ADAPTING DRINKING WATER TREATMENT STRATEGIES TO CHANGING SOURCE WATER QUALITY UNDER THE STRESS OF CLIMATE IMPACTS

by

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ABSTRACT

Over the last few decades, noticeable chemical and microbiological changes in water quality have been observed in Atlantic Canada lakes as a result of recovery from acidification and climatic drivers (e.g. warming temperature, increased precipitation and droughts). These factors are causing changes in pH, alkalinity, dissolved organic matter (DOM) concentrations, and increased occurrence, intensity, and frequency of harmful algae blooms (HABs). This dynamic nature of source water quality has multiple implications for drinking water treatment in unconventional plants (i.e. without sedimentation or flotation), in both the quality and quantity of drinking water produced, causing increased concentrations of disinfection by-products (DBPs), the potential for algal toxins in drinking water, and plugging of unit processes (e.g. adsorption clarifiers, filters).

Two drinking water utilities in Atlantic Canada that were built prior to the observed changes in source water quality are experiencing or anticipating the aforementioned consequences. These plants will ultimately require significant infrastructure and process upgrades; however, immediate solutions are needed to mitigate the problem while more long-term sustainable designs are implemented. The objective of the presented research was to investigate both immediate strategies and potential longer-term solutions to adapt to long-term changes and seasonal fluctuations in lake water quality.

The impacts of adjusting coagulation parameters (i.e. coagulant type, dose, and coagulation pH) on natural organic matter (NOM) and aluminum (Al) removal was conducted at both the bench- and pilot-scale. Results determined that the partial substitution of aluminum sulphate (alum) with cationic polyelectrolyte did not improve NOM removal, nor did it improve the unit filter run volumes (UFRV) in a direct filtration pilot plant. It was determined that DBP precursor material remaining in the filtrate was likely resistant to coagulation, and as such, additional treatment processes are recommended to improve their removal. However, the addition of polyelectrolyte did improve effluent turbidity when alum was underdosed, which may be beneficial in controlling turbidity spikes caused by heavy precipitation and storms. Studies adjusting the pH and alum dose for treatment of the two source waters had conflicting results. However, the importance of considering the downstream effects when implementing these strategies at the full-scale was highlighted as optimal operating parameters for treatment of NOM and Al often caused poor filter hydraulic performance.

With respect to longer-term solutions, pilot-scale tests concluded that increasing the effective size of filter media, while maintaining the bed length to depth ratio, extended filter run cycles without compromising the quality of the effluent. This strategy could be used to offset the unintended consequences of altering coagulation parameters (e.g. reduced filter run cycles) to produce high quality drinking water. Another long-term solution considered was upgrading an adsorption clarification plant to ballasted flocculation and sedimentation. In comparing contaminant removal through subsequent treatment steps for each process, it was determined that the upgrade would have minimal impact on drinking water quality and process operation. Further, the switch to ballasted flocculation would reduce the sensitivity of the plant to HABs.

LIST OF ABBREVIATIONS AND SYMBOLS USED

AD	Alzheimer’s disease
Al	Aluminum
Alum	Aluminum sulphate
ANOVA	Analysis of variance
BA	Ballasting agent
BF	Ballasted flocculation
Ca	Calcium
cm	Centimeter
d	Depth
DBP	Disinfection by-product
DBPfp	Disinfection by-product formation potential
DOC	Dissolved organic matter
DOM	Dissolved organic matter
ES	Effective size
Fe	iron
FSP	Full-scale plant
HAA	Haloacetic acid formation potential
HAAfp	Haloacetic acid formation potential
HAB	Harmful algae bloom
HIA	Hydrophilic acid
HIB	Hydrophilic base
HIN	Hydrophilic neutral
HON	Hydrophobic neutral
hr	Hour
JDKWSP	J.D. Kline Water Supply Plant
L	Litre
L	length

m	Meter
MAC	Maximum allowable concentration
mg	Milligram
MLD	Mega-litres per day
mm	Millimeter
Mn	Manganese
MW	Molecular weight
MWTP	Moncton Water Treatment Plant
nm	Nanometer
NOM	Natural organic matter
NTU	Nephelometric turbidity units
OG	Operational guideline
PAC	Powdered activated carbon
PACl	Polyaluminum chloride
PES	Polyethersulfone
PP	Pilot plant
SUVA	Specific ultraviolet absorbance
TCU	True color units
THM	Trihalomethane
THMfp	Trihalomethane formation potential
TOC	Total organic carbon
UFRV	Unit filter run volume
UV_{254}	Ultraviolet absorbance at 254 nm
µg	Microgram
µm	Micrometer

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CHAPTER 1: INTRODUCTION

Over the last few decades, increasing concentrations of natural organic matter (NOM), measured as dissolved organic carbon (DOC), have been recorded in many regions across Northern America and Europe (Garmo 2020; Garmo et al. 2014; Monteith et al. 2007). This trend has often been associated with ‘recovery from acidification’, a phenomenon defined as increasing acid neutralization capacity, alkalinity, or pH in response to reduced atmospheric acid deposition (Evans and Monteith 2001; Stoddard et al. 1999). However, the composition and character of NOM in surface waters is also impacted by climatic factors, including precipitation events (e.g. increased rainfall and droughts) and warming temperatures. These additional drivers often lead to amplified seasonal fluctuation in surface water quality (Imtiazy et al. 2020; Meyer-Jacob et al. 2020; Strock et al. 2016; De Wit et al. 2016; Xiao, Rohrlack, and Riise 2020)

Global increases in frequency, intensity, and duration of harmful algae blooms (HABs) have also been reported in the last few decades (Huisman et al. 2018; Moore et al. 2008; O’Neil et al. 2012). Blooms of blue-green algae, or cyanobacteria, are of particular concern due to their production of toxic, secondary metabolites, called cyanotoxins (Huisman et al. 2018; O’Neil et al. 2012). The drivers behind the proliferation of cyanobacteria are vast and diverse, making it difficult to pin-point the individual impacts of the various factors (O’Neil et al. 2012; Wagner and Adrian 2009); however, increasing temperatures due to climate warming and increasing lake color, also referred to as brownification, have proven to stimulate the growth of cyanobacteria (Creed et al. 2018; Moore et al. 2008; O’Neil et al. 2012; Urrutia-Cordero, Ekvall, and Hansson 2016; Wagner and Adrian 2009).

This dynamic nature of lake water quality has multiple design implications for drinking water treatment. NOM is the primary precursor material for disinfection by-products (DBPs), cancerous compounds that are regulated by Health Canada (2019). As such, higher concentrations of NOM in the supply can result in higher concentrations of DBPs in the treated water if the plant is unable to effectively mitigate the increasing organic load. Further, the presence of HABs in drinking water sources presents the concern of cyanotoxins. Although intracellular cyanotoxins can be removed with coagulation/flocculation, extracellular cyanotoxins are not effectively removed through conventional treatment processes and can cause liver damage, and neurological and reproductive effects (Huisman et al. 2018; Noyma et al. 2017). Additionally, both increasing concentrations of dissolved organic matter (DOM) and HABs add to the solids loading on treatment plants, which may lead to plugging of unit processes (e.g. filtration, adsorption clarification), greater chemical demand, and reduced overall plant productivity (Anderson et al. 2017; Ghernaout, Ghernaout, and Saiba 2010; Marston et al. 2015).

On top of shifts in source water quality, the advancement of science has led to more awareness regarding contaminants in drinking water and changes in treatment regulations and guidelines. Recently, Health Canada proposed new guidelines for Al, including halving the current operational guideline (OG) to 50μg/L and adding a maximum allowable concentration (MAC) of 2.9 mