., 1999).

For several decades, decreased acid deposition has given rise to surface water recovery from acidification throughout North America and Europe, a phenomenon defined by increasing pH, acid neutralization capacity (ANC) or alkalinity, and often associated with increasing concentrations of dissolved organic carbon (DOC) (e.g., brownification) (Evans & Monteith, 2001; Monteith et al., 2007; Skjelkvåle et al., 2001; Stoddard et al., 2002; Sverdrup et al., 2002). While recovery is currently being experienced in parts of North America and Europe, it is anticipated that the effects could be observed on a broader scale in the future as the use of coal will potentially be phased out globally by 2050 under the Paris Agreement (Rocha et al., 2016), further reducing atmospheric acid deposition to surface waters. The effects of recovery from acidification are also expected to be amplified by climate change (e.g., increasing temperature, more frequent and severe flooding and droughts) and changing land use (De Wit et al., 2016; Hongve et al., 2004; Roulet, 2006; Weyhenmeyer et al., 2016; Whitehead et al., 2009; Kritzberg et al., 2020).

Engineered water infrastructure in many communities relies on surface water as a drinking water source. In the United States, 61% of the total withdrawals for public water supply were from surface water in 2015 (Dieter et al., 2018). In Canada, surface water sources provided 89% of the total volume of potable water produced in 2011 (Statistics Canada, 2013). Thus, changing surface water quality is an important design consideration that must be well understood to provide sustainable water treatment solutions, as most water treatment infrastructure was designed based on historical water quality.

It is expected that the synergistic effects of climate change, recovery from acidification, and other anthropogenic pressures will impact engineered drinking water processes. This is important given the relevance to the United Nations Sustainable Development Goals (SDGs) priorities of clean water (SDG 6) and climate action (SDG 13), which together emphasize the societal need for high-quality drinking water under a changing climate. Although the links between climate change and surface water quality are well-documented (Whitehead et al., 2009), a review of the potential effects of recovery from acidification, climate, and other brownification drivers is lacking, particularly concerning water treatment infrastructure. Accordingly, the purpose of this chapter is to 1) provide a comprehensive review of surface water quality responses to decreased sulfate deposition and other brownification drivers (e.g., changing climate, land use) in the northern hemisphere with a focus on natural organic matter (NOM) dynamics, 2) to identify the potential impacts of these responses on water treatment infrastructure, and 3) identify the key research needs to understand future risk from surface water quality responses.

2.3. Methods

Multiple databases (e.g., Scopus, Web of Science, ScienceDirect) were used to search for studies on topics related to increasing NOM (TOC, DOC, color, etc.) or browning in surface waters throughout the northern hemisphere with an emphasis on climate or reversal of acidification as drivers. Keywords used alone or in combination included: acidification, lake recovery, chemical recovery, reversal of acidification, acid deposition, DOC, TOC, NOM, DOM, CDOM, color, brownification, browning, climate change, trace metals, drinking water treatment, surface water, freshwater, water supply.

Information was gathered from academic sources published in peer-reviewed journals. The literature search focused on studies published between the late 1990s and early 2000s given that this period was typically when trends in recovery from acidification were initially reported. Generally, this resulted in studies that were based in Europe and North America with both global and regional scales. The publications were screened based on the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines (Moher et al., 2009) to ensure reliability and validity among studies and to evaluate biases and uncertainty of measurements across outcomes, even within a study.

2.4. Recovery from acidification and climate change contribute to widespread browning

Over the last several decades, evidence of recovery from acidification has been reported throughout the Northern Hemisphere, particularly in regions across Europe (e.g., Fennoscandian countries and the UK), the Northeastern United States, and Eastern Canada. Recovery has been identified by observing regional trends in ANC or alkalinity, acid anion (e.g., SO_4^{2-}, NO_3^-, Cl^-) concentrations, and pH. Numerous studies have investigated global trends in recovery across the Northern Hemisphere over periods from the 1980s to 2010s (Garmo et al., 2014, 2020; Skjelkvåle et al., 2005; Stoddard et al., 1999). While the degree of recovery is varied across geographical locations, the consensus was observed improvements in either alkalinity or ANC (and sometimes pH) – often correlating with decreases in acid deposition.

Site-specific studies have been completed in both Europe and North America. Results from European monitoring sites provided strong evidence for recovery from acidification, with overall increasing trends in pH (Evans et al., 2001). Popular study sites in the United States include the Appalachians, New England, the Adirondacks, and Eastern Canada, all of which have shown evidence of recovery in the last 30 years through decreases in surface water sulfate concentration and concomitant increases in pH or ANC (Burns et al., 2006; Clair et al., 2011; Driscoll et al., 2003; Lawrence et al., 2011; Leach et al., 2019; Meyer-Jacob et al., 2020; Redden et al., 2021; Stoddard et al., 2002; Strock et al., 2014; Waller et al., 2012). Figure 1 summarizes the magnitude of annual trends in sulfate concentration reported in the literature for surface waters in the regions commonly reported as experiencing recovery. Information, including the general conclusion of each highlighted paper and the magnitude of change in acid deposition, for studies presented in Figure 1 is provided in Table A1 (Appendix A).

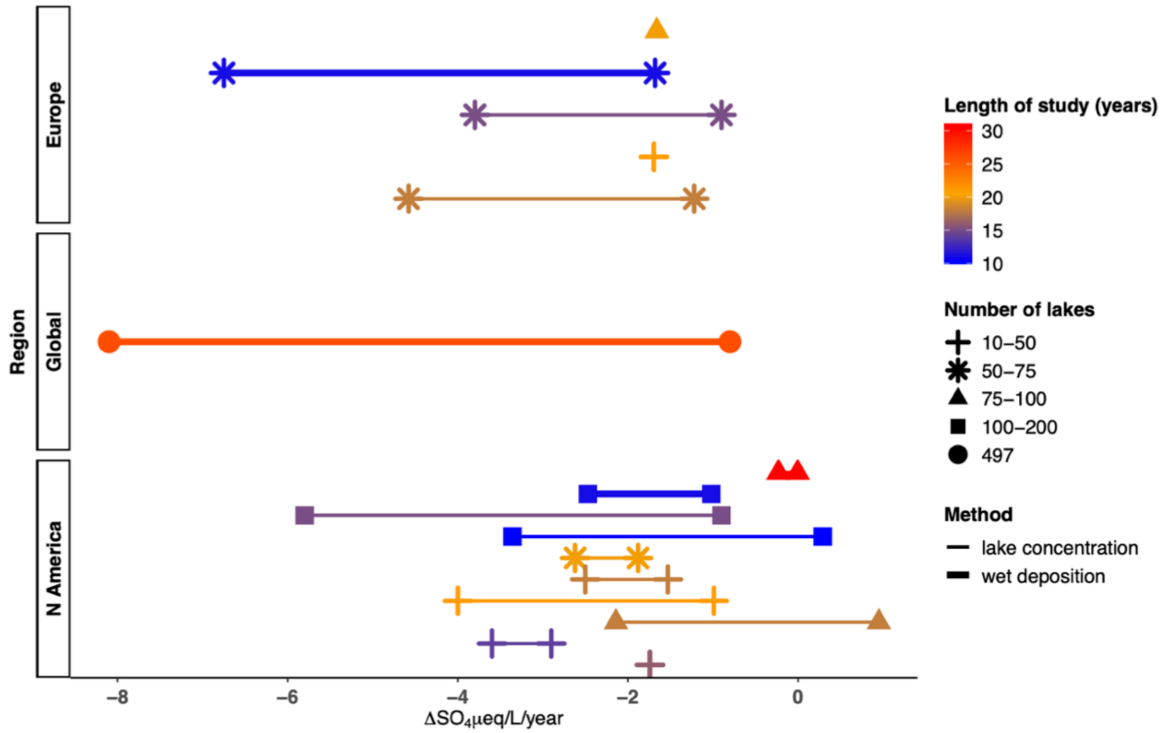

Figure 1. Range in magnitude of annual trends in SO_4 concentration and wet deposition as a function of number of lakes and study length (in years) reported in the literature for surface waters in various regions experiencing recovery.

Despite the widespread decrease in sulfate deposition observed in the Northern Hemisphere, the degree of recovery from acidification in many surface waters has been less than expected, indicating that there are additional factors impacting the progression of recovery to pre-industrial states. These factors include an increase in concentrations of acidic organic compounds (i.e., DOC), depletion of base cations (BCs) in the catchment soils, and release of legacy sulfate from the catchment and sediment. Additional information on factors impeding recovery is provided in Appendix A (Section A1).

2.4.1. Chemical responses to recovery from acidification

2.4.1.1. Increasing concentration of NOM and brownification

2.4.1.1.1. Regional trends in surface water quality indicate recovery in Europe and North America

Surface water recovery is often associated with abiotic water quality parameters including NOM, as measured by DOC. Throughout the Northern Hemisphere, surface waters in natural settings have been exhibiting higher concentrations of DOC, particularly in areas that were previously exposed to chronic sulfate deposition through acid rain. For example, multiple studies comparing trends in surface water chemistries across North America and Europe have reported decreasing sulfate concentrations corresponding with increasing DOC concentrations (e.g., Garmo et al., 2020; Monteith et al., 2007; Skjelkvåle et al., 2005). Regional trends in surface water DOC concentrations reported in studies across Scandinavia, the UK, Northeastern US, and Eastern Canada are summarized in Figure 2. More specific details are provided in Appendix A (Table A2).

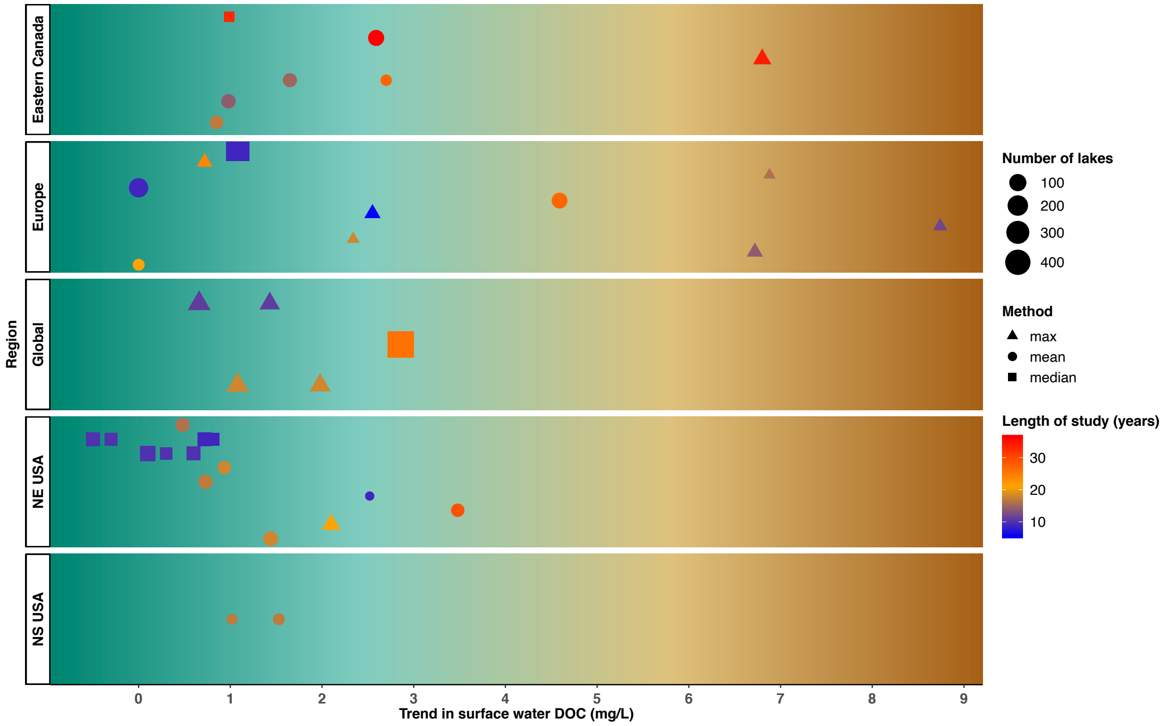

Figure 2. Reported magnitude of annual trends in surface water DOC concentration as a function of number of lakes and study length (in years) reported in the literature for surface waters in various regions experiencing recovery.

2.4.1.1.2. Quantifying pre-acidification water quality with paleolimnology

A lack of long-term historical datasets is one of the challenges in quantifying recovery status. More recently, a paleolimnological approach using lake sediment cores has been applied to infer trends in lake water organic matter concentrations across longer time scales (Meyer-Jacob et al., 2017, 2019; Xiao et al., 2020). The extended history of inferred water chemistry enables a comparison of pre-industrial and post-acidification conditions. Sediment inferred TOC values and in-lake TOC trends have been proven to be well-matched in Canadian and Scandinavian lakes (Meyer-Jacob et al., 2017). Meyer-Jacob et al. (2019) compared DOC trends over the past 200 years using cores from high and low acid-sensitive lakes in Ontario, Canada and found that DOC concentrations had exceeded background levels, suggesting climate factors and reduction in acid deposition may push DOC concentrations past pre-industrial levels. Similarly, Meyer-Jacob et al. (2020) found that sediment-inferred DOC in Ontario lakes has been approaching pre-industrial levels. Russell et al. (2021) reconstructed sediment inferred DOC for UK lakes and observed increases in DOC, noting that increases pre-dated acidification and that terrestrial productivity may have driven brownification. Myrstener et al. (2021) evaluated long-term trajectories of sediment inferred TOC in Swedish lakes and observed an increase in TOC due to processes such as recovery from acidification and reforestation.

Studies have also used paleolimnology to evaluate the impacts of increasing DOC on physical, chemical, and biological lake properties. Brown et al. (2017) used a paleolimnological approach to evaluate the consequence of increasing DOC on lake thermal structure and noted that increases in DOC could alter the physical and biological structure (e.g., a shift in mixing depth, change in community structure) of lakes. Recently, Fowler et al. (2022) conducted a paleolimnological comparison of changes in clear versus brown water lakes over two centuries in the northeastern United States and noted that both lakes showed signs of recovery from acid deposition and that brown water lakes showed more subtle responses to climate changes. Accordingly, this approach could be used to understand past and future trends in DOC concentration as well as physical, chemical, and biological properties in surface waters lacking long-term monitoring data.

2.4.1.1.3. Mechanisms related to atmospheric acid deposition for explaining NOM increase

Monteith et al. (2007) offered two possible mechanisms (both associated with decreasing acid deposition) responsible for the widespread increase in DOC concentrations in North America and Europe. The first mechanism involved a reduction in the acidity of soils, rendering soil organic matter more soluble. SanClements et al. (2012) presented a similar hypothesis and Evans et al.

(2012) found a positive relationship between DOC concentration and soil acidity observed at all study sites. Using one of the same study sites, Oulehle et al. (2013) also determined that changes in soil pH have significant effects on interstitial soil concentrations; however, leaching of DOC to soil pore water was limited by biological controls (i.e., vegetation and biomass productivity).

The second proposed mechanism by Monteith et al. (2007) was a reduction in ionic strength of soil solutions. Haaland et al. (2010) suggested changes in concentrations of H^+ and mobile anion concentrations (e.g., SO_4^{2-}, NO_3^-, Cl^-) in precipitation would result in a reduction in ionic strength of soil solutions, which in turn would increase the export of colored organic matter to surface waters. Clark et al. (2011) conducted batch experiments to simulate chemical regulation of DOC release from organic soils because of changes in acidity and ionic strength from the addition of sulfate. They found that over 20 hours, DOC release decreased by 21-60% in response to the addition of sulfuric acid. Studies in Norway (De Wit et al., 2007), the Czech Republic (Hruska et al., 2009), and the Adirondack region of New York (Lawrence and Roy, 2021) found that decreasing ionic strength in soil solutions was the main driver of increased solubility of DOC and subsequent transport to catchments.

2.4.1.1.4. Potential shifts in NOM character and changes in reactivity in brown waters

The character of NOM in surface waters depends on photochemical, hydrological, and biological properties, as well as the regional climate and extreme weather events (e.g., drought, heavy precipitation). NOM can be categorized based on its polarity as hydrophobic or hydrophilic in nature—hydrophobic components contain mostly high molecular weight humic and fulvic acids, whereas hydrophilic components contain low molecular weight proteins, carbohydrates, and amino acids (Sillanpää et al., 2018).

Some studies have shown that NOM is becoming more hydrophobic and colored in nature and this has been linked to the declining ionic strength of soils caused by reductions in sulfate deposition (Worrall and Burt, 2009), as described above. Erlandsson et al. (2008) observed that the ratio of UV absorbance to DOC concentration (i.e., specific ultraviolet absorbance [SUVA]) was increasing in Sweden between 1987 and 2004, suggesting a shift toward a more hydrophobic NOM. Clark et al. (2011) found similar results, reporting a decrease in the proportion of colored aromatic humic acids with increasing acidity, suggesting that DOC quality and quantity change with the addition of sulfate. Worrall and Burt (2010) used the DOC-color ratio to test for long-term changes in the composition of NOM in over 70 British rivers from 1974 to 2005. Results showed that the amount of color per unit of DOC increased in the 1990s, suggesting a shift towards more humic-rich NOM (e.g., hydrophobic acids). The quality of NOM was characterized using fluorescence spectroscopy in nine-acid sensitive lakes in Maine (SanClements et al. 2012) and all lakes with increasing DOC trends had NOM representative of more terrestrial (hydrophobic) sources. On the other hand, Dawson et al. (2009) found a decline in the hydrophobicity of DOC when studying the SUVA relationship in two surface waters in Scotland, the UK between 1986 and 2007. The surface waters studied showed an increase in DOC concentration of 0.15 and 0.28 mg/L/year, but the decreasing trend in SUVA values over time indicated a decline in the proportion of hydrophobic DOC.

The photo and biodegradation of NOM within the aquatic environment can also contribute to the transformation and alteration of NOM character. UV radiation from sunlight can generate photooxidants that may accelerate the degradation of NOM in surface waters. More specifically, the aromatic, colored fraction of NOM absorbs sunlight, potentially initiating photochemical reactions that can mineralize NOM to CO_2 or can produce partially oxidized compounds with altered chemical composition (e.g., lower in molecular weight, less aromatic). Lower molecular weight and less aromatic compounds are typically more bioavailable, and thus can undergo further microbial processing (e.g., biodegradation) (Graneli et al., 1996; Lindell et al., 2000). The effects of lake acidification on the photoreactivity of NOM have been studied previously (e.g., Gennings et al., 2001; Aneslo et al., 2003). For example, Aneslo et al. (2003) noted that photooxidation rates were higher under acidic conditions compared to ambient pH, and that an increase in NOM photo reactivity by acidification could explain water transparency and DOC removal in acidic lakes.

However, studies on brown lakes are only more recently gaining attention. Calderaro and Vione (2020) observed that with regards to browning waters, a shallower and more NOM-rich epilimnion can alter photodegradation processes. Paneer Selvam (2016) noted that biodegradation plays a dominant role in NOM transformation in brown lakes while photodegradation plays a larger role in clear water lakes. According to Magyan et al. (2021), photodegradation is more important compared to biodegradation on short time scales (e.g., weeks), and that photodegradation of terrestrial NOM can occur for up to 90 days. In 7-day experiments, Dempsey et al., (2020) recently found that photodegradation can lead to larger changes in NOM concentration and character than biodegradation (Dempsey et al., 2020). They also compared the sensitivity of different sources of terrestrial DOC on photodegradation in lakes and found that changes in DOC concentration were strongest for brown lakes, while changes in SUVA were more notable for oligotrophic and eutrophic lakes (Dempsey et al., 2020). Thus, brownification may alter photo and biodegradation processes which could contribute further to changes in NOM character (e.g., optical properties, molecular weight, etc.) in surface waters, particularly as acidification-related drivers subside and other drivers (e.g., climate, changing land use) become more prominent. Wasswa et al. (2022) demonstrated the contrasting impact of microbial and photochemical processing of terrestrial (e.g., brown) NOM in the formerly acidic Adirondack lakes, highlighting a need for a better understanding of these processes, particularly in browning lakes. Wasswa et al. (2020) also noted a need for additional research on photoreactivity and photochemical processes in response to surface water browning. Slavik et al. (2021) discuss the implications of solar radiation impacts to NOM character from a drinking water supply perspective.

2.4.1.2. Increases in trace metals associated in part with brownification

Many surface waters with increasing DOC have also had changes in trace metals cycling, although the drivers are not well understood. For example, Iron (Fe) concentrations have been increasing in many browning lakes in regions with reduced acid deposition. Neal et al. (2008) examined temporal trends in the concentration of Fe in UK surface waters and found that Fe correlated with DOC concentration— the greatest rates of Fe increase coincided with those for DOC. Kritzberg and Ekström (2012) evaluated the role of Fe concerning brownification and found that Fe-NOM interactions are likely responsible for maintaining Fe in solution. However, they also noted that the rate of Fe increase was greater than that of NOM, indicating that changes in NOM concentration or composition were not the sole explanations. Weyhenmeyer et al. (2014) compared the contributions of Fe and DOC to water color in boreal freshwaters in Sweden and Canada and found widespread increasing trends in DOC and Fe in study lakes. Björnerås et al. (2017) analyzed temporal trends in Fe concentration in over 300 water bodies in Europe and North America and found that Fe increases coincided with NOM increases. They also noted that increases in Fe and NOM may not be directly mechanistically linked but may be responding to common regional drivers such as declining sulfate deposition. Brezonik et al. (2019) found that color and dissolved Fe were correlated in the surface waters in the Upper Great Lakes states.

In addition to Fe, there have been varied reports of changing aluminum (Al) concentration in browning surface waters. It is understood that acidification mobilizes toxic monomeric inorganic Al from soil to surface waters, resulting in harm to aquatic life. Due to reductions in atmospheric acid deposition, there have been decreases in the inorganic Al concentration, which is not surprising, as DOC can co-transport Al (Bailey et al., 1995; Driscoll & Newton, 1985) and affect Al speciation. For example, Lawrence et al. (2021) recently evaluated the status of Al chemistry in Adirondack streams and noted that inorganic levels of Al continue to decline and that increases in DOC are shifting speciation to non-toxic organically complexed Al. Others have reported increases in organically complexed Al where increasing DOC has been observed. In Atlantic Canada, Sterling et al. (2020) noted that Al concentrations increase during periods of elevated TOC concentration and the observed increases in total Al were likely in the form of organically complexed Al. Redden et al. (2021) evaluated chemical recovery and browning of Nova Scotia surface waters (81 lakes and rivers) and found apparent color increased in 54 of 64 lakes, while Al increased in 36 lakes. Further, Redden et al. (2021) noted that Al was often bound to organic and Fe-based colloids, which implied that NOM increased the binding capacity for metals. Similarly, Anderson et al. (2021) used field flow fractionation coupled with UV and IC-PMS detection to investigate the metal-NOM interactions in Nova Scotia lakes and found increasing Fe, Al, and color in the study lakes, and Fe and Al were in part bound to NOM (Anderson et al., 2021). Accordingly, browning lakes may see increases in organic colloids that are rich in Fe and Al. Despite the shift in speciation of Al in less acidic surface waters, inorganic Al exceeds thresholds for aquatic life (15 μg/L) in some surface waters despite elevated NOM levels (Sterling et al, 2020). These studies demonstrate the importance of speciation of metals like

Fe and Al in monitoring programs to understand the division between organic and inorganic forms and their drivers of change.

2.4.2. Climate change and other processes drive browning as recovery processes stabilize

Climate change and other factors (e.g., changing land use) act in concert with reductions in atmospheric deposition to contribute to widespread trends in browning in natural settings. Multiple studies have reported significant effects of climatic factors in addition to reversal of acidification on temporal trends of DOC concentration (Porcal et al., 2009; Couture et al., 2012; De Wit et al., 2016; Evans et al., 2005; Finstad et al., 2016; Imtiazy et al., 2020; Kopáček et al., 2019; Meyer-Jacob et al., 2020; Riise et al., 2018; Ma et al., 2019; Meingast et al., 2020; Marty et al., 2021; Lee et al., 2020; Nelson et al., 2021; Lepistö et al., 2021; Zhang et al., 2021; Jelji et al., 2022). Further, DOC has increased in some lakes that were not acidified and thus did not undergo recovery, suggesting other drivers (Evans et al. 2005; Gavin et al. 2018; Keller et al. 2008). In some regions, variation in climate was the dominant driver controlling DOC concentrations since the 2000s (Imtiazy et al., 2020; Riise et al., 2018). Moreover, climate has been proven to strongly impact catchment characteristics, which dictate many of the processes and mechanisms controlling the chemistry and recovery process in surface waters (Riise et al., 2018). Lapierre et al. (2021) evaluated color and DOC in hundreds of northeastern US lakes and observed widespread increasing trends, but although browning may be more pronounced in areas where recovery from acidification and climate are dominant drivers, their effects may be more muted in landscapes with more anthropogenic activity.

The most prominent climatic factors impacting water quality are precipitation and temperature. Increases in precipitation can lead to greater connectivity in the watershed and more mobile DOC, both of which can lead to larger exports of terrestrial DOC from the catchment (De

Wit et al., 2016; Mitchell & Likens, 2011; Strock et al., 2016; Xiao et al., 2020). De Wit et al. (2016) reported strong relationships between median annual precipitation and organic content for lakes in Norway, Sweden, and Finland. The relationship between increasing trends in rainfall and organic content was strongest in dry regions, and the impact weakened as precipitation increased, likely due to the dilution of organic content at the high rainfall sites. Wei et al. (2021) identified key environmental factors explaining temporal DOC patterns in the United States across watersheds of different sizes and land-use conditions and found that precipitation was the dominant factor for DOC export on an annual timescale, but atmospheric deposition was also significant over time. Periods of drought have also been shown to significantly impact water chemistry—increased acidification, readily caused by oxidation of legacy sulphur stored in soils leads to suppression of DOC (Clark et al., 2005; Strock et al., 2016; Watmough et al., 2016). Strock et al. (2016) observed a ~2.5 mg/L decrease in DOC concentrations during dry periods and an increase of ~0.5-1.0 mg/L during wet periods in the Northeastern United States. Additionally, patterns in precipitation can impact the character of NOM, where more hydrophilic NOM has been observed during drought and more hydrophobic NOM was recorded post-drought (Clark et al., 2011; Scott et al., 1998; Watts et al., 2001).

Rising atmospheric temperatures have also impacted DOC concentrations through processes that are largely driven by increased biological activity (Couture et al., 2012; Evans et al., 2005; Finstad et al., 2016). Warming of surface waters has been linked to increased microbial activity, which contributes to increased NOM (Xiao et al., 2020), potentially amplifying the effects of recovery. Higher atmospheric temperatures can also increase weathering and reduce ice coverage in northern regions, which can lead to more base cations in the soil and a larger buffering capacity of the catchment (Houle et al., 2010; Strock et al., 2014). Further, climate warming extends growing seasons which can significantly alter catchment soil and vegetation properties (e.g., greening), and in turn, the storage and leaching of NOM and sulfate in watersheds (Xiao et al., 2020). Despite the complexity of these systems, it is evident that climate pressures will play a significant role in the browning of surface waters and as deposition levels off these factors may become more prominent. There is also evidence to suggest that climatic factors have shifted the baseline state of ecosystems such that they will not completely recover to their pre-acidified conditions (Keller et al., 2019; Meyer-Jacob et al., 2020).

Finally, the increasing importance of additional drivers (e.g., changing land use and type) of browning has been highlighted in more recent literature, as atmospheric acid deposition stabilizes (Garmo et al., 2020). For example, Skerlep et al. (2020) noted that land use has received less attention compared to climate and recovery processes. They found that 75% of the long-term variation was explained by a combination of precipitation, temperature, deposition, and land-use change, and disentangling the contributions of these factors to rising DOC will continue to be challenging given that long-term datasets describing them are lacking (Skerlep et al., 2020). Klante et al., (2021) highlighted the importance of precipitation and temperature in relation to seasonal variations in browning, while on a decadal scale change in land use (e.g., forestry) play an important role. Clutterbuck and Yallop (2010) observed that changes in acid deposition and temperature could explain 20-30% of the increase in humic DOC from upland peat soils in the UK, while changing land use could explain finer scale variation in DOC. Kritzberg et al. (2020) and others (e.g., Kritzberg et al., 2017; Ritson et al., 2019) also demonstrate the importance of changing land use in addition to climate change and recovery from acidification as factors contributing to browning.

2.5. Impacts of browning on surface water treatment

The increases in NOM concentration and shifts in its composition described in this review will impact the efficacy of various surface drinking water treatment processes. Most notably, widely used conventional NOM removal processes such as coagulation and flocculation, clarification, and filtration may be impacted substantially. Inadequate removal may impact downstream process efficiency and/or lead to the formation of disinfection by-products (DBPs). Elevated NOM concentration may also indirectly impact other treatment processes such as pre-oxidation for the removal of soluble Fe and Mn. As long-term episodes of browning continue, more advanced monitoring and treatment solutions for NOM will be necessary.

2.5.1. Aspects of conventional drinking water treatment challenged by browning

2.5.1.1. Pre-oxidation for iron and manganese removal influenced by NOM

The most used pre-oxidants for Fe and Mn removal include permanganate ($KMnO_4$), chlorine (Cl_2), and chlorine dioxide (ClO_2), however, $KMnO_4$ may be preferred given that Cl_2 and ClO_2 have been shown to form regulated DBPs. Although $KMnO_4$ has been used as a pre-oxidant for decades, its reactions with NOM remain poorly understood (Laszakovits et al., 2020). Typically, $KMnO_4$ is dosed on a theoretical or stoichiometric basis (1.92 mg $KMnO_4$ per mg Mn (II), and 0.94 mg $KMnO_4$ per mg Fe (II)), and the oxidant demand of Fe must be satisfied before Mn will be oxidized (Cleasby, 1975). Knocke et al. (1987) showed that in source waters with low TOC (<3 mg/L) the required $KMnO_4$ doses were near the stoichiometric requirement for Mn, but with high TOC levels (e.g., >8 mg/L), no Mn oxidation occurred until the oxidant dose was increased to satisfy the NOM demand. Thus, in browning waters, the oxidant dose may need to be optimized to meet the demand of NOM before oxidation of Mn (and Fe) can occur.

Organically complexed Fe caused by browning may also challenge pre-oxidation processes. Knocke et al. (1992) evaluated the removal of Fe-NOM complexes via $KMnO_4$, Cl_2 and ClO_2 and noted that complexation rendered the Fe stable against oxidation and that Fe complexed by high molecular weight (e.g., humic) DOC is more amenable to removal via alum coagulation rather than oxidation. Knocke et al. (1987) also observed that the degree of oxidation of Fe and Mn was impacted by the degree of complexation with DOC. Similarly, Laszakovits et al. (2020) noted that contaminants (e.g., Fe) that can partition into hydrophobic NOM pockets may not be accessible for $KMnO_4$ oxidation. Accordingly, a lack of Fe and Mn removal via chemical oxidation may also be a result of complexation with NOM, in addition to the direct or competitive oxidant demand exhibited by NOM. This sheds light on the need for better characterization of NOM-metal complexes (see Locsin et al., 2022 for a review of appropriate characterization methods) and differentiation between truly dissolved and complexed metals in surface water supplies. This contrasts with the convention of quantifying dissolved material via separation through a 0.45 µm filter adopted by the drinking water industry.

2.5.1.2. Elevated coagulant doses are required to overcome increasing NOM

It is well accepted that enhanced coagulation is one of the most widely used NOM removal processes in drinking water treatment. Enhanced coagulation is the process of increasing coagulant dose and controlling pH to favour the removal of NOM and minimize the formation of DBPs (Edzwald & Tobiason, 1999). As such, enhanced coagulation dose determination is a direct function of NOM concentration and quality (as opposed to turbidity) thus both long-term browning trends and short-term or climate event-based increases in NOM content will undoubtedly have an impact on coagulant requirements. Previous reviews (e.g., Matilainen et al., 2010b; Ivancev-Trumbas, 2014) provide more insight on enhanced coagulation for NOM removal.

With regards to browning, Eikebrokk et al. (2004) quantified the impacts of increasing NOM levels on treatment and found that a long-term increase in source water color from 20 to 35 mg Pt/L resulted in an increase in coagulant dose by 64% which led to nearly doubling of sludge production. According to Sharp et al. (2006b), an increase in DOC as well as a change in the charge density, particularly during autumn and winter periods over the past decade(s), has increased coagulant demand. More recently, Anderson et al. (2017) found that in response to decreasing sulfate deposition in Atlantic Canada, source water color increased by nearly four times causing the coagulant demand to increase at a similar rate (e.g., alum dose increased from ~15 mg/L to >50 mg/L over the study period). Per Edzwald and Van Benschoten (1990), the coagulant demand exerted by humic NOM can be as high as 2 mg alum (as Al^{3+}) per mg of humic-DOC, which can provide some context around how much coagulant demand may increase due to browning.

In addition to the long-term browning, the impacts of acute changes in NOM concentration induced by climate events should also be considered as they can also impact enhanced coagulation on a smaller timescale. Hurst et al. (2004) examined the impact of heavy precipitation events on coagulation and clarifier performance and noted an increase in NOM concentrations (40%, from 3.9-5.5 mg/L to 14.4 mg/L) significantly impaired coagulation resulting in elevated settled water turbidity. Such treatment challenges may occur more frequently given the expected increase in heavy precipitation events because of climate pressures.

Increasing the coagulant dose may be a viable option for managing elevated NOM load at treatment facilities with a clarification stage, however, this will lead to both increased waste disposal and the embedded carbon footprint of plant operations. Further, increased coagulant dosing will cause significant operational challenges for direct filtration facilities. Anderson et al. (2017) showed that long-term browning in surface water (TOC increase from 2.4 to 3.4 mg/L, color increase from ~12 to 21 TCU from 1999 to 2015) supplying a direct filtration plant caused the facility to operate at the upper operational limits (as defined by Crittenden et al., 2012) for direct filtration based on TOC (<4 mg/L) and color (≤20 TCU). DeMont et al. (2021) assessed strategies to improve the efficiency of NOM removal in direct filtration, including the partial substitution of alum with a high-density cationic polyelectrolyte in various dose combinations (10-12 mg/L alum and 0-1 mg/L polyelectrolyte) but found no improvement in TOC removal. Alternative strategies, including the use of clarification, may be required to adapt to increased NOM load at direct filtration treatment facilities where browning is a concern.

The previously mentioned changes in the character of NOM will also impact enhanced coagulation. It is well known that enhanced coagulation and flocculation processes are better suited for compounds with high molecular weight (Collins et al., 1986); hydrophobic compounds (Sharp et al., 2006a); and compounds with higher specific absorbance (White et al., 1997). A shift towards more hydrophobic NOM fractions may yield water quality that is more "treatable" by enhanced coagulation processes, but it will still become more costly for utilities due to increased chemical and energy demands. Conversely, drought-induced shifts towards hydrophilic NOM may be more difficult to remove via coagulation. This emphasizes the importance of site-specific trend analysis before treatment design, as well as the need for online monitoring tools that can monitor both the quantity and quality of NOM in source waters and during coagulation.

2.5.1.3. Filter performance impacted by increasing NOM

Greater organic loading on drinking water treatment plants and subsequent increases in coagulant demand may have downstream impacts on filter performance. As mentioned above, the effects are particularly pronounced in direct filtration plants, which do not have a clarification step to buffer the varying organic load (Valade et al., 2009; DeMont et al., 2021). Eikbrokk et al.,

(2004) reported an 87% increase in the number of daily backwashes in a direct filtration plant when the raw water color increased from 20 to 35 mg Pt/L. Similarly, DeMont et al. (2021) reported decreasing filter run times with increasing organic loading and higher coagulant doses. Although they found that increasing the effective size of the filter media improved the unit filter run volume (3 to 16 m^3/m^2), the larger effective size filters were more susceptible to turbidity breakthrough (DeMont et al., 2021). Additionally, greater concentrations of DOC, if not effectively removed through coagulation/clarification, may impact GAC contactors or filters by accelerating the exhaustion of the media, as NOM occupies binding sites in the GAC pores and saturates the media (Bhatnagar & Sillanpaa, 2017; Moona et al., 2018).

2.5.1.4. Distribution system water quality impacted by poor NOM removal

2.5.1.4.1. Risk of elevated disinfection by-product formation

The widespread increase in NOM concentrations observed throughout the Northern Hemisphere may also promote the formation of DBPs in distribution systems. Increased NOM remaining after coagulation and other pre-treatments may require an increased disinfectant dose both because of a higher demand exerted by NOM as well as the need for adequate free chlorine residual. However, few studies have directly linked an increase in DBP formation with increased NOM levels caused by long-term browning. According to Sharp et al. (2006b), decadal increases in DOC particularly during autumn and winter periods have resulted in greater production of DBPs although quantitative data was not provided. Kovacs (2013) noted that because NOM is present at higher amounts, a greater amount of disinfectant (e.g., Cl_2) was necessary (5-15%), resulting in significantly higher concentrations of DBPs (5-30%). DeMont et al. (2021) determined that increased TOC removal from a browning source water did not reduce DBP formation potential in pilot-plant operations, suggesting that residual DBP precursors were potentially resistant to coagulation as evidenced by low specific UV-absorbance. The characteristics of the aromatic hydrophobic humic material tend to form higher THM levels and therefore the impact of changes in both concentration and character of NOM on the formation of DBPs should be considered in treatment design and optimization.

Although there is limited information published on the formation of DBPs in surface water treatment facilities challenged by long-term browning, there has been increased attention to the impact of climate. Delpla and Rodriguez (2016) evaluated the variability in raw water DBP formation following rain events. Although there were only slight impacts on NOM concentration (TOC increase from 4.3 to 5.2 mg/L) and reactivity (e.g., SUVA increase from 4.2 to 4.5 L-mg/m), there was a 2-fold increase in THM formation observed after heavy rain (approx. 50 mm total). Delpla et al., (2016) evaluated estimated variations of DBPs in drinking water according to climate change scenarios. The worst-case climate special report emissions scenario estimate (2080, 4.9 °C/y, 147 mm/y) indicated considerable impacts on THMs formation, with a 34% increase during the winter months, 16% during the spring, and ~4% during the fall. No clear trends were observed for summer THM formation (Delpla et al., 2016). More recently, Valdivia-Garcia et al. (2019) predicted the impact of climate change (e.g., temperature and DOC increase) on THM formation in Scottish drinking water treatment plants. They found that a mid-range climate scenario (22.7% DOC increase per °C, 1.8 °C temperature increase) yielded a 39% increase in summer THM formation by 2050, and the effect of warming climate on surface water DOC levels was the main contributor (33.5%) to this increase, in addition to water temperature (5.4%) (Valdivia-Garcia et al., 2019). Additional research on quantifying DBP formation in treatment facilities that draw from surface waters impacted by brownification will help inform future DBP mitigation strategies for drinking water suppliers.

2.5.1.4.2. NOM as a vector for lead release

Unoptimized treatment of browning surface waters will pose a risk not only to elevated DBP formation but also has implications for controlling lead (Pb) during distribution. NOM has been shown to reduce and dissolve Pb, delay Pb precipitation, complex dissolved Pb and stabilize Pb-bearing colloids. Colling et al. (1992) observed that increasing the humic content corresponded with higher Pb concentrations in waters that were previously considered to have low plumbosolvency— treated waters with the highest TOC concentration (>3 mg/L) were more plumbosolvent, compared to low TOC (<0.6 mg/L). Korshin et al. (2005) noted that the concentrations of soluble Pb increased several-fold in the presence of NOM, and that NOM inhibited the formation of corrosion scales (e.g., cerussite). Zhou et al. (2015) found that increasing NOM (from 1 to 7 mg/L DOC) resulted in significant Pb release in an experiment with simulated partial lead service line (LSL) replacements. Trueman et al. (2017) suggested that the presence of humic substances increased Pb release by more than 4-fold and that orthophosphate (a corrosion inhibitor) was less effective in the presence of humic material (Trueman et al., 2017). Further, it has been reported through multiple studies that lead mobilized by NOM is predominately captured in a colloidal size fraction and advanced techniques are required to quantify corrective action (Loscin et al., 2022)

de Mora et al. (1987) showed that higher NOM removal was associated with lower Pb concentrations in treated drinking water. Winning et al. (2017) noted that the removal of 50% of total NOM resulted in a 75% reduction in Pb release. Zhao et al. (2018) noted that the removal of NOM during water treatment may have the added benefit of minimizing the mobility of Pb-containing colloids. Accordingly, in water systems that do not have optimized removal of NOM, Pb contamination events may be driven by elevated NOM concentration, and optimized coagulation or adsorption processes can minimize the effect of organic matter on Pb mobilization (King et al., 2022).

2.5.2. Fluorescence-based NOM monitoring for source waters and treatment facilities impacted by browning

Drinking water treatment facilities will need to adopt better strategies for NOM monitoring, particularly regarding the character of NOM in surface waters and treatment plants impacted by both long-term and acute browning. Many treatment facilities depend on the UV absorbance of a sample at 254 nm normalized to the DOC concentration (e.g., SUVA) to assess the character of NOM in source and coagulated waters, where a SUVA > 4 indicates mainly hydrophobic and aromatic material (Edzwald and Tobiason, 1999; Weishaar et al., 2003). Sepp et al. (2018) evaluated different traditional metrics for monitoring NOM (e.g., TOC, DOC, color, chemical oxygen demand) and highlighted the importance of absorbance and fluorescence spectroscopy as key sensors to include in brownification monitoring programs.

In the past decade, techniques to distinguish different types of NOM have become more readily available to the water treatment industry. Most notably, fluorescence spectroscopy is a straightforward tool that generates an excitation-emission matrix (EEM) when used in 3D mode, which can provide a "fingerprint" of fluorescent NOM in a sample. Many have highlighted the benefit of fluorescence spectroscopy for NOM characterization (Fellman et al., 2010; Bridgeman et al., 2011; Matilainen et al., 2011; Nebbioso and Piccolo, 2013; Zhang et al., 2021). Chen et al. (2003) identified EEM regions to characterize the components of NOM including aromatic proteins, fulvic acid-like and humic acid-like compounds, and microbial by-products that have since been used to provide valuable information on the removal of NOM types in drinking water treatment. Coble (1996) identified humic-like fluorescence into "peak A" (λ_{ex} = 250-260 nm, λ_{em}

= 380-480 nm) and “peak C” (λ_{ex} = 330-350 nm, λ_{em} = 420-480 nm), and protein-like fluorescence into tyrosine-like “peak B” (λ_{ex} = 270-280 nm, λ_{em} = 300-320 nm) and tryptophan-like “peak T” (λ_{ex} = 270-280 nm, λ_{em} = 320-350 nm). Further, ratios of these peak intensities can be used to provide additional information on NOM character, for example, the ratio of peaks T and C can be sensitive to changes in the character of DOC and indicates a shift from protein-like to humic-like NOM (Shutoya et al., 2016). In addition, parallel factor analysis (PARAFAC) is also highly valuable for decomposing fluorescence EEM data, as described in the review by Ishii and Boyer (2012). Sciscenko et al. (2022) provide a review of EEM-PARAFAC for water treatment applications, and many recent works (e.g., Ndiweni et al., 2020; Maqbool et al., 2020; Xu et al., 2021; Wilske et al., 2021; Philbert et al., 2022) have highlighted the value in using PARAFAC to monitor NOM removal in drinking water treatment.

Optical sensors based on fluorescence spectroscopy can be implemented for in-situ monitoring of the various types of NOM in source waters and treatment plants. Hoffmeister et al. (2020) used a commercially available in-situ fluorescence-based optical sensor (λex/λem = 365 ± 5/480 ± 40 nm), to estimate DOC concentrations for drinking water production and found that it may be useful for optimizing coagulation processes. Recently, Carstea et al. (2020) provided an in-depth review of advancements in in-situ fluorescence measurements of NOM, including freshwater applications.

An added benefit of fluorescence-based NOM monitoring is its predictive ability. Most commonly, fluorescence EEMs have been commonly used to predict DBP formation in drinking water treatment (Johnstone and Miller, 2009; Hua et al., 2010; Peleato and Andrews, 2015; Trueman et al., 2016; Peleato et al., 2018). Others have predicted NOM treatability with fluorescence measurements (Philibert et al., 2022). If the browning of surface waters continues, fluorescence-based approaches to NOM monitoring will be highly valuable to drinking water providers.

2.5.3. Water safety plans as a tool to understand treatment risk with browning supplies

As drinking water sources continue to experience browning, treatment plants that are ill-equipped to mitigate the increasing NOM load will need tools to understand the risks to their systems. Developed by the World Health Organization (WHO), Water Safety Planning (WSP) is a framework that uses system knowledge and risk management strategies to improve drinking water quality (WHO, 2011). The WSP framework is cyclical and adaptive in nature using hazard identification, risk mitigation and operator knowledge (Lane et al., 2022) and spans from catchment to consumer or source to tap. The WSP approach is used to shift from reactive control or "end of pipe" water quality monitoring, toward preventative management for the entire water supply chain. WSPs have been used to minimize the risk of microbiological contamination in drinking water (Gunnarsdottir et al., 2012; Muoio et al., 2020). For example, Gunnarsdottir et al. (2012) showed how implementing WSPs could significantly reduce heterotrophic plate counts (HPC, a measure of microbiological water quality) resulting in 14% fewer clinical cases of gastrointestinal illness. WSPs could have been used to avoid a 2014 "do not drink" advisory (Jetoo et al., 2015) and a state of emergency caused by elevated levels of microcystin in the treated water.

Thus, WSPs could be implemented as a tool to routinely assess the risk associated with brownification in drinking water treatment. Lane et al. (2022) developed a WSP-based web application focused on risk assessment for chlorine disinfection and distribution systems, which included hazards such as DBPs as well as the absence of chlorine residual, both of which are associated with elevated NOM concentrations and demonstrate how aspects of NOM could be incorporated into WSPs. Routine use of WSPs could help to inform monitoring programs in browning source waters, to identify weaknesses in the treatment system (e.g., poor NOM removal), and distribution impacts (e.g., insufficient disinfectant residual caused by elevated DOC, elevated DBPs, NOM-related Pb release at the tap) all of which can be used to improve treatment and inform adaptations or upgrades. Given the flexible nature of WSPs, they could also encompass aspects beyond the source and treatment plant such as atmospheric deposition or climate monitoring which would further enhance their value to browning sources.

2.5.4. Catchment level strategies for adapting browning to surface water supplies

Drinking water providers may want to pay increased attention to source protection and should closely consider catchment level strategies as one of the control measures for browning. Kritzberg et al. (2020) provide an overview of various local-level mitigation strategies for browning surface waters from a Swedish perspective, but with relevance to many other regions. Specific forest management strategies (e.g., thinning coniferous cover and actively planting deciduous tree species in targeted zones) are highlighted as a measure that could possibly halt browning at a local level (Kritzberg et al., 2020). Skerlep et al. (2020) also explained that long-term variability in DOC was explained by an increase in conifers and that catchment management could be beneficial. However, it is important to note that this strategy could take decades or longer to impact DOC concentration. Forest management (e.g., clear cutting) can also increase DOC export and therefore should be minimized to control browning (Kritzberg et al., 2020). Ritson et al. (2019) note that catchment management should consider all sources of DOC within a catchment, including forested areas. Ditch network maintenance may also be used to control DOC concentration although it depends on the soil type, and additional detail can be found in Kritzberg et al. (2020) and Nieminen et al. (2018). Finally, increasing water retention time and restoring peatlands have been highlighted as other potential control measures (Kritzberg et al., 2020). Overall, it appears that forestry management near surface water supplies will be of increasing importance and offers promise for some potentially long-term controls on brownification at the source.

2.5.5. Possible treatment adaptations for browning surface water supplies

The sections below provide a detailed review on some of the possible treatment adaptations for browning surface water supplies. Figure 3 below provides a summary of some the recommended adaptation strategies for consideration by drinking water utilities experiencing brownification.

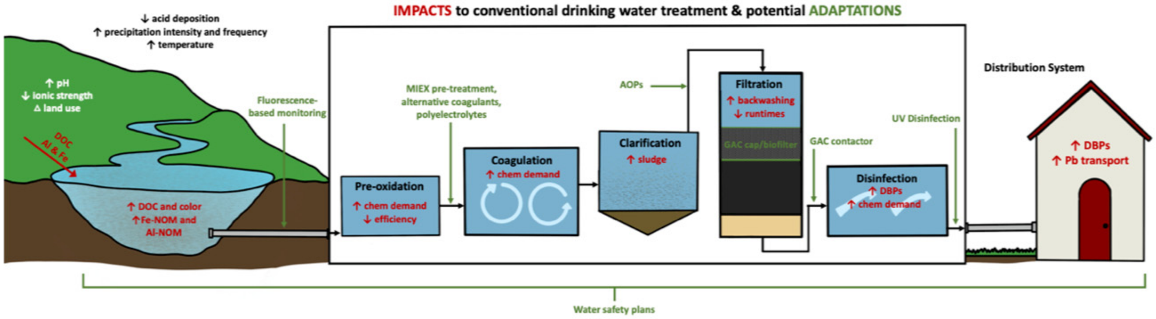

Figure 3. Overview of some of the possible treatment adaptations for conventional treatment facilities impacted by browning source waters.

2.5.5.1. Chemical strategies to improve NOM removal

As DOC concentrations increase in drinking water sources, alternative coagulants may enhance NOM removal, and subsequently, reduce the formation of DBPs. For example, the use of polyelectrolytes as primary coagulants or coagulant aids has been shown to improve NOM removal (Bolto et al., 2001; Bolto & Gregory, 2007; Matilainen et al., 2010b) and reduce solids loading on downstream unit processes, improving unit filter run times (McCormick and King, 1982; Pernitsky et al., 2011). However, conflicting results have also been reported and the use of polyelectrolytes should be considered on a system-by-system basis (DeMont et al., 2021). Likewise, switching from Al- to Fe-based metal salts has also shown improved removal of higher and intermediate molecular weight DOC and may be a short-term solution for treating surface water experiencing browning (Dayarathne et al., 2021; Sillanpaa et al., 2018; Matilainen et al., 2010a; Matilainen et al., 2010b).

The implementation of conventional ion exchange (e.g., strong base) (Finkbeiner et al., 2018; Finkbeiner et al., 2020; MacKeown et al., 2021) or magnetic ion exchange resin (MIEX) as a pre-treatment for coagulation has also been shown to enhance coagulation efficiency, reducing coagulant dose and DBP formation (Singer & Bilyk, 2002; Singer et al., 2009; Matilainen et al., 2010b; Chen et al., 2018). Jarvis et al. (2008) showed that the implementation of MIEX before coagulation led to a 50-70% reduction in coagulant doses and improved DBP formation compared to coagulation alone. Caltran et al. (2020) evaluated NOM removal via MIEX and noted that it could remove 40 to 60% of NOM, targeting primarily humic fractions and resulting in lower coagulant dose and energy consumption. Thus, MIEX is well-suited for high DOC waters (Karpinska et al., 2013) and may offer solutions to treatment facilities drawing from browning surface waters.

2.5.5.2. Advanced oxidation processes and biofiltration to augment NOM removal

According to a review on AOPs for NOM removal by Sillanpaa et al. (2018), AOPs may assist in coping with increasing amounts of NOM in natural waters, as well as controlling the formation of DBPs. The most common AOPs include combinations of an oxidant (typically ozone or hydrogen peroxide) with a catalyst or ultraviolet (UV) irradiation, all of which generate hydroxyl radicals that react non-selectively with organic compounds in the water matrix (Sillanpaa et al., 2018).

Complete mineralization of DOC is typically not realized at doses practically applied in drinking water treatment (Sillanpaa et al., 2018), therefore AOPs are best used to transform the properties of NOM (e.g., hydrophobicity and biodegradability) after conventional processes (e.g., coagulation), rather than as a standalone unit process to remove DOC. There is extensive evidence demonstrating that AOPs effectively degrade high molecular weight NOM into lower molecular weight compounds (Chin and Berube, 2005; Gardoni et al., 2012; Sarathy & Monsheni, 2007; Sarathy & Monsheni, 2010; Matilainen et al., 2010b; Lamsal et al., 2011; Agbaba et al., 2016; Sillanpaa et al., 2018). Lower molecular weight organic compounds are often more biodegradable, and more easily removed through biological NOM removal processes (e.g., biofiltration). A review article by Basu et al. (2016) on the applications of biofiltration in drinking water treatment noted that the combination of ozone and biofiltration could yield DOC removals of 15-50%, and THM precursors by 40-80%. Ozone (O_3) doses of 1-2 mg O_3/mg TOC appeared to be effective for biodegradation of NOM before biofiltration (Basu et al., 2016). Similarly, Toor et al. (2007) used UV-peroxide (H_2O_2) followed by biologically active carbon (BAC) filtration to reduce TOC and DBPs by 43 and 52%, respectively. Beniwal et al. (2018) showed that pre-oxidation with O_3 and H_2O_2/O_3 enhanced DOC removal but the impact on DBP reduction was limited. Sidhu et al. (2018) showed that O_3 and H_2O_2/O_3 could improve DOC removal by 15 and 23%, respectively. In the same study, THMFP was reduced by 38 and 14% and HAAFP by 36 and 20% for O_3 and H_2O_2/O_3 compared to BAC alone (Sidhu et al., 2018). Ødegaard et al. (2010) also discusses the application of oxidation and biofiltration for NOM removal in Norwegian surface waters, which have undergone substantial browning in recent decades. Slavik et al., (2021) recommend ozonation-biofiltration as a promising strategy to cope with NOM-related climate-related challenges (e.g., changes in NOM properties due to increased solar radiation). In comparison to conventional NOM removal approaches, the addition of AOPs with biofiltration may provide enhanced NOM removal following coagulation and may be a well-suited adaptation technology for brownification.

2.5.5.3. Activated carbon for enhanced NOM removal

Granular activated carbon (GAC) has been widely identified as an effective post-filtration unit process for the removal of low molecular weight and recalcitrant DOC – although the efficacy will vary depending on the other water constituents, and the type, size, and age of the GAC (Ritson et al., 2014; Bhatnagar and Sillanpaa, 2017). Multiple studies have shown improved removal of NOM and DBPs after treatment with GAC (Kim & Jung, 2008; Iriarte-Velasco et al., 2008; Bhatnagar and Sillanpaa, 2017; Marais et al., 2018; Golea et al., 2020; Cuthberson et al., 2019). Moreover, BAC has also proven to be an effective solution for the treatment of elevated concentrations of DOC and DBPs formed during pre-chlorination (Matilainen et al., 2010b; Fu et al., 2017; Stoddart & Gagnon, 2015; Korotta-Gamage & Sathasivan, 2017). A recent review by Yuan et al. (2021) provides additional insight on BAC for NOM removal in drinking water treatment. Integrative processes such as pre-ozonation and BAC are often applied to improve biodegradation efficiency, as smaller oxidized compounds are more prone to biodegradation (Ødegaard et al., 2010; Fu et al., 2021).

The addition of ballast with adsorptive properties may improve treatment performance in facilities that are challenged by browning surface waters. Powdered activated carbon (PAC) has been shown to increase the removal of DOC (Fabris et al., 2004; Matilainen et al., 2010b; Kristiana et al., 2011; Park et al., 2021), and can be used as a ballast in flocculation, improving residual turbidity (Shutova et al., 2020; Gaikwad & Munavalli, 2019; Younker & Walsh, 2016; Huang et al., 2021; Wongcharee et al., 2020).

2.5.5.4. Membrane treatment as a strategy for improved NOM removal

Membrane filtration has also gained popularity to enhance NOM removal. Membrane filtration (e.g., ultrafiltration (UF) and nanofiltration (NF)) has been gaining popularity for enhancing NOM removal, particularly in Nordic countries where surface water supplies are browning. According to Odegaard et al. (2010), the NF process is often selected in Norway when color is >30 color units/L and turbidity is <1 NTU, which is characteristic of many brown surface water supplies. Matilainen et al., (2010b) provide added detail on coagulation and membranes for NOM removal under similar source water conditions. Keucken et al. (2017) noted that a novel capillary NF system combined with a low dose (e.g., 0.5-0.7 mg/L) in line coagulation pre-treatment could provide upwards of 90% removal of DOC and UV254. Further, higher coagulant dosages (0.9-1.2 mg/L) were tested for expected increases in NOM concentration and were successfully applied in the coagulation NF system (Keucken et al., 2017). A similar system described Kohler et al. (2016) provided comparable NOM removals. Kohler et al. (2016) also noted that coagulation will need to be supplemented with additional processes to maintain DOC removal given the increasing concentration in raw water. According to Winter (2017), humic substances are not considered a substantial contributor to the fouling of NF membranes, which shows promise for browning water supplies.

Voigtländer et al. (2020) investigated the use of coagulation and UF for NOM removal (raw water DOC range 8-14 mg/L) in Sweden to understand its effectiveness as a technology for increasing NOM. Approximately 50% removal could be achieved at an alum dose of 6 mg Al/L, raw waters with TOC > 15 mg/L would remain a challenge for this type of system (Voigtländer et al., 2020)). Further, humic substances, which are dominant in browning source waters, are some of the relevant NOM fractions that can contribute to reversible and irreversible fouling for UF membranes (Jermann et al., 2007; Ma et al., 2018; Zhang et al., 2018). Thus, the removal of humic NOM prior to UF is an important factor to consider for membranes as a possible adaptation for browning water supplies. Others have also used ozonation (Bu et al., 2019; Yu et al., 2018; Ouali et al., 2022) and PAC (Li et al., 2011; Ivancev-Tumbas et al., 2014; Wang et al., 2016; Xing et al., 2019) in conjunction as UF pre-treatment. Bu et al. (2019) investigated the combination of coagulation and ozonation as a pre-treatment for UF and found that although both combinations improved NOM removal efficiency, coagulation followed by ozonation and UF produced the lowest fouling. Wang et al. (2016) investigated NOM removal and membrane fouling in a combined PAC, coagulation and UF process at pilot scale and found that the presence of PAC during coagulation increased NOM removal (e.g., humic substances) which contributed to a reduction in membrane fouling. MIEX has also been applied for UF pre-treatment to enhance NOM removal and for fouling reduction (Son et al., 2005; Kabsch-Korbutowicz et al., 2008; Imbrogno et al., 2018; Xu et al., 2019; Yu et al., 2019). A recent review by Peters et al. (2021) covers NOM removal by UF and pre-treatment mitigation strategies.

Overall, NOM removal via membrane treatment in conjunction with coagulation or other pre-treatments may serve a more prominent role in the treatment of browning surface waters in the future, although fouling should be carefully considered.

2.5.5.5. Disinfection strategies to control DBPs while minimizing Pb release

The reduction of DBPs in drinking water treatment is commonly achieved through two primary strategies – removing DBP precursor material before chlorination, and alternative disinfection strategies. Due to more stringent standards, switching from chlorine to chloramine has been well-established to minimize the formation of regulated THMs and HAAs (Siedel et al., 2005; Bond et al., 2014; Rosario-Ortiz et al., 2016). This may appear like a promising adaptation for treatment plants facing browning, however, it does not address the formation of unregulated DBPs, and it can have significant implications for Pb release. When the secondary disinfectant is switched from chlorine to monochloramine, reductive dissolution or destabilization of PbO_2 can cause elevated Pb levels at the tap (Xie et al., 2010; DeSantis et al., 2020). For example, the use of chloramine to replace chlorine was responsible for the lead crisis in Washington D.C. in the early 2000s (DeSantis et al., 2020). Consequently, DBP control should be achieved through NOM removal before disinfection (e.g., coagulation, GAC adsorption, etc.) to minimize the impacts on Pb release (Trueman et al., 2017).

UV-LEDs are a viable alternative disinfectant in drinking water treatment that does not produce chlorinated DBPs (Chen et al., 2017, Jarvis et al., 2019; Chatterley & Linden, 2010; Song et al., 2016). They are energy-efficient, long-lasting, easily tailored for specific operations, and compact in design (Chen et al., 2017). While UV disinfection does not offer the benefit of residual disinfectants in the distribution system, there is significant potential for the application of UV-LEDs outside of the treatment plant, however, research is required in this field to understand the implications for the distribution system before full-scale application (Linden et al., 2019).

2.6. Conclusion

Based on this review, it is evident that surface waters throughout the Northern Hemisphere are experiencing elevated NOM concentrations and changes in composition because of recovery from acidification in addition to other factors such as climate change and land use. This comprehensive review has identified two research areas to be addressed: 1) a need for comprehensive monitoring programs (e.g., larger timescales; consistency in measurements) to assess climate change impacts on recovery responses and NOM dynamics, and 2) a better understanding of impacts on drinking water treatment vulnerabilities and the transition towards robust treatment technologies and solutions that can adapt to climate change and other drivers of changing water quality.

Although the chemical responses to recovery from acidification are relatively well defined, several gaps need to be investigated. There is a lack of high-quality monitoring data concerning NOM concentration and quality over larger time scales (decades). Water utilities should implement monitoring programs that consider multiple parameters for quantifying NOM concentration, including conventional analytes as well as metrics such as fluorescence spectroscopy that can also provide information on quality. Such programs should also consider the speciation of metals (as opposed to the convention of measuring total concentrations), as browning surface waters also exhibit increasing levels of organically complexed Fe and Al. The role of climate change, as well as changing land use, should also be incorporated into such programs, as they can also influence NOM concentration and character.

There is also a need for tools to evaluate the recovery status of lakes where adequate water quality monitoring data is limited. A paleolimnological approach using sediment cores to reconstruct past trends in lake water TOC concentrations would provide information on historical water quality in lakes missing adequate monitoring data and could help shed light on the pre-acidification conditions. Such methods could also help address the questions related to how high NOM concentration could become in lakes that are undergoing recovery or experiencing deteriorating water quality due to climate pressures or changes in land use. This is particularly important given that as reductions in atmospheric acid deposition stabilize, other drivers (e.g., climate) will likely dominate.

As a result of changes in NOM concentration and character, treatment plants may be under designed and unable to accommodate increased NOM loads without compromising downstream treatment processes. In this context, there is a need for studies to identify treatment optimization and operational strategies for water treatment processes that are drawing from browning lakes. Given that treatment plant optimization work can take months to years, these studies should also consider treatment practices (e.g., coagulant change or optimization) that can be implemented immediately and temporarily while more long-term solutions are researched, designed, and constructed. Further, climate-based optimization studies should consider the use of risk-based planning tools (e.g., water safety plans) and build considerations to understand the unintended consequences impacting distribution system water quality.

Since it is not known how high NOM concentrations will become or how the quality of NOM will change, establishing design targets will be challenging. The highly variable nature of climate change impacts (e.g., degrees of warming, heavy precipitation), further complicates the design. This highlights a need for long-term solutions that incorporate risk-based approaches (e.g., water safety planning), and for a transition towards robust treatment technologies and solutions that can adapt to climate change and other drivers of changing water quality.

3. CHAPTER 3: LAKE BROWNIFICATION THROUGH REDUCED SULPHATE DEPOSITION: A NEW PARADIGM FOR DRINKING WATER TREATMENT

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L.E.A was responsible for article conceptualization, original draft preparation, writing-reviewing and editing.

3.1. Abstract

This study examined sulfate deposition in Nova Scotia from 1999-2015, and its association with increased pH and organic matter in two protected surface water supplies (Pockwock Lake and Lake Major) located in Halifax, Nova Scotia. Sulphate deposition in the region decreased by 68%, while pH increased by 0.1-0.4 units over the 16-year period. Average monthly color concentrations in Pockwock Lake and Lake Major increased by 1.7 and 3.8x, respectively, suggesting brownification of the water supplies. Accordingly, the coagulant demand increased by 1.5 and 3.8x for the water treatment plants supplied by Pockwock Lake and Lake Major. Not only was this coagulant increase costly for the utility, but it also resulted in compromised filter performance, particularly for the direct-biofiltration plant supplied by Pockwock Lake that was found to already be operating at the upper limit of the recommended direct filtration thresholds for color, total organic carbon and coagulant dose. Additionally, in 2012-2013 geosmin occurred in Pockwock Lake, which could have been attributed to reduced sulfate deposition as increases in pH favor more diverse cyanobacteria populations. Overall, this study demonstrated the impact that ambient air quality can have on drinking water supplies.

3.2. Introduction

As a result of successful air emissions control, several studies have shown evidence of recovery from acidification (Stoddard et al., 1999; Skjelkvåle et al., 2005; Garmo et al., 2014). Such recovery is defined by increasing acid neutralization capacity (ANC), alkalinity and/or pH (Evans & Monteith, 2001), and is often associated with increasing natural organic matter (NOM) as measured by dissolved organic carbon (DOC). As described in Chapter 2, increasing concentrations of DOC (often referred to as brownification) in surface waters in the Northern hemisphere have been reported in areas that were previously exposed to chronic sulfate (SO_4) deposition through acid rain (Skjelkvåle et al., 2001; Jeffries et al., 2002; USEPA, 2003; Monteith et al., 2007), and therefore increasing DOC and brownification is often viewed as evidence for recovery from acidification. For example, Monteith et al. (2007) studied the spatial distribution of DOC trends in data collected in six North European and North American countries between 1990 and 2004 and found widespread significant upward trends in DOC in the northeastern portion of the United States (US), southern Nordic regions, and in the United Kingdom (UK), which Monteith and co-workers related to reductions in atmospheric deposition of SO_4 across large areas. Garmo et al. (2014) analyzed trends in surface water chemistry for 12 sites in Europe and North America and found that during the period between 1990 and 2008, sulfate deposition declined at 87% of study sites, corresponding with increasing DOC concentrations. Other instances of increasing DOC, pH and diversity have occurred in lakes without associated increases in nutrient levels, leading to the concept that lakes are undergoing some form of change, observed through increased NOM and subsequent brownification, which may be associated with recovery from acidification.

In drinking water, NOM may contribute to taste, color, and odor issues that can be problematic from a consumer standpoint. As well, NOM from source water like the lakes studied have shown to contribute to the formation of chlorinated disinfection by-products (DBPs) following chlorination (Singer, 1999; Kent et al., 2014). Accordingly, coagulation processes are widely used to destabilize negatively charged particulate matter (Faust & Aly, 1998) and through enhanced coagulation, conventional treatment processes can be adapted to remove NOM (Edwards, 1997). It has been suggested that surface waters recovering from acidification produce NOM with a greater hydrophobic fraction as the solubility of NOM increases (Worrall & Burt, 2010; Ekstrom et al., 2016; SanClements et al., 2012), which will have potential to increase coagulant demand. See Chapter 2 for additional detail on the impact on drinking water treatment.

Such changes in influent water quality will also have implications for energy use and carbon emissions associated with water treatment processes. The operational embodied energy for a water treatment facility represents the energy needed to produce a unit volume of drinking water and consists of direct and indirect energy. Direct energy is comprised of electricity and fuel consumption, and indirect energy is from the production and transport of water treatment chemicals. Santana et al. (2014) showed that increases in chemical dosing at a water treatment plant in Florida was responsible for 14.5% of the total operational embodied energy for the facility. Accordingly, increases in NOM concentration and changes in composition associated with recovery from acidification and brownification are anticipated to have significant impact on water treatment, though there are limited data reported in the literature. Chapter 2 and Anderson et al. (2023) provides a detailed review on the potential impact of brownification on drinking water treatment processes.

In addition to abiotic water quality indicators for recovery (e.g., increasing NOM concentration), changes in biotic water quality in terms of species richness and taxonomic composition are among the best-known indicators of biological recovery from acidification (Vinebrook & Graham, 1997). Experimental acidification of lakes has demonstrated loss of algal species (Turner et al., 1995; Findlay et al., 1999), reduced species richness, and changes in algal community structure as the phytoplankton community shifts from cyanobacteria to large dinoflagellates (Schindler et al., 1990; Findlay et al., 1999; Vinebrook et al., 2002; Findlay, 2003). Anthropogenic acidification has also caused long-term changes in algal community abundance, spatial distribution, and taxonomic composition (Schindler et al., 1990; Findlay et al., 1999; Vinebrook et al., 2002; Findlay, 2003. Findlay et al. (1999) showed that experimental and anthropogenic acidification had an impact on the species diversity of phytoplankton, which was positively correlated with pH. Findlay et al. (1999) also noted that cyanobacteria were significantly reduced below pH 5.1 and increased during recovery at a pH between 5.5 and 5.8. In the northeastern US, decreased sulfate deposition throughout the 1980's-2000's and subsequent increases in ANC corresponded with increased phytoplankton species richness (Sutherland et al., 2015). It has been widely reported that some cyanobacteria produce taste and odor compounds in surface waters (Gerber & LeChevalier, 1965; Hrudey et al., 1995; Suffet et al., 1995). For example, one of the most prevalent taste and odor compounds—geosmin (trans-1,10-dimethyl-trans-9-decalol) is produced by a subset of filamentous cyanobacteria and is a common challenge for drinking water utilities. In Fall 2012, previously unreported incidents of geosmin were identified in Pockwock Lake Wright et al., 2014). Prior to 2012, geosmin was not a water quality concern for Halifax Water. Consumer complaints regarding the earthy, musty smell of geosmin in treated tap water began in 2012, which initialized Halifax Water's geosmin monitoring routine.

The objective of this study is to examine the impact of decreased sulfate deposition and its effect on lake water quality (with a focus on NOM) and water treatment practices over the period

1999-2015. This study focuses on two lakes that are used as drinking water supplies in Nova Scotia, Canada. It also contributes to understanding the impact of decreased sulfate deposition on water treatment practices and has implications to water utilities in regions with surface waters that have been impacted by anthropogenic emissions of sulfur dioxide (SO_2) to the atmosphere.

3.3. Materials and methods

3.3.1. Study sites

Lake Major and Pockwock Lake are protected watershed areas and are not impacted by wastewater discharges. Both lakes are used for drinking water supply and are operated by Halifax Water located in the Halifax Regional Municipality of Nova Scotia, Canada. Pockwock Lake is characterized as a low-pH (pH<6), low-turbidity (<0.5 nephelometric turbidity units (NTU)) and low-alkalinity (<5 mg $CaCO_3$/L) source water (Vadasarukkai et al., 2011; Knowles et al., 2012). Pockwock Lake is the water supply for the J.D. Kline Water Supply Plant (JDKWSP), which has an average daily flow of 85 million litres per day (MLD). The JDKWSP, commissioned in 1973, underwent conversion from direct filtration (i.e., no clarification step before filtration) to direct biofiltration through removal of pre-chlorination in 2013 (Stoddart and Gagnon, 2015). Lake Major also has a low pH (pH<6), low alkalinity (<5 mg $CaCO_3$/L) and low turbidity (<0.5 NTU) and is the water supply for the Lake Major Water Supply Plant (LMWSP) which is a 45 MLD (average daily production) conventional filtration plant (commissioned in 1999) with upflow clarification.

3.3.2. Water quality analysis and data acquisition

Historical raw water quality data for both Lake Major and Pockwock Lake were obtained from records provided by Halifax Water staff. Reported raw water pH and turbidity data were measured by Halifax Water operations staff using a bench-top probe and turbidimeter, respectively, unless otherwise specified. Raw water color was determined by Halifax Water operations staff using a bench-top spectrophotometer (Hach Company, Loveland CO). Color data are presented in True Color Units (TCU). Water quality data for both lakes were obtained from an online data historian for the period January 1, 1999 to December 31, 2015. However, pH was recorded on a limited basis during the period 1999-2003 for Pockwock Lake and was not reported in this study. Additional pH data for Pockwock Lake was obtained from Environment Canada's Freshwater Quality Monitoring and Surveillance Program (Environment Canada, 2015a) during the period beginning in May 2000 to November 2012, when samples were collected from Pockwock Lake approximately once per month. DOC data for surface water bodies in Atlantic Canada (New Brunswick (NB), Prince Edward Island (PE), Newfoundland (NL)) was also obtained from Environment Canada's Freshwater Quality Monitoring and Surveillance Program for the period between 1990-2013. The Environment Canada Freshwater Quality Monitoring and Surveillance Program database did not contain sufficient DOC data for Nova Scotia surface waters during this period.

Compliance samples collected by Halifax Water staff were analyzed for sulfate by an independent laboratory and entered into Halifax Water's compliance software (WaterTrax). Sulphate data (annual averages) for this work were obtained from the WaterTrax database from the period 2004-2015. For the period between 1999-2003, sulfate data were obtained from Annual Water Quality Reports published by Halifax Water (Halifax Water, 2015). Annual mean total organic carbon (TOC) data were obtained from Annual Water Quality Reports and unpublished data from a NOM dataset developed by the Centre for Water Resources Studies (CWRS) at Dalhousie University in Halifax, Nova Scotia, which contains several years of TOC data acquired from various projects. Samples for TOC were collected headspace-free, acidified to pH < 2 with phosphoric acid, and were analyzed with a TOC-V CPH analyzer (Shimadzu Corporation, Kyoto, Japan).

Chemical dosages for the period 1999-2015 were obtained from Halifax Water's operational reports completed by operations staff. Mean monthly dosages were computed from daily values. Geosmin data for Pockwock Lake were also obtained from Halifax Water. Geosmin was measured in raw water from Pockwock Lake and in treated water from the JDKWSP between 2 and 4 times per month beginning in 2012. Samples collected by Halifax Water staff were sent to an independent external laboratory (SGS Lakefield Research Ltd., Lakefield, Ontario) that used gas chromatography with mass spectrometer detection (GC/MS) for geosmin analysis. Indirect embodied energy estimates for chemical use at the LMWSP were calculated using the procedure outlined by Santana et al. (2014).

3.3.3. Atmospheric deposition and climate data

Sulphate deposition data were obtained from Environment Canada's Canadian Air and Precipitation Monitoring (CAPMoN) program collected at Kejimkujik Lake (Environment Canada, 2015b). Sulphate deposition data were not available for Lake Major and Pockwock Lake; therefore Kejimkujik Lake (44°24'11.020" N, 65°12'11.070" W) was chosen to approximate wet deposition in Halifax due to data completeness at this site, and proximity to the study area (141 km from Lake Major, 117 km from Pockwock Lake). Sulphate deposition data were obtained from the CAPMoN database at Kejimkujik for the period January 1984 to September 2015. Data were sea salt corrected (e.g., marine aerosol contribution was subtracted) by Environment Canada. Daily sea salt corrected sulfate deposition data (mg/L) and daily total precipitation (mm) were used to calculate total annual sea salt corrected sulfate deposition (kg/ha/year). Others (Clair et al., 2002; Clair, 2011) have also used the Kejimkujik CAPMoN site to represent deposition in Nova Scotia.

Mean monthly temperature and precipitation levels for Halifax (1999-2015) were obtained from Environment Canada’s National Climate Archives (Environment Canada, 2015c).

3.3.4. Statistical methods

For each water quality parameter, the annual and monthly arithmetic mean was calculated to minimize the effect of variable sampling frequency on the ability to detect trends. The Mann Kendall Test (MKT) (Hirsch & Slack, 1984) was applied to annual means and the Seasonal Mann Kendall Test (SMKT) was applied to monthly arithmetic means (when available) to statistically evaluate temporal trends in historical water quality parameters and atmospheric sulfate deposition data. The MKT, a form of nonparametric monotonic trend regression analysis for data with serial dependence, analyzes the sign of the difference between later measured and earlier measured data, and is used to determine the statistical significance of the identified trend ($\alpha=0.05$). Sen’s slope estimation (m) was used to calculate the magnitude of significant trends identified using MKT and SMKT (Sen, 1968). Sen’s slope estimate represents the median of all pairwise slopes in the data set. Kendall’s tau correlations (τ) were applied to monthly means to understand the relationship between various water quality parameters. All statistical analyses were computed using MATLAB R2015b (The Mathworks, Inc).

3.4. Results and discussion

3.4.1. Sulphate deposition and sulfate concentration in study lakes

Figure 4 depicts trend in total annual wet deposition of sulfate (sea salt corrected) at the Kejimkujik Lake CAPMoN site for the period 1985-2015. It is likely that sulfate deposition at the Lake Major and Pockwock Lake study sites were higher due to proximity to localized sources of sulfate such as the Tufts Cove Generating Station which burned coal from 1965-2004. Wet deposition sulfate data at the Kejimkujik CAPMoN site showed a significant decreasing trend

($p<0.05$) at a rate of 0.3 kg/ha/year (Sen's slope estimate) from 1984-2015. The overall decrease in sulfate deposition was approximately 83%. The reductions of sulfate deposition were consistent with the decrease in SOx emissions over a similar period (1990-2014) published by Environment Canada as the total annual SOx emissions were reduced by 63% for the period between 1990 and 2014 (Environment Canada, 2014).

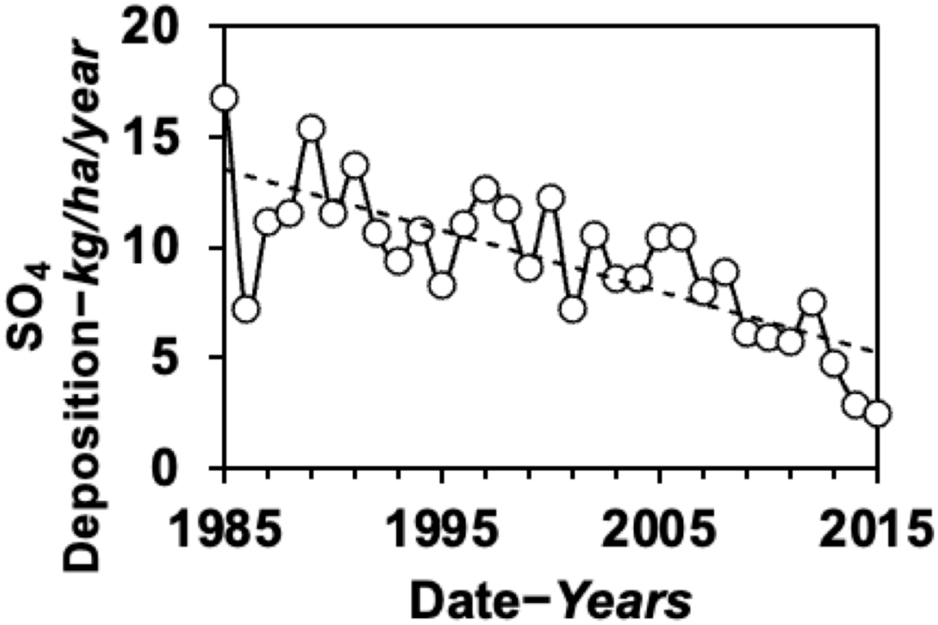

Figure 4. Total sea salt corrected wet deposition sulfate trends from the CAPMoN site at Kejimkujik, Nova Scotia. Dashed line represents approximation of linear trend ($p<0.05$, m=-0.3 kg/ha/year).

Sulphate is typically the dominant anion in acidified lakes of eastern North America, northwestern Europe, and Scandinavia (Henriksen, 1980) and hence has been widely used as a measure of the intensity of lake acidification (Dillon et al., 1984). Although chloride ions primarily dominate Nova Scotia lakes as a result of proximity to the Atlantic Ocean, data corrected for marine contributions generally show that Nova Scotia lakes were also dominated by sulfate

(Underwood et al., 1987). Thompson & Hutton (1985) demonstrated a correlation between annual sulfate deposition and sulfate concentration in watersheds of eastern Canada.

Significant decreasing trends in sulfate concentrations were observed in Lake Major ($p<0.05$, $m=-0.2$ kg/ha/year) (Table B1, Appendix B) and to a lesser extent in Pockwock Lake ($p<0.10$, $m=-0.1$ kg/ha/year) (Table B2, Appendix B) over the study duration. In 2015 sulfate concentrations in Pockwock Lake and Lake Major were reduced by 38% and 52%, respectively, from 1999 levels. These findings were consistent with other studies investigating the effects of acidic deposition on surface water quality in Atlantic Canada (e.g., Clair et al., 2002; Clair, 2011; Jeffries et al., 2003).

The decrease in atmospheric deposition of sulfate was higher compared to the reductions in lake sulfate concentration for both Pockwock Lake and Lake Major. This difference can be explained by several factors including the release of sulfate retained in catchment soils during previous periods of high sulfate deposition (Thompson & Hutton, 1985; Eimers et al., 2004).

3.4.2. Abiotic indicators of recovery from acidification

There have been several reports of increasing pH as a result of reduced sulfate deposition in the northeastern US (Garmo et al., 2014; Monteith et al., 2007; Driscoll et al., 2003; Lawrence et al., 2011; Waller et al., 2012), the UK (Garmo et al., 2014; Evans et al., 2001; Monteith et al., 2007) and Scandinavian countries (Skjelkvåle et al., 2001; Monteith et al., 2007; Garmo et al., 2014). Figure B1 (Appendix B) depicts average monthly raw water pH for Pockwock Lake. Data from plant records prior to 2004 were omitted, as they were deemed to be incomplete due to missing pH data during this time period. As described previously, additional pH data was obtained from Environment Canada's Freshwater Quality Monitoring and Surveillance Program (Environment Canada, 2015a) in order to capture seasonal trends in pH for Pockwock Lake before

2004. Statistical analysis with SMKT confirmed that Pockwock Lake pH increased significantly ($p<0.05$, $m=0.06$ pH units/year) over the time period studied. The average annual pH in Pockwock Lake increased from 5.2 in 2004 to 5.6 in 2015. Average monthly raw water pH for Lake Major is provided in Figure B2 (Appendix B). The average annual pH increased from 5.3 in 1999 to 5.4 in 2015 for Lake Major. Because of the size of the dataset, the increase in annual pH was also significant over the time period studied ($p<0.05$, $m=0.01$ pH units/year). A cyclic trend in the mean monthly pH was observed throughout the study period for both Lake Major and Pockwock Lake. For most years, pH was lower from November through to May, and increased from June through October during biologically productive months (Ziegler & Pfafflin, 2012).

The frequency of days where pH was below 5 was evaluated for both lakes (Figure 5). The pH of 5 was selected as a reference point for sustaining fish habitat in Atlantic Canadian lakes (Lacoul et al., 2011). In 2002 there were 153 days where pH was less than 5 in Lake Major; whereas for the period between 2010 and 2015, there were less than 10 days in total when the pH was lower than 5. Similarly, in Pockwock Lake there were 162 days in 2005 where pH was less than 5, and from 2010-2015 there were only 7 days in total that had a pH < 5.

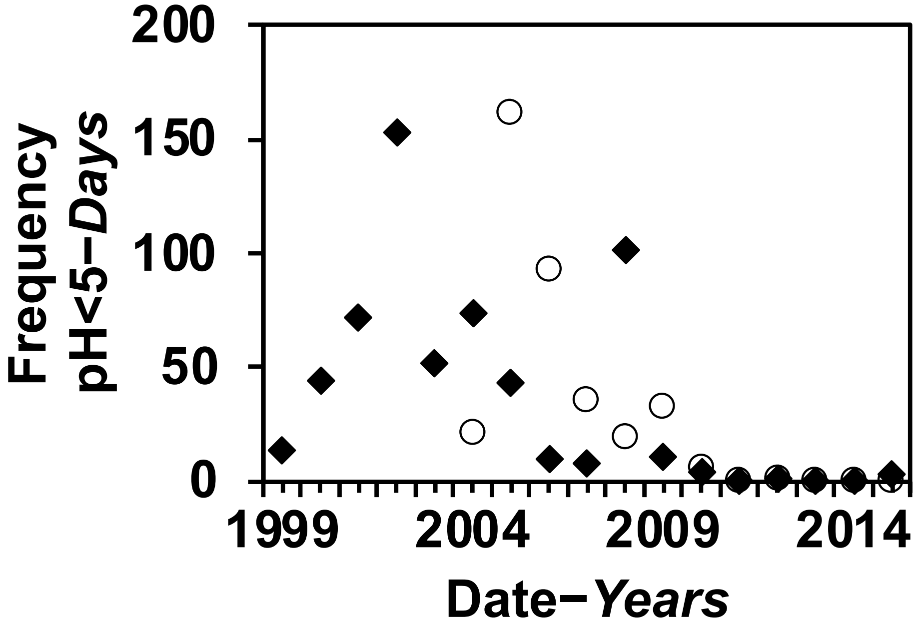

Figure 5. Frequency of low pH (days where pH < 5) in Lake Major and Pockwock Lake. Diamonds denote Lake Major, while circles denote Pockwock Lake.

Many surface waters in the Northern hemisphere have experienced increases in color concentration and brownification along with corresponding decreases in sulfate deposition and increases in pH (Hongve et al., 2004; Haaland et al., 2010). Figure B3 (Appendix B) and Figure 6 depict average monthly color concentrations for both Pockwock Lake and Lake Major, respectively. Color was selected as an indicator for NOM, as daily TOC and/or DOC data were not available for the entire study duration. Tables B1 and B2 (Appendix B) show average annual TOC concentrations for Lake Major and Pockwock Lake, during a limited time period. For lakes in Atlantic Canada, color has been shown to correlate strongly with TOC (MacPhee, 1992; Waller et al., 1996). Statistical analysis with SMKT confirmed that mean color in both Lake Major (m=1.6 TCU/year) and Pockwock Lake (m=0.55 TCU/year) increased significantly ($p<0.05$) over the time period studied. Average color doubled in Lake Major from 1999-2015. Additionally, average annual TOC concentrations in Pockwock Lake (Table B2, Appendix B) and Lake Major (Table

B1, Appendix B) increased by approximately 1 mg/L since 1999. Thus, Pockwock Lake and Lake major appear to be undergoing brownification as a result of changes to atmospheric deposition.

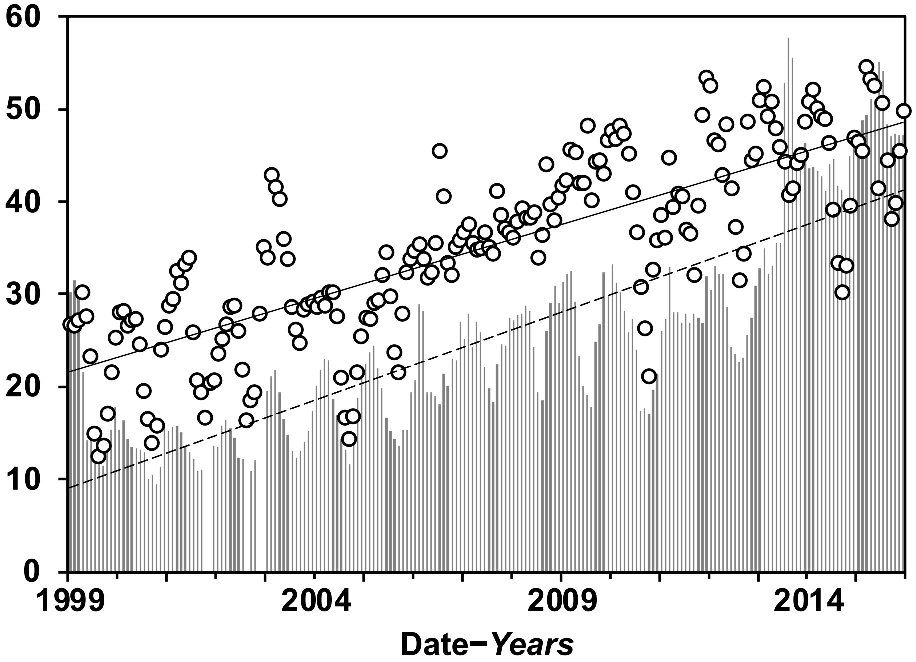

Figure 6. Monthly mean color in Lake Major and corresponding alum consumption at the Lake Major Water Supply Plant since commissioned in 1999. Circles denote lake water color (TCU), columns denote alum dose (mg/L). Solid line represents approximation of linear trend for color (p<0.05, m= 1.6 TCU/year), dashed line represents approximation of linear trend for alum dose (p<0.05, m=1.7 mg/L/year).

This trend is not localized to the Halifax area. Analysis of data from Environment Canada's Freshwater Quality Monitoring and Surveillance Program (Figure 7) shows that during the period ranging between 1990 and 2013, many other surface water bodies throughout Atlantic Canada have also been experiencing an increasing trend in organic matter concentrations measured as DOC. Additionally, there are more instances of increasing DOC in Atlantic Canadian surface waters than there are decreasing.

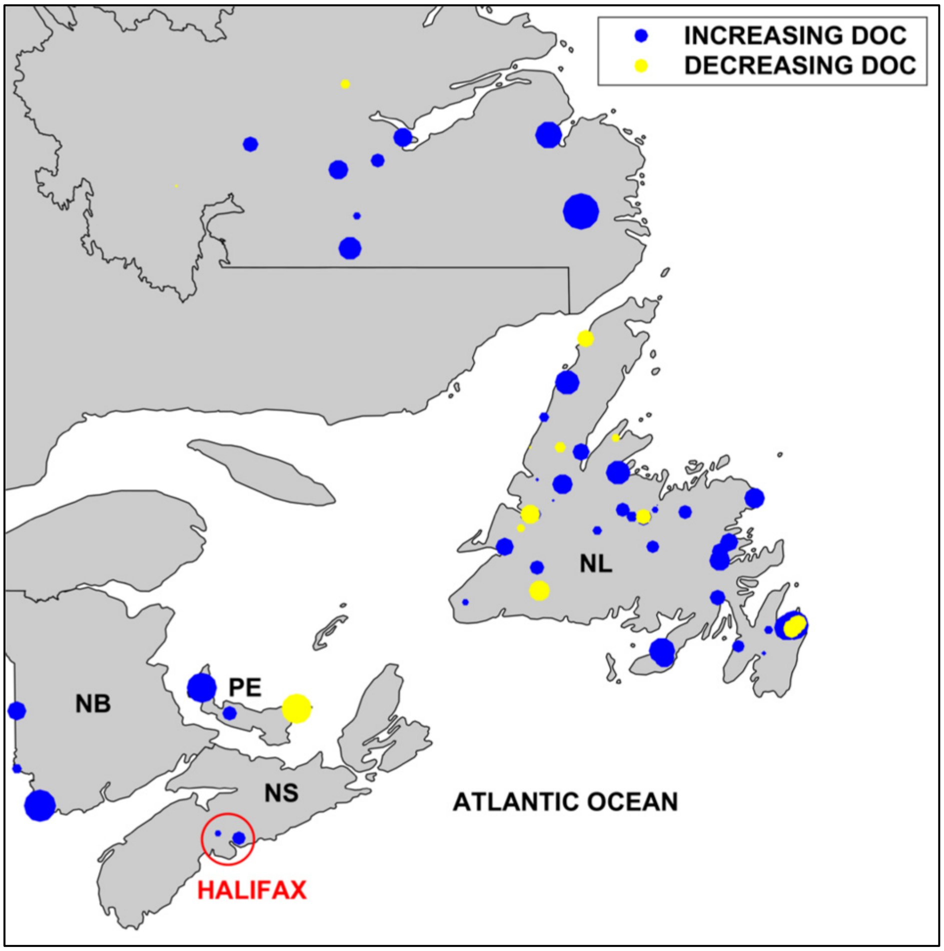

Figure 7. Change in dissolved organic matter concentration for Atlantic Canadian surface water bodies. Data for NB, PE, and NL interpreted from Environment Canada's Freshwater Quality Monitoring and Surveillance Program. Data for Halifax, NS (Pockwock Lake and Lake Major) interpreted from Tables B1 and B2. Point size is proportional to the magnitude of the linear trend between 1990 and 2013.

Both drinking water supplies studied were considered to have low color and had water treatment plants that were designed based on this concept. For example, in 1999 the year the LMWSP was commissioned there were 70 days when color concentration in Lake Major was <15 TCU (the aesthetic objective for color in the Guidelines for Canadian Drinking Water Quality), and in 2015 there was only one day where color was <15. Similarly, for Pockwock Lake, there were 179 days in 1999 and 43 days in 2015 where color was <15. Tropea et al. (2007) also noted low color levels in Pockwock Lake during the period from 1990–2000.

During the period between 1990-2000, Hongve et al. (2004) found that color and organic acid concentrations increased by as much as 50% in Norwegian lakes, which also showed decreased sulfate concentrations during the same period. Vogt et al. (2004) also reported a strong correlation between sulfate deposition and the characteristics of dissolved NOM, where NOM with high molecular weight, aromaticity and color was observed at locations that received low sulfate deposition.

Several researchers have explained the mechanism for increased NOM concentration in surface water, and additional insight on these mechanisms is provided in Chapter 2. The solubility and mobility of organic matter has been shown to increase with decreased ionic strength, which would be the case with decreasing inputs of sulfate ion (Monteith et al., 2007; Haaland et al., 2010; Ekström et al., 2016). For example, Vogt (2006) noted that declining ionic strength would increase the repulsion forces between organic molecules, decreasing the ability to precipitate out of water, resulting in highly colored water. Worrall & Burt (2010) noted that reductions in the ionic strength of soil pore water would lead to increases in DOC solubility that in turn could cause more hydrophobic compounds to become mobile. Others (SanClements et al., 2012; Ekström et al., 2016) have also shown that such increases in DOC solubility correspond with a shift of NOM quality towards more hydrophobic, aromatic and colored NOM with higher molecular weights.

In addition to reduced acidic deposition, others have attributed increasing NOM concentrations to climatic factors including increasing precipitation levels and/or temperature. For example, de Wit et al. (2016) noted that the current increasing trend in surface water NOM concentration will be further impacted by a wetter climate. Specifically, de Wit et al. (2016) projected a 30 to 50% increase in organic carbon concentrations in regions of Scandinavia that had a 10% increase in precipitation level. This was related to an increase in mobilization of NOM to freshwaters through lateral flows across catchment soils. NOM concentrations have also been known to increase with temperature as NOM decomposition and solubilisation rates are more rapid at higher temperatures (Ritson et al., 2014).

For this work, precipitation and temperature data for Halifax were analyzed to consider whether changes in climate contributed significantly to the color increases observed in Pockwock Lake and Lake Major. First, the correlations between mean monthly lake color with average air temperature and precipitation levels (both on a monthly time scale) were considered. Results showed that color in Lake Major was weakly correlated with precipitation levels ($\tau = 0.07$) and air temperature ($\tau = -0.08$), while mean color in Pockwock Lake showed similar results ($\tau = 0.02$ and $\tau = -0.17$ for precipitation and air temperature, respectively). Analysis with SMKT revealed that both monthly precipitation levels and average air temperature in Halifax did not show any significant ($p = 0.22$ and 0.38, respectively) increase throughout the period 1999-2015. In fact, temperature and precipitation levels remained relatively consistent throughout the study period. Based on these weak correlations and the lack of significant change in local climate, it was determined that neither temperature nor precipitation levels were primarily responsible for the increase in color levels in Pockwock Lake and Lake Major. However, climate change acts in concert with reductions in atmospheric deposition to contribute to increasing NOM and brownification and will likely have a more pronounced effect as deposition continues to stabilize in the region.

Previous studies (Erlandsson et al., 2010; Holmgren et al., 2014) have found that increased DOC concentration can sometimes retard the recovery of pH caused by decreasing sulfate deposition. Erlandsson et al. (2010) noted that increased DOC in recent decades has slowed the recovery from acidification by up to 1 pH unit for some lakes. Many other studies have examined the impact of buffering by organic acids on retarding the recovery in pH (Driscoll et al., 2003; Evans et al., 2008; Erlandsson et al., 2010; Erlandsson et al., 2011). This study demonstrated that reduced acid deposition may in fact be contributing to recovering pH, even in lakes with poorly buffered soils and low alkalinity such as those throughout Atlantic Canada. Kent et al. (2014) studied six lakes in Atlantic Canada that were dominated by hydrophilic neutrals (53% of NOM in Pockwock Lake) and hydrophobic acid (28% of NOM in Pockwock Lake) fractions, which are the weakest in carboxyl acidic strength compared to hydrophilic acids (12% of NOM in Pockwock Lake).[12] Therefore, it is possible that pH in Pockwock Lake was able to recover because the NOM fractions present are predominately comprised of neutral and weak acids as opposed to the stronger hydrophilic acid fraction that would have more of an effect on pH (Kent et al., 2014).

3.4.3. Impact on plant operations

Historical operational data from Halifax Water was used to quantify and assess the impacts of reduced acid deposition and corresponding increases in pH and organic matter concentration in Pockwock Lake and Lake Major on the direct-biofiltration (JDKWSP – Pockwock Lake) and conventional coagulation (LMWSP - Lake Major) treatment facilities drawing from these lakes. It is probable that water utilities in Scandinavia, the UK, in the northeastern US, and more recently in Atlantic Canada, will experience similar operational challenges as lake recovery and increasing NOM concentrations are well documented in these regions.

In recent years, the JDKWSP has experienced reduced filter run times, as well as the need to increase their alum ($Al_{2(}SO_4)_3$) dose to 12 mg alum/L after consistently dosing at 8 mg alum/L for the last 35 years. Direct filtration treatment plants are commonly used to treat high quality surface waters with moderate to low color (≤ 20 TCU), and low TOC (<4 mg/L) (Crittenden et al., 2012). Waller et al. (1996) described median color and TOC concentrations for Pockwock Lake in 1992-1993 at 9 TCU and 2.6 mg/L, respectively. Since the JDKWSP was built in the 1970's, the Pockwock Lake water supply as described by Waller et al. (1996) in the 1990s remained well suited for direct filtration based the thresholds described by Crittenden et al. (2012). As shown in Table B2 (Appendix B), TOC concentrations in Pockwock Lake have increased from 2.4 mg/L in 1999 to 3.4 ± 0.2 mg/L in 2015 while color concentrations have increased from 12 ± 6 to 21 ± 5 TCU over the same period. Consequently, the treatment system at the JDKWSP is approaching the upper thresholds (i.e., ≤20 TCU, <4 mg/L) for direct filtration in terms of both color and TOC, which has been shown by the need for increased aluminum sulfate (alum) dosage and shorter filter run times. Hutchinson (1976) and others (Wagner & Hudson, 1982) have suggested an upper limit of 15 mg/L for alum dosing in direct-filtration plants. Accordingly, the JDKWSP is also approaching the suggested upper limit for alum dosing in direct filtration plants.

As mentioned previously, researchers have suggested that not only the quantity, but the composition of NOM is changing as more hydrophobic fractions are becoming prevalent in surface waters recovering from acidification. Kent et al. (2014) showed that Pockwock Lake was dominated by hydrophilic neutrals (53% of NOM in Pockwock Lake), and hydrophobic acid (28% of NOM in Pockwock Lake). It is widely reported that coagulant demand is predominately generated by hydrophobic NOM fractions (White et al., 1997; Sharp et al., 2006; Ghernaout, 2014) and therefore a shift towards more hydrophobic NOM in Pockwock Lake would create an increase in coagulant demand. Further NOM characterization studies (e.g., fractionation) are necessary to fully understand the impacts on treatment at the JDKWSP. It is probable that water utilities in Atlantic Canada and in other regions currently experiencing recovery from acidification and subsequent increases in NOM concentration will face similar operational challenges as direct-filtration plants were generally well suited for highly acidified surface waters with low NOM concentrations.

In addition to the process issues associated with elevated NOM concentrations, Pockwock Lake has also experienced geosmin occurrences. Figure 8 depicts geosmin concentrations measured in Pockwock Lake from 2012-2015.

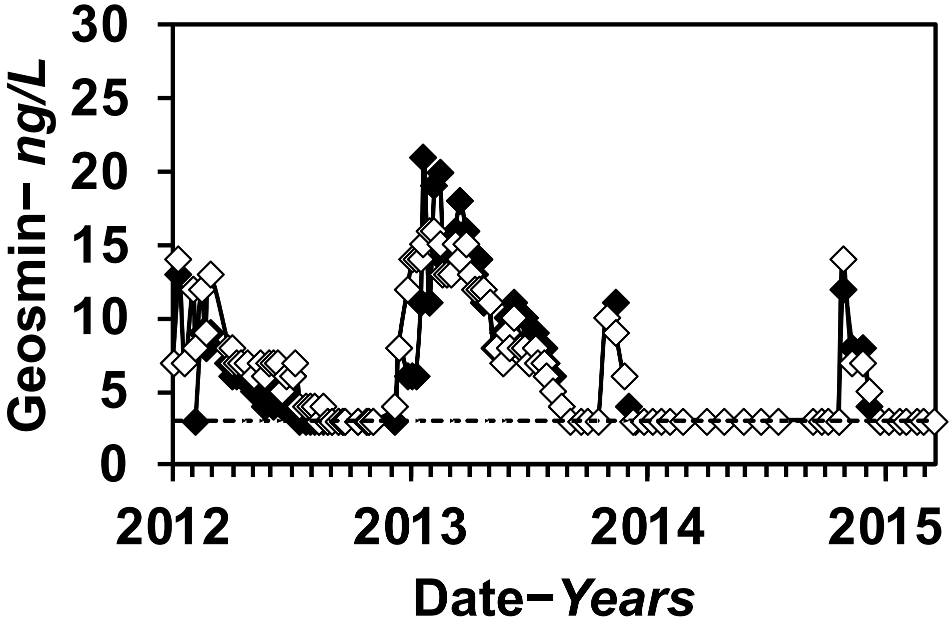

Figure 8. Geosmin concentrations in Pockwock Lake throughout the period 2012 to 2015. Filled diamonds denote raw water geosmin concentration, white diamonds denote treated water geosmin concentration, and dashed line represents minimum detection limit for geosmin.

The first indication of geosmin in Pockwock Lake was in October 2012. Prior to 2012, Halifax Water had not experienced water quality issues associated with geosmin (e.g., earthy and musty taste/odor) in Pockwock Lake and therefore had not routinely tested for it. Consequently, the presence or absence of geosmin in Pockwock Lake before 2012 cannot be confirmed. It generally persisted throughout the winter of both 2012 and 2013 reaching maximum concentrations of 12 and 21 ng/L in October 2012 and November 2013, respectively. In 2014 and 2015, the period of geosmin occurrence was shorter, as it only reemerged in August and September at maximum concentrations of 11 and 14 ng/L for 2014 and 2015, respectively. The maximum concentrations of geosmin experienced in Pockwock Lake were generally above the odor threshold concentration for humans ranging between 4 to 10 ng/L (Young et al., 1996; Rashash et al., 1997).

The main source of geosmin in freshwater systems are cyanobacteria (e.g., blue green algae) (Watson, 2004; Watson et al., 2008). Accordingly, the occurrence of geosmin in Pockwock Lake may be linked to biological responses to chemical recovery as it is well documented that increases in pH generally favor more rich/diverse cyanobacteria populations. The main genera of cyanobacteria that are known to contain geosmin-producing species are *Anabaena, Aphanizomenon, Lyngba, Oscillatoria, Planktothrix, and Symploca* (Izaguirre et al., 1982; Rashash et al., 1996; Jüttner & Watson, 2007). Although the preferred growth conditions vary by species and are dependent upon several environmental factors, it is generally known that cyanobacterial production of geosmin occurs at a pH between 6 and 9 at temperatures ranging between 15 and 30°C. *Anabaena* has been identified as the dominant geosmin producing species in the Pockwock watershed (Halifax Water, unpublished data). *Anabaena* has been reported to grow at pH 6 (Rao, 1989; Thomas et al., 2005) although lower pH values (i.e., pH<6) can be deleterious to the growth of *Anabaena* cyanobacteria (Giraldez-Ruiz et al., 1997). In 2013, the pH in Pockwock Lake began seasonally approaching pH 6 (Figure S1 in SI) which coincided with the most prevalent occurrence of geosmin and the detection of *Anabaena*.

Reductions in sulfate deposition have been connected to changes in phytoplankton species richness and community structure elsewhere (Findlay, 2003; Rönicke, 2010; Sutherland et al., 2015). For example, geosmin has been abundant in the Great Lakes (Watson et al., 2008), a region that has been undergoing recovery from acidification (Keller et al., 2007). Findlay (2003) studied the response of phytoplankton communities to recovery from acidification in several Ontario lakes and found that changes in phytoplankton community assemblages were observed in species richness and diversity, both of which were significantly correlated with pH. Rönicke et al. (2010) studied the effects of chemical neutralization of a highly acidified lake on changes in the phytoplankton community and found that with increasing pH, the community became more diverse as diatoms, chrysophyceans and blue green algae contributed significantly to biomass. Finally, Sutherland et al. (2015) documented biotic recovery in Brooktrout Lake as a response to reductions of sulfate deposition throughout the 1980's-2000's and observed increased phytoplankton species richness corresponding with decreased sulfate deposition.

The LMWSP has also faced serious treatment challenges associated with increasing NOM (i.e., color and TOC) in Lake Major (Figure 6; Table B1 in Appendix B). Mean color concentrations in Lake Major have more than doubled, and TOC concentrations have increased by 1.1 mg/L since the plant was commissioned in 1999. To assess the impact of increasing NOM on coagulant demand, daily historical coagulant (alum) dosages at the LMWSP were consulted (Figure 6).

Average coagulant dosages at the LMWSP showed significant ($p<0.05$) increase during the period between 1999 -2015. Between 2000 (the first full year post-commissioning) and 2015, the average alum dose at the LMWSP increased by nearly 4x (12.9 to 49.5 mg/L). Other factors affecting coagulant dosing such as raw water temperature and turbidity were also investigated (Table B1 in Appendix B). During the period of 1999-2015, monthly mean turbidity in Lake Major was poorly correlated with monthly mean alum dose ($\tau=0.01$) at the LMWSP, while temperature showed an inverse correlation with alum dose ($\tau=-0.23$) as expected, since seasonal cold water conditions often warrant increases in coagulant dose. Based on these weak correlations, it was determined that changes in turbidity and temperature were not the primary cause for increasing coagulant dose at the LMWSP. In contrast, mean monthly color had the strongest correlation with alum dose (τ=0.63). Furthermore, the alum dose at the LMWSP was increasing at a similar rate to color concentration in Lake Major (Sen's slope estimates for color and alum dose at 1.6 TCU/year and 1.7 mg/L/year, respectively), and therefore it is likely that increasing color concentrations were the main driver for coagulant increase at the LMWSP. There is also potential for shifts in NOM composition in Lake Major causing increases in NOM solubility that in turn could cause more hydrophobic, aromatic and colored NOM compounds to become mobile (Worrall & Burt, 2010; SanClements et al., 2012; Ekstrom et al., 2016). This would create an even greater coagulant demand at the LMWSP, as hydrophobic NOM generally controls coagulant requirements.

In addition to increased alum consumption, further analysis of chemical use at the LMWSP revealed that lime (a chemical used to adjust pH/alkalinity during coagulation) consumption has also increased by 1.75x since 2000, while average water production rates decreased by approximately 26% (51.5 MLD in 2000 to 38 MLD in 2015). This increase in lime consumption was attributed to the significant increase in alum dosing, as adding more coagulant requires further addition of lime to maintain target coagulation pH. As described previously, significant amounts of energy are required to produce and transport the chemicals used in water treatment facilities. This energy is commonly referred to as indirect embodied energy or production and transport energy, and it represents a fraction of the total embodied energy for a water treatment facility (the remaining fraction is associated with fuel and electricity). The production and transport embodied energy for alum and lime have been estimated by Santana et al. (2014) as 10.8 and 8.12 MJ/kg, respectively. Based on these estimates, the transport and production energy associated with alum and lime consumption at the LMWSP was approximately 4x10^6 MJ in the year 2000 and 9.7x10^6 MJ in the year 2015, an overall increase in indirect embodied energy of 58.5% which is substantial considering the decrease in average water production rates.

3.5. Conclusion

This work evaluated changes in water quality (e.g., pH, NOM concentration) associated with atmospheric sulfate deposition in Nova Scotia over a 16-year period (1999-2015) in two protected surface water supplies (Pockwock Lake and Lake Major). The effect of lake water chemistry on drinking water treatment processes was also considered. Overall, this study demonstrated the impact that ambient air quality can have on drinking water supplies, particularly with respect to brownification. Sulphate deposition in the region decreased by 68%, corresponding to an increase of 0.1-0.4 units over the study period. Average monthly NOM concentration (measured as color increased by 1.7 and 3.8x, respectively, for Pockwock Lake and Lake Major drinking water supplies, corresponding to coagulant demand increases of 1.5 and 3.8x at the JDKWSP and LMWSP. This increase resulted in compromised filter performance, particularly for the JDKWSP direct-biofiltration facility supplied by Pockwock Lake, which is operating at the upper limit of the recommended direct filtration thresholds. Further, the occurrence of geosmin in Pockwock Lake may have also been attributed to improvements in pH that favor more diverse cyanobacteria populations. Ultimately, utilities with surface water supplies experiencing increased NOM concentrations will not only be faced with increasing costs associated with chemical consumption, but environmental costs associated with increased energy and carbon emissions from the use of greater quantities of water treatment chemicals that are extremely energy intensive to produce and transport. In addition to Atlantic Canada, this will be of significance for eastern US, northwestern Europe, and Scandinavia, which were regions heavily impacted by acidic deposition.

4. CHAPTER 4: CHARACTERIZATION OF COLLOIDS IN A REGION WITH BROWNING SURFACE WATERS AND POTENTIAL IMPLICATIONS FOR DRINKING WATER TREATMENT

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Anderson, L. E., Trueman, B. F., Dunnington, D. W., & Gagnon, G. A. (2021). Relative importance of organic-and iron-based colloids in six Nova Scotian lakes. *npj Clean Water*, *4*(1), 1-10.

L.E.A was responsible for bench-top laboratory analysis, contributed to data analysis, conceptualization and original draft preparation, writing- reviewing and editing.

4.1. Abstract

NOM concentrations have been increasing in parts of the northern hemisphere for several decades. This process—brownification—often accompanies increasing iron and aluminum, but the metal–DOM interactions these concurrent trends imply are poorly described. Brownification represents a significant challenge for drinking water treatment systems, and metal-NOM interactions can impact the efficacy of various water treatment processes. Here, field-flow fractionation coupled with UV and ICP-MS detection was used to measure the size distribution of colloidal iron, aluminum, manganese, copper, uranium, and NOM in six lakes over six months. Five of these lakes have browned to some degree in the past three decades, with linear increases in organic carbon and color ranging from 0.01–0.13 mg C/L-yr and 0.13–1.94 PtCo/yr. Iron and aluminum were present in two primary fractions, sized nominally at 1 and 1000 kDa. The 1 kDa fraction included the primary NOM signal, suggesting that NOM colloids bind significant quantities of iron and aluminum. The 1000 kDa fraction absorbed minimally at 254 nm and likely represents iron-rich (oxyhydr)oxides. Colloidal manganese was sized at 1000+ kDa, whereas colloidal copper and uranium occurred primarily at 1 kDa. These associations fit with a pattern of

increasing DOC, iron, aluminum, and color in the region’s lakes. They represent a significant challenge for drinking water treatment systems. Given that browning trends are expected to continue, monitoring plans would better inform treatment process design and operation by characterizing NOM and iron-rich, primarily inorganic colloids that contribute to adverse water quality outcomes.

4.2. Introduction

Dissolved organic carbon (DOC) concentrations have been increasing in many lakes across Scandinavia, the UK, and northeastern North America for several decades. Some European lakes have seen increases of up to 0.15 mg C/L-yr. A concurrent increase in water color—brownification—is common (Monteith et al., 2007; Kritzberg et al., 2017). Brownification is attributed to climate change (Weyhenmeyer & Karlsson, 2009; De Wit et al., 2016; Meyer Jacob et al., 2019), declining atmospheric acid deposition, and changes in land use (Evans et al., 2006; Meyer Jacob et al., 2015; De Wit et al., 2016; Finstad et al., 2016). It is often accompanied by increasing iron (Lawrence et al., 2011; Kritzberg & Ekstrom, 2012; Björnerås et al., 2017) and aluminum concentrations (Visser, 1984; Rotteveel & Sterling, 2019).

Brownification has important implications for the provision of safe drinking water. As DOC concentrations increase, so do the chemical inputs required to maintain drinking water quality. Some treatment facilities are challenged with aging infrastructure that was designed to treat acidified surface waters with low color (Anderson et al., 2017) Moreover, the aromatic carbon associated with water color is particularly reactive with chlorine, yielding large quantities of toxic disinfection by products (Reckhow et al., 1990; Singer, 1999; Chen et al., 2019).

Brownification implies greater concentrations of humic and fulvic acids (Miele & Ingram, 1991; Tipping & Hurley, 1992; Kent et al., 2014), which can bind metals and stabilize iron, aluminum, and other metal (oxyhydr)oxides (Tipping et al., 1988; Gu et al., 1995; Catrouillet et al., 2014). Increasing NOM in European and North American freshwater bodies has accompanied increases in iron (Evans et al., 2006; Bjorneras et al., 2017; Kritzberg & Ekstrom, 2012) and aluminum (Visser, 1984; Rotteveel & Sterling, 2019). This may be causal, but the extent of metal-NOM binding is limited due to challenges in measuring these interactions in the environment. Dissolved NOM and metal oxide colloids contribute to the mobility of lead and other toxic metals, representing a potential risk to human health if they are not removed during treatment. Further, the efficacy of treatment processes used for the removal of certain metals (e.g., iron and manganese), may be impacted by the presence of NOM, through the formation of metal-NOM colloids (Knocke et al., 1987).

Conventionally, particulate and dissolved analyte fractions are separated by filtration at 0.45 µm. Colloids—dispersed particles 1–1000 nm in at least one dimension—have not often been considered a unique size fraction. They have been measured in the past by ultrafiltration (Bolea et al., 2006), size-exclusion chromatography (Neubauer et al., 2013), and field-flow fractionation (FFF) (Siripinyanond et al., 2005). Flow FFF, an FFF subtype, separates colloids based on hydrodynamic diameter. Separation is typically paired with online detection by UV-Vis absorbance, light scattering, or mass spectrometry (Dubascoux et al., 2010; Baalousha et al., 2011). Field-flow fractionation has been used to characterize colloid interactions with trace elements in surface waters, (Lyven et al., 2003; Stolpe et al., 2010; Baalhousha et al., 2011) demonstrating that NOM and iron-based colloids are major metal carriers. Given the significance of brownification, it is important that methods for quantifying the organically complexed and inorganic colloidal fractions of metals are considered in water quality monitoring and in drinking water treatment decision making, however the convention of 0.45 μm separation is typically applied in practice.

The objective of this study was to investigate the relationship between NOM and metal colloids, from a drinking water perspective, in six lakes representing a range of DOC levels characteristic of Nova Scotia, a region whose surface waters are browning significantly. The elemental composition as a function of size using flow FFF with UV absorbance and ICP-MS detection (FFF-UV-ICP-MS) was determined and these data were supplemented with fluorescence spectra and a suite of conventional water quality metrics. The abundance and relative importance of larger iron-rich, primarily inorganic colloids and smaller NOM colloids in browning lakes was assessed, with the hypothesis that high DOC lakes the strongest browning trends would have the highest concentrations of trace metals bound to colloids. These findings were interpreted from a drinking water treatment perspective, as these data have implications for drinking water sources undergoing brownification that can adversely impact treatment.

4.3. Materials and methods

4.3.1. Study area and sampling

Water samples were collected from six lakes in the Halifax Regional Municipality to characterize the variability of colloids over time and among lakes with different characteristics (Figure C1, Appendix C). Three lakes with low DOC concentrations (Albro Lake, Bayers Lake, and Chocolate Lake) and three lakes with high DOC concentrations (Frasers Lake, Long Lake, and Powers Pond), were selected for this study based on their DOC concentration. All six lakes were previously included in a sampling program of Halifax-area lakes conducted in 1991, 2000, and 2011, as shown in Table 1 (Clement et al., 2007; Clement & Gordon, 2019). The catchments of Frasers Lake, Long Lake, and Powers Pond are 2–5% wetland, while Albro, Bayers, and Chocolate Lakes do not have wetlands in their catchments. The catchments of Bayers Lake and Chocolate Lake are underlain in part by the Cunard Formation, which has produced uncharacteristically acidic surface waters following disturbance of the bedrock due to commercial and industrial activity (Tarr & White, 2016)

Table 1. Summary of data collection. When only a subset of the total number of samples are available for a given parameter, the size of the subset is listed in parenthesis after that parameter.

Collected	# of samples	Parameters	Source (reference #)
2019	24	FFF, pH, turbidity, TOC, DOC (18), color, EEM, UV_{254}, IPC-MS (6)	This study
2011	6	True color, DOC	Clement & Gordon, 2019
2000	9	True color, DOC	Clement et al., 2007
1991	4	True color, DOC	Clement et al., 2007

Samples were collected every six weeks from spring turnover until the time of strongest stratification (September). Samples were collected from the mixed layer (0.5 m depth) at the approximate center of each lake from an inflatable kayak. We used acid-washed bottles (1 L HDPE) for sample collection and stored samples at 4°C before analysis.

4.3.2. Water quality analysis and data acquisition

Element-specific size distributions for each water sample were generated using asymmetric flow field-flow fractionation (FFF). Specifics of our FFF method are available in Appendix C (Section C.1) and elsewhere (Trueman et al., 2019). In brief, a 10 mL aliquot from each sample was filtered using a 0.45 µm cellulose nitrate membrane immediately before analysis. Each filter was cleaned with 20 mL of ultrapure water followed by 20 mL of sample. We separated each sample using an asymmetric flow FFF system (PostNova AF2000 Multiflow) with a 300 Da polyethersulfone (PES) membrane and a manual injection valve with a 1 mL polyether ether ketone (PEEK) sample loop. The system was coupled first to a UV-Vis detector (Shimadzu SPD-20A) and then to a quadrupole ICP-MS (Thermofisher X series II). During separation, NOM was monitored by measuring absorbance at a wavelength of 254 nm. The mobile phase for all separations was 50 mM tris-HCl (pH 7.1).

The FFF procedure separated samples into three primary fractions, with approximate sizes of 1, 1000, and >2000 kDa (P1, P2, and P3, respectively) (Figure C2). The UV detector response in P2–P3 may be due at least in part to light scattering but is not explained by carry-over from P1; this was ensured by separating Suwannee River NOM at a concentration chosen to achieve a comparable detector response to that of Powers Pond (Figure C3). Aluminum, copper, and manganese fractograms featured a prominent void peak (P0), representing ionic forms of these elements and unfocused sample material.

As a supplement to the FFF data, the pH, turbidity, and total organic carbon (TOC) content of unfiltered lake water samples were measured. The optical properties (true color, UV_{254}, fluorescence) dissolved organic carbon content (DOC), and elemental composition of filtered water samples were also characterized. Samples for non-FFF analysis were filtered using using 0.45 µm PES membrane filters (GE Water and Process Technologies) precleaned with 500 mL of ultrapure water.

Turbidity was measured on a laboratory turbidimeter (Hach 2100AN) and pH was measured using a benchtop meter (Accumet XL50, Fisher Scientific). True color and UV_{254} were measured on a UV-Vis spectrophotometer (Hach DR5000, Hach Company, Loveland, CO, methods 8025 and 10054, respectively). TOC and DOC samples were collected, headspace-free, in 40 mL clear glass vials and preserved with concentrated phosphoric acid to pH < 2. Vials were washed and then baked at 105˚C for at least 24 h before use. TOC and DOC were quantified using a TOC-V CPH analyzer with a Shimadzu ASI0-V autosampler and a catalytically-aided combustion oxidation non-dispersive infrared detector with a method detection limit of 0.08 mg/L (Shimadzu Corpotation, Kyoto Japan) (APHA, 2017a). Turbidity, true color, UV_{254}, organic carbon and elemental concentrations are reported as nephelometric turbidity units (NTU), true color units (platinum cobalt units, PtCo), cm^{-1}, and mg/L, respectively. Element concentrations in the bulk water samples were quantified by ICP-MS (Thermofisher X-series II) (APHA, 2017b), with instrument detection limits of 0.67, 0.20, 0.80, 0.12, and 0.08 µg/L for Fe, Cu, Al, Mn, and U. Samples were acidified with nitric acid to pH < 2 and held for at least 24 hours before analysis.

A benchtop fluorometer (Horiba Aqualog) with excitation and emission ranges of 230–610 nm and 250–620 nm, respectively, was used to generate all fluorescence excitation-emission matrices (EEMs). The integration interval and spectral resolution were 0.1 seconds and 3 nm. Before acquiring data, an ultrapure water blank was used to measure the signal-to-noise ratio of the water Raman peak at 350 nm (excitation) and 397 nm (emission). Each EEM was processed by subtracting the blank, correcting inner filter effects, and removing 1st and 2nd order Raleigh scattering, as described elsewhere (Brophy et al., 2019). Intensities were normalized against the Raman water peak at an excitation wavelength of 350 nm. The median length of time between collection and EEM analysis was 3 days (1–17 days).

4.3.3. Statistical analyses

4.3.3.1. Trend analysis

The change in true color and DOC over time in the high DOC study lakes was modelled using cubic regression splines, fit using the *mgcv* package in R (R Core Team, 2019). Linear regression slopes in true color and DOC for all six study lakes were determined using ordinary least-squares linear regression. Additional details are available in Appendix C (Section C.2).

4.3.3.2. Principal components analysis

The variation in the FFF-ICP-MS data was summarized using principal components analysis, via the *prcomp()* function in R (R Core Team, 2019) (the input matrix included a row for each lake sample and a column for each instantaneous concentration of Al, Cu, Fe, Mn, and U). To limit the influence of outliers (e.g., high concentrations of colloidal Mn and Fe in the July sample of Powers Pond), a natural-log transformation was applied to the data and all variables were mean-centered before computing the principal components analysis. The transformed data were not multivariate normal according to a Shapiro-Wilk test (Jarek, 2012). No values were imputed or deleted.

The variation in DOC and color over time in the study lakes was also summarized via principal components analysis. DOC and color were mean-centered and scaled to unit variance, but no outliers were removed, and no values were imputed. The input matrix was not bivariate normal according to a Shapiro-Wilk test (Gonzalez-Estrada & Villasenor-Alva, 2013).

4.4. Results and discussion

4.4.1. Water quality trends

The six lakes studied fall into two broad categories based on their typical DOC concentrations (Table 2). The low DOC lakes—Albro, Bayers, and Chocolate Lakes—had a median DOC concentration of 2.5 mg/L (range: 0.34–5.9). The high DOC lakes—Frasers Lake, Long Lake, and Powers Pond—had a median of 7 mg/L (5.9–8.7). TOC and DOC were comparable, with a median difference of 0.2 mg/L; most of the organic carbon in these lakes is “dissolved” (<0.45 μm).

Median true color was 8.3 PtCo (range: 0–25) and 69 PtCo (55–110) in the low and high DOC lakes, respectively. Fluorescence was greater in the high DOC lakes and was generally dominated by humic and fulvic-like fluorophores (Figure 9); protein-like fluorescence comprised a relatively minor component. The fraction of total fluorescence attributable to humic-like fluorophores was greater in high DOC lakes (67–68%) than in low DOC lakes (42–65%). The trend in protein-like fluorescence was opposite: the fractional fluorescence attributable to proteins was greater in the low (2.2–13%) relative to the high DOC lakes (0.92–1.4%).

Humification indices (HIX) ranged from 9–19 in the high DOC lakes, with a median of 14. This consistent with the occurrence in these lakes of high molecular weight, strongly aromatic NOM of terrestrial origin (Huguet et al., 2009; Tedetti et al., 2011). Humification indices ranged from 0.77–6.4 in the low DOC lakes, with a median of 3.7. This implies that autochthonous NOM was present in samples yielding HIX in the lower half of this range (HIX < 4) (Tedetti et al., 2011). Consistent with the HIX, median biological indices (BIX) were greater in the low compared to the high DOC lakes (0.7 *vs.* 0.51). These values imply low NOM production across all lakes, although the differences among lakes suggest a greater fraction of NOM in the low DOC lakes was of autochthonous origin (Huguet et al., 2009; Tedetti et al., 2011). Specific UV absorbance—SUVA, the ratio of UV_{254} to DOC—is highly correlated with the percent aromaticity of NOM (Weishaar et al., 2003). The high DOC lakes had a median SUVA of 4.9 L-mg/m (range: 4.3–5.7) which accords with high HIX and the presence of wetlands in the lake catchments. The low DOC lakes had a median SUVA of 2.4 L-mg/m (0.89–14), lower HIX, and no wetlands in their catchments.

Table 2. Water quality summary of study lakes (April - September 2019); element concentrations represent 0.45 µm-filtered samples.

Lake type	Parameter	Median	Range	Units	N
High DOC	Al	0.18	0.16–0.24	mg/L	3
	BIX	0.51	0.47–0.53	mg/L	12
	Ca	3.8	2.1–5.1	mg/L	3
	Colour	69	55–110	PtCo	12
	Cu	0.0012	0.001–0.0013	mg/L	3
	DOC	7	5.9–8.7	mg/L	9
	Fe	0.12	0.091–0.16	mg/L	3
	HIX	14	9–19	mg/L	12
	Humic-like	67	67–68	% of total fluorescence	12
	Mn	0.029	0.019–0.04	mg/L	3
	P	0.084	0.019–0.18	mg/L	3
	pH	6	5.4–6.1	-	9
	Protein-like	1.1	0.92–1.4	% of total fluorescence	12
	SUVA	4.9	4.3–5.7	L-mg/m	12
	TOC	8	5.9–11	mg/L	9
	Turbidity	1.1	0.26–2	NTU	9
	U	<MDL	5e-04–0.16	µg/L	3
	UV_{254}	0.37	0.28–0.51	cm^{-1}	12
Low DOC	Al	0.048	0.0082–0.057	mg/L	3
	BIX	0.7	0.22–0.96	mg/L	12
	Ca	13	8.6–15	mg/L	3
	Colour	8.3	0–25	PtCo	11
	Cu	0.001	0.00096–0.0034	mg/L	3
	DOC	2.5	0.34–5.9	mg/L	9
	Fe	0.037	0.025–0.12	mg/L	3
	HIX	3.7	0.77–6.4	mg/L	12
	Humic-like	62	42–65	% of total fluorescence	12
	Mn	0.15	0.032–0.37	mg/L	3
	P	0.27	0.17–0.42	mg/L	3
	pH	6.1	5.3–7	-	9
	Protein-like	2.9	2.2–13	% of total fluorescence	12
	SUVA	2.4	0.89–14	L-mg/m	12
	TOC	2.6	0.31–5.3	mg/L	9
	Turbidity	0.96	0.25–3.7	NTU	9

U	<MDL	<MDL - <MDL	µg/L	3
UV_{254}	0.07	0.003–0.14	cm^{-1}	12

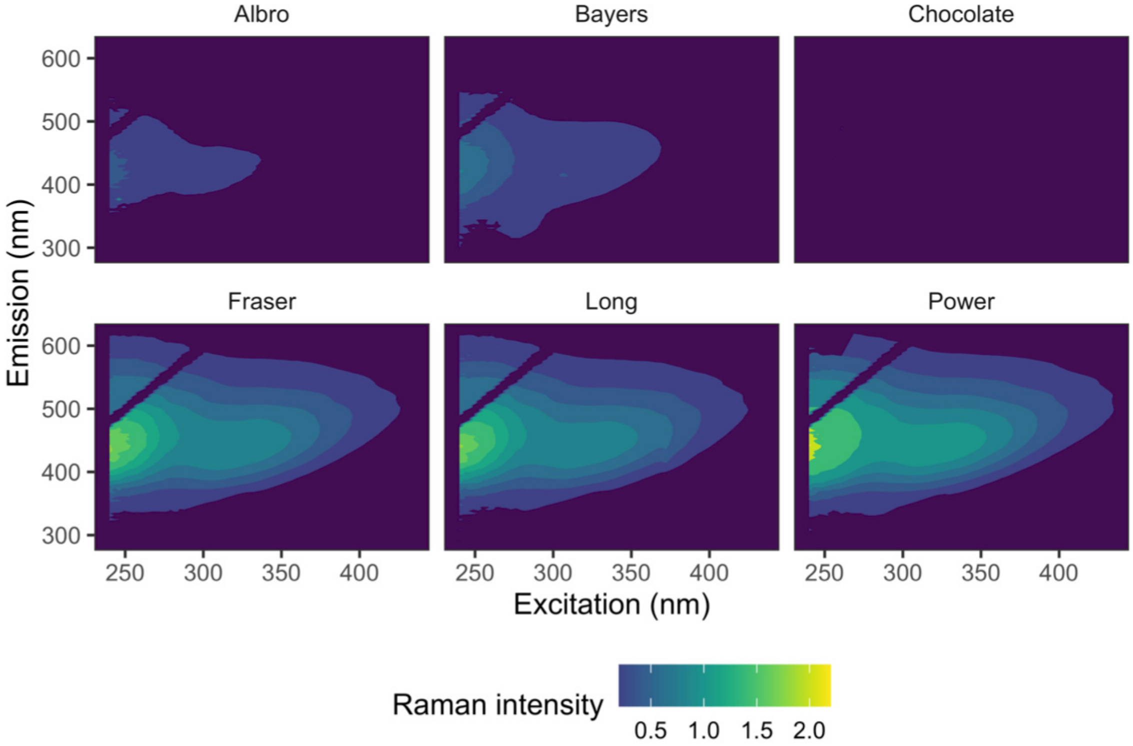


Figure 9. Fluorescence excitation-emission matrices (EEMs) representing the six lakes in the dataset (top row: three low DOC lakes; bottom row: three high DOC lakes). The Raman intensity at each excitation-emission coordinate represents an average of multiple EEMs.

Most of the study lakes have browned significantly in the past three decades based on historical data (1991 - 2011) (Clement et al., 2007; Clement & Gordon, 2019) and those collected for this study. The overall browning trend in the high DOC lakes is summarized in Figure 10 via time series of true color, DOC, and the first principal component describing variation in color and DOC as a summary metric for colored NOM (trends for each lake reported in Table C2 and Figure C4, Appendix C). Over the period 1991 - 2019, linear regression slopes describing variation in color ranged from 0.96–1.94 and -0.29–0.55 PtCo/yr in the high and low DOC lakes, respectively.

Trends in DOC ranged from 0.06–0.12 and 0.00–0.13 mg C/L-yr. While browning was most prominent in the high DOC lakes, DOC and color increased in all but Chocolate Lake, which exhibited a decreasing color trend (-0.29 PtCo/yr) and a negligible DOC trend. These browning trends are consistent with regional trends (e.g., Redden et al., 2021), such as those described in Chapter 2 and 3 (e.g., Anderson et al., 2017; Anderson et al., 2023) as well as those reported elsewhere (see Anderson et al., 2023 for a detailed review on trends in the northern hemisphere).

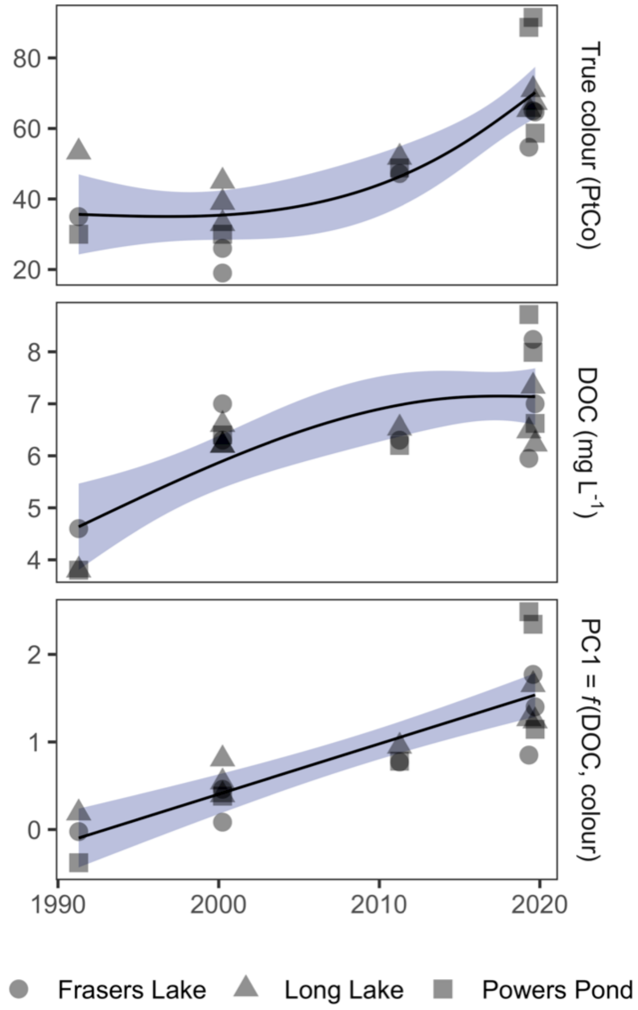


Figure 10. Colour (a) and DOC (b) have increased over the past three decades in the high DOC study lakes. (c) The first principal component (PC1, 70% of total variance) describing variation in DOC and color is used as a summary metric for colored NOM; PC1 scales with the sum of (standardized) DOC and color (PC1 = 0.7 DOC + 0.7 color). The

solid lines in all panels represent cubic regression splines fit to the data, and the shaded regions define a pointwise 95% confidence interval on the fitted values.

4.4.2. Colloid characterization via field flow fractionation

Fractograms (i.e., analyte intensities as functions of time) were generally bi- or tri-modal, with peaks at approximate retention times of 13 (P1), 20 (P2), and 29 (P3) minutes (Figure C2). P1 and P2 correspond to approximate molecular weights of 1 and 1000 kDa, respectively (Figure 11). P3 was estimated at >2000 kDa, but P3 occurred beyond the calibration range (0.69–2000 kDa) and represents signal acquired without a crossflow.

Peaks at 1 and 1000+ kDa (e.g., P1 and P2) represent primarily organic and inorganic colloids (Cuss et al., 2017; Westerhoff et al., 2018), respectively. The majority of UV absorbance at 254 nm (UV_{254}) was due to P1 (1 kDa), which, consistent with previous work (Cuss et al., 2017; Trueman et al., 2019), likely represents organic material. P2 and P3 were rich in iron, which agrees with previous reports of largely inorganic metal oxide-based colloids in this size range (Cuss et al., 2017). Iron also occurred at 1 kDa, suggesting that it was complexed with colloidal NOM. P3 was relatively prominent in the manganese fractograms, which also featured peaks at 20 minutes (P2, 1000 kDa) but only negligibly at 13 minutes (P1, 1 kDa). That is, manganese was identified in inorganic colloids—or in dissolved forms—but not to any significant degree as an adsorbate on NOM colloids in P1. Copper and aluminum occurred primarily in P1, implying that these elements were largely bound to NOM.

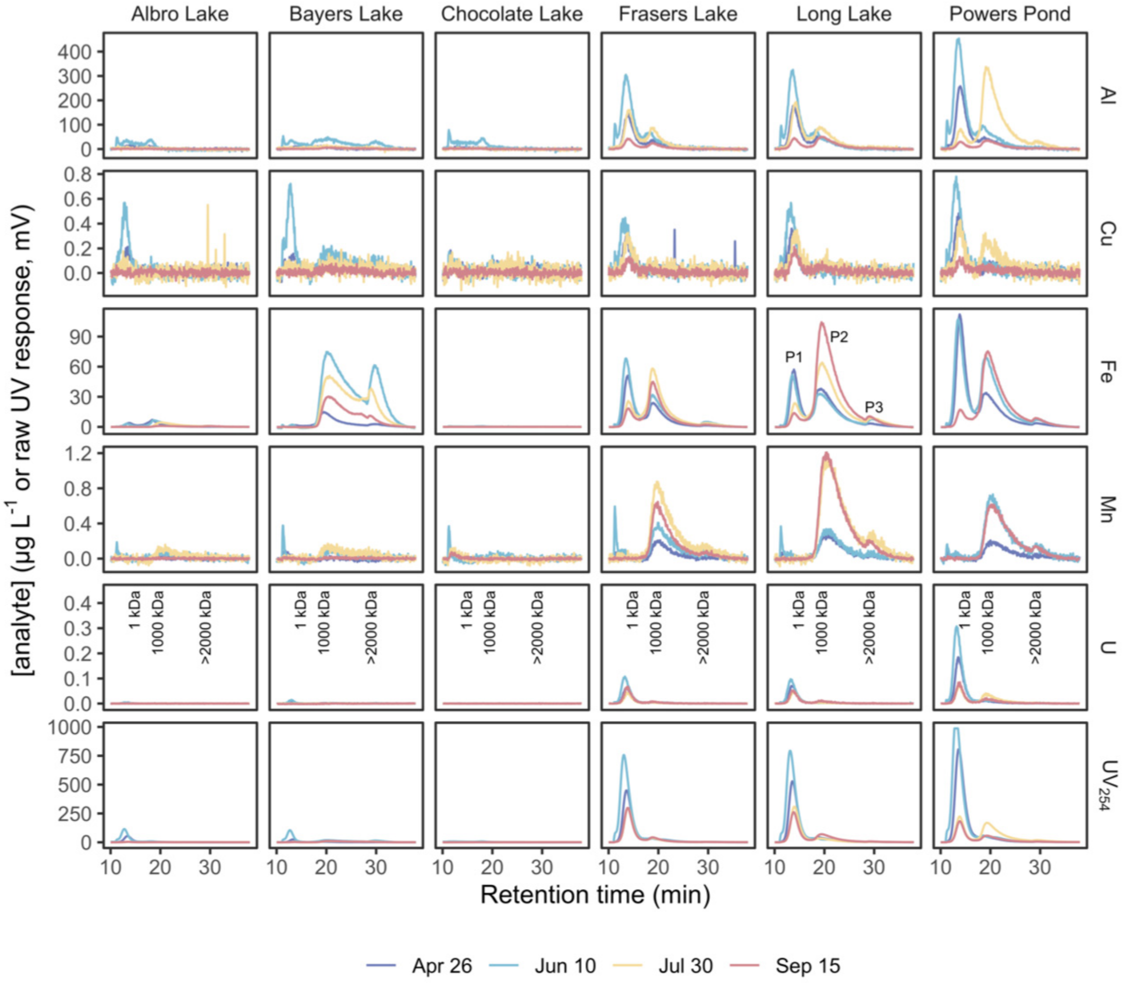
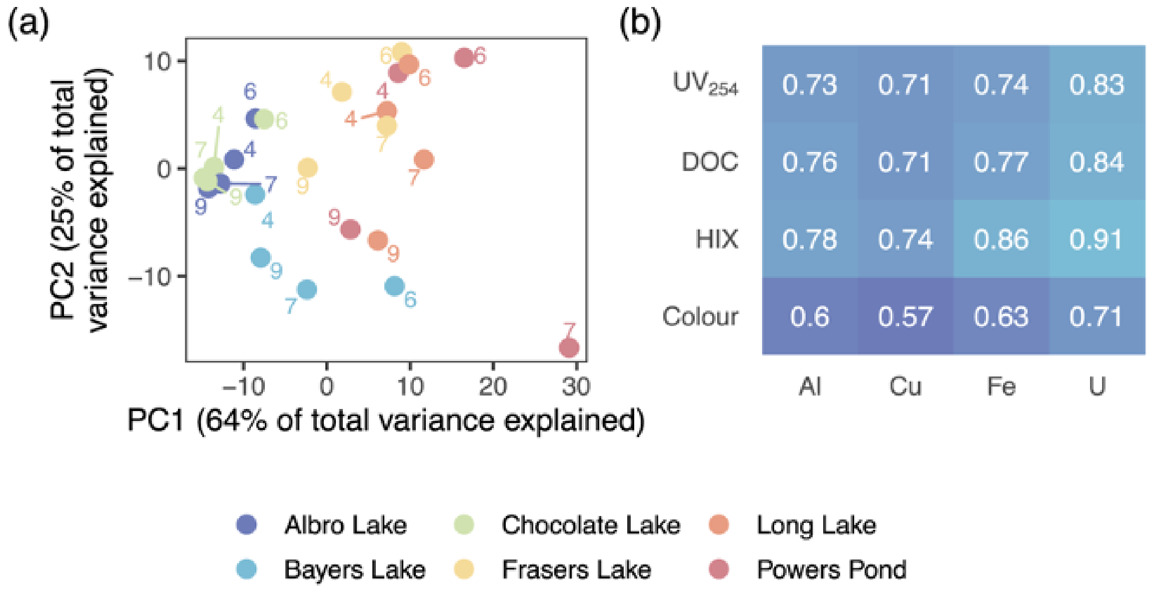


Figure 11. Semiquantitative fractograms representing the six study lakes (three low DOC lakes on the left, three high DOC lakes on the right); the July Fe and Mn data representing Powers Pond are omitted for clarity of presentation due to anomalously high concentrations.

Semiquantitative aluminum, iron, copper, and uranium concentrations in P1 (FFF data) were correlated with DOC, UV$_{254}$, true color, and the humification index (HIX) (Figure 12b). That is, concentrations of these metals at 1 kDa were greater in the three high DOC lakes than in the three low DOC lakes. Principal component analysis accorded with these associations, highlighting two axes of variability: one (PC1) aligned with UV$_{254}$, analytes (e.g., aluminum, iron, copper, and uranium) primarily associated with the organic P1 1 kDa colloids, and one (PC2) aligned with manganese and iron dominated by the primarily inorganic P2 - 3 (1000 + kDa) colloids (Figure

12a). The first two components together accounted for 89% of total variation in the FFF data (Figure C6, Appendix C). The high DOC lakes scored higher on the first principal component (PC1, Figure 12a). Further, in the high DOC lakes, scores on PC2 became more negative from spring to summer, reflecting increasing dominance of larger P2 and P3 colloids during the summer when NOM is at a seasonally low concentration. Likewise, negative scores on PC2 for samples representing Bayers Lake are consistent with the high intensity of colloidal Fe in that lake relative to the other low DOC lakes.



	Al	Cu	Fe	U
UV_{254}	0.73	0.71	0.74	0.83
DOC	0.76	0.71	0.77	0.84
HIX	0.78	0.74	0.86	0.91
Colour	0.6	0.57	0.63	0.71

Figure 12. a) FFF data representing all six study lakes, projected onto the space spanned by the first two principal components. Sample month is annotated numerically. (b) Except for manganese, semiquantitative element concentrations in the 1 kDa size fraction were correlated with UV_{254}, true color, DOC, and HIX (Table 2). Values represent Spearmen rank correlation coefficients.

The contribution of each fraction to the overall size distribution was estimated by deconvolution (Figure 13) (Trueman et al., 2019). A median 81% of UV absorbance was accounted for in the three high DOC lakes by P1 (range: 35–89%). The remainder was explained by P2 and P3. In the low DOC lakes, larger colloids (P2–P3) dominated absorbance fractograms, particularly in the summer months (Figure 13): the respective median shares were 37 and 22%, while P1 accounted for a median of 32%.

Iron fractograms representing the high DOC lakes were dominated by P2 (1000 kDa), with a median share of 67%. P1 and P3 accounted for a median 26 and 6% of total colloidal iron, respectively. In the low DOC lakes, P2 iron was even more dominant, with a median signal share of 72%, and P3 replaced P1 as the second-most abundant fraction with a median share of 20%. This pattern was particularly evident in Bayer's Lake, which had significant concentrations of iron in P2 and P3 (Figure 11, Figure 13).

Aluminum in the high DOC lakes occurred primarily in P1 (median: 55%), although P2 was sometimes significant (median: 43%). In the low DOC lakes, P2 aluminum was more prominent, accounting for a median share of 58% among samples where it was detected. High DOC lakes were richer in manganese, but unlike iron and aluminum, it was present almost exclusively in larger colloids (P2–P3, 1000+ kDa) with a median of 1% attributable to P1.

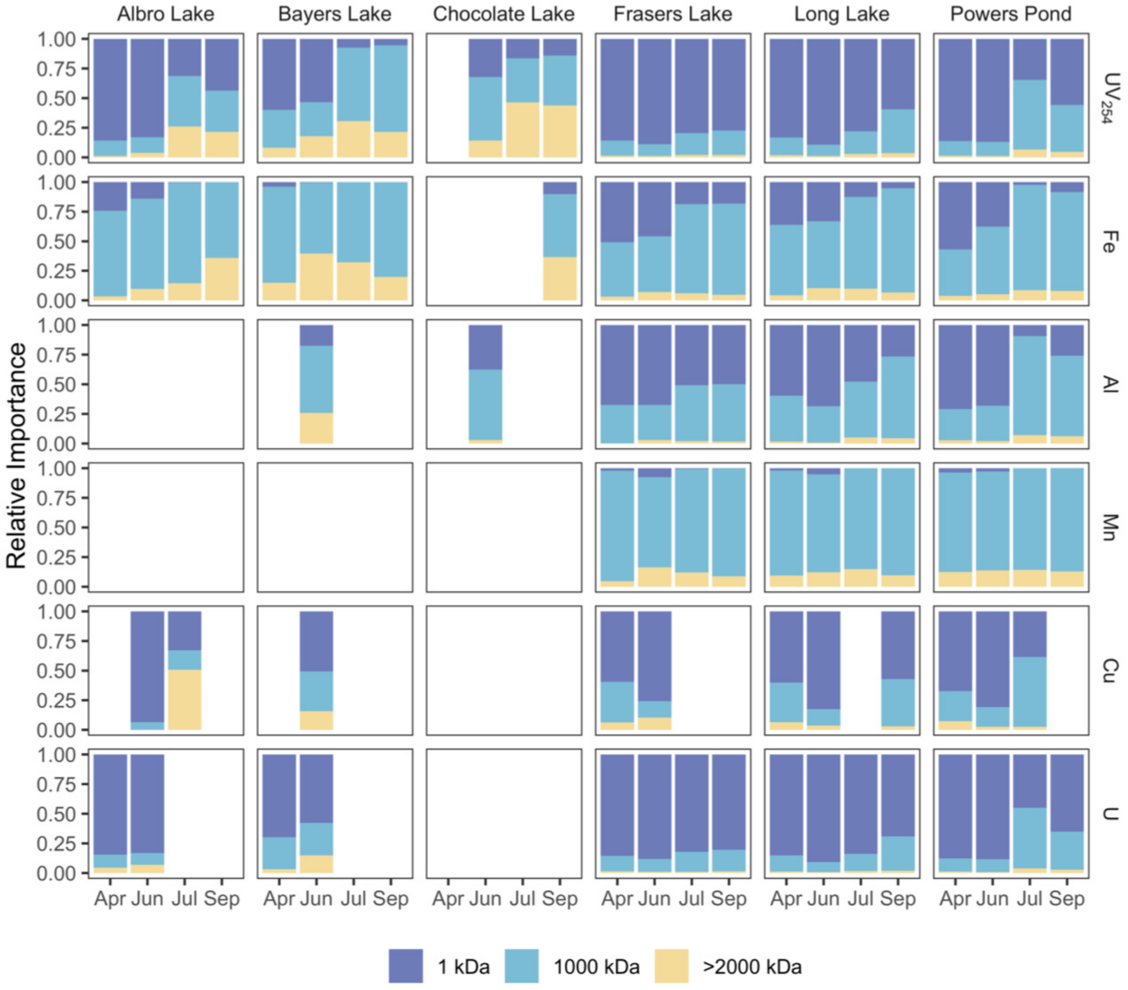


Figure 13. Contribution of the nominal 1 kDa, 1000 kDa, and >2000 kDa size fractions to each fractogram, estimated by deconvolution. Fractograms with nonquantifiable peaks were omitted.

Previous studies (Gallego-Urrea et al., 2010; Westerhoff et al., 2018) have reported a bi-modal colloid distribution in surface waters, where the smaller peak comprises NOM and NOM–metal complexes (approximately 1 - 10 nm) and the larger, transition metal oxides (>50 nm) with adsorbed NOM and trace metals. Consistent with these results, the study lakes in this work contained two primary colloid fractions: a metal–NOM peak (P1) at approximately 1 kDa, and an iron and manganese rich, primarily inorganic peak (P2) at approximately 1000 kDa. These colloids were present at significantly higher concentrations in the high DOC lakes.

4.4.2.1. Primarily organic (1 kDa) fraction (P1)

The molecular weight estimate for P1 is consistent with the reported range for humic and fulvic acids (Thurman et al.,1982) and NOM extracts from surface waters (Cuss et al., 2017). It agrees with previous work showing that these colloids are typically less than 10 kDa (Thurman et al., 1982; Rosario-Ortiz et al., 2007). The data presented in this work suggest that a substantial fraction of colloidal iron and nearly all colloidal aluminum, copper, and uranium is bound to NOM (P1). This is consistent with mechanistic studies of metal binding to the phenolic and carboxylic functional groups that are well-represented in high molecular weight NOM (Thurman et al., 1987; Masini et al., 1998).

In Nova Scotian surface waters, aluminum is often correlated with TOC (Rotteveel & Sterling, 2019), and Al–NOM complexation is relatively well documented (Driscoll et al., 1980; Driscoll, 1985; Bailey et al., 1995). Aluminum in P1 likely explains the elevated levels in the high DOC study lakes. These lakes have pH near the solubility minimum of aluminum hydroxide (e.g., 6 to 6.1, Table 2) a possible solubility-controlling phase—and without considering colloidal interactions, expected solubility would be low. Al–NOM complexation also explains the correlation between semiquantitative P1 aluminum concentrations and various NOM metrics (Figure 12b).

Iron in P1 was also higher in the high DOC study lakes, which is consistent with the expected binding of iron to NOM colloids. Complexation provides a partial explanation for high "dissolved" iron (Table 2). Considering only simple inorganic ligands, ferric iron is highly insoluble above pH 4, with a typical equilibrium concentration below 1 μM (Zinder et al., 1986). In the presence of complexing organic ligands, however, ferric iron solubility can be much greater.

Similar patterns have been reported elsewhere: Cuss et al. (2017) reported that aluminum was present exclusively in ionic/small forms or associated with NOM colloids in the Athabasca River and its tributaries. Rotteveel & Sterling (2019) observed that seasonal maximum Al concentrations, likely present as Al associated with organic colloids) in rivers in the study region (also characterized by numerous wetlands within catchments) are driven by peak TOC concentrations during periods of low flow. Iron was also associated with NOM colloids, albeit to a lesser degree. Dupré et al. (1999) fractionated river water by ultrafiltration, finding that organic colloids were important for aluminum and iron transport. Baalousha et al. (2006) detected and aluminum and NOM in a common size fraction sized below 10 nm by FFF, and Morrison & Benoit (2004) showed that at least some aluminum was bound to organic colloids in freshwater samples from six Connecticut rivers. Several studies (Lyven et al., 2003; Stolpe et al., 2010; Cuss et al., 2018; Morrison & Benoit, 2004; Tipping et al., 2010) have found that copper and uranium are primarily associated with organic colloids.

While the data in this study provide no clear evidence of Mn–NOM complexation at 1 kDa, Cuss et al. (2018) attributed at least a minor fraction of colloidal Mn to NOM in all samples. Lyvén et al. (2003) attributed 70% of manganese in a freshwater sample to carbon-based colloids and Baalousha et al. (2011) found that manganese was bound to NOM colloids less than 10 nm in diameter. Other studies (Chiswell & Mokhtar, 1986; Baalousha et al., 2006; Stolpe et al., 2010; Cuss et al., 2018) have reported manganese association with iron-based colloids, which is more consistent with the results in this study. It is also possible that adsorption sites on NOM were largely occupied by aluminum and iron, which were present at much higher levels than manganese. But the capacity for NOM to bind these metals may be increasing over time: positive trends in surface water DOC have often accompanied a shift to more hydrophobic, aromatic, and coloured NOM with a greater density of metal binding sites (SanClements et al., 2012; Ekstrom et al., 2016).

4.4.2.2. Primarily inorganic (1000+ kDa) fraction (P2–P3)

Given the study lakes' water chemistry, NOM-stabilized iron (III) (oxyhydr)oxides were expected to account for the iron in P2 and P3 (Gu et al., 1995; Stolpe et al., 2010). Stabilization occurs when high molecular weight NOM partition to iron colloids via surface complexation. Negatively charged functional groups and organic polymer chains extend outwards into the water phase, providing electrostatic and steric repulsion (Gu et al., 1995; Baalousha et al., 2009). In light of its stabilizing effect, adsorbed NOM might account for variation in the size of iron-rich colloids, allowing aggregation and growth at lower concentrations (Baalhousha et al., 2009). Previous work (Stolpe et al., 2010) has described a positive shift in the size distribution of colloidal iron in moderate, relative to high, DOC surface waters.

All elements were associated to some degree with large, Fe-rich colloids (1000+ kDa, P2–P3), albeit only a small fraction in the case of uranium and copper. A significant fraction of total colloidal aluminum was present in P2–P3, in contrast to Cuss et al., (2018) who did not report any significant association of aluminum with large Fe-rich colloids.

Manganese in P2 likely occurred as (oxyhydr)oxides or mixed iron/manganese phases (Davison, 1993). In surface waters, manganese occurs in three oxidation states: soluble Mn(II) (stable in anoxic waters), Mn(III) (e.g., as MnOOH), and Mn(IV) (e.g., as MnO_2) (Davison, 1993). A range of manganese (oxyhydr)oxides form in well-oxygenated waters at the lake surface, unless seasonal mixing distributes dissolved Mn(II) across the water column (Davison, 1993). Stratification of the study lakes typically peaks in late summer or early fall, which may explain the greater magnitude of P2 in July and September as well as the apparent presence of ionic manganese (void volume, P0) in June when the lakes would have been more fully mixed (Figure 11). Consistent with our data, Cuss et al. (2018) reported that large Fe-rich colloids accounted for a substantial fraction of Mn in the Athabasca River.

4.5. Implications for drinking water treatment

The browning trends reported in this work fit with a pattern of increasing DOC, iron, aluminum, and color in the region's lakes (Clair et al., 2011; Anderson et al., 2017; Redden et al., 2021). These trends may have adverse impacts on drinking water quality as lakes become more difficult to treat (Edzwald & Tobiason, 1999; Keeley et al., 2016; Anderson et al., 2017; Kritzberg et al., 2020). In one of the region's most important drinking water supplies, for instance, source water color increased nearly four-fold over 16 years (1999–2015), necessitating a proportional increase in coagulant addition to maintain treated water quality (Anderson et al., 2017).

This work highlights the importance of NOM removal in drinking water treatment and could inform future treatment plant design. Conventional treatment practice focuses on removing dissolved metals and NOM independently. Dissolved metals are typically removed by oxidation and NOM is removed by coagulation, sedimentation, and filtration. The metal–NOM binding we report here suggests that treatment facilities should adapt to brownification by optimizing NOM removal first, and technologies commonly used for removing metals may become less effective due to the presence of colloids. A study by Carlson et al. (1997) demonstrates the impact of inadequately dosing oxidants when metals are present in the form of colloids, as opposed to truly dissolved species, highlighting the importance of colloid characterization and the removal of colloids via optimized solid-liquid separation processes. If colloids are not removed during treatment, they facilitate lead release from legacy plumbing via complexation or partitioning to

NOM-stabilized metal (oxyhydr)oxides (Trueman et al., 2019; Trueman & Gagnon, 2016; Gora et al., 2020). Furthermore, aluminum, iron, and manganese are the subjects of current or proposed regulations or monitoring requirements (Health Canada, 2009; Health Canada, 2019a; Health Canada, 2019b). Treatment facilities that are ill-equipped to manage increasing metal and NOM loads in drinking water supplies may fail to meet increasingly stringent drinking water guidelines.

4.6. Conclusion

DOC concentrations have been increasing in many lakes throughout the northern hemisphere for several decades due to reductions in atmospheric acid deposition, climate change, and changing land use. Brownification is often accompanied by increases in metal concentration such as iron and aluminum. The objective of this work was to characterize the size distribution of colloidal iron, aluminum, manganese, copper, uranium, and NOM in six lakes with varying degrees of browning using field-flow fractionation coupled with UV and ICP-MS detection.

Linear increases in NOM measured as DOC and color were observed in five of the six study lakes, ranging from 0.01–0.13 mg C/L-yr and 0.13–1.94 PtCo/yr, which agrees with brownification of surface waters in the region. Through FFF-UV-ICPMS, two primary fractions were observed – sized nominally at 1 and 1000 kDa. The 1 kDa fraction primarily included NOM and significant quantities of iron and aluminum, suggesting that NOM colloids bind iron and aluminum. The 1000 kDa fraction had minimal NOM signal and represented colloidal iron. Colloidal manganese was present in the 1000+ kDa fraction and was likely associated with Fe rich colloids. These trends agreed with increases in DOC, color, iron and aluminum in the region.

These colloids represent a significant challenge for drinking water treatment systems, and this work highlights the importance of NOM removal in drinking water treatment and could inform future treatment plant design. Conventional treatment practice focuses on removing dissolved metals and NOM independently. Dissolved metals are typically removed by oxidation and NOM is removed by coagulation, sedimentation, and filtration. The metal–NOM binding reported here suggests that treatment facilities should adapt to brownification by optimizing NOM removal first, and technologies commonly used for removing metals may become less effective due to the presence of colloids. Treatment facilities that are not equipped to manage increasing metal and NOM loads in drinking water supplies may fail to meet increasingly stringent drinking water guidelines.

NOM increases are expected to continue given the anticipated effects of climate change and the ongoing reductions in atmospheric acid deposition. With continued browning, we can expect increases in NOM-associated metals, as well as the concomitant impacts on ecosystem services. Future monitoring and management plans, then, would better serve the public by characterizing NOM and iron-rich, primarily inorganic colloids that contribute to adverse water quality outcomes, especially in catchments that include wetlands. Such plans could inform process design, selection, and operation of unit processes, and drinking water source selection.

5. CHAPTER 5: ROBUSTNESS OF GRANULAR ACTIVATED CARBON (GAC) AS A WATER TREATMENT ADAPTATION STRATEGY FOR BROWNIFICATION

This chapter was prepared for submission to AWWA Water Science for publication and is currently under revision.

Anderson, L. E., Tchonlla, M., Earle, M. & Gagnon, G. A. (2023). Robustness of Granular Activated Carbon (GAC) as a Water Treatment Adaptation Strategy for Brownification. Submitted to *AWWA Water Science*.

L.E.A was responsible for data analysis, conceptualization and original draft preparation, writing-reviewing and editing.

5.1. Abstract

Widespread increases in natural organic matter (NOM) concentration (e.g., brownification) and in some cases, concurrent increases in metals (e.g., Fe or Mn) in source waters together have created challenges for drinking water treatment, particularly those using direct filtration. A pilot-scale study was conducted to assess adaptation strategies (e.g., implementation of clarification, use of alternative filter media such as GAC) for direct filtration facilities under the stress of increasing NOM through brownification of surface water supplies. Given that metals removal may be impacted by brownification, a secondary objective was to assess the removal of dissolved (<0.45 µm) metals including Fe and Mn across the different treatment configurations, including $KMnO_4$ pre-oxidation. The use of GAC caps or full-GAC media replacement may be a promising alternative to direct or conventional filtration (e.g., Ant/Sand) for adapting to brownification of source waters, providing between ~40 and 58% (mean, from raw water levels) removal of DOC and ~77 to 83% of UV254 (compared to ~42 to 44% for DOC and ~69 to 72% for UV254 for conventional filters). The GAC filters also had the greatest reduction in DBPfp with ~35 µg/L of THMfp and 13 µg/L of HAAfp, respectively, compared to THMfp of 55 to 59 and HAAfp of 22-

24 µg/L for conventional filters. In contrast, there was little removal of Mn and Fe through pre-treatment with $KMnO_4$. We hypothesized that the addition of $KMnO_4$ was ineffective due to the presence of colloidal Mn and Fe, as opposed to dissolved. It was hypothesized that $KMnO_4$ reacted with other substances (e.g., humic NOM) to generate MnO_x colloids that were deposited onto the filters, which was followed by the release of dissolved Mn due to reducing conditions in the filters. The filters typically released Mn at levels higher than the influent and negated any (although limited) removal that occurred during pre-treatment. The GAC capped and full-GAC sand filters released the most dissolved Mn at up to ~29% increase from pre-filter levels. This work highlights the source water complexities that are anticipated through brownification and the need for considering robust adaptation water treatment solutions that consider many factors in addition to NOM, including Mn and Fe.

5.2. Introduction

In recent decades, there have been widespread increases in the concentration of natural organic matter (NOM) as indicated by color, dissolved organic carbon (DOC) or total organic carbon (TOC) in surface waters throughout the Northern hemisphere. This phenomenon has been referred to as the brownification of surface waters and is generally believed to be a result of multiple anthropogenic and climate stressors. Many studies (e.g., Skjelkvåle et al., 2005; Monteith et al., 2007; Anderson et al., 2017; Garmo et al., 2020; Redden et al., 2021; Anderson et al., 2023) have reported on brownification trends in surface waters in Europe and North America. Collectively, these studies have identified relationships between increased DOC concentration and lower levels of atmospheric acid deposition. More recently, the importance of climate change (Finstad et al., 2016; Riise et al., 2018; Kopáček et al., 2019; Imtiazy et al., 2020; Meyer-Jacob et al., 2020; Marty et al., 2021; Nelson et al., 2021; Lepistö et al., 2021) and changing land use (e.g., Skerlep et al., 2020; Garmo et al., 2020; Kritzberg et al., 2020) have been highlighted as additional drivers of increasing DOC concentration, particularly as acid deposition stabilizes.

The efficacy of many aspects of water treatment processes including the dosing of treatment chemicals (e.g., coagulant, oxidant) and the selection, implementation, design, and operation of unit processes are dependent on the concentration and properties of NOM present. NOM is the major precursor material to the formation of regulated disinfection-by products including trihalomethanes and haloacetic acids (Hua and Reckhow, 2007; Bond et al., 2011). Insufficient NOM removal can contribute to undesirable colour, taste, and odour problems, can impact the biological stability of distributed water (Hammes et al., 2010) and can act as a carrier of trace metals (e.g., Pb) in distribution systems (Trueman et al., 2017).

Considering that brownification of surface waters is occurring on a global scale (see Anderson et al., 2023a and Chapter 2 for a detailed review), there is a need to consider treatment adaptations that can accommodate large fluctuations in NOM concentration, particularly for direct filtration facilities (DeMont et al., 2020). Granular activated carbon (GAC) adsorption can be a cost-effective strategy for enhanced NOM removal and is attractive due to its improved control of DBP precursors (Kim and Kang, 2008; Iriarte-Velasco et al., 2008; Bhatnagar and Sillanpää, 2017; Golea et al., 2020; Cuthbertson et al., 2019)~~.~~ Supplementing conventional treatment with GAC may be a promising adaptation approach for treating browning source waters, given its ability to minimize DBP formation even with high levels of NOM (Garcia and Moreno, 2009).

In addition to NOM removal processes, brownification may also impact the removal of metals including Fe and Mn. Previous work, including Chapter 4, has demonstrated the impact of brownification and increasing NOM concentration on metal cycling in lakes, where browner lakes experience concurrent increases in Fe and other metals (Anderson et al., 2021; Kritzberg et al., 2020; Bjorneras et al., 2017). NOM can form stable complexes with metals—Anderson et al. (2021) observed colloids of approximately 1 kDa that were identified as complexes of NOM and Fe in browning lakes, and although high DOC lakes were rich in Mn, it was present as larger colloids that were likely associated with Fe-oxides. Lyven et al. (2003) and Baalousha et al. (2011) also found that Mn was associated with NOM colloids. These colloids can interfere with removal via pre-oxidation, given that oxidants are typically applied to Fe and Mn that are in the reduced (soluble) form (Knocke et al., 1987; Cherry Leal et al., 2015). As brownification continues, drinking water providers may not only need to consider the direct impact of brownification on NOM removal processes, but also the secondary impacts on other treatment processes like pre-oxidation for the removal of Fe and Mn.

The objective of this work was to investigate changes in NOM removal due to various adaptation strategies for direct filtration facilities under the stress of surface water brownification. Specifically, we conducted a pilot-scale comparison simulating current full-scale plant conditions - direct filtration with anthracite/sand filters- to various brownification adaptation scenarios including 1) implementing sedimentation but keeping the anthracite/sand filters, 2) implementing sedimentation and adding GAC caps to anthracite/sand filters, and 3) implementing sedimentation and changing filter media to GAC. Given that trace metal removal may be impacted by brownification, a secondary objective was to assess the effectiveness of potassium permanganate as a pre-oxidant for the removal of Fe and Mn across the different treatment configurations.

5.3. Materials and methods

5.3.1. J.D. Kline Water Supply Plant and Pockwock Lake

The J. Douglas Kline Water Supply Plant (JDKWSP) is a direct filtration drinking water treatment plant operated by Halifax Water located in Nova Scotia, Canada. This facility is the largest water supply plant in Atlantic Canada with a design capacity of approximately 220 million litres per day (MLD) and an average flow of 85 MLD. The JDKWSP consists of pre-screening, pre-oxidation, coagulation, flocculation, and direct filtration. Since the facility was built in 1973, raw water has been treated with 0.15 mg/L as $KMnO_4$ (stochiometric dose for Fe and Mn) of $KMnO_4$ at a pH between 9.6 and 10 (achieved via the addition of lime) for oxidation of low levels of Fe and Mn. Pre-chlorination is used for seasonal control of algal biomass, although dosing is applied so that there is no free chlorine residual in the filter influent. Aluminium sulfate (alum) is the primary coagulant and is added at an average dosage of 18.5 mg/L Al_2SO_4. A target coagulation pH of 6.2 is achieved through the addition of CO_2. Cationic polymer (FLOPAM, SNF Canada) is applied to reduce floc time and maintain turbidity performance, at an average dosage ranging between 0.015 to 0.03 mg/L, and 0.05 mg/L during the winter. Coagulated water flows to a tapered three-stage flocculation basin, where flocculation occurs for a time ranging from 30 to 45 minutes. Coagulated water is then distributed between eight dual-media anthracite (600 mm, ES = 0.9 mm) and sand (300 mm, ES = 0.45 mm) filters.

The source water for the JDKWSP is supplied from Pockwock lake which has low nutrient content, low turbidity, pH, and alkalinity alongside moderate NOM concentration. In recent years, Pockwock Lake has been subjected to brownification through increasing NOM concentration (Anderson et al., 2017; DeMont et al., 2021). Raw water characteristics for the period of study

(May to December 2022), based on bi-weekly (e.g., twice per week) analysis, are presented in Table 3.

Table 3. Raw water characteristics during period of study (July to December 2022).

Analyte	n	Median	Range
pH	88	5.68	5.43-5.99
Turbidity – NTU	88	0.56	0.34-1.7
UV_{254} – cm^{-1}	86	0.093	0.079-0.118
TOC – mg/L	76	3.0	2.7-3.4
DOC – mg/L	65	2.8	2.6-3.5
SUVA – L-mg/m	65	3.1	2.6-3.6
Total Mn – µg/L	86	59.0	22.4-686.6
Dissolved Mn – µg/L	86	21.2	8.7-28.1
Total Fe – µg/L	82	50.7	23.3-196.5
Dissolved Fe – µg/L	82	15.0	7.5-37.7

*Due to supply chain issues with DOC filter papers, there were fewer DOC measurements relative to TOC, during the study period.

5.3.1.1. Pilot plant description

The JDKWSP is equipped with a research pilot plant which consists of two identical and parallel treatment trains (Figure 14), both capable of simulating direct filtration, with the added capacity to implement sedimentation. Each train independently carries out coagulation, flocculation, and filtration processes. Raw water coming from Pockwock lake feeding the full-scale plant is also used to feed the pilot plant, at an average of 10 L/min into each treatment train. Raw water first enters through a series of three rapid mechanical mixer tanks where chemicals such as lime, $KMnO_4$, and alum ($Al_2(SO_4)_3 \cdot 14H_2O$, Chemtrade) were dosed. Leaving the rapid mix tanks, water flows into a series of three 189 L mechanical flocculation tanks with paddle mixers and then into the optional sedimentation tank. The sedimentation tank is a 330 L basin with 30 adjustable plates with a settling area of 0.1 m^2. Flocculated or clarified water (depending on whether the clarifier was being operated) is then pumped to the filtration skid on each train. Each filtration skid consisted of three 200 mm filter columns through which the flow is evenly distributed at ~2.4 L/min per filter. Although periodic pre-chlorination was employed to control algal biomass during summer months, dosing was applied so that there was no available free chlorine residual in the filter influent, therefore, the filters were operated as passive biofilters. On each filtration skid, the first filter (labelled as Ant/Sand) contains 61 cm of anthracite (ES = 0.9 mm) and 30.5 cm of silica sand (ES = 0.52). The second filter (labelled as GAC/Ant/Sand) contains 30.5 cm of silica sand (ES = 0.52), 61cm of anthracite (ES = 0.9 mm), and is capped with 30.5 cm of GAC (ES = 0.8 to 1.0 mm). The third filter (labelled GAC/Sand) contains 61 cm of GAC (ES = 0.8 to 1.0 mm) and 30.5 cm of silica sand. The Ant/Sand filter and GAC/Sand filters had 12 min total EBCT, while the GAC/Ant/Sand had a total EBCT of 16 min. Prior to this study, the GAC/Ant/Sand filter was operated for approximately 26,700 Bed Volumes (BV) (based on a GAC EBCT = 4 min), while the GAC/Sand filter was operated for approximately 11,800 BV (based on a GAC EBCT = 8 min) which represented approximately 74 and 65 operational days, respectively. The GAC media was installed during the SARS-CoV-2 pandemic (April 2021), when sample collection for water quality parameters was limited due to restricted access to the facility. Figure D1 (Appendix D) provides a detailed schematic of the different filter configurations used in this study.

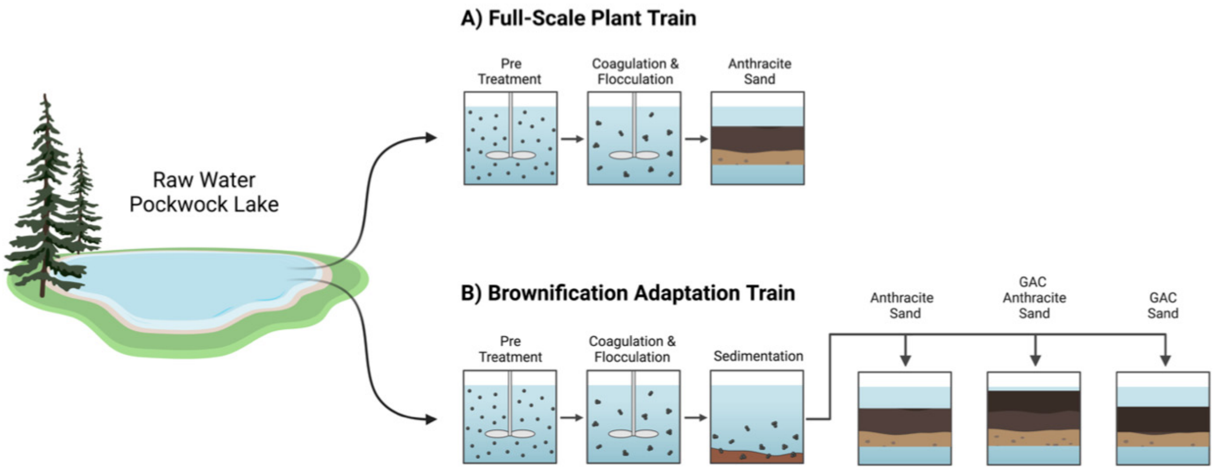


Figure 14. Schematic of pilot plant setup used in this study. The full-scale plant (FSP) train (A) mimics treatment conditions at the JDKWSP, while the adaptation train (B) was used to assess sedimentation and alternative filter configurations using granular activated carbon (GAC).

5.3.2. Experimental and operational procedures

For this study, one train (labelled as "Full-Scale Plant (FSP) Train") was used as a control and was operated as direct filtration to mimic the full-scale facility, where the sedimentation tank was bypassed and the flow from the last floc tank went directly to an anthracite sand filter (ANT/Sand). The second train (labelled as "Adaptation Train") was operated with sedimentation to allow for higher coagulant dosing and improved filter hydraulic performance. On this train we also assessed the use of GAC filter media (e.g., GAC/ANT/Sand, GAC/Sand). The study period ranged from early July to mid-December 2022. On both trains, the premix pH was maintained at 10.5 while the coagulation pH was maintained at 6.0 to 6.2 for the entire study period (collected pH data not reported in this study). Prior to this study, both pilot treatment trains were paired for one month so that they produced statistically equivalent water quality, according to Knowles et al. (2012).

A secondary objective was to assess Fe and Mn removal through the different treatment configurations given that trace metal removal efficacy may be impacted by brownification. To accomplish this, we varied chemical dosing (e.g., $KMnO_4$ and alum) on the adaptation train throughout four different study phases (Table 4) and assessed Fe and Mn removal during pre-treatment as well as across the filters.

Table 4. Chemical dosing and operational conditions for the FSP train and adaptation train used throughout the study period. The FSP train was operated as direct filtration under plant operating conditions for the entire study, while the adaptation train was operated as sedimentation with varied chemical dosing.

Phase	Date (2022)	Alum (mg/L)		$KMnO_4$ (mg/L)	
		FSP train	Adaptation train	FSP train	Adaptation train
A	July 5 – August 8	18	18	0.15	0.15
B	August 9 to October 2	18	30	0.15	0
C	October 3 to December 20	18	18-30*	0.15	0.15

*Alum dose was reduced back down to 18 mg/L due to operational issues with sludge accumulation and floc carryover in clarifier, and for maintenance. Alum dose was gradually increased back up to 30 mg/L during this period.

Throughout the study, 1-L samples were collected from the FSP train Ant/Sand filter and adaptation train Ant/Sand, GAC/Ant/Sand, and GAC/Sand filters near the end of a filter run. At the same time as filter sample collection, paired 1-L samples were collected from both the FSP train and the adaptation train from raw water (labelled as raw), and post flocculation or post clarification (labelled as prefilter). These samples were analyzed for pH, turbidity, UV_{254}, TOC, DOC, and total and dissolved Fe and Mn. In addition, SUVA (the UV absorbance at 254 nm normalized to DOC) was also used to understand the bulk properties of NOM across the treatment stages. Samples for disinfection by-product formation potential (DBPfp) were collected from raw and filtered water, also at the end of a filter run. Filter hydraulic performance was evaluated based on filter run time (FRT), unit filter run volume (UFRV), as well as turbidity and head loss profiles measured via in-line sensors. The end of a filter run was based on either reaching turbidity breakthrough (>0.2 NTU), terminal head loss (>2.15 m), or run time (80 hours), which are the same setpoints used at full-scale. Filters were backwashed with filter effluent. Backwash consisted of an air scour phase, a combined air scour and water wash phase, and three water wash phases.

5.3.3. Analytical procedures

The pH (Accumet XL50, Fisher Scientific), turbidity (2100 AN, HACH) and UV_{254} (DR4000 UV/VIS spectrophotometer, HACH) were measured immediately after sample collection. Before analysis, UV_{254} samples were filtered through a 0.45-μm polyethersulfone (PES) filter membrane that had been pre-rinsed with 500 mL of deionized water. TOC and DOC on samples were prepared according to Standard Methods (5310) (APHA, 2005) and measured with a TOC analyzer (Shimadzu TOC-V_{CPH}). All metal samples were acidified to a pH below 2 using nitric acid (Trace MetalGrade, Fisher Scientific) for <16 hr then measured for total and dissolved concentrations via inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo Scientific iCAP™ RQ ICPMS), having a reported detection limit of 0.67 μg/L for Fe and 0.12 μg/L for Mn. Dissolved metals were filtered through a PES 0.45-μm filter membrane that had been pre-rinsed with 500 mL of deionized water. Soluble Fe and Mn in the text refer to 0.45 μm filtrate. Samples from summer (July 2022) and fall (November 2022) were characterized for Fe and Mn colloids using field flow fractionation coupled with UV and ICPMS detection, as described in Chapter 4 and Anderson et al., (2021).

Samples for trihalomethane formation potential (THMfp) and haloacetic acid formation potential (HAAfp) were prepared following an adapted version of Standard Methods (5710) (AHPA,2005). Samples were buffered to pH 8 and chlorine was dosed such that the free chlorine residual was 1.0 ± 0.4 mg/L after a 24-hour incubation period (Summers, 1996). The concentrations of HAAs and THMs were measured using gas chromatography with electron capture (US Environmental Protection Agency methods 552.2 and 551.1, respectively). Samples were analyzed for four THM compounds: chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform, and for 9 haloacetic acids (HAA9): monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA) and tribromoacetic acid (TBAA). Reported detection limits for THMs were 8.0 μg/L for chloroform, BDCM, DBCM, and bromoform, and 3.0, 2.0, 2.5, 2.5, 2.5, 3.0, 3.0, 3.0, and 3.0 for MCAA, MBAA, DCAA, TCAA, BCAA, DBAA, BDCAA, CDBAA, and TBAA, respectively.

5.3.4. Statistical analyses

Experimental data were analyzed using R (Version 1.4.1717) (R Core Team, 2023). Two-sided Wilcoxon-signed rank tests were used to compare samples under the assumption that repeated measurements from individual trains were independent. The level of significance for all statistical tests was 0.05. Data in this text are reported as median and interquartile range (IQR).

5.4. Results and discussion

5.4.1. Pilot-scale evaluation of brownification adaptation strategies for direct filtration facilities

5.4.1.1. Implementing sedimentation and GAC adsorption for improving NOM removal

Previous work reported increased DOC concentration through brownification in Pockwock Lake (Anderson et al., 2017) and broadly in many lakes in Nova Scotia (Redden et al., 2021). Since the early 2000's, DOC increased from ~2.3 to 2.7 (Anderson et al., 2017) to 4.1 mg/L (this study) in Pockwock Lake. Pilot scale direct filtration fed 18 mg/L of alum performed similarly to the FSP and was used as the basis of comparison for the adaptation train (Figure 15, Table D1 in Appendix D). Increasing the alum dose to 30 mg/L and utilizing sedimentation created a small but significant improvement to UV254 removal (FSP train median 68.2%, IQR 5.4%), adaptation train (median 70.9%, IQR 5.3%). Differences in DOC removal was not significant and both trains produced similar water quality after pre-treatment with DOC < 2 mg/L and UV254 < 0.03 cm^{-1}. Enhanced coagulation removed a substantial portion of the humic NOM, as evidenced by the ~40% reductions in which is typical for coagulated waters (Edzwald and Tobiason, 1999). The Ant/Sand filters on the FSP and adaptation train did not provide improved NOM removal relative to pre-treatment.

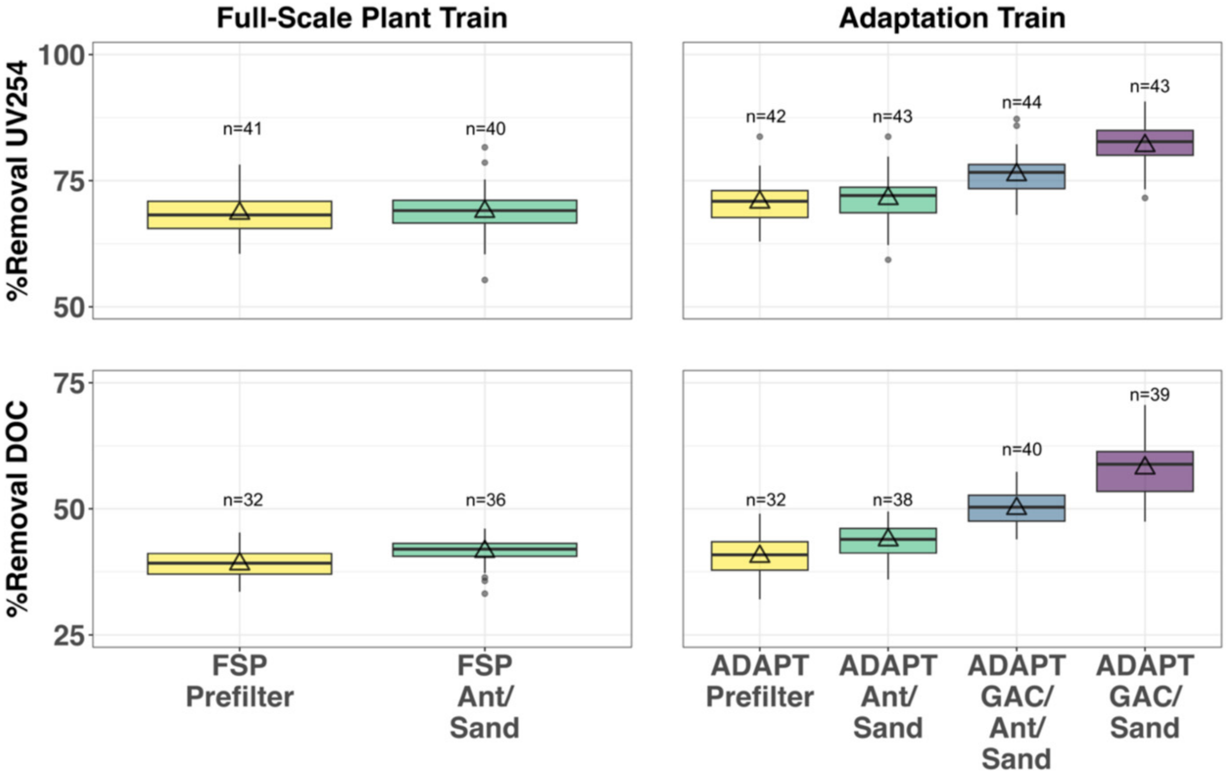


Figure 15. UV254 (top) and TOC (bottom) removal (from raw water levels) on the FSP train (direct filtration with anthracite/sand filters, left) and the adaptation train (sedimentation with anthracite/sand, GAC/Ant/Sand and GAC/Sand filters, right). Triangle indicates mean values. Median raw water UV254 and DOC were ~0.094 cm^{-1} and ~3 mg/L, respectively. Percent removal values below zero were omitted.

As expected, the GAC filters on the adaptation train provided statistically significant improvements in DOC and UV254 removal in comparison to the Ant/Sand filters. Specifically, the Ant/Sand filter with a GAC cap provided median removals of 76.6% (IQR 4.8%) of UV254 (filtered water median concentration of 0.023, IQR 0.004 cm^{-1}) and 50.2% (IQR 5.3%) of DOC (1.5 mg/L), while the full GAC filters removed median 82.7% (IQR 4.9%) of UV254 and 58.8% (IQR 7.9%) of DOC. This is comparable to previous work (Bridgehouse et al., 2023) who observed improved NOM removal from the addition of shallow GAC caps (15 cm) on conventional filters as well as Thomson (2019) who observed improved NOM removal performance in a full GAC/Sand filter compared to a GAC capped anthracite filter.

Median THMfp and HAAfp on the FSP train Ant/Sand filter were 58.9 μg/L (IQR 10.7 μg/L) and 23.9 μg/L (IQR 1.8 μg/L), respectively, and were not significantly different than the Ant/Sand filter on the adaptation train (Figure 16). In comparison, the GAC/Ant/Sand filter and GAC/Sand filter had considerably lower median THMfp at 41.5 μg/L (IQR 4.1 μg/L) and 34.8 μg/L (IQR 3.1 μg/L), respectively, as well as HAAfp of 18.5 μg/L (IQR 3.7 μg/L) and 13.2 μg/L (IQR 3.3 μg/L) (Figure 3). These results are in line with other work that have demonstrated the effectiveness of GAC for controlling THMs and HAAs and DBP precursor material (Cuthbertson et al., 2019; Marais et al., 2018; Fu et al., 2017; Liu et al., 2017). All filters produced THMfp and HAAfp concentrations well below the regulatory limits of 100 and 80 μg/L, respectively (Health Canada, 2006; Health Canada, 2008), however THMfp and HAAfp are not always representative of true distribution system DBP concentrations. Regulations for THMs and HAAs are expected to become more stringent, and the use of GAC caps or full-GAC media replacement may be a promising adaptation strategy.

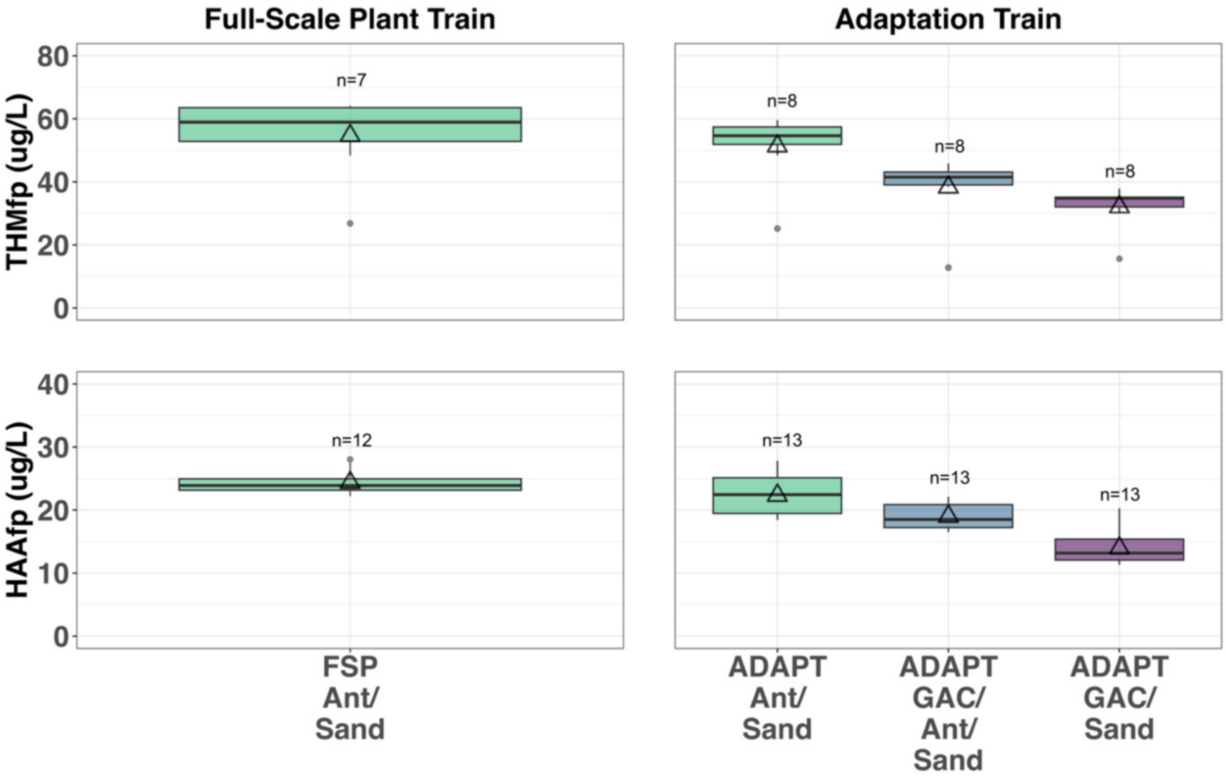


Figure 16. Filtered water THM formation potential (top) and HAA formation potential (bottom) for the FSP train (direct filtration with anthracite/sand filters, left) and adaptation train (sedimentation with anthracite/sand, GAC/Ant/Sand, and GAC/Sand filters, right). Triangle indicates mean values. Median raw water THMfp and HAAfp were ~143 and ~86-103 μg/L, respectively.

One of the downsides of using GAC media is the saturation of adsorption sites, requiring routine regeneration and/or replacement which can be costly to utilities. The GAC media used in this study had been operated previously (26,700 BV for the GAC/Ant/Sand filter and 11,800 BV for the full GAC filter), therefore media exhaustion in terms of NOM removal was also assessed throughout the study period (Figure 17). At the beginning of this study the GAC/Ant/Sand filter was partially exhausted, removing ~25 to 30% of DOC (from prefilter values) and was reduced to <10% for by the end of this study (total of ~63,000 BV cumulative, EBCT ~ 4 min for GAC). The full-GAC filters were also partially exhausted, removing ~50 to 60% of DOC and decreased to approximately ~15 to 20% for DOC and (~27,000 BV cumulative, EBCT ~8 min for GAC) by the end of the study. Babi et al. (2007) observed a GAC bed life of ~63,000 BV (EBCT ~9.5 min), while Terry and Summers (2018) reported ~75,000 BV for GAC exhaustion (EBCT ~ 10 min). Conversely, Doederer et al. (2017) reported exhaustion at lower BVs (~30,000, EBCT ~10 min), as did Golea et al. (2020) (>20,000 BV, EBCT ~20 min). Cuthbertson et al. (2019) noted that GAC was effective for removing DBP precursor material and reducing DBP formation even after treating >20,000 BV (EBCT ~15 to 20 min).

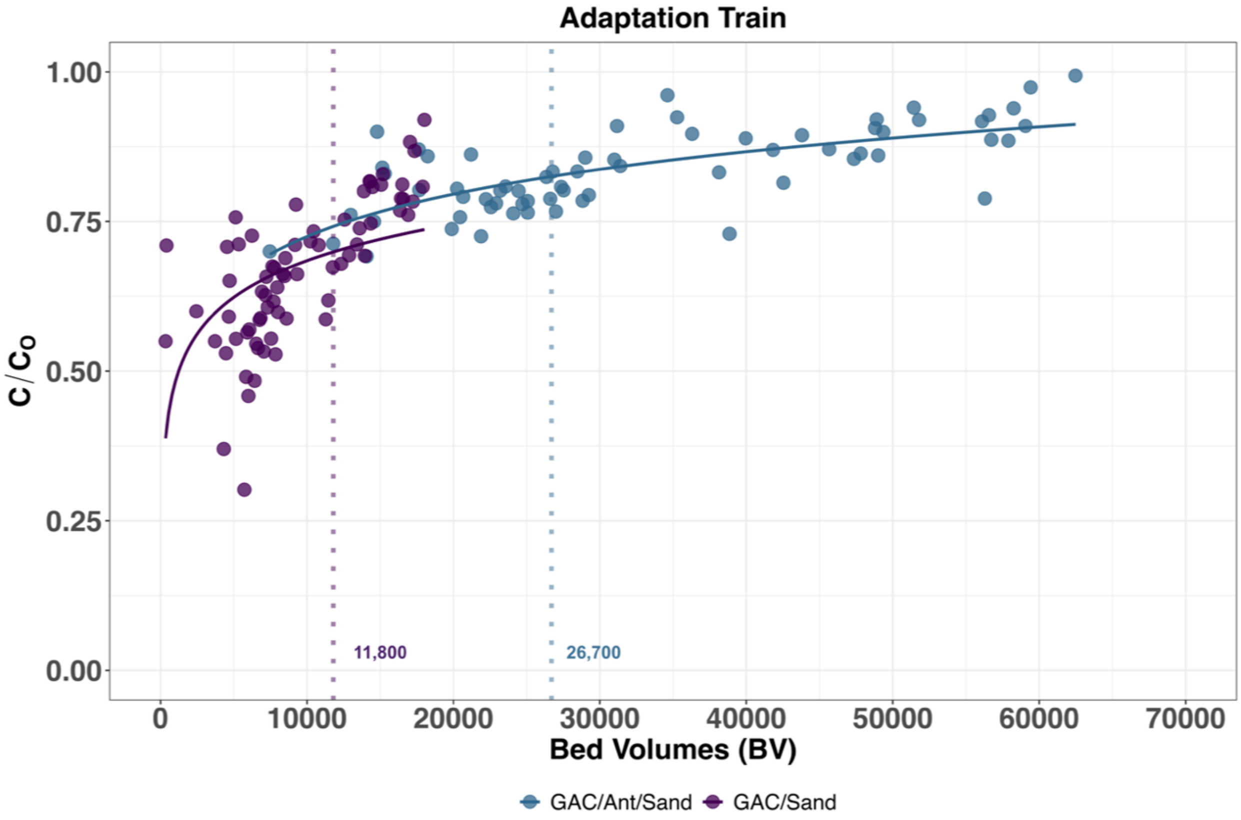


Figure 17. NOM removal rates (from pre-filter values) of GAC/Ant/Sand (blue) and GAC/Sand (purple) filters on the adaptation train. Median filter influent was C_o=1.7 mg/L. Prior to this study, the GAC/Ant/Sand filter was operated for 26,700 BV (GAC EBCT = 4 min) and the GAC/Sand filter for 11,800 BV (GAC EBCT = 8 min), as indicted by the vertical dashed lines.

Accordingly, the GAC/Ant/Sand filter in this study appears to be at or close to exhaustion for NOM removal and may be near the end of its operational life, while the GAC/Sand filter may continue to have some capacity to remove NOM. Despite being close to saturation, it outperformed the conventional filters. Some of this removal may be driven by biodegradation as opposed to adsorption (Korotta-Gamage & Sathasivan, 2017; Brown et al., 2020; Anderson et al., 2022) given that these filters are passive biofilters (e.g., no free chlorine residual in filter influent).

Information on the hydraulic performance of the different filter configurations is provided in the SI (Figure D2). All filters had comparable filter effluent (<0.1 NTU). The adaptation GAC/Ant/Sand filter had the longest FRT (median 69.7 h, IQR 14.1 h) and highest UFRV (median 313 m^3/m^2, IQR 57.8 m^3/m^2) with comparable or better performance in terms of head loss accumulation (median 1.98 m, IQR 0.28 m) relative to the other study filters (Table D5, Table D6, Appendix D).

5.4.1.2. Assessing Fe and Mn removal across the various adaptation strategies

Figure 18 depicts dissolved (0.45 µm filtrate here and throughout the text) Mn and Fe removal during pre-treatment for the different study phases. During Phase A, $KMnO_4$ was dosed on both trains at 0.15 mg/L as $KMnO_4$. The removal of dissolved Fe during pre-treatment on both trains was comparable and not significantly different (median 77% (IQR 7.8%) for FSP and 79.5% (IQR10.7%) for adaptation) (Figure 18, Table D2 and D4). However, there was little removal of dissolved Mn (median 5.9% (IQR 3.7%) on the FSP train and 11.7% (IQR 11.8%) on the adaptation train), and differences were not significant (Table S4). During Phase B the FSP train continued receiving 0.15 mg/L as $KMnO_4$, while the adaptation train received no $KMnO_4$ but increased the coagulant from 18 to 30 mg/L as alum. Like Phase A, the removal of dissolved Fe during pre-treatment was comparable on both trains (median 70.7% (IQR 6.3%) on FSP train, 67.9% (IQR 11.3%) on the adaptation train). On the FSP train, there was substantial increase in dissolved Mn concentration (up to 93%) after the addition of $KMnO_4$ (median -7.4%, IQR 61.3%) although high variability in these measurements meant they were not significant (Table D4) compared to the adaptation train (median -2.3%, IQR 7.1%). Finally, during Phase C, both the FSP train and the adaptation train received 0.15 mg/L as $KMnO_4$ (like Phase A). Like in previous phases, the removal of dissolved Fe was comparable FSP (median 81.6%, IQR 9.9%) and adaptation trains (median 80.5%, IQR 16.4%). The removal of dissolved Mn through $KMnO_4$ addition during this phase was significantly higher on both the FSP (median 39.9%, IQR 26.2%) and adaptation trains (median 35.7%, IQR 23.3%) compared to previous phases.

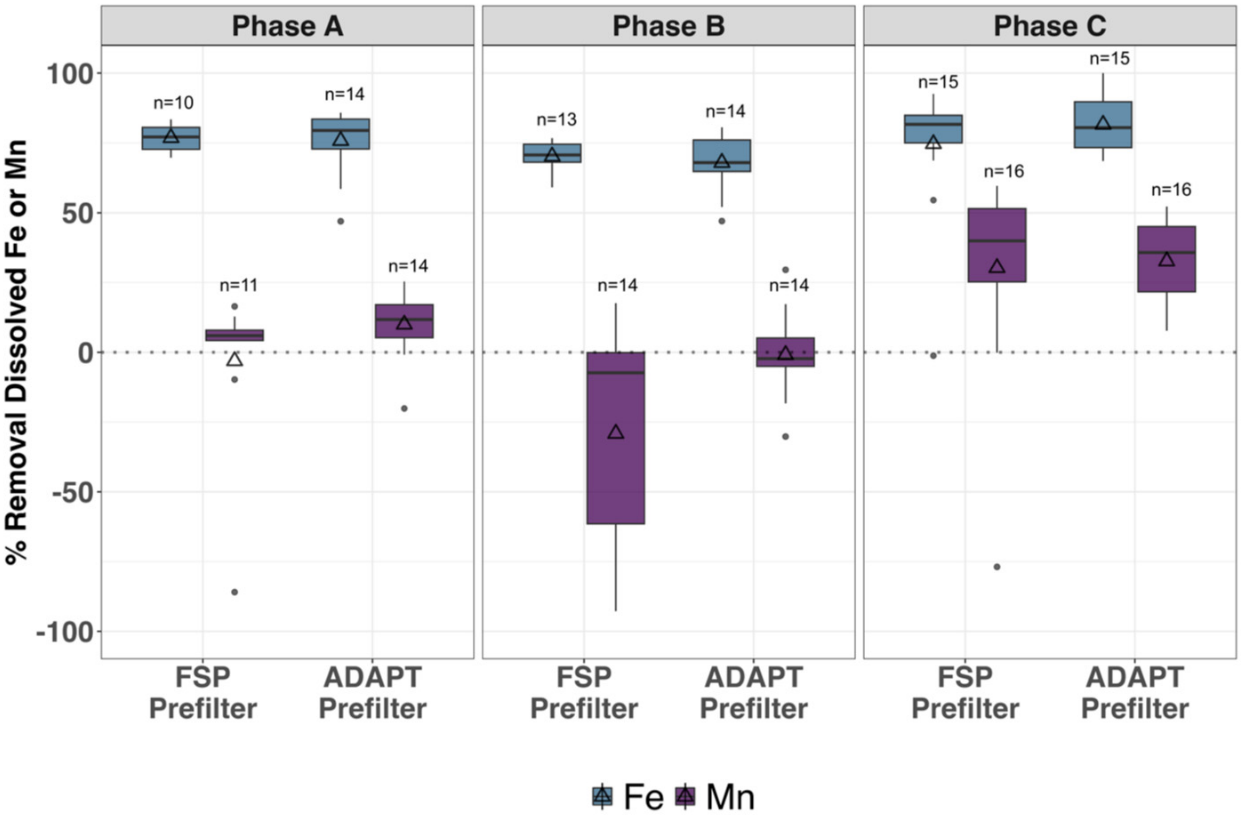


Figure 18. Dissolved (<0.45 µm) Fe and Mn removal during pre-treatment on the FSP (direct filtration) and Adaptation (sedimentation) trains. During Phases A (July 5 to August 8) and C (October 3 to December 20), $KMnO_4$ was dosed at 0.15 mg/L on both trains, while during Phase B (August 9 to October 2), $KMnO_4$ was turned off on the adaptation train. Mean values are indicated by triangles.

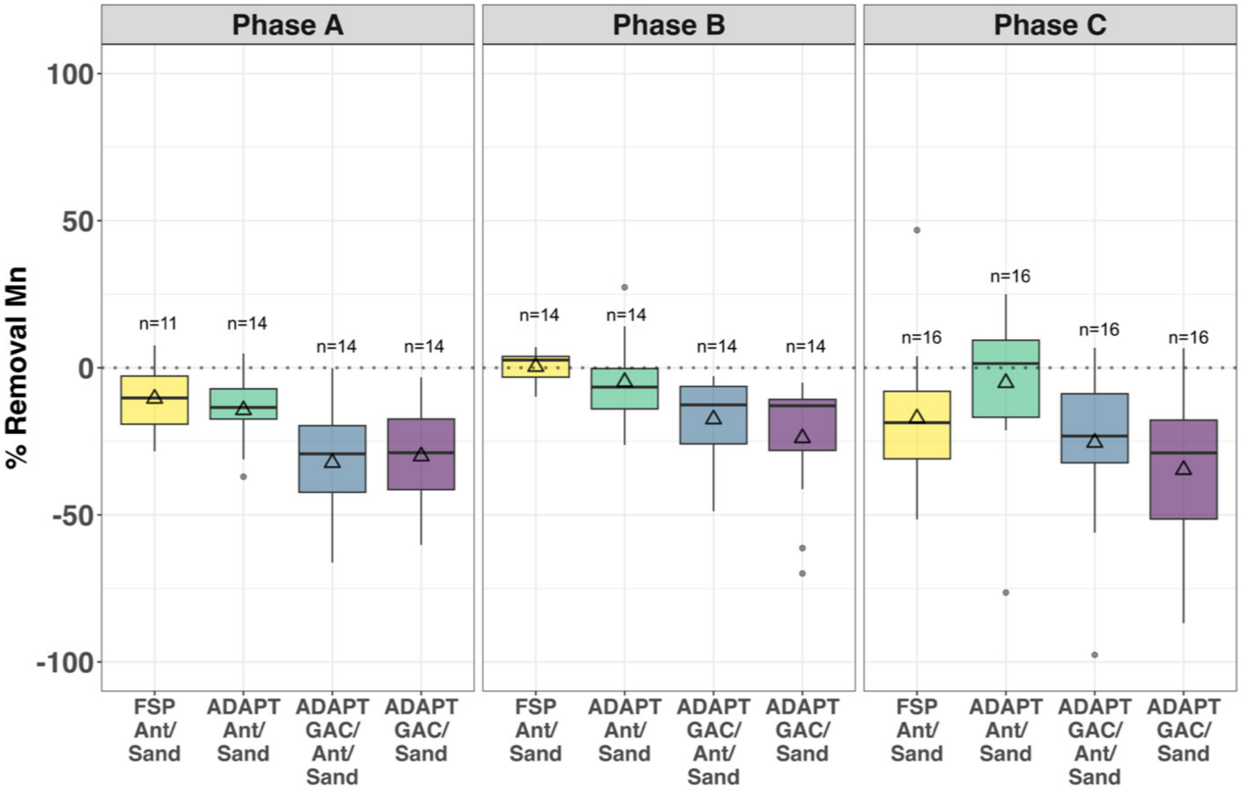
It is hypothesized that a lack of dissolved Mn removal during Phases A and B may be attributed to the presence of colloidal (as opposed to soluble) Mn in the raw water, rendering the addition of $KMnO_4$ ineffective (Carlson et al., 1997). Carlson et al. (1997) observed similar outcomes at a facility that was dosing $KMnO_4$ when the raw water Mn was already oxidized (e.g., colloidal). The instances of increase in dissolved Mn on the FSP train (Phase B) also indicates the presence of soluble $KMnO_4$ species that may be a result of overdosing (in the absence of dissolved Mn) (Carlson et al., 1997). The improvements of dissolved Mn removal in Phase C are likely a result of a change in Mn speciation during seasonal turnover. The raw water intake for the

JDKWSP is at mid-depth, and therefore when the lake is stratified in the summer (Phases A and B) would be drawing from the epilimnion where the majority of Mn would be oxidized and in a colloidal form. When the lake mixes during seasonal fall turnover (Phase C), soluble Mn from the hypolimnion mobilizes throughout the water column (Tobiason et al., 2016) and would be the dominant form of Mn in the raw water. Eventually the Mn would return to its oxidized, colloidal state when the lake reaerates and there is no longer an anoxic zone in the hypolimnion. The consistent removal of dissolved Fe across all phases regardless of $KMnO_4$ addition implies that it was likely colloidal and removed through coagulation. Previous work in the region (Anderson et al., 2021) demonstrated that colloidal Mn and Fe in the 1000+ kDa size range was predominant in browning surface waters. Attempts were made to characterize colloidal Fe and Mn in the raw water during this work using field flow fractionation coupled with UV and ICPMS detection as described in Chapter 4, and showed similar results as Anderson et al., (2021) for Fe, with Fe-NOM colloids present at 1 kDa and Fe oxides at 1000 kDa, confirming that Fe was present as colloidal material as opposed to dissolved Fe (Figure D). However due to low Mn concentration the signal presented as noise and was not interpretable.

Further, we would have observed higher dissolved Mn after pre-treatment, and/or discolored water, if excess Mn were simply a function of permanganate overdosing or a lack of oxidant demand. Instead, we often observed increases (in some cases >100%, Table D2) in total Mn after pre-treatment, which suggests that $KMnO_4$ was reacting with something other than soluble Mn^{2+} (which as described previously was hypothesized to be unavailable in the raw water). Permanganate can react with various constituents including NOM to form colloidal Mn oxides (Tobiason et al., 2016; Chen et al., 2018). Such colloids are finely dispersed and may have an impeded ability (compared to organic Fe colloids) to be removed through conventional processes

(Cherry Leal et al.,2015; Chiswell and Huang, 2006). In this study, it is possible that natural Mn colloids as well as those generated through ineffective $KMnO_4$ treatment were poorly removed, resulting in their accumulation in downstream processes.

Dissolved Mn and Fe removal across the different filter configurations were also assessed (Figure 19a and 19b). In all the phases, the filters typically released dissolved Mn (total Mn $\approx$ Mn < 0.45 μm) relative to the filter influent (Figure 19a). Median Mn release was significantly worse from the filters when $KMnO_4$ was applied (e.g., Phases A and C). Further, there was some release of dissolved Mn even when $KMnO_4$ was not added (Phase B), likely due to previously accumulated MnO_x on the filters. The Ant/Sand filters on the FSP and adaptation trains typically released comparable amounts of Mn when $KMnO_4$ was on. For example, the FSP Ant/Sand filter released median 10.3% (IQR 16.3%) and 118.7% (IQR 22.9%) during Phases A and C, and the adaptation Ant/Sand filter released 13.5% (IQR 10.3%) during Phase A. This was in exception to Phase C, where the adaptation Ant/Sand filter did not release Mn (median 1.5%, IQR 26.2%). Further, the GAC filters typically more dissolved Mn compared to the Ant/Sand filters and was often worse on the GAC/Sand filter. The adaptation GAC/Ant/Sand released up to 29.3% (IQR 22.6%), while the GAC/Sand released comparable amounts. This may be caused by higher accumulation on GAC media due to favourable surface interactions in the porous media compared to anthracite (McCormick et al., 2021). The filters typically released dissolved Mn at levels that were often higher than the filter influent and raw water concentrations (Table D2), which negates any removal achieved through $KMnO_4$ treatment. There was no substantial release of dissolved Fe from the filters (Figure 19b) and there were there were no significant differences in Fe removal across the different filter configurations within the phases. Dissolved Fe removal was highest during Phase B, with median removals between ~16 and 18% (Figure 19b, Table D2). This was likely because the colloidal Fe present in raw water was effectively removed during pre-treatment, resulting in less accumulation of Fe-NOM and Fe oxide colloids on the filters.



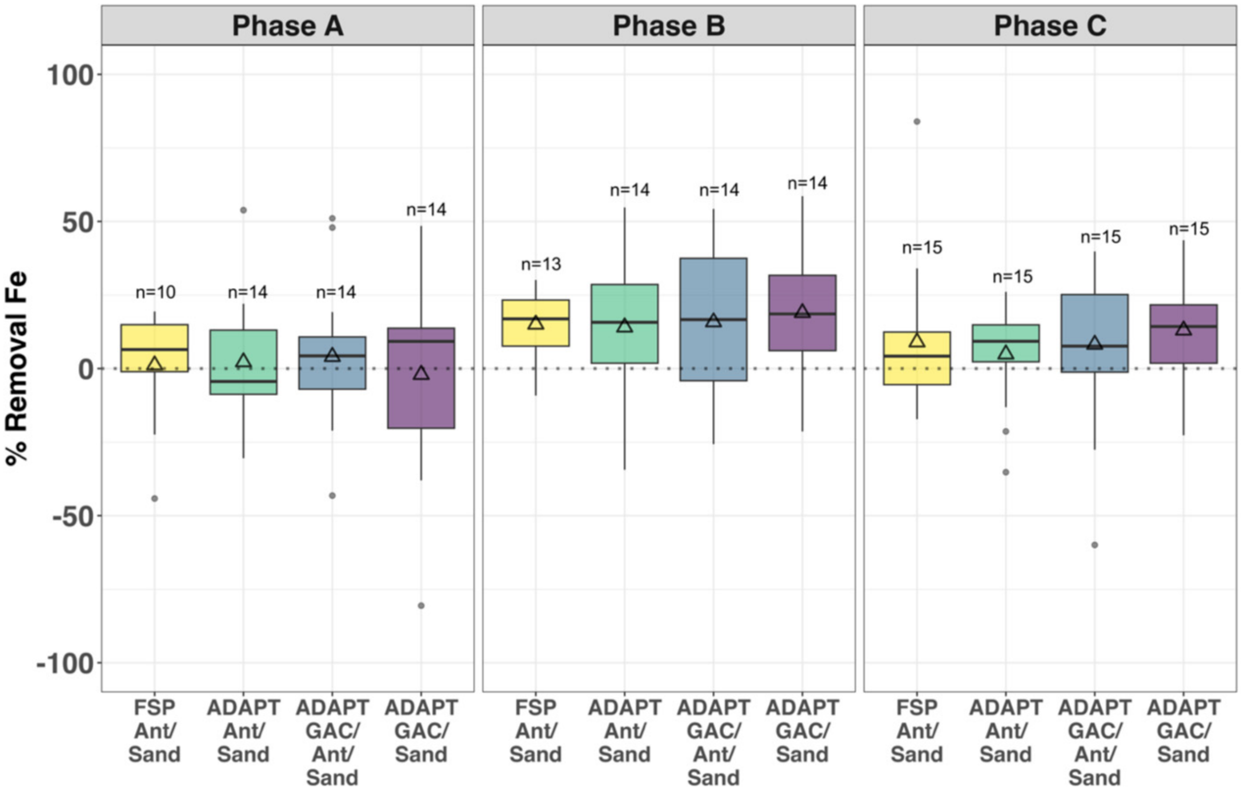


Figure 19 a and b. Dissolved (<0.45 µm) Mn (top, 19a) and Fe (bottom, 19b) removal from prefilter levels through on the FSP Ant/Sand filter compared to the adaptation train filters including Ant/Sand, GAC/Ant/Sand, and GAC/Sand. During Phases A (July 5 to August 8) and C (October 3 to December 20), $KMnO_4$ was dosed at 0.15 mg/L on both trains, while during Phase B (August 9 to October 2), $KMnO_4$ was turned off on the adaptation train. Mean values are indicated by triangles.

Carlson et al. (1997) found similar results at a treatment facility that was applying $KMnO_4$ to Mn that was not in truly soluble, also observing dissolved Mn release from filters. However, the authors attributed this to the microbiological reduction of Mn by anaerobic activity in the clarifier (Carlson et al., 1997). In this work, a substantial increase in dissolved Mn during pre-treatment (aside from Phase B) was typically not observed, and therefore we believe that dissolved Mn release was isolated to the filters. Accordingly, it is hypothesized that the previously mentioned ineffective $KMnO_4$ addition during pre-treatment contributed to the accumulation of MnO_x

(possibly formed through the reaction of MnO_4^- with NOM or other constituents aside from dissolved Mn and Fe) and eventual release of soluble Mn^{2+} from the filters.

Most studies reporting the release of dissolved Mn involve transition to biofiltration (Gabelich et al., 2006; Kohl and Dixon, 2012) through the termination of pre-chlorine used to promote Mn^{2+} surface adsorption followed by catalytic oxidation on the MnO_x surface (e.g., catalytic Mn filtration). There was no pre-chlorination during our study. However, other significant chemical or biological changes in the filters can cause the release of Mn into the treated water (Arnold et al., 2021). For example, a change in the redox (e.g., oxidation reduction potential) in the filters could cause the dissolution of the accumulated MnO_x on the filter media. Since the oxidation of Mn to insoluble oxides is reversible, a very positive oxidation reduction potential would need to be maintained across the filters to avoid reducing conditions. An electrode potential (E_H) of >0.5 V at pH would be required would be required to maintain MnO_x on the filters or would require pH adjustment to >7 (Mouchet, 1992), and therefore low redox conditions resulting in the dissolution of MnO_x to Mn^{2+} is a possible explanation for elevated dissolved Mn in the filter effluent. Additionally, this E_H and pH borders the region where $Fe(OH)_3$ is stable, where slight reductions in E_H at pH 6 would cause the dissolution of Fe^{2+}. This could explain why there was some periodic but inconsistent release of Fe from the filters in this study, in comparison to Mn.

An alternative explanation for dissolved Mn release from GAC media could be competitive adsorption- desorption equilibria or displacement of Mn. For example, higher NOM concentrations can result in earlier breakthrough of GAC for some co-contaminants due to competitive adsorption (Kennedy et al., 2021). Accordingly, the competitive adsorption of between NOM and Mn could force any previously adsorbed Mn, naturally occurring MnO_x, or Mn oxides formed through reactions between $KMnO_4$ and NOM, to be displaced back into solution as Mn^{2+}. As shown on the breakthrough curves for dissolved Mn (Figure 20), it is evident that there was no breakthrough curve for Mn – the filters were consistently releasing Mn ($C/C_o>1$), particularly when $KMnO_4$ was on (Phases A and C). Since we hypothesized that the Mn in this study was likely colloidal in nature, adsorption would not be the dominant removal mechanism. Colloidal Mn is more likely to be trapped in the GAC pores as precipitates, or within the biofilms, and released as dissolved Mn if redox conditions favoured dissolution. Given that the inert anthracite filters also released Mn, it is likely that competitive adsorption/desorption was not the dominant mechanism for dissolved Mn release from the filter media. However, measurements from the virgin GAC were unavailable for this study and therefore the initial adsorption capacity and exhaustion cannot be assessed.

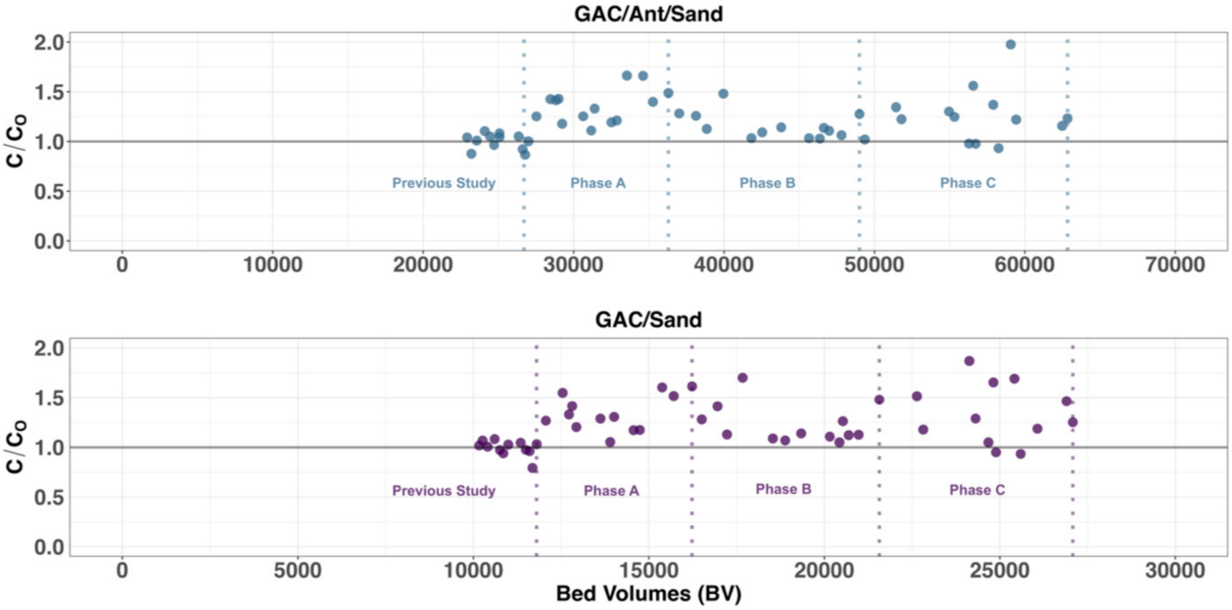


Figure 20. Mn removal rates (from pre-filter values) of GAC/Ant/Sand (blue) and GAC/Sand (purple) filters on the adaptation train. During Phases A and C, $KMnO_4$ was dosed at 0.15 mg/L, while during Phase B $KMnO_4$ was turned off. Median filter influent was C_o=14 to 24 µg/L. Prior to this study, the GAC/Ant/Sand filter was operated for 26,700 BV (GAC EBCT = 4 min) and the GAC/Sand filter for 11, 800 BV (GAC EBCT = 8 min), with no $KMnO_4$ pre-treatment.

5.5. Conclusion

The use of GAC caps or full-GAC media replacement may be a promising alternative to direct or conventional filtration (e.g., Ant/Sand) for adapting to brownification of source waters, outperforming direct filtration with Ant/Sand, providing between ~50 and 59% (median, from raw water levels) removal of DOC and ~77 to 83% of UV254. The GAC filters also had the greatest reduction in DBPfp with THMfp concentrations between 35 and 41 μg/L and HAAfp between 13 and 18 μg /L for GAC/Ant/Sand and GAC/Sand, respectively.

However, the release of dissolved Mn (<0.45 μm), particularly from GAC filters could be a major unintended consequence of converting to GAC media as an adaptation strategy for source water brownification. It was hypothesized that due to the presence of colloidal Mn (e.g., not soluble), the addition of $KMnO_4$ was ineffective for Fe and Mn removal. When $KMnO_4$ was not added, there was no change in the removal of dissolved (<0.45 μm) Mn. It was hypothesized that $KMnO_4$ reacted with humic NOM or other substances to generate MnO_x colloids that were deposited onto the filters due to insufficient colloid removal during pre-treatment. The filters typically released dissolved Mn at levels higher than the influent and negated any removal that occurred during pre-treatment, and the GAC filters released more dissolved Mn than the anthracite filters.

For this facility, implementing GAC adsorption (in the presence of ineffective $KMnO_4$) to improve NOM removal considering brownification would result in a new water challenge for the utility. It may be beneficial for the utility to only dose $KMnO_4$ seasonally when a portion of Mn is truly dissolved, during lake turnover. Optimizing the removal of naturally occurring Mn colloids through coagulation and clarification may reduce Mn release from filters. Alternative clarification strategies such as dissolved air flotation could also improve the removal of colloids**.** Further, the use of an alternative oxidant (e.g., ozone) ahead of the filters to stabilize any residual MnO_x could also minimize the release of soluble Mn from filter media. The use of chlorine as a pre-filter oxidant is not recommended given the potential for increased DBP formation with continued browning of surface waters. The continued use of $KMnO_4$ in the full-scale plant is possibly resulting in the release of soluble Mn to finished water and eventual accumulation of colloidal or particulate Mn in the distribution system, which is a concern given the potential for legacy manganese issues, as well as the risk for increased lead release (Trueman et al., 2019).

This work demonstrates the importance of source water characterization in terms of fractionating Fe and Mn (e.g., total, colloidal, and truly dissolved), which would inform the appropriate use of $KMnO_4$ or alternative technologies for Fe and Mn control. This is becoming even more relevant considering that the binding capacity of NOM for metals may be increasing with time through brownification (e.g., increasing humic NOM with a greater density of metal binding sites (Anderson et al., 2021). It also emphasized the importance of monitoring redox conditions across filters (Earle et al., 2020). This work highlights the source water complexities that are anticipated under emerging climate change pressures and the need for considering robust adaptation water treatment solutions that can accommodate brownification.

6. CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

This research was guided by the following research questions:

1. How is water quality in drinking water reservoirs and surface waters in Nova Scotia responding to anthropogenic pressures such as atmospheric deposition and climate change?
2. What are the vulnerabilities to surface drinking water treatment systems in Nova Scotia in response to changing source water quality, including brownification?

These questions were addressed through a series of objectives that focused on the concept of brownification of surface drinking water supplies because of reduced atmospheric acid deposition and climate change pressures, and the subsequent impacts on drinking water treatment.

6.1.1. Research Question 1: How is water quality in drinking water reservoirs and surface waters in Nova Scotia responding to anthropogenic pressures such as atmospheric deposition and climate change?

Through the work in Chapter 2, over 100 peer-reviewed publications were reviewed to understand the drivers of brownification and subsequent impacts to drinking water treatment. A summary of key conclusions from this work were that increasing NOM concentration and brownification are prevalent throughout the northern hemisphere, including Europe, the United States, and eastern Canada. Through this review, hundreds of surface waters have been identified as experiencing brownification. Key drivers of brownification trends identified were the reduction in atmospheric acid deposition (e.g., recovery from acidification), in addition to climate change (e.g., warming temperature, increasing precipitation) and changing land use, primarily related to forestry. This work highlighted that as atmospheric acid deposition stabilizes, other drivers, particularly climate change, will become increasingly important.

Chapter 3 examined historical atmospheric acid deposition (e.g., SO_4) in Atlantic Canada over the period from 1999-2015, as well as the associated water quality responses in two large surface drinking water supplies with an emphasis on NOM. A summary of key conclusions from Chapter 3 were that SO_4 deposition in Atlantic Canada has decreased significantly (nearly 70%), resulting in slight improvements in pH (0.1 to 0.4 units). It was determined that these drinking water supplies are "recovering" from their previously acidified state, and because of reduced acid inputs there has been a substantial increase in NOM concentration in both supplies. Specifically, the color concentration in Pockwock Lake and Lake Major increased by 1.7 and 3.8-fold, respectively, which had major implications for the treatment facilities drawing from these lakes.

In Chapter 4, field-flow fractionation coupled with UV and ICP-MS detection was used to measure the size distribution of colloidal metals and NOM in six lakes with a range of DOC concentration (low DOC 0.3 to 6 mg/L, high DOC 6 to 9 mg/L). Key conclusions from this work were that the lakes in this study were also found to be undergoing brownification in recent decades, which was in line with findings in previous work (Chapters 2 and 3). Five of the six lakes underwent brownification since the 1990's, with increases in DOC and color ranging from 0.01–0.13 mg C/L-yr and 0.13–1.94 PtCo/yr. Through FFF-UV-ICPMS, two primary fractions were identified – a 1 kDa fraction primarily included NOM and significant quantities of iron and aluminum, suggesting that NOM colloids bind Fe and Al, and a 1000+ kDa fraction that had minimal NOM signal and represented colloidal Fe and Mn that was likely associated with Fe rich colloids. Through brownification processes, there will likely be more humic NOM with a greater density of metal binding sites, making colloid characterization increasingly important for drinking water providers.

Accordingly, through anthropogenic pressures including declining atmospheric deposition and climate change the quality of drinking water reservoirs are experiencing brownification, which is expected to have a substantial impact on drinking water treatment processes as discussed below.

6.1.2. Research Question 2: What are the vulnerabilities to surface drinking water treatment systems in Nova Scotia in response to changing source water quality, including brownification?

In Chapter 2, the impact of brownification on surface drinking water treatment processes were evaluated through a in depth review of peer reviewed publications examining hundreds of surface waters in the northern hemisphere, and demonstrated that because of changing source water quality, and brownification, drinking water providers may be challenged with increasing chemical dosing (e.g., coagulant) to overcome elevated NOM load, which can impact filter operations. Without adequate NOM removal, utilities may be faced with increased formation of DBPs. This work revealed the vulnerabilities of conventional treatment facilities, which were typically designed based on historical water quality which is no longer representative. As a result of changes in NOM concentration and potential shifts in character, treatment plants may be under designed and unable to accommodate increased NOM loads without compromising downstream treatment processes. This work identified a need for long-term solutions and a transition towards robust treatment technologies and solutions that can adapt to climate change and other drivers of changing water quality. More advanced treatment technologies including adsorption via GAC, ion exchange (e.g., MIEX), membranes (UF and NF), as well as advanced oxidation processes will become more relevant as water quality continues to change.

In Chapter 3, the brownification (1.7 to 3.8-fold increases in color) of drinking Nova Scotia water reservoirs associated with reductions in atmospheric acid deposition corresponded directly with increases in coagulant demand at both facilities (1.5 and 3.8-fold for the JDKWSP and LMWSP, respectively), and compromised filter performance at the JDKWSP which is a direct filtration plant. This work also found the JDKWSP on Pockwock Lake to already be operating at the upper limit of the recommended direct filtration thresholds, highlighting a need for upgrades to accommodate changes in source water quality. This work also demonstrated that drinking water utilities in regions challenged with brownification and increasing NOM will be faced with increasing costs associated with chemical consumption, but environmental costs associated with increased energy and carbon emissions from the use of greater quantities of water treatment chemicals that are extremely energy intensive to produce and transport.

The work in Chapter 4 determined that organic and inorganic colloids present in browning lakes would present a significant challenge for drinking water treatment systems in the region. For example, processes for the removal of metals including oxidation are designed for truly dissolved/soluble metals, as opposed to colloids. The metal–NOM binding in this work suggests that treatment facilities should adapt to brownification by optimizing NOM removal first, and that the technologies commonly used for removing metals may become less effective due to the presence of colloids. This work also demonstrated the importance of colloid characterization in source waters to inform specific treatment needs. Given that brownification of surface waters is expected to continue with changing climate, there will likely be more humic NOM with a greater density of metal binding sites, making colloid characterization increasingly important for drinking water providers.

In Chapter 5, a pilot-scale study was conducted at the JDKWSP on Pockwock lake to assess various adaptation strategies (e.g., implementation of clarification, use of alternative filter media such as GAC) for direct filtration facilities under the stress of brownification. As described in Chapter 4, the removal of metals may be impacted by brownification, and therefore a secondary objective was to assess the removal of dissolved (<0.45 µm) Fe and Mn across the different treatment configurations. A summary of key conclusions from this work (Chapter 5) were that the use of GAC filter media, in the form of GAC caps or full-GAC filters was a very promising strategy to enhance NOM removal and minimize DBP formation in browning source waters. However, an unintended consequence of this work was the significant release of dissolved Mn from the filters. It was hypothesized that pre-oxidation via $KMnO_4$ was ineffective, likely due to the presence of colloidal Mn as opposed to truly dissolved Mn, in the raw water. The GAC filters released dissolved Mn levels higher than the influent and negated any removal that occurred during pre-treatment, and the GAC filters released more dissolved Mn than the anthracite filters. As with Chapter 4, this work demonstrated the importance of source water characterization in terms of Fe and Mn (e.g., total, colloidal, and truly dissolved), which would inform the appropriate use of $KMnO_4$ or alternative technologies for Fe and Mn control.

Overall, this work highlighted the source water complexities that are anticipated through brownification and the vulnerabilities of the drinking water facilities drawing from brown lakes. There is a need for considering robust adaptation water treatment solutions that consider many factors in addition to NOM, including Mn and Fe.

6.2. Recommendations

Based on the findings and limitations of this work, there are several recommendations for future research. These recommendations have been organized in terms of integrated water quality monitoring, and treatment recommendations below.

6.2.1. Recommendation 1: Integrated water quality monitoring that acknowledges atmospheric and climate processes

This work (Chapters 2, 4) identified a need for comprehensive monitoring programs that cover larger timescales, with consistency in measurements, to assess the impacts of climate change, as well as other drivers (e.g., atmospheric deposition, changing land use) of source water brownification. These monitoring programs will be key to inform future water treatment needs, since it is not known how high NOM concentrations will become or how the quality of NOM will change, making the establishing of design targets challenging.

As discussed in Chapter 2, as atmospheric acid deposition stabilizes, other drivers such as climate change, will become increasingly important. The Climate Atlas of Canada is a tool that allows for analysis of climate variables at a regional level and provides climate change projections under different greenhouse gas emissions scenarios (Climate Atlas of Canada, 2022). The Climate Atlas of Canada uses two representative concentration pathways (RCP) to portray future climate change scenarios— a high emissions scenario using RCP 8.5, which is the highest emissions scenario where emissions continue to rise throughout the 21st century, and a moderate scenario, where emissions peak at 2040 and then decline. For Halifax, the Climate Atlas of Canada suggests that under the RCP 8.5 scenario, annual precipitation could increase from a baseline of 1398 mm (1976-2005) to up to 1722 mm for the period 2021-2050, with precipitation increasing each season.

Under the RCP 4.5 scenario, precipitation predictions are still high at >1700 mm for the same period. Mean temperatures are also projected to increase under both scenarios –annual temperature is expected to go from a mean of 6.7°C for the period 1976 -2005, to 9.9°C for 2021-2050 under RCP 8.5, and to 9.7°C under RPC 4.5 (Climate atlas of Canada, 2022). Accordingly, regardless of the emission scenario, we can expect significant changes to precipitation and temperature in the region, which will undoubtedly impact the quality of surface drinking water supplies and will influence brownification processes.

Such increases in temperature and precipitation will impact lake dynamics (e.g., seasonality), and brownification processes, significantly. According to Lipczynska-Kochany (2018), increased temperature will enhance biodegradation of soil organic matter, leading to a production of NOM which will be exported to surface waters through increased precipitation (flooding, runoff). This will promote further brownification of surface waters (Lipczynska-Kochany, 2018). Further, climate induced changes to humic substances may lead to the re-mobilization of metals from humic substances contained in soil and sediments. Further increases in NOM through brownification, as well as warming temperatures, will increase the thermal stratification of lakes due to decreased water transparency (Pilla et al., 2018), which will impact lake mixing regimes (e.g., longer, and more intense stratification periods resulting in later seasonal turnover).

Accordingly, source water monitoring programs should be broadened to consider regional climate variables, such as those provided by the Climate Atlas of Canada, to promote a better understanding of the diverse changes in source water quality expected through further brownification. The use of climate data should be an emphasis in future research on brownification, as it can be integrated with historical water quality and other data (e.g., atmospheric deposition, land use) to develop models to predict future changes in source water quality under various climate scenarios.

Given the complexity of changing climate and brownification processes, source water monitoring programs should also consider more advanced characterization approaches, in addition to more conventional NOM metrics. Fluorescence is a valuable characterization tool that can provide a “fingerprint” of NOM (Yan et al., 2000), and a single fluorescence EEM provides high-resolution data that is sensitive to changes in NOM character. Fluorescence-based NOM monitoring will be particularly informative in regions prone to browning and may be a valuable tool for predictive modelling applications, particularly in relation to climate change. Vione et al. (2021) notes that common organic matter fluorophores including humic substances and proteins are responsive to climate change (warming temperature, more intense precipitation events). Given that fluorescence spectroscopy has emerged as a valuable tool for the characterization and monitoring of NOM over the past decade(s), in addition to considerable uptake by the industry, there exist new opportunities for research investigating temporal changes in the nature of NOM in sources where long-term fluorescence datasets are available. Paired with climate and other water quality data, these datasets present an opportunity to further our understanding of brownification trends in drinking water supplies, as well as the ability to predict future relationships. Such predictions could help to inform future treatability studies for browning source waters.

Future research into source water monitoring strategies should also consider the routine characterization of NOM-metal as well as inorganic colloids, as browning surface waters are expected to have increased binding capacity for metals through increasing concentrations of humic substances. Chapters 2, 4 and 5, shed light on the importance of characterization of these NOM-metal complexes and differentiation between truly dissolved and complexed or colloidal metals in surface water supplies. This contrasts with the convention of quantifying dissolved material via separation through a 0.45 µm filter adopted by the drinking water industry. Characterization approaches can be analytically complex, such as FFF-UV-ICPMS (e.g., Trueman et al., 2019), SEC-UV-ICPMS (e.g., Redden et al., 2021), or as simple as fractionating metals (e.g., Fe, Mn, Al) and NOM into soluble, colloidal, and particulate fractions via separation with sequential filtration (0.2 um followed by 30K ultrafiltration) (e.g., Carlson et al., 1997). Such approaches will be critical for informing appropriate process design, selection, and operation of unit processes, and drinking water source selection. Inadequate characterization (e.g., using the convention of total vs. dissolved) of organic (e.g., NOM-metal) and inorganic colloids could result in inappropriate process selection, as evidenced in Chapter 5. For example, the JDKWSP on Pockwock Lake has been dosing $KMnO_4$ since the plant began operations in 1974 to control low levels of Mn and Fe, however it has become apparent in Chapter 5 that $KMnO_4$ may not be the appropriate treatment process due to the presence of colloidal, as opposed to truly dissolved metals in the source water. Such strategies should also be adopted within the treatment facilities, to understand the removal (or lack thereof) of organic and inorganic colloids throughout various unit processes (e.g., clarification and filtration).

6.2.2. Recommendation 2: Robust adaptation treatment solutions that consider source water complexities associated with climate and atmospheric processes

This work (Chapters 2, 3, and 5) highlighted a need for a better understanding of impacts on drinking water treatment vulnerabilities and the transition towards robust treatment technologies and solutions that can adapt to climate change and other drivers of changing water quality. As noted in Chapter 3, drinking water supplies in regions prone to brownification can expect increasing coagulant dosages to overcome elevated NOM loads. Treatment facilities may be under designed and unable to accommodate increased NOM loads without compromising downstream treatment processes. However, increasing chemical dosing alone may not be sufficient to adapt to brownification and other unit processes that can remove excess NOM and minimize DBP formation will become increasingly necessary as source waters continue to change.

Chapter 5 demonstrated the potential for using GAC as an adaptation strategy for browning source water. However, additional research using GAC media should be conducted. Only one type of GAC media was studied, and therefore other types of media (e.g., coal based, coconut based) with varying properties (e.g., effective size, uniformity coefficient, pore size, specific surface area) should be considered in future research. Rapid small scale column tests, as well as pilot-scale trials of different GAC types would be beneficial, particularly in understanding the exhaustion rates of different media under varying levels of NOM. Further, this work only considered GAC in filter configurations (e.g., GAC cap, or full-GAC media), however post-filter GAC contactors may also be relevant as they allow for different modes of operation (e.g., seasonal use) that could prolong the operational life of GAC media in terms of NOM exhaustion. Post-filter GAC contactors may become increasingly beneficial for other contaminants of concern (e.g., taste and odour compounds, algal toxins). GAC biofiltration has been identified as a promising treatment approach for the removal of algal toxins (Ho & Newcombe, 2007), as well as taste and odour compounds such as geosmin (Persson, 2007), both of which are expected to become more prevalent through increasing temperatures as a result of cyanobacterial activity (Journey et al., 2013). However, the adsorption of these compounds, in conjunction with elevated levels of NOM, should be considered in future work.

Future research should also assess the mechanisms for Mn release from GAC filters, as presented in Chapter 5, should be investigated in future pilot studies. This could also be achieved in RSSCT or future pilot work, however monitoring (e.g., metals, NOM, ORP) needs to occur from the onset of GAC installation in order to adequately assess desorption or dissolution mechanisms. As described previously, in depth colloid characterization would also help to inform the removal pathways, or lack thereof, of metals like Fe and Mn throughout treatment, including GAC.

Another aspect of GAC research that could use additional research with regards to brownification processes is advanced oxidation coupled with biologically active GAC (BAC) filtration. For example, advanced oxidation processes (AOPs) including UV/H_2O_2 coupled with BAC, or O_3/H_2O_2 have proven to be effective for minimizing DBP formation (Matilainen & Sillanpaa, 2010; Tak & Vellanki, 2020), however specific bench-and pilot-scale studies that consider future browning scenarios should be conducted in order to assess their feasibility for full-scale implementation. The removal of other contaminants such as metals (e.g., Fe and Mn) should be considered in these studies to understand any unintended consequences, such as those observed in Chapter 5 (e.g., metals release from filters).

Future research should consider also other unit processes that provide enhanced NOM removal, in addition to GAC or BAC as part of adaptation to brownification. For example, anion exchange, has shown promise as a NOM removal technology (Jarvis et al., 2008; Karpinska et al., 2013; Levchuk et al., 2018; Caltran et al., 2020) and may become increasingly relevant as brownification of source waters continue, and could be a relevant alternative to GAC adsorption. Bench and pilot-studies that compare both GAC and anion exchange under various brownification scenarios may be important aspects of future research.

Finally, given that the formation of regulated DBPs (e.g., THMs and HAAs) is driven primarily by chlorination of NOM, alternative disinfection strategies that minimize chlorine use should also be considered in future works. Implementing UV disinfection for primary disinfection may be a strategy for minimizing DBP formation within a treatment facility, however some have shown evidence of increased DBP formation after secondary disinfection (chlorination) of UV treated water (Choi & Choi, 2010).

Further, UV-LEDs are becoming a viable, more energy efficient alternative disinfectant in drinking water treatment (Chen et al., 2017, Jarvis et al., 2019; Carra et al., 2020). They are energy-efficient, long-lasting, easily tailored for specific operations, and compact in design (Chen et al., 2017). However, research is required in this field to understand the implications for the distribution system before full-scale application (Linden et al., 2019), as well as the formation of unregulated DBPs.

In all future research activities, attempts should be made to challenge test the vulnerability of different treatment solutions at bench and pilot-scale under high NOM concentrations as predicted through climate modelling scenarios described above.

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APPENDIX A: SUPPORTING DATA FOR CHAPTER 2

Table A1. Summary of peer reviewed evidence of recovery from acidification.

Spatial scope	Source	Region	N lakes/streams	Duration of study	Magnitude of change	Type of statistic	Unit of change	Evidence of chemical recovery from acidification
Global	(Stoddard et al., 1999)	Europe	39 surface waters	1980-1989	-0.8 to -3.8	Seasonal Kendall	μeq/L/year SO_4 lake concentration	Seven of eight regions reported decreasing rates of acidic deposition. All regions of Europe showed recovery in alkalinity, while only one of five regions in North America were recovering – likely due to the decline in base-cation concentrations exceeding decreases in sulfate concentrations.
		North America	129 surface waters		-1.2 to -1.7		μeq/L/year SO_4 lake concentration	
		Europe	74 surface waters	1990-1995	-0.9 to -5.8		μeq/L/year SO_4 lake concentration	
		North America	131 surface waters		-0.9 to -5.8		μeq/L/year SO_4 lake concentration	
	(Skjelkvåle et al., 2005)	Europe	73 surface waters	1990-2001	-1.68 to -6.75	Seasonal Kendall with simple linear regression	μeq/L/year SO_4 deposition	Significant decreasing sulfate concentrations observed for 11 of the 12 geographical regions (divided geographically based on acid-sensitivity). Improvements in ANC and pH were observed on a wide spatial distribution in response to decreased acid deposition.
		North America	116 surface waters		-1.02 to -2.47		μeq/L/year SO_4 deposition	
	(Garmo et al., 2014)	Europe	73 surface waters	1990-2008	-1.22 to -4.58	Seasonal Kendall with Sen's slope estimator	μeq/L/year SO_4 lake concentration	Increases in ANC, concomitant with decreases in sulfate deposition, were reported across all regions studied.
		North America	100 surface waters		0.95 to -2.14		μeq/L/year SO_4 lake concentration	
	(Garmo, 2020)	North America + Europe	497 surface waters (13 regions)	1990-2016	-8.1 to -0.8	Regional Kendall with Sen's slope estimator	μeq/L/year SO_4 deposition	

Europe	(Evans et al., 2001)	Italy, Slovakia, Czech Republic, Germany, Finland, Sweden, Norway, UK	24 lakes + 32 streams	1971-1988 to 2000	NA	Mann Kendall with Sen’s slope estimator	NA	Significant decreasing trends in sulfate were observed in 38 of 56 sites. 27 sites had increasing ANC, and 19showed significant increases in pH.
	(Kopáček et al., 2006)	Poland, Slovakia	91 lakes	1984, 1994, 2004	~ -1.66	NA	μeq/L/year SO_4 lake concentration	Atmospheric deposition of sulfate decreased by approximately 57% over the span of the study. No changes in ANC were observed from 1984-1994 but did increase from 1994-2004.
	(Broadmeadow et al., 2019)	UK	12 streams	1991-2012	-1.694	Seasonal Kendall	μeq/L/year SO_4 lake concentration	Significant declining trend in sulfate concentrations observed with corresponding and increases in pH and ‘charge-balance based’ ANC.
	(Kopáček et al., 2021)	Poland, Slovakia	30 lakes	2003-2020	-0.66 to -1.68	Linear regression	μeq/L/year SO_4 lake concentration	Declines in acid deposition contributed to recovery, and the effect of climate change on recovery increased since the 2000’s.
	(Moiseenko et al., 2022)	Russia	75 lakes	1990-2018	NA	NA	NA	Sulfate concentrations decreased significantly over the study period – in 1990 38% of lakes were dominated by sulfate, reducing to 8% by 2018.
Canada	(Keller et al., 2019)	Sudbury	42 lakes	1981-2015	-0.45 to -0.17	Linear mixed-effect model	mg/L/year SO_4 lake concentration	Increasing trends in pH observed for all lakes studied with concomitant decline in regional sulfate deposition.
	(Clair et al., 2011)	Atlantic Canada	66 lakes (since 1983) + 25 lakes (starting 1990)	1983-2007	NA	NA	NA	General negative trend in atmospheric sulfate deposition corresponded to decreasing lake sulfate concentration in all regions studied, although recovery was delayed due to

								acid-base characteristics of natural organic acids and concurrent reductions in dissolved base cations.
	(Houle et al., 2003)	Quebec	43 lakes	1985-1999	-2.9 to -3.6	NA	μeq/L/year SO_4 lake concentration	Climate variations (i.e., higher annual temperatures) were more correlated to increasing pH and ANC than decreasing rate of sulfate deposition. However, sulfate deposition declined at 40/43 lakes studied.
	(Marty et al., 2021)	Quebec	1 watershed	1981-2016	-0.004	Mann Kendall with Sen's slope estimator	Mg/L/year SO_4 stream concentration	Stream concentrations within the watershed showed a 50% reduction over the study period.
	(Redden et al., 2021)	Nova Scotia	60 lakes + 17 rivers	1985-2016	-0.0051 to -0.23	Mann Kendall with Sen's slope estimator	mg/L/year SO_4 lake concentration	Sulfate concentrations decreased in 60/62 lakes and 14/17 rivers, while pH increased in 55 lakes and 11 rivers.
	(Houle et al., 2021)	Atlantic Canada	78 lakes	1986-2018	-0.562	Mann Kendall with Sen's slope estimator	μeq/L/year SO_4 wet deposition concentration	Recovery was observed around the year 2000 with significant increase in pH, after which an increase in organic acidity decreases ANC recovery.
	(Watmough et al., 2021)	Ontario	7 lakes	1982-2015	-1.7	Mann Kendall with Sen's slope estimator	μeq/L/year SO_4 lake concentration	Increases in ANC, pH and alkalinity concomitant with decreases in sulfate deposition, were reported.
	(Webster et al., 2021)	Ontario	9 catchments	1982/83-2017/18	-0.071	Mann Kendall with Sen's slope estimator	mg/L/year SO_4 wet deposition concentration	Concentration of SO_4 decreased in all catchments, while and pH (8/9 catchments), alkalinity (6/9 catchments), and ANC (6/9 catchments) occurred in many catchments. DOC generally increased.

	(Hall et al., 2021)	Ontario	44 lakes	1981-2018	-0.24	Mann Kendall with Sen's slope estimator	mg/L/year SO_4 lake concentration	.Strong recovery from acidification was observed in the region evidenced by increases in pH and decreases in SO_4 concentration.
	(Coutourier et al., 2022)	Ontario	15 lakes	1980-2017	-0.07 to -0.13	Mann Kendall with Sen's slope estimator	mg/L/year SO_4 lake concentration	Evidence of recovery from acidification through abatement of SO2 deposition.
Northeastern USA	(Lawrence et al., 2011)	Adirondacks	12 streams	1980-2008	NA	NA	NA	Atmospheric sulfur decreased by 50% in the region, resulting in 13 meq/L increase in ANC and a pH increase of 0.28 units.
	(Driscoll et al., 2003)	Adirondacks	17 lakes (from 1982) + 35 lakes (1992)	1982-2000	-1.53 to -2.5	NA	μeq/L/year SO_4 lake concentration	Decreases in sulfate and nitrate concentrations have resulted in increases in ANC and pH. Results suggested that chemical recovery of Adirondack Lakes will be several decades under current levels of acid deposition.
	(Burns et al., 2006)	Adirondack + Catskill	12 lakes + 5 streams	1984-2001	NA	NA	NA	Decreasing sulfate, nitrate and base cation concentrations corresponded with increasing pH. ANC increased in around half of Adirondack lakes and one Catskill stream.
	(Strock et al., 2014)	New England	31 lakes	1990-2010	-1.88 to -2.06	Simple linear regression	μeq/L/year SO_4 lake concentration	Recovery of ANC and pH was variable in the two regions studied, likely due to depletion of base cations and dissolved organic carbon concentrations, despite accelerated reductions in atmospheric sulfate deposition since the 1980s.
		Adirondacks	43 lakes		-2.0 to -2.62		μeq/L/year SO_4 lake concentration	
	(Stoddard et al., 2002)	Adirondacks	48 lakes	1990-2000	-2.26	Seasonal Kendall with Sen's	μeq/L/year SO_4 lake concentration	Decreasing trends in sulfate concentrations, with corresponding increases in ANC, were observed for four of the five
		New England	24 lakes		-1.77			

		Northern Appalachians	9 streams		-2.27	slope estimator		regions studied; however, the decline in base cations likely limited recovery of ANC and pH.
		Ridge & Blue Ridge	69 streams		0.29			
		Upper Midwest	38 lakes		-3.36			
	(Waller et al., 2012)	Adirondacks	42 lakes	1991-2007	-1.74	Mann Kendall with Sen's slope estimator	μeq/L/year SO_4 lake concentration	The number of acidified lakes in the Adirondacks has decreased from 15.5% to 8.3% since the implementation of the Acid Rain Program and the Nitrogen Budget Program. Decreases in sulfate concentrations have generally corresponded with increasing ANC.
	(Driscoll et al., 2016)	Adirondacks	48 lakes	1992-2013	-0.99 to -4	Seasonal Kendall	μeq/L/year SO_4 lake concentration	All lakes showed significant declines in sulfate concentrations. 42 of 48 lakes reported increasing ANC and 33 of 48 observed increases in pH.
	(Harmon et al., 2021)	Shenandoah National Park	13 streams	1995-2016	-0.027 to -0.14	Seasonal Kendall with Sen's slope estimator	μeq/L/year SO_4 concentration	Minor change in ANC and sulfate concentration in acid sensitive watersheds and streams.

Table A2. Summary of changes in natural organic matter, in terms of DOC or TOC concentration, as a result of recovery from acidification.

Spatial scope	**Source**	**Region**	**N lakes/streams**	**Duration of study**	**Magnitude of change (mg DOC/L/year)**	**Type of statistic**	**Evidence of chemical recovery from acidification**
Global	(Skjelkvåle et al., 2005)	Europe	73 surface waters	1990-2001	0.05 to 0.13	Seasonal Kendall with simple linear regression	Ten of the twelve regions exhibited positive trends in

		North America	116 surface waters		-0.04 to 0.06		DOC concentrations, with six significant trends. Trends in sulfate concentrations for all ten regions were negative and significant.
	(Monteith et al., 2007)	North American + Europe	522 lakes	1990-2004	~0.02 to 0.15	Mann Kendall with Sen's slope estimator	Wide-scale trends increasing trends in DOC concentrations can be explained by changes in deposition chemistry and catchment acid-sensitivity. DOC concentrations were rising in proportion to declines in atmospheric sulfur deposition.
	(Garmo et al., 2014)	Europe	73 surface waters	1990-2008	0.04 to 0.11	Seasonal Kendall with Sen's slope estimator	Across all regions, 22% of surface waters exhibited significant increasing trends, where 76% were increasing but not significant. DOC trends were strongly correlated with deposition chemistry.
		North America	100 surface waters		-0.02 to 0.06		
	(Garmo, 2020)	North American + Europe	497 surface waters (13 regions)	1990-2016	0.03 to 0.11	Regional Kendall with Sen's slope estimator	All regions where data were available, except the Appalachia region, exhibited increasing DOC concentrations, which was strongly correlated to deposition chemistry and the sensitivity of the catchment to said deposition.
	(Rodriguez-Cardona et al., 2022)	Northern hemisphere	74 streams	1975 to 2010-2015	-0.13 to 0.05 (median 0.003)	Sen's slope estimator	Results indicated that DOC concentrations are experiencing fundamental change due to recovery from atmospheric acid deposition.
Europe	(Haaland et al., 2010)	Norway	4 lakes	1983-2008	NA	NA	The observed long-term trend of increasing colored dissolved organic matter was found to be largely related to

							reductions in sulfate and chloride concentrations in precipitation.
	(Kopáček et al., 2006)	Poland, Slovakia	91 lakes	1984, 1994, 2004	NA	NA	Concentrations of DOC increased in eight of ten Tatra forest lakes and decreased in two. The increasing trend was likely a result of decreasing ionic strength from reduced acidic deposition. No temporal trends in DOC were observed in alpine lakes.
	(De Wit et al., 2007)	Norway	3 catchments	1985-2003	0.06 to 0.13	Mann Kendall with Sen's slope estimator	Increases in TOC concentrations ranged from 14 to 36% over period of study and were largely explained by reduction in atmospheric acid deposition.
	(Finstad et al., 2016)	Norway	70 Lakes	1986-2013	0.17	Mann Kendall with Sen's slope estimator	General increasing trends in DOC were observed over the regions studied, with the strongest increases in more acidified areas. The increase in DOC was largely attributed to reductions in sulfate deposition, however climatic factors and land use changes also impact the level of organic matter in surface waters.
	(Evans & Monteith, 2001)	UK	11 lakes + 11 streams	1988-2000	0.072 to 0.7284	Seasonal Kendall with Sen's slope estimator	Significant increasing DOC concentrations were described in 20 of 22 streams. Increases in sites unaffected by acidification suggest climatic factors also contributed to the positive trend.

	(Davies et al., 2005)	UK	11 lakes + 11 streams	1988-2003	0.06 to 0.48	Seasonal Kendall	Significant increases in DOC concentrations were observed at all sites; however, both climate and acid deposition drivers were likely to influence the trends in organic concentration.
	(Forsius et al., 2003)	Finland	163 lakes	1990-1999	NA	NA	Only 10% of lakes had significant increases in TOC concentrations over the period of study. Decreasing trends were observed in the Central Finland region.
	(Lepisto et al., 2021)	Finland	12 catchments	1990-2019	0.09 to 0.38	Seasonal Kendall with Sen's slope estimator	TOC increased in 7 to 10 out of 12 catchments over the 30 year study period and were related to recovery and climate.
	(Skjelkvåle et al., 2001)	Finland, Norway, Sweden	163 + 100 + 81 lakes	1990-1999	NA	NA	TOC showed significant positive trends in 12% of lakes studied, largely situated in Norway. The increasing concentrations were a likely result of regional changes in climate. Recovery from acidification may have also impacted the lake chemistry.
	(De Wit et al., 2016)	Finland, Norway, Sweden	290 lakes + 184 running waters	1990-2013	NA	NA	Increasing trends in DOC concentrations were consistent across climate gradients and catchment sizes. Median concentrations increased by 1.4% per year, with largest trends in areas with steepest reductions in atmospheric sulfate deposition.
	(Broadmeadow et al., 2019)	UK	12 streams	1991-2012	NA	NA	Seven of the twelve streams indicated significant increases in DOC, with larger

							increases in forest catchments.
	(Hruška et al., 2009)	Czech Republic	2 catchments	1992-2008	0.42 and 0.43	Seasonal Mann Kendall	DOC concentrations increased significantly in both catchments, by approximately 65%, over the period of study. Increases were associated with declining ionic strength in the soil-water caused by reductions in sulfate deposition.
	(Kopáček et al., 2019)	Tatra Mountains	31 lakes	1992-2018	0.007 to 0.116	Simple linear regression	Highest increase in lake DOC concentrations occurred in regions with acidic, soil-rich catchments, suggesting that soil recovery from acidification was one of the probable drivers of increased DOC export from catchment soils into the receiving water.
	(Moiseenko et al., 2022)	Russia	75 lakes	1990-2018	NA	NA	DOC concentrations increased above natural values or stabilized, as a result of reduced acid input and climate warming.
	(Evans et al., 2005)	UK	11 lakes + 11 streams	1998-2003	0.06 to 0.51	Seasonal Kendall with Sen's slope estimator	Average DOC concentrations have increased by more than 90%. The rises in organic concentrations have been largely associated to reduced sulfate in acidified waters and climate factors in non-acidified waters.
Canada	(Keller et al., 2019)	Sudbury	42 lakes	1981-2015	0.025 to 0.2	Linear mixed effect models	The vast majority (37/42) of the study lakes showed significant increasing concentrations of DOC. This was attributed to reductions

							in sulfate deposition; however, climate factors are also likely to impact the level of organic matter.
	(Meyer-Jacob et al., 2020)	Sudbury, Ontario	75 lakes	1981-83 to 2016-18	0.046 to 0.023	Mann Kendall with Sen's slope estimator	DOC concentrations increased by 1.6 ± 1.0 mg/L in acid sensitive lakes and 0.9 ± 0.6 mg/L in buffered lakes over the period of study. Further, a diminishing influence of sulfate deposition was observed, suggesting climate drivers and vegetation cover are becoming increasingly influential on lake DOC concentrations.
	(Watmough & Eimers, 2020)	Ontario	7 lakes	1982-2015	0.02 to 0.07	Mann Kendall with Sen's slope estimator	Significant increasing trends in DOC were reported for all seven study lakes with concomitant significant declining trends in sulfate concentrations. Results determined that increasing DOC concentrations had a minimal impact on the delay of lake recovery.
	(Clair et al., 2011)	Atlantic Canada	66 lakes (from 1983) + 25 lakes (1990 onward)	1983-2007	NA	NA	Significant increasing DOC concentrations were observed in the four regions studied over the period of study, with one exception. Significant positive trends were reported for all four regions from 2000 onward.
	(Imtiazy et al., 2020)	ELA, Ontario	4 lakes	1983-2015	NA	NA	No significant trend in DOC was observed in ELA lakes from 2000-2015, however increasing trends were reported from 1983-2000.

							Precipitation was the main driver of DOC concentration, as opposed to sulfate deposition.
	(Houle et al., 2003)	Quebec	43 lakes	1985-1999	~0.07	NA	Of the 43 lakes monitored, 18 displayed significant increases in DOC concentrations with a mean regional change of 13% over the period of study.
	(Redden et al., 2021)	Nova Scotia	87 lakes + 17 rivers	1985-2016	NA	NA	Apparent color has increased in 54 of 62 lakes and 13 of 17 rivers. The increase in color was positively correlated with aluminum and iron concentrations, implying greater binding capacity for metals in surface waters.
	(Imtiazy et al., 2020)	Dorset, Ontario	8 lakes	1988-2015	0.1	Multiple linear regression	Increasing DOC was evident in both study regions, with sulfate deposition and precipitation explaining 24-54% and 21-49% of variance in DOC concentration over study period, respectively.
	(Couture et al., 2012)	Quebec	30 lakes	1989-2006	0.05	Seasonal Kendall	Significant increases in DOC concentrations were observed in the majority of the lakes studied. Results suggest concentrations were driven by reduced sulfate deposition and long-term temperature variables.
	(Imtiazy et al., 2020)	Nova Scotia	37 lakes	2000-2015	0.11	Multiple linear regression	Increasing DOC was evident in both study regions, with sulfate deposition and precipitation explaining 24-54% and 21-49% of variance in DOC concentration over study period, respectively.

	(Houle et al., 2021)	Atlantic Canada	78 lakes	1986-2018	NA	NA	A portion of the study lakes showed increasing DOC over the study period, particularly after 2001.
	(Webster et al., 2021)	Ontario	9 catchments	1982/83-2017/18	0.13 (max)	Mann Kendall with Sen’s slope estimator	DOC concentrations increased in 7 out o f9 catchments and were linked to recovery from acidification and changing climate.
	(Watmough et al., 2021)	Ontario	7 lakes	1982-2015	0.03	Mann Kendall with Sen’s slope estimator	DOC concentrations increased over the study period, with clear evidence of recovery after 2005 which aligned with dramatic declines in atmospheric deposition.
	(Hall et al., 2021)	Ontario	44 lakes	1981-2018	0.05	Mann Kendall with Sen’s slope estimator	DOC concentration varied substantially, however increases in DOC were related to decreasing sulfate concentration and increasing pH. Atmospheric deposition and climate change were noted as primary mechanisms for increasing DOC.
	(Coutourier et al., 2022)	Ontario	15 lakes	1980-2017	0.01 to 0.02	Mann Kendall with Sen’s slope estimator	Increases in DOC coincided with decreases in sulfate deposition however differences in local drivers (regional climate, hydrology) can influence DOC.
	(Marty et al., 2021)	Quebec	1 watershed	1981-2016	0.0625	NA	A decrease in sulfate deposition was related to increases in DOC, however the role of climate will increase in the future.
Northeastern USA	(Driscoll et al., 2003)	Adirondacks	17 lakes (from 1982) + 35 lakes (1992)	1982-2000	0.0792	NA	All lakes reported significant decreases in sulfate concentration, however, only 7 of 17 original study sites

							had significant increases in DOC concentrations. Increase in DOC concentrations contributed to limited increase in ANC.
	(Burns et al., 2006)	Adirondacks + Catskill	12 lakes + 5 streams	1984-2001	NA	NA	Significant increasing trends in DOC concentrations were reported in 75% of the Adirondack lakes and 80% of the Catskill streams.
	(Gavin et al., 2018)	Maine	29 lakes	1986-2015	0.12	Simple linear regression	All 29 lakes studied showed positive trends in DOC, however, only 19 lakes had significant increases. The strongest predictors of DOC concentrations were the lake sulfate concentration and climate variables (e.g., air temperature).
	(Stoddard et al., 2002)	Adirondacks	48 lakes	1990-2000	0.06	Seasonal Kendall with Sen's slope estimator	Positive significant trends in DOC concentrations were reported for three of the five regions studied. One region exhibited an increasing, but not significant, trend. The largest rates of DOC increase were observed at sites with strongest decrease in sulfate deposition.
		New England	24 lakes		0.03		
		Northern Appalachians	9 streams		0.03		
		Ridge & Blue Ridge	69 streams		NA		
		Upper Midwest	38 lakes		0.06		
	(Waller et al., 2012)	Adirondacks	42 lakes	1991-2007	0.03	Mann Kendall with Sen's slope estimator	Increasing DOC concentrations were reported in 69% of the lakes for the entire period of study; however, in the first 13 years (up to 2004), a larger percentage of lakes showed increasing trends (81%).

	(Driscoll et al., 2016)	Adirondacks	48 lakes	1992-2013	NA	NA	DOC has significantly increased in 29 of the 28 sites, while two exhibited decreasing trends.
	(SanClements et al., 2012)	Maine	9 lakes	1993-2009	~0.1	Simple linear regression	Five of the nine study lakes showed significant increasing DOC concentrations, three of which exhibited significant negative correlations between sulfate and DOC concentration. Further, the five lakes with significant positive DOC trends also showed significant decreasing trends in fluorescence index (i.e., more terrestrial NOM).
	(Lawrence et al., 2013)	Adirondacks	42 lakes	1994-2011	~0.043	Seasonal Kendall	Significant increases in annual mean DOC concentrations were reported for 27 of the study lakes and 8 lakes showed non-significant increases. Results suggest that studied lakes may be returning to their natural state prior to acidic deposition.
	(Leach et al., 2019)	Adirondacks	28 lakes	1994-2012	0.052	Mann Kendall and Sen's slope	The annual rate of DOC increase for all study lakes was 0.052 mg/L/year. The reduced water clarity from brownification was a likely driver of change in primary producers.
	(Lawrence and Roy, 2021)	Adirondacks	2 streams	2001-2019	~0.18	Linear regression	DOC concentrations showed linear increases throughout the study period. DOC trends have continued although deposition rates are low

							suggesting alternative drivers.
	(Strock et al., 2014)	Adirondacks	43 lakes	1990-2010	0.09, then -0.03	Simple linear regression	Significant increases in DOC concentrations were observed in both regions from 1990-2000, however negative (insignificant) trends were reported from 2000 to 2010. Results suggest that DOC concentrations have not consistently increased in acid-sensitive lakes in the region.
		New England	31 lakes		0.08, then -0.05		
	(Nelson et al., 2021)	Northern Appalachians and Adirondacks	257 ponds	1978-2019	0.001 median (max 0.042)	Mann Kendall and Sen's slope	DOC increased significantly at 54% of ponds, attributed to reduced acid deposition and climate.
	(Meingast et al., 2020)	Michigan	1 watershed of Lake Superior	1988-2013	0.14	Linear regression	Increases in DOC were related to SO4 deposition, but future increases may be related to climate (temperature, snowmelt, runoff).
	(Diamond et al., 2022)	Vermont	1 lake	2001-2019	0.04	NA	Chemical recovery was identified as a reason for increasing DOC throughout the study period, significant DOC increases occurred after 2001 breakpoint.

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Section A1: Factors impeding chemical responses to recovery from acidification

Despite the widespread decrease in sulfate deposition observed in the Northern Hemisphere, the degree of recovery from acidification in many surface waters has been less than expected, indicating that there are additional factors impacting the progression of recovery to pre-industrial states. These factors include increase in concentrations of acidic organic compounds (i.e., DOC), depletion of base cations (BCs) in the catchment soils, and release of legacy sulfate from the catchment.

Muted increases in pH in some surface waters, despite reductions in sulfate deposition, have been attributed to increased DOC concentrations, although the increase in organic anions was not necessarily caused by the changes in sulfate deposition (Strock et al., 2014; Watmough et al., 2016). Similarly, the lack of pH increases in Atlantic Canadian lakes (Clair et al., 2011; Redden et al., 2021), Scandinavian (Skjelkvåle et al. 2001), and UK (Evans et al., 2008) surface waters has been linked to increases in DOC concentrations over the same periods of time. Additionally, increasing concentrations of DOC have also been linked to sulfate desorption as the organic ions compete with sulfate for adsorption sites, leading to sulfate leaching in the lake and impeding recovery (Sokolova & Alekseeva, 2008).

Inhibited, lack of, or reversed recovery from the loss of catchment soil BCs has been frequently observed in Eastern North America (Clair et al., 2011; Houle et al., 2006; Reid & Watmough, 2015; Robison et al., 2013; Strock et al., 2014; Watmough et al., 2016; Watmough & Eimers, 2020) and Europe (Watmough et al., 2005). When subject to acid deposition, the BCs bound in the catchment soil, often summarized by concentrations of Ca^{2+} and Mg^{2+}, are exchanged with incoming H^+ ions. Soils formed from bedrock with high content of buffering material (e.g., limestone), have a significant pool of exchangeable BCs, and thus a greater capacity to buffer acid deposition (Clair et al., 2011). This mechanism may explain the absence of acidification in surface waters that drain base-rich catchments (Dan et al., 2019). When base-poor soils are subject to atmospheric sulfate deposition, the initial exchangeable pool will buffer against changes in pH; however, it is ultimately depleted and surface waters may remain acidified if subject to further acid deposition (Clair et al., 2011; Driscoll & Wang, 2019). If exchangeable pools are depleted, recovery may be delayed until the rate of BC replenishment from weathering exceeds the rate of leaching from acidic anions (Clair et al., 2011; Driscoll & Wang, 2019; Redden et al., 2021; Reid & Watmough, 2015; Strock et al., 2014). With increasing temperatures and greater rates of precipitation, bedrock weathering is anticipated to increase (Strock et al., 2014), suggesting that climatic factors will also play a role in the rate of replenishment of BCs in catchment soils and thus the rate of recovery in the surface waters (Houle et al., 2010).

Recovery from acidification may also be muted by internal loading of legacy sulfate, which is largely accumulated as adsorbed sulfates in soil solutions, plant tissues, and soil organic matter and can be released slowly over time, enhancing, or extending the period of acid deposition (Robison et al., 2013; Sokolova & Alekseeva, 2008). Mass balance budget analysis on multiple watersheds in the Northern Hemisphere found that the export of sulfate to receiving water bodies exceeded the atmospheric deposition, indicating an internal source within the catchments (Evans et al., 2006; Mitchell et al., 2013; Mitchell & Likens, 2011; Robison et al., 2013; Watmough et al., 2016). Drivers such as mineralization (Mitchell & Likens, 2011; Sokolova & Alekseeva, 2008), the degree of soil weathering (Houle et al., 2010; Mitchell & Likens, 2011), concentration of aluminum and iron oxides and hydroxides (Robison et al., 2013; Sokolova & Alekseeva, 2008), dilution of soil pore water (Mitchell & Likens, 2011), and oxidation of organic/inorganic sulfur (Clark et al., 2005; Evans et al., 2006; Gavin et al., 2018; Watmough et al., 2016) will all impact the rate of legacy sulfur release. Where climate factors (e.g., temperature, precipitation) can impact these drivers, it may also be influential on internal sulfur loading. With decreasing atmospheric sulfate deposition and increasing discrepancies in mass balance budgets, lake recovery may be delayed until the internal sources are depleted (Mitchell & Likens, 2011; Robison et al., 2013).

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APPENDIX B: SUPPORTING DATA FOR CHAPTER 3

Table B1. Average Annual Raw Water Quality Data for Lake Major.

Plant	Year	pH	Turbidity — *NTU*	SO_4—*mg/L*	Colour— *TCU*	TOC —*mg/L*	Temperature—*℃*
Lake Major (LMWSP)	1999	5.30 (0.23)	0.27 (0.08)	5[a, e]	22 (7)	4[a, e]	13.4 (7.6)[e]
	2000	5.20 (0.28)	0.25 (0.04)	5[a, e]	23 (6)	3.8[a, e]	10.5 (7.6)
	2001	5.23 (0.30)	0.26 (0.06)	8.0[a, e]	26 (7)	3.1[a, e]	10.5 (7.8)
	2002	5.02 (0.30)	0.26 (0.08)	5.5[a, e]	25 (6)	2.4[a, e]	10.1 (7.5)
	2003	5.34 (0.38)	0.29 (0.05)	6.0[a, e]	33 (7)	2.8[a, e]	10.3 (7.8)
	2004	5.31 (0.40)	0.27 (0.06)	4.0[a, e]	24 (6)	2.9[a, e]	10.0 (7.5)
	2005	5.36 (0.43)	0.27 (0.07)	4.0[a, e]	29 (5)	4.1[a, e]	10.3 (7.7)
	2006	5.24 (0.13)	0.24 (0.07)		36 (5)		11.0 (7.1)
	2007	5.23 (0.15)	0.28 (0.06)	4.0[a, e]	37 (3)	4.0[a, e]	10.3 (7.2)
	2008	5.14 (0.27)	0.32 (0.07)	3.0[a, e]	38 (4)	5.1[a, e]	10.1 (7.5)
	2009	5.23 (0.13)	0.32 (0.07)	3.0[a, e]	44 (5)	4.0[a, e]	10.0 (7.0)
	2010	5.30 (0.17)	0.30 (0.05)	3.0[b, e]	38 (10)	4.0[a, e]	11.0 (7.4)
	2011	5.37 (0.15)	0.31 (0.07)	3.0[b, e]	41 (9)	3.9[a, e]	10.3 (7.0)
	2012	5.49 (0.27)	0.31 (0.06)	2.5 (0.2)[b, e]	44 (10)	5.10 (0.55)	11.1 (7.6)
	2013	5.35 (0.13)	0.28 (0.06)	2.5 (0.3)[b, e]	47 (6)	5.47 (0.26)	10.4 (7.6)
	2014	5.41 (0.26)	0.29 (0.03)	2.4 (0.3)[b, e]	44 (10)	5.04 (0.48)	10.3 (7.5)
	2015	5.41 (0.22)	0.28 (0.05)	2.1 (0.3)[b, e]	48 (7)	5.10 (0.52)	9.6 (7.7)

Unpublished plant operations data unless otherwise specified;
pH, turbidity and color were measured using benchtop probe, turbidimeter or spectrophotometer unless otherwise specified
Standard deviation given in parentheses
[a] Halifax Water Annual Report, reported as 'typical value'; [b] Halifax Water "WaterTrax" database; [c] Centre for Water Resources Studies (CWRS) NOM dataset; [d] Stoddart and Gagnon, 2015; [e] Incomplete year represented

Table B2. Average Annual Raw Water Quality Data for Pockwock Lake.

Plant	Year	pH	Turbidity – NTU	SO_4—*mg/L*	Colour—*TCU*	TOC —*mg/L*	Temperature—*ºC*
Pockwock Lake (JDKWSP)	1999	5.5 (0.1)	0.35 (0.25)	4.8[a, e]	12 (6)	2.4[a, e]	10.7 (7.7)
	2000	5.31 (0.2)[f]	0.32 (0.12)	4.8[a, e]	13 (6)	2.3[a, e]	10.2 (7.0)
	2001	5.16 (0.1)[f]	0.29 (0.13)	5.0[a, e]	13 (6)	2.4[a, e]	10.2 (7.5)
	2002	5.28 (0.1)[f]	0.29 (0.12)	4.8[a, e]	12 (7)	2.7[a, e]	9.8 (7.4)
	2003	5.22 (0.1)[f]	0.32 (0.07)[e]	5.0[a, e]	15 (6)	2.9[a, e]	9.9 (7.4)
	2004	5.24 (0.15)	0.31 (0.14)	5.7[a, e]	13 (5)	2.7[a, e]	9.5 (7.2)
	2005	5.01 (0.14)	0.41 (0.10)	6.0[a, e]	18 (5)	2.9[a, e]	10.3 (7.0)
	2006	5.09 (0.17)	0.38 (0.06)		20 (4)		10.5 (6.8)
	2007	5.24 (0.13)	0.33 (0.06)	6.0[a, e]	16 (3)	2.9[a, e]	
	2008	5.23 (0.13)	0.38 (0.05)	6.0[a, e]	16 (4)	2.9[a, e]	8.8 (7.1)
	2009	5.16 (0.13)	0.45 (0.08)	4.0[a, e]	17 (5)	2.5[a, e]	9.4 (7.3)
	2010	5.39 (0.14)	0.41 (0.07)	4.0[b, e]	15 (5)	2.82 (0.36)[c, e]	10.9 (7.3)
	2011	5.35 (0.11)	0.40 (0.08)	4.0[b, e]	19 (5)	2.86 (0.16)[c, e]	10.3 (6.9)
	2012	5.47 (0.25)[d]	0.44 (0.18)[d]	3.9 (0.15)[b, e]	19 (7)	2.93 (0.28)[d, e]	10.8 (7.4)
	2013	5.73 (0.19)[d]	0.35 (0.10)[d]	3.8 (0.35)[b, e]	19 (9)	2.97 (0.18)[d, e]	10.1 (7.1)
	2014	5.65 (0.33)[d]	0.35 (0.07)[d]	3.1 (0.4)[b, e]	19 (5)	3.05 (0.26)[d, e]	10.2 (7.1)
	2015	5.54 (0.15)	0.33 (0.07)	3.3 (0.3)[b, e]	21 (5)	3.37 (0.20)[c,e]	9.7 (7.2)

Unpublished plant operations data unless otherwise specified;

pH, turbidity and color were measured using benchtop probe, turbidimeter or spectrophotometer unless otherwise specified

Standard deviation given in parentheses

[a]Halifax Water Annual Report, reported as 'typical value; [b]Halifax Water "WaterTrax" database; [c]Centre for Water Resources Studies (CWRS) NOM dataset; [d]Stoddart and Gagnon, 2015; [e]Incomplete year represented; [f]Environment Canada's Freshwater Quality Monitoring and Surveillance Program

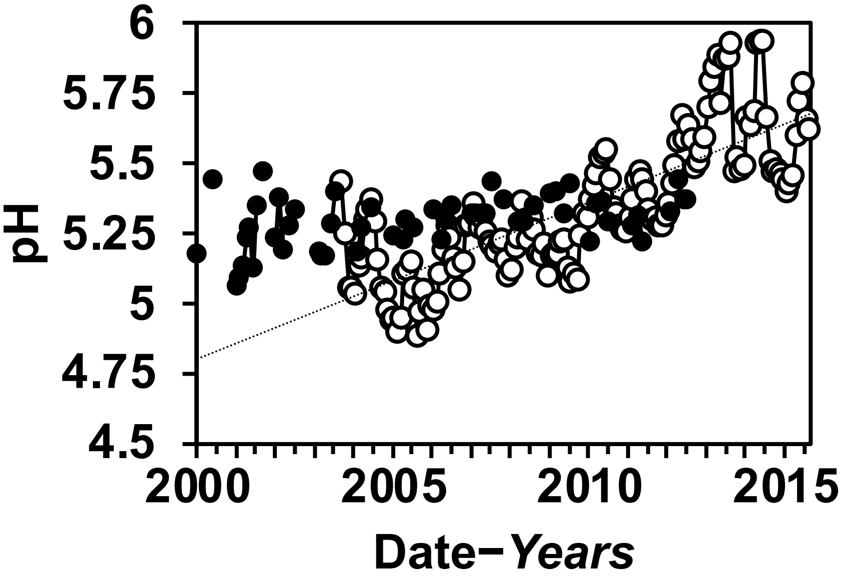

Figure B1. Increasing monthly mean pH in Pockwock Lake from 2000 to 2015. Dashed line represents approximation of linear trend ($p<0.05$, $m=0.06$ pH units/year). Filled circles denote Environment Canada pH data, while empty circles denote Halifax Water pH data.

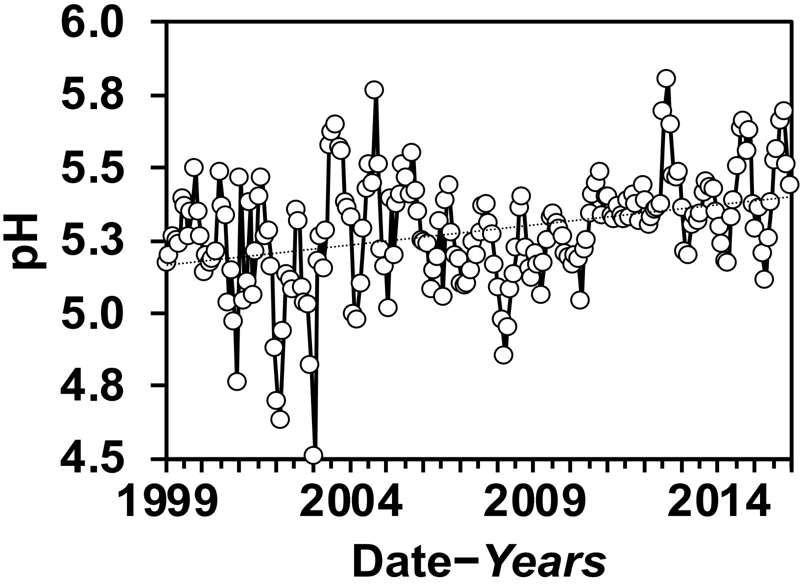

Figure B2. Increasing monthly mean pH in Lake Major from 1999 to 2015. Dashed line represents approximation of linear trend ($p<0.05$, $m=0.01$ pH units/year).

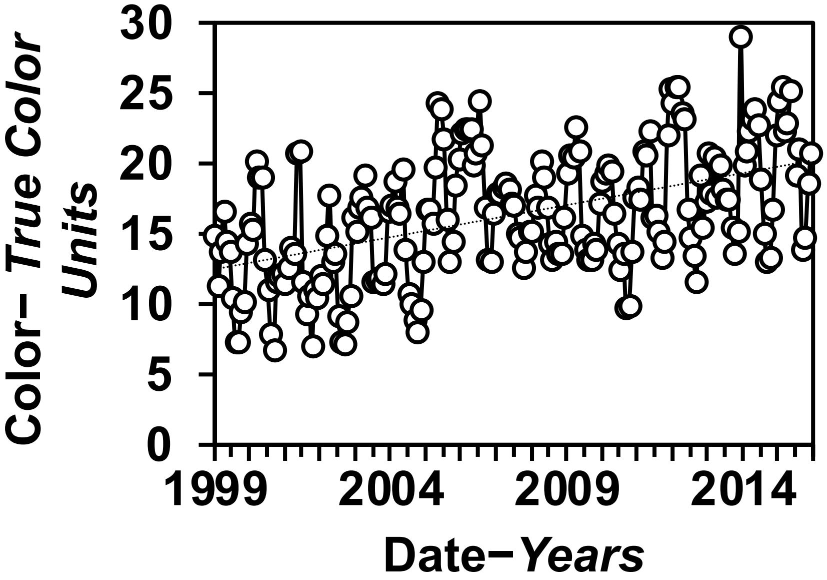

Figure B3. Increasing monthly mean color in Pockwock Lake from 1999 to 2015. Dashed line represents approximation of linear trend (p<0.05, m=0.55 TCU/year).

APPENDIX C: SUPPORTING DATA FOR CHAPTER 4

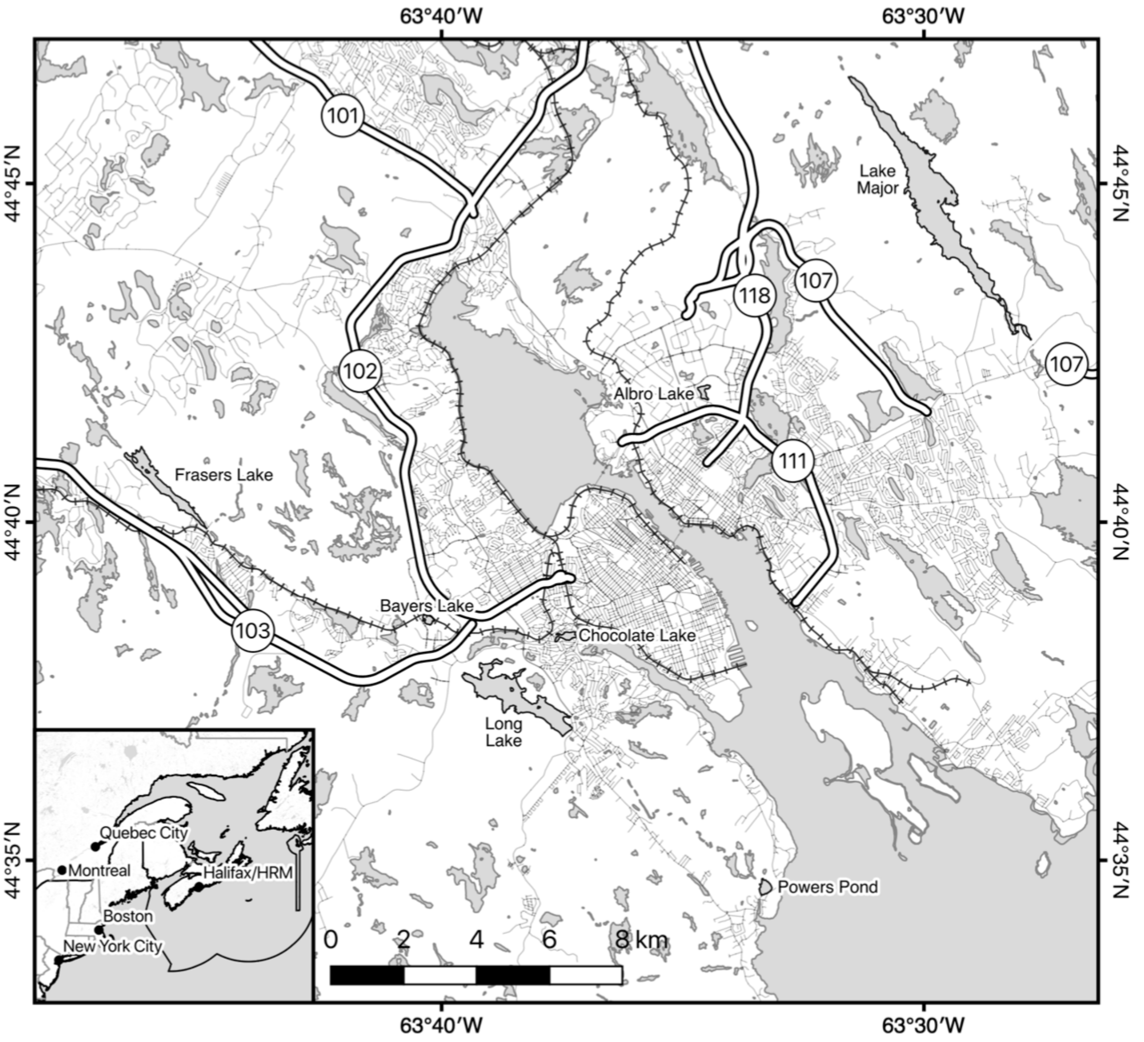

Figure C1. Locations of lakes included in this study.

C.1 Additional information on the FFF method

An initial cross-flow of 2.5 mL/min and 10 minutes of focusing time was used for FFF analysis. After focusing, the cross-flow was maintained for 6 minutes and then decayed linearly over 2 minutes to 0.1 mL/min, separating free and organically complexed metals from larger iron-rich colloids. A second population of large colloids was detected after the cross-flow was set to zero at 28 minutes. Analyte recoveries were estimated as the ratio of total integrated peak area with and without a cross-flow. FFF separation recovered approximately 48, 24, 62, 39, and 45% of Al, Cu, Fe, Mn, and U, respectively, from a sample representing Powers Pond. These estimates reflect losses of ionic and small forms of each element that occur by design, in addition to losses due to adsorption to the membrane. Such non-ideal interactions may impact the relative importance of size fractions as described in the results section. Recovery of UV_{254} was estimated using a sample of Suwannee River natural organic matter at 57%.[43] Similar recoveries of NOM and metals have been reported previously for similar samples and separation conditions,[43,44] although recovery of iron was somewhat higher here.

We calibrated the FFF system using bromophenol blue (0.69 kDa) and blue dextran (2000 kDa) at 590 nm; tannic acid (1.7 kDa) at 254 nm; and ferritin (440 kDa) and ovalbumin (44 kDa) at 280 nm. Linear decay of the crossflow necessitated a quadratic fit to the molecular weight (MW) calibration data: $\log_{10}(MW) = 11.76 - 1.89v_r + 0.07v_r^2$ ($R^2 = 0.98$, where v_r is the retention volume.

The ICP-MS was calibrated on each analysis day using multielement standards in 2% HNO_3, containing Al, Mn, Fe, Cu, and U at 25, 50, 100, 150, and 250 μg/L. Each was spiked with 50 μg/L Sc, In, and Tb as internal standards. Calibration curves yielded median R^2 values (across all runs) of 0.9474, 0.9999, 0.9997, 0.9999, and 0.9998, respectively. Quality control spikes in the same matrix (75 μg/L) yielded 83.8, 99.6, 98.2, 100.7, and 101.6% recoveries of Al, Mn, Fe, Cu, and U, respectively. An independently-prepared spike at 40 μg/L yielded 80.5, 99.3, 96.9, and 100.3% recoveries of Al, Mn, Fe, and Cu. Standards were introduced to the nebulizer by means of the ICP-MS autosampler after mixing with FFF channel effluent via the mixing tee. Flow rates were similar between calibration and separation, differing by less than 10%; this difference was minimized with adjustments to the peristaltic pump speed. Detection limits were estimated using the 3σ method (Table C1), with σ calculated separately for the elution step of a total of six blanks collected on different analysis days.

Table C1. Estimated detection limits by element.

Element	Median (µg/L)	Interquartile range (µg/L)
Al	11.196	7.531
Cu	0.109	0.048
Fe	0.386	0.412
Mn	0.055	0.075
U	0.002	0.001

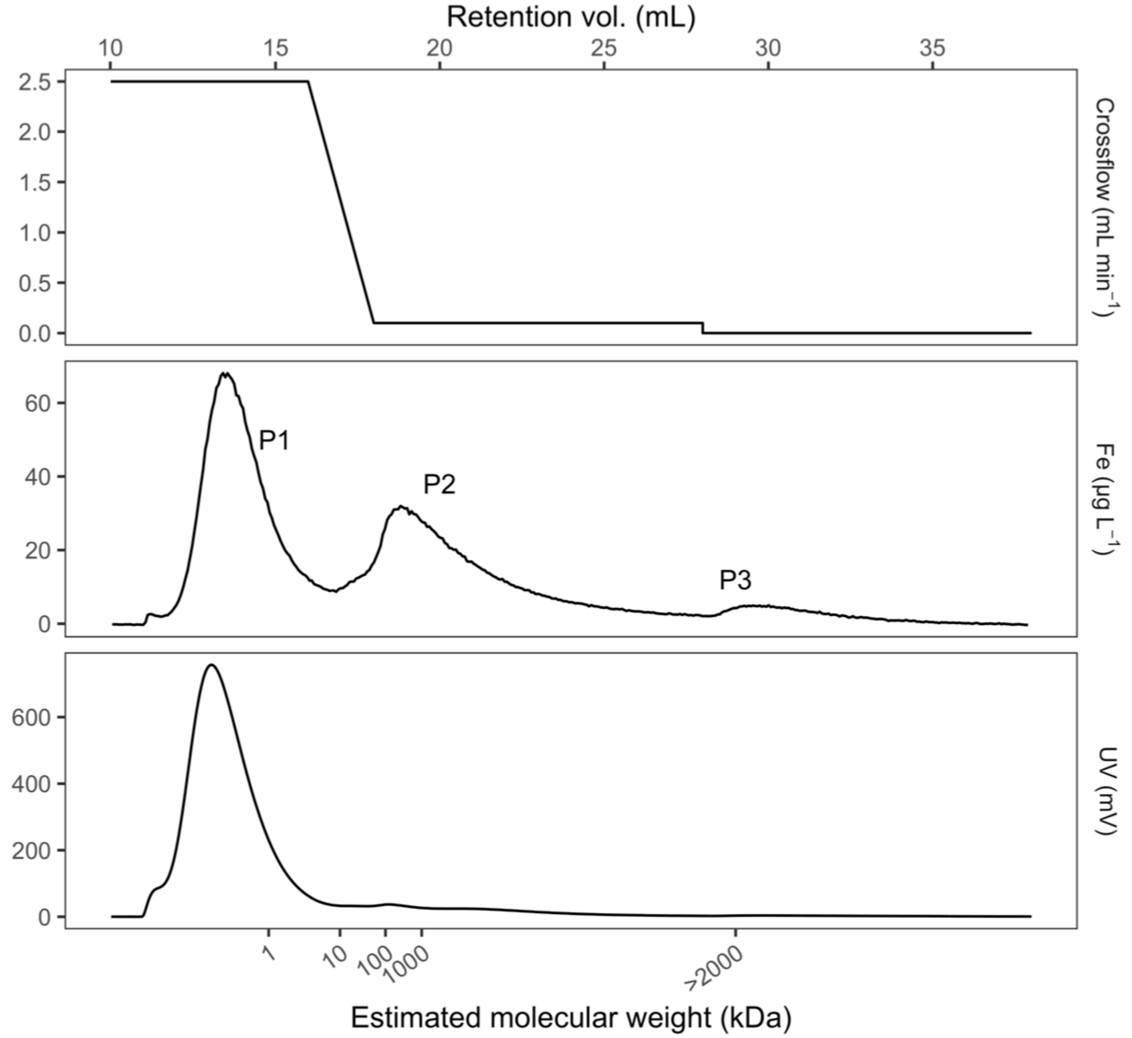

Figure C2. A sample Fe and UV fractogram from the dataset (Fraser Lake, June 10), along with the cross-flow program over the analytical run.

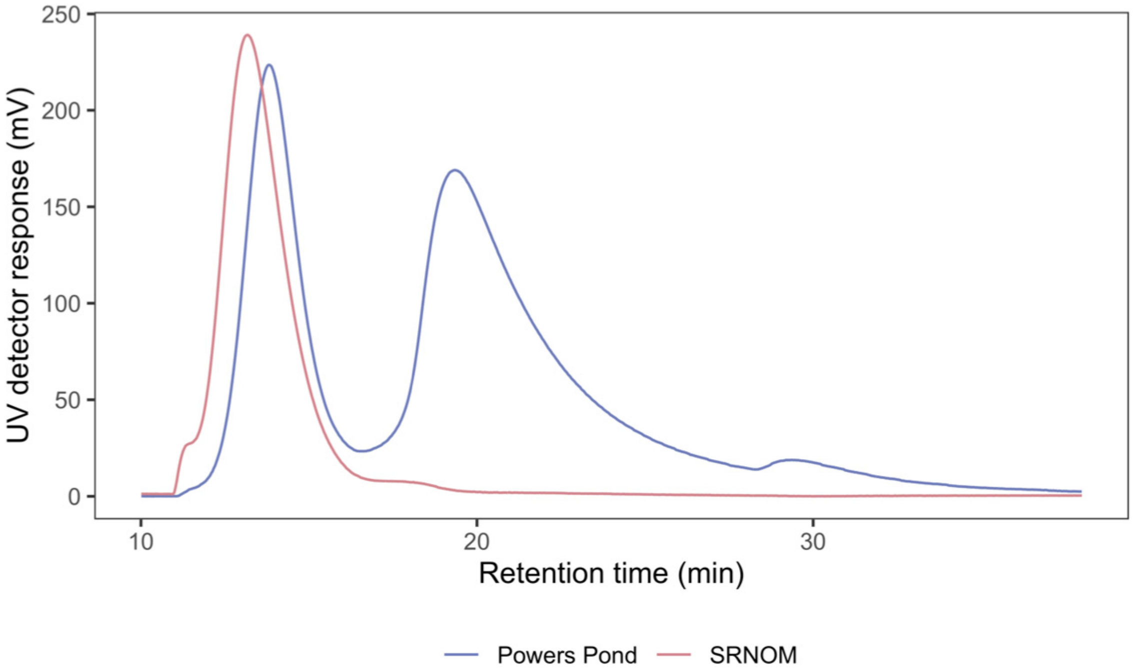

Figure C3. Elution profiles of Suwannee River natural organic matter (SRNOM) and Powers Pond (July sample) compared.

C2. Additional information on statistical analyses

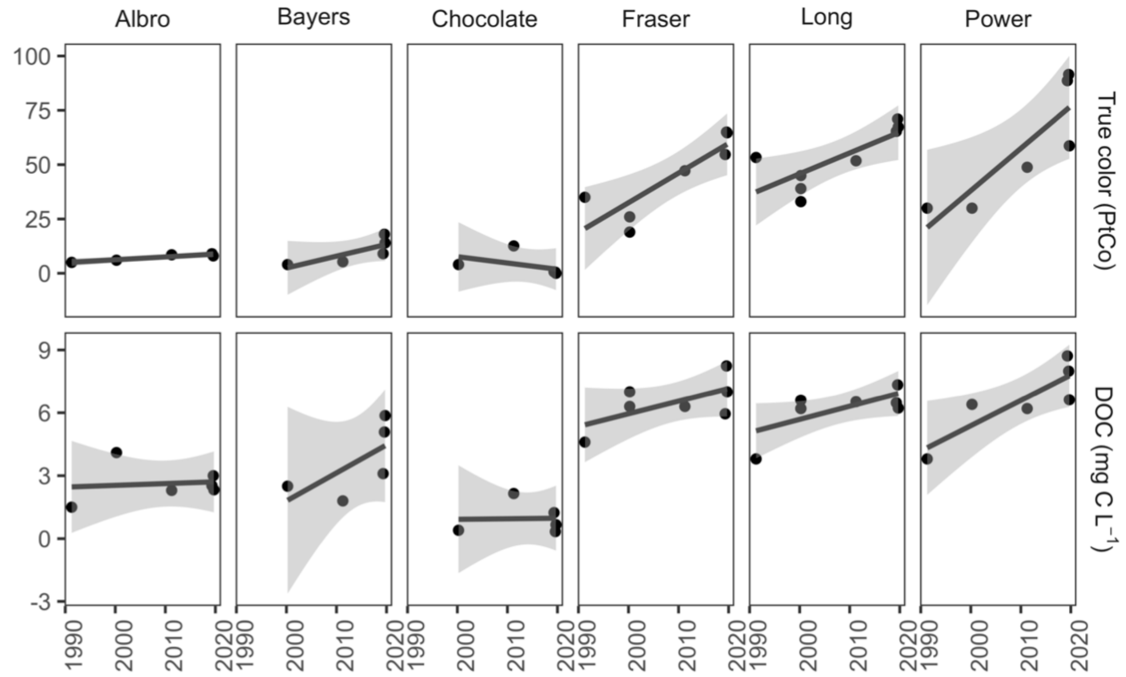

Figure C4. Time series of DOC and true color representing the six study lakes. Each solid line represents a linear fit to the data, and the grey shaded regions define a pointwise 95% confidence interval on the fitted values.

Table C2. Linear slopes describing the change in DOC and true color in the six study lakes.

Lake	Type	Parameter	Unit	Slope (unit/yr)	p-value
Albro	Low DOC	DOC	mg C/L-yr	0.01	0.83
Albro	Low DOC	True color	PtCo	0.13	0.02
Fraser	High DOC	DOC	mg C/L-yr	0.06	0.13
Fraser	High DOC	True color	PtCo	1.36	0.01
Long	High DOC	DOC	mg C/L-yr	0.06	0.06
Long	High DOC	True color	PtCo	0.96	0.03
Power	High DOC	DOC	mg C/L-yr	0.12	0.03
Power	High DOC	True color	PtCo	1.94	0.03
Bayers	Low DOC	DOC	mg C/L-yr	0.13	0.23
Bayers	Low DOC	True color	PtCo	0.55	0.12
Chocolate	Low DOC	DOC	mg C/L-yr	0.00	0.96
Chocolate	Low DOC	True color	PtCo	-0.29	0.43

The smooth functions fit to the time series in Figure 10 take the form

$$y = \beta_0 + f(t) + \epsilon$$

where y is the response, t is a time variable, β_0 is the intercept, ϵ is the error term, and $f(t)$ is a linear combination of basis functions:

$$f(t) = \sum_{j=1}^{k} b_j\,(t)\beta_j$$

where β_j is the weight associated with the jth basis function.

Here, each function is a weighted sum of two cubic basis functions (Figure C5); models are further described in Table C3.

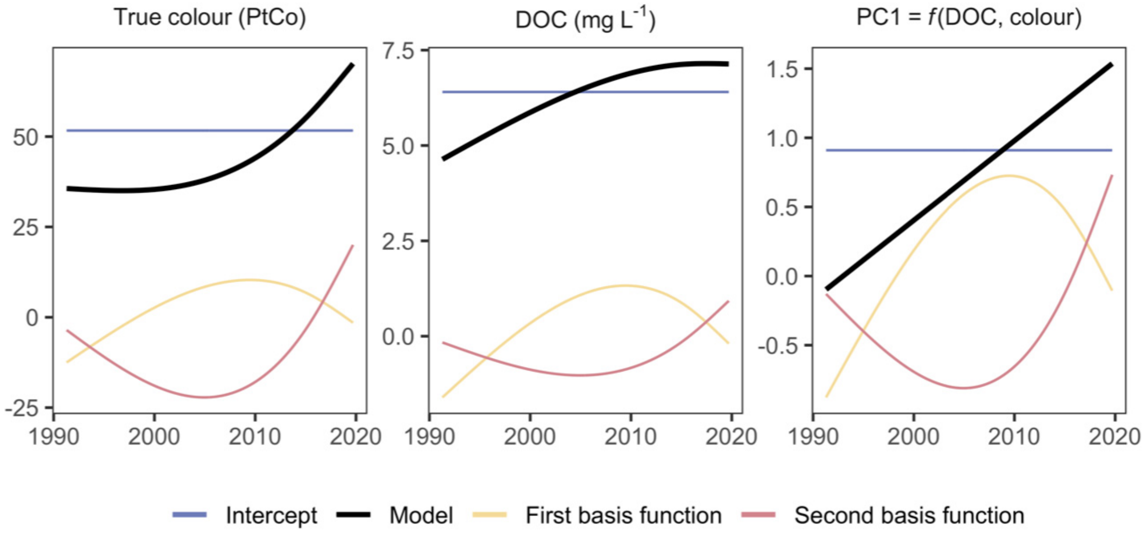

Figure C5. The smooth functions fit to the time series in Figure 10 are weighted sums of cubics.

Table C3. Terms, p-values, and r-squared values associated with each smooth function.

Parameter	Term	Estimate	p-value	Adjusted r-squared
True color (PtCo)	Intercept	51.70	<0.001	0.691
	f(date)	NA	<0.001	
DOC (mg/L)	Intercept	6.40	<0.001	0.55
	f(date)	NA	<0.001	
PC1 = *f*(DOC, color)	Intercept	0.91	<0.001	0.708
	f(date)	NA	<0.001	

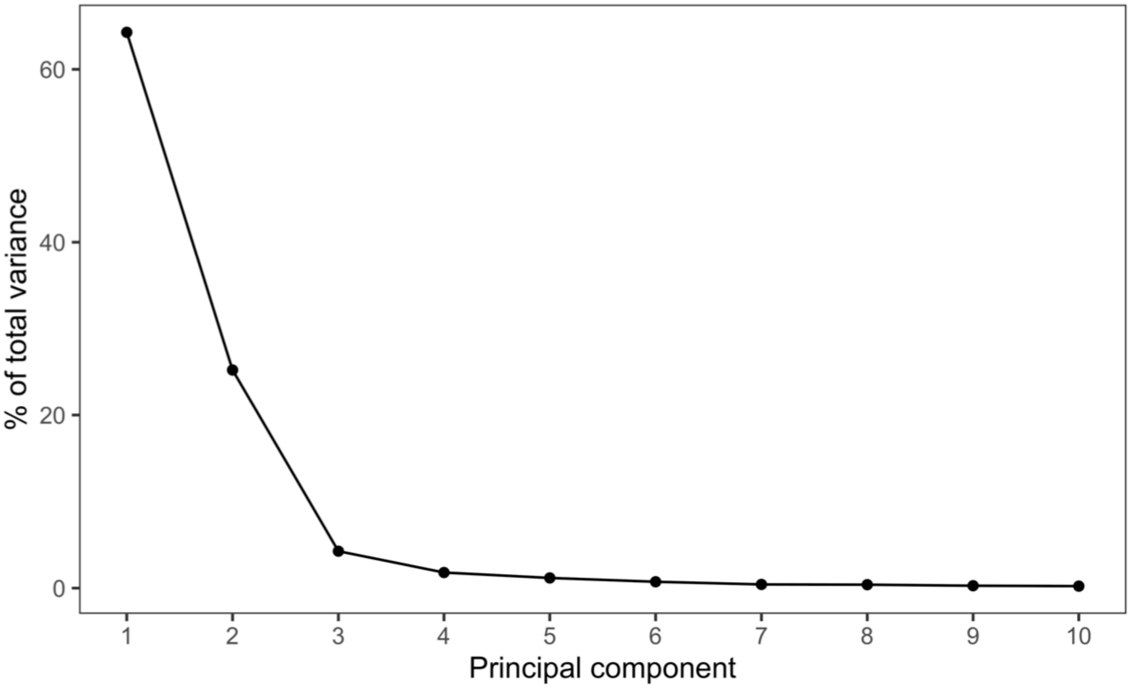

Figure C6. Scree plot summarizing the proportion of total variance accounted for by each principal component.

References for Appendix C

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APPENDIX D: SUPPORTING DATA FOR CHAPTER 5

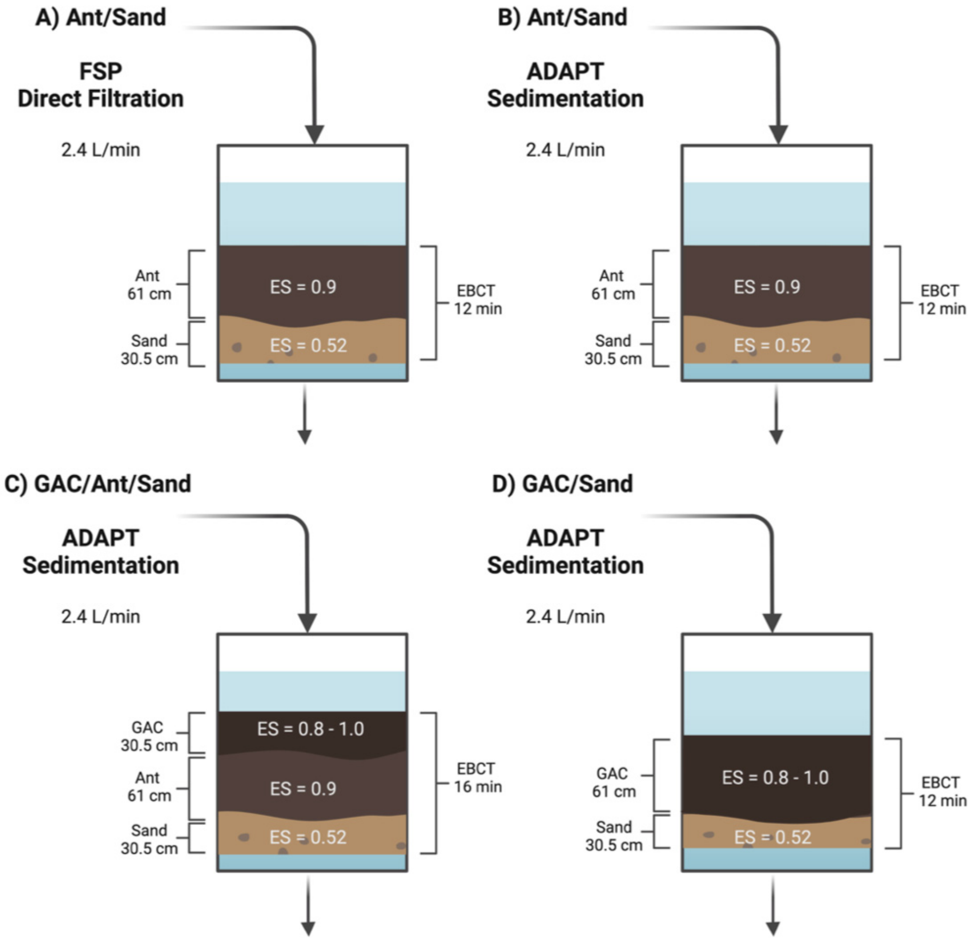

Figure D1. Detailed schematic of filter media configurations used in this study. The FSP Ant/Sand (A) filter was fed with unclarified water (direct filtration), while the adaptation (ADAPT) Ant/Sand (B), GAC/Ant/Sand (C), and GAC/Sand (D) filters were fed with clarified water. The GAC/Ant/Sand and GAC/Sand filters were previously operated for 26,700 (GAC EBCT = 4 min) and 11,800 BV (GAC EBCT = 8 min), respectively.

Table D1. Summary of NOM and DBP formation potential concentrations and removal rates for the full-scale plant (FSP) and adaptation (ADAPT) trains. Percent removals are calculated from raw water concentrations. Note that values represent median and parentheses indicate interquartile range. For % removals, values below zero were omitted.

Train	n	UV254 (cm^{-1})	n	UV254 (% Removal)	n	DOC (mg/L)	n	DOC (% Removal)	n	SUVA (L-mg/m)	n	SUVA (% Removal)	n	THMfp (µg/L)	n	HAAfp (µg/L)
FSP – Raw Water	43	0.093 (0.015)		NA	37	3.0 (0.27)		NA	37	3.3 (0.28)		NA	3	143.2 (4.6)	3	102.7 (14.9)
ADAPT – Raw Water	47	0.094 (0.017)		NA	39	3.1 (0.37)		NA	39	3.2 (0.48)		NA	3	143.3 (15.1)	3	85.8 (3.9)
FSP – Prefilter	43	0.031 (0.003)	41	68.2 (5.4)	32	1.8 (0.17)	31	39.2 (4.1)	27	1.7 (0.12)	27	47.1 (4.7)		NA		NA
ADAPT – Prefilter	45	0.028 (0.004)	42	70.9 (5.3)	32	1.7 (0.17)	31	40.9 (5.6)	26	1.6 (0.20)	26	47.6 (6.2)		NA		NA
FSP – Ant/Sand	42	0.029 (0.005)	40	69.0 (4.5)	36	1.7 (0.17)	36	42.0 (2.6)	32	1.7 (0.16)	27	48.3 (8.2)	7	58.9 (10.7)	12	23.9 (1.i8)
ADAPT – Ant/Sand	45	0.027 (0.006)	43	71.8 (5.2)	38	1.7 (0.18)	38	44.0 (4.9)	28	1.6 (0.17)	28	47.8 (5.4)	8	54.6 (5.5)	13	22.5 (5.7)
ADAPT – GAC/Ant/Sand	47	0.023 (0.004)	44	76.6 (4.8)	40	1.5 (0.12)	39	50.2 (5.3)	29	1.5 (0.18)	28	49.4 (8.0)	8	41.5 (4.1)	13	18.5 (3.7)
ADAPT – GAC/Sand	45	0.017 (0.006)	43	82.7 (4.9)	39	1.2 (0.16)	38	58.8 (7.9)	29	1.3 (0.27)	28	57.0 (13.1)	8	34.8 (3.1)	13	13.2 (3.3)

Table D2. Summary of Fe and Mn concentration and removal rates for the full-scale plant (FSP) and adaptation (ADAPT) trains. Percent removals are calculated from pre-filter values. Note that values represent median, and parentheses indicate interquartile range.

Train	Phase	n	Total Fe (µg/L)	n	Total Fe (% Removal)	n	Dissolved Fe (µg/L)	n	Dissolved Fe (% Removal)	n	Total Mn (µg/L)	n	Total Mn (% Removal)	n	Dissolved Mn (µg/L)	n	Dissolved Mn (% Removal)
FSP – Raw Water	***A***	10	49.0 (5.7)		NA	10	17.8 (7.7)		NA	11	30.8 (14.9)		NA	11	14.3 (5.2)		NA
	B	13	37.2 (24.1)			13	10.2 (1.9)			14	102.0 (209)			14	23.4 (3.1)		
	C	15	53.1 (27.2)			15	22.6 (11.2)			16	47.7 (74.0)			16	17.9 (7.7)		
ADAPT – Raw Water	***A***	14	51.8 (11.0)		NA	14	17.9 (7.6)		NA	14	45.7 (25.0)		NA	14	24.0 (3.5)		NA
	B	14	48.9 (55.9)			14	10.2 (2.0)			14	98.9 (195.3)			14	17.3 (3.0)		
	C	15	64.3 (15.5)			15	20.7 (9.3)			16	63.4 (59.7)			16	23.7 (2.3)		
FSP – Prefilter	***A***	10	102.6 (36.1)	10	-100.1 (58.2)	10	3.5 (0.52)	10	77.1 (7.8)	11	84.7 (23.5)	11	-176.1 (143.1)	11	20.7 (3.7)	11	5.9 (3.7)
	B	13	89.9 (38.5)	13	-110 (236)	13	2.8 (0.84)	13	70.7 (6.3)	14	36.0 (53.9)	14	64.0 (103.1)	14	16.8 (2.7)	14	-7.4 (61.3)
	C	15	81.4 (23.1)	15	-64.2 (64.2)	15	3.9 (2.0)	15	81.6 (9.9)	16	72.9 (17.8)	16	-30.2 (145.3)	16	12.7 (2.8)	16	39.9 (26.2)
ADAPT – Prefilter	***A***	14	76.1 (22.4)	14	-43.2 (76.8)	14	3.4 (0.8)	14	79.5 (10.7)	14	86.6 (63.8)	14	-83.8 (147.2)	14	20.8 (3.1)	14	11.7 (11.8)
	B	14	71.0 (8.3)	14	-34.3 (128.5)	14	3.1 (0.9)	14	67.9 (11.3)	14	54.8 (54.9)	14	54.2 (110.8)	14	16.9 (3.3)	14	-2.3 (10.2)
	C	15	92.9 (53.3)	15	-58.2 (149.8)	15	3.5 (3.1)	15	80.5 (16.4)	16	99.5 (55.6)	16	-2.7 (117.9)	16	15.2 (3.2)	16	35.7 (23.3)
FSP – Ant/Sand	***A***	10	3.3 (0.6)	10	96.6 (1.9)	10	3.4 (0.4)	10	6.5 (16.0)	10	23.2 (2.0)	11	73.5 (9.9)	10	22.4 (1.7)	11	-10.3 (16.3)
	B	13	2.8 (0.9)	13	96.5 (2.1)	13	2.6 (0.6)	13	16.9 (15.6)	13	16.7 (3.6)	14	44.4 (35.6)	13	16.1 (2.6)	14	2.7 (7.1)
	C	15	4.0 (1.3)	15	95.5 (1.7)	15	3.2 (1.8)	15	4.3 (17.8)	16	16.2 (2.9)	16	78.4 (5.3)	16	15.8 (3.0)	16	-18.7 (22.9)
ADAPT – Ant/Sand	***A***	13	3.4 (0.7)	14	94.8 (1.6)	14	3.3 (0.6)	14	-4.4 (21.8)	14	25.6 (5.6)	14	72.2 (13.1)	13	24.3 (4.8)	14	-13.4 (10.3)

	B	14	3.2 (0.7)	14	95.3 (1.1)	14	2.6 (0.3)	14	15.7 (26.7)	13	19.5 (4.9)	14	56.1 (53.1)	13	18,.6 (3.0)	14	-6.5 (13.6)
	C	15	3.6 (1.9)	15	96.1 (4.4)	15	3.3 (2.2)	15	9.3 (12.5)	16	16.5 (3.3)	16	83.2 (9.3)	16	15.8 (4.3)	16	1.5 (26.2)
ADAPT – GAC/Ant/Sand	***A***	14	3.4 (0.5)	14	95.1 (1.9)	14	3.4 (0.8)	14	4.3 (17.7)	14	27.2 (3.7)	14	68.9 (19.6)	14	27.8 (4.0)	14	-29.3 (22.6)
	B	14	3.1 (0.7)	14	95.6 (1.4)	14	2.6 (0.4)	14	16.6 (41.6)	14	22.5 (7.3)	14	59.3 (48.4)	14	23.4 (7.5)	14	-12.6 (19.5)
	C	15	3.7 (1.7)	15	96.1 (4.4)	15	3.4 (1.5)	15	7.6 (26.3)	16	18.1 (6.6)	16	81.8 (18.3)	16	18.8 (6.7)	16	-23.2 (23.5)
ADAPT – GAC/Sand	***A***	14	3.1 (0.3)	14	95.1 (1.3)	14	3.5 (0.7)	14	9.3 (33.9)	13	28.7 (2.6)	14	68.8 (25.2)	14	26.6 (2.9)	14	-28.8 (23.9)
	B	14	2.9 (0.5)	14	96.0 (0.9)	14	2.5 (0.2)	14	18.5 (25.6)	13	24.7 (8.1)	14	56.4 (50.6)	14	24.7 (7.6)	14	-12.9 (17.3)
	C	15	3.4 (2.3)	15	95.9 (3.7)	15	3.0 (1.4)	15	14.3 (19.8)	16	20.6 (9.0)	16	77.2 (22.1)	16	19.6 (6.5)	16	-28.9 (33.6)

Table D3. Results from two-sided Wilcoxon-signed rank tests on median NOM parameters and DBP formation potential for the different treatment comparisons. Symbols indicate level of significance, * = <0.05, ** = <0.01, * = <0.001, N.S. = not significantly different (p > 0.05).**

Comparison	UV254 (cm-1)	UV254 (% Removal)	DOC (mg/L)	DOC (% Removal)	SUVA (L-mg/m)	SUVA (% Removal)	THMfp (µg/L)	HAAfp (µg/L)
FSP Prefilter vs. ADAPT Prefilter	0.01009*	0.01209*	0.04917 N.S.	0.151 N.S.	0.6159 N.S.	0.8798 N.S.	NA	NA
FSP Ant/Sand vs. ADAPT Ant/Sand	0.05456 N.S.	0.294 N.S.	0.344 N.S.	0.2942*	0.4315 N.S.	0.576 N.S.	0.2243 N.S.	0.221 N.S.
FSP Ant/Sand vs. ADAPT GAC/Ant/Sand	6.387e-11***	7.174e-06***	5.096e-10***	7.204e-06***	0.0004316***	0.06958 N.S.	0.01767*	2.493e-05***
FSP Ant/Sand vs. ADAPT GAC/Sand	1.065e-13***	6.462e-08***	1.095e-13***	1.642e-07***	2.124e-06***	0.001124**	0.01767*	2.493e-05***
ADAPT Ant/Sand vs. ADAPT GAC/Ant/Sand	9.753e-08***	4.848e-05***	1.21e-08***	0.0001661***	0.008644**	0.1582 N.S.	0.01008*	0.01034*
ADAPT Ant/Sand vs. ADAPT GAC/Sand	2.055e-13***	3.553e-08***	6.673e-14***	1.088e-06***	2.176e-05***	0.002689**	0.01008*	5.094e-05***
ADAPT GAC/Ant/Sand vs. ADAPT GAC/Sand	4.788e-10***	4.208e-05***	6.228e-12***	5.93e-05***	0.0062**	0.02975*	0.01359*	0.00012***

Table D4. Results from two-sided Wilcoxon-signed rank tests on median total and dissolved Fe and Mn for the different treatment comparisons across the different study Phases (A and C used $KMnO_4$ pre-treatment, Phase C had no $KMnO_4$). Percent removals are relative to filter influent. Symbols indicate level of significance, * = <0.05, ** = <0.01, * = <0.001, N.S. = not significantly different ($p > 0.05$).**

Comparison	Phase	Total Fe (µg/L)	Total Fe (% Removal)	Dissolved Fe (µg/L)	Dissolved Fe (% Removal)	Total Mn (µg/L)	Total Mn (% Removal)	Dissolved Mn (µg/L)	Dissolved Mn (% Removal)
FSP Prefilter vs. ADAPT Prefilter	***A***	0.04337*	0.09516 N.S.	0.5387 N.S.	0.6605 N.S.	0.6774 N.S.	0.7035 N.S.	1 N.S.	0.1688 N.S.
	B	0.05527 N.S.	0.344 N.S.	0.9034 N.S.	0.7896 N.S.	0.8722 N.S.	0.9085 N.S.	0.9817 N.S.	0.1821 N.S.
	C	0.8357 N.S.	0.9842 N.S.	0.7716 N.S.	0.7716 N.S.	0.1576 N.S.	0.8358 N.S.	0.7716 N.S.	0.4419 N.S.
FSP Ant/Sand vs. ADAPT Ant/Sand	***A***	0.6418 N.S.	0.06732 N.S.	0.8768 N.S.	0.6418 N.S.	0.4757 N.S.	0.8768 N.S.	0.4757 N.S.	0.4025 N.S.
	B	0.7196 N.S.	0.1662 N.S.	0.7583 N.S.	0.7196 N.S.	0.04024*	0.7196 N.S.	0.3299 N.S.	0.09059 N.S.
	C	0.3738 N.S.	0.4408 N.S.	0.89 N.S.	0.6468 N.S.	0.3964 N.S.	0.2662 N.S.	0.5847 N.S.	0.02046*
FSP Ant/Sand vs. ADAPT GAC/Ant/Sand	***A***	0.7474 N.S.	0.2081 N.S.	0.9766 N.S.	0.93 N.S.	0.00375**	0.7035 N.S.	0.003107**	0.00917**
	B	0.9806 N.S.	0.2968 N.S.	0.8651 N.S.	1 N.S.	0.008177**	0.5768 N.S.	0.005267**	0.0002716***
	C	0.4891 N.S.	0.5665 N.S.	0.7073 N.S.	0.4306 N.S.	0.0009745***	0.9549 N.S.	0.00349**	0.6494 N.S.
FSP Ant/Sand vs. ADAPT GAC/Sand	***A***	0.1629 N.S.	0.2512 N.S.	0.9259 N.S.	0.8768 N.S.	0.001737**	0.6869 N.S.	0.006981**	0.01006*
	B	0.5727 N.S.	0.6816 N.S.	0.6444 N.S.	0.5383 N.S.	0.002936**	0.4119 N.S.	0.002481**	5.094e-05***
	C	0.5396 N.S.	0.5665 N.S.	0.6783 N.S.	0.229 N.S.	0.0003191***	0.6109 N.S.	0.001101**	0.1672 N.S.
ADAPT Ant/Sand vs. ADAPT GAC/Ant/Sand	***A***	0.4233 N.S.	0.2159 N.S.	0.7896 N.S.	0.8271 N.S.	0.04938*	0.2541 N.S.	0.0186*	0.008177**
	B	0.5441 N.S.	0.6104 N.S.	0.4233 N.S.	1 N.S.	0.2159 N.S.	0.7524 N.S.	0.1264 N.S.	0.1008 N.S.
	C	0.9249 N.S.	0.9249 N.S.	0.9249 N.S.	0.5854 N.S.	0.009832**	0.1935 N.S.	0.01849*	0.004159**
ADAPT Ant/Sand vs. ADAPT GAC/Sand	***A***	0.01594*	0.09059 N.S.	0.6444 N.S.	0.9183 N.S.	0.05133 N.S.	0.3299 N.S.	0.02404*	0.02745*
	B	0.1239 N.S.	0.2184 N.S.	0.2184 N.S.	0.6081 N.S.	0.137 N.S.	0.356 N.S.	0.08123 N.S.	0.01833*

	C	0.1095 N.S.	0.8127 N.S.	0.02679*	0.104 N.S.	0.003937 N.S.	0.1809 N.S.	0.005702**	0.004676**
ADAPT GAC/Ant/Sand vs. ADAPT GAC/Sand	***A***	0.2159 N.S.	0.6448 N.S.	0.8651 N.S.	0.8271 N.S.	1 N.S.	0.9034 N.S.	0.7159 N.S.	0.7159 N.S.
	B	0.1667 N.S.	0.3693 N.S.	0.7159 N.S.	0.68 N.S.	0.6104 N.S.	0.5768 N.S.	0.4233 N.S.	0.4119 N.S.
	C	0.06877 N.S.	0.9127 N.S.	0.02679*	0.3334 N.S.	0.4397 N.S.	0.7487 N.S.	0.5194 N.S.	0.407 N.S.

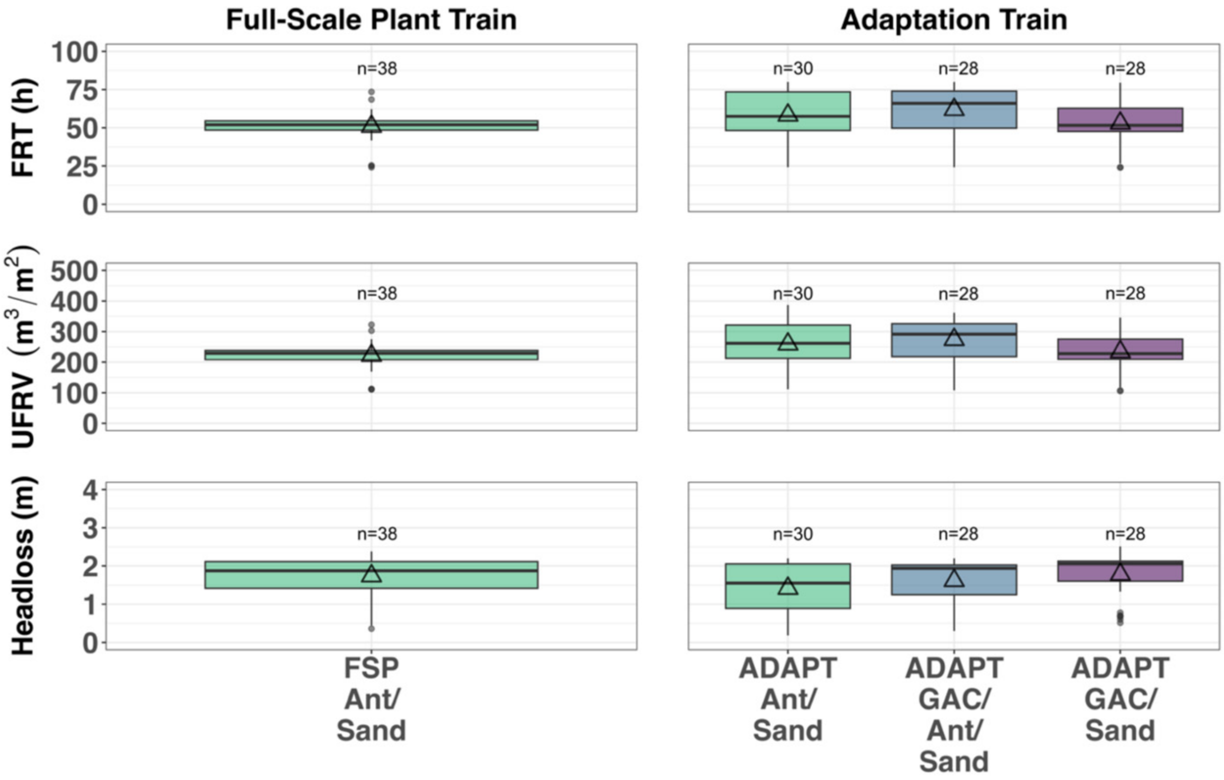

Figure D2. Filter run time (top), Unit Filter Run Volume (middle) and headloss (bottom) for the FSP (direct filtration with anthracite/sand filters, left) and adaptation train (sedimentation with anthracite/sand, GAC/Ant/Sand, and GAC/Sand filters, right). Triangle indicates mean values.

Table D5. Summary of turbidity and hydraulic performance in terms of filter run time (FRT), unit filter run volume (UFRV) and headloss rates for the full-scale plant (FSP) and adaptation (ADAPT) trains. Note that values represent median, and parentheses indicate interquartile range.

Train	n	Turbidity (NTU)	n	FRT (h)	n	UFRV (m^3/m^2)	n	Headloss (m)
FSP – Raw Water	42	0.54 (0.22)		NA		NA		NA
ADAPT – Raw Water	46	0.58 (0.23)		NA		NA		NA
FSP – Prefilter	42	3.6 (1.1)		NA		NA		NA
ADAPT – Prefilter	44	3.0 (4.0)		NA		NA		NA
FSP – Ant/Sand	41	0.07 (0.04)	38	52.3 (5.7)	38	230 (26.7)	38	2.0 (0.55)
ADAPT – Ant/Sand	44	0.07 (0.04)	30	66.1 (23.75)	30	288 (103)	30	1.61 (0.75)
ADAPT – GAC/Ant/Sand	46	0.07 (0.04)	28	69.7 (14.1)	28	313 (57.8)	28	1.98 (0.28)
ADAPT – GAC/Sand	44	0.07 (0.05)	28	58.1 (15.1)	28	249 (65.9)	28	2.1 (0.11)

Table D6. Results from two-sided Wilcoxon-signed rank tests on median filter turbidity and hydraulic performance parameters for the different treatment comparisons. Symbols indicate level of significance, * = <0.05, ** = <0.01, * = <0.001, N.S. = not significantly different ($p > 0.05$).**

Comparison	Turbidity (NTU)	FRT (h)	UFRV (m^3/m^2)	Headloss (m)
FSP Prefilter vs. ADAPT Prefilter	0.2183 N.S.	NA	NA	NA
FSP Ant/Sand vs. ADAPT Ant/Sand	0.2546 N.S.	0.00185**	0.001136**	0.03521*
FSP Ant/Sand vs. ADAPT GAC/Ant/Sand	0.2801 N.S.	5.089e-07***	2.877e-07***	0.8916 N.S.
FSP Ant/Sand vs. ADAPT GAC/Sand	0.7382 N.S.	0.07026 N.S.	0.06082 N.S.	0.035*
ADAPT Ant/Sand vs. ADAPT GAC/Ant/Sand	0.8086 N.S.	0.2123 N.S.	0.2278 N.S.	0.06079 N.S.
ADAPT Ant/Sand vs. ADAPT GAC/Sand	0.1803 N.S.	0.0927 N.S.	0.08553 N.S.	9.702e-05***
ADAPT GAC/Ant/Sand vs. ADAPT GAC/Sand	0.2167 N.S.	0.001011**	0.0005286***	0.002368**

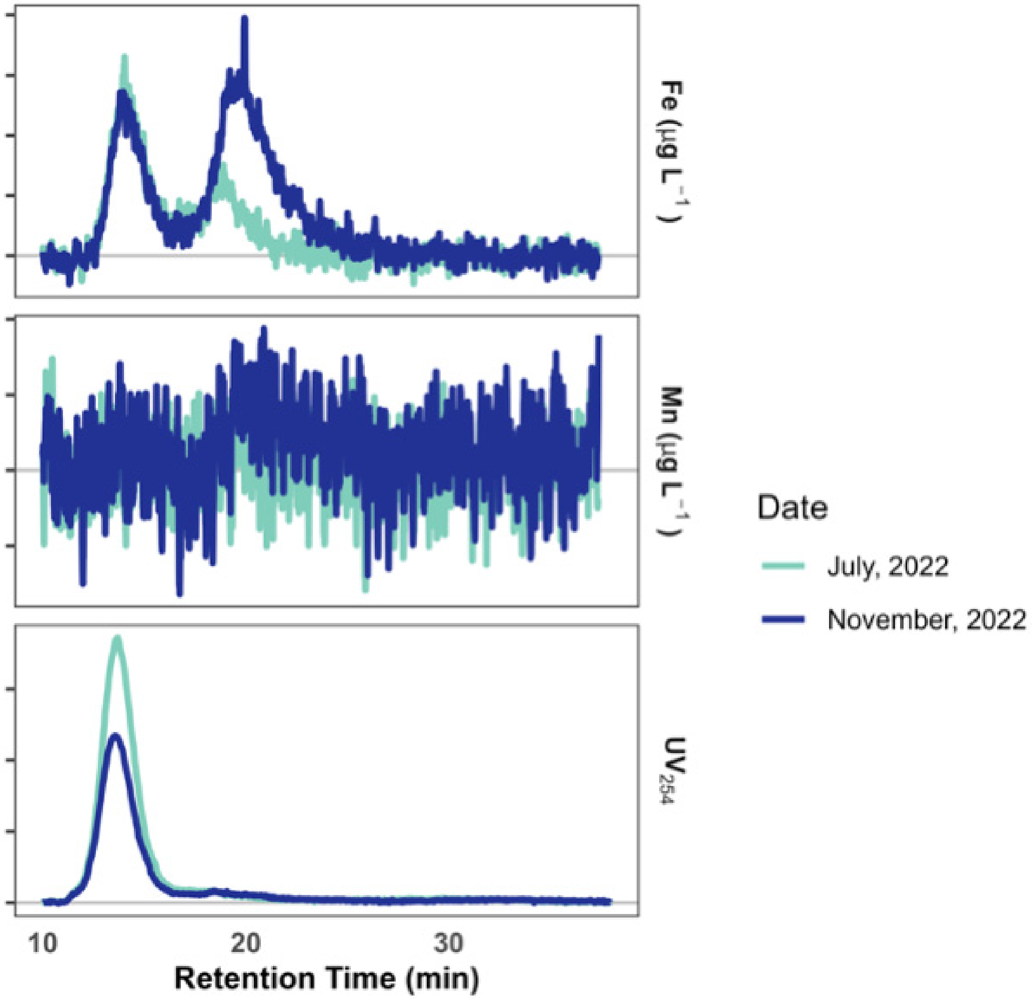

Figure D3. Figure D3. FFF-UV-ICPMS fractograms for raw water collected in Pockwock Lake in summer (July 2022) and fall (November 2022).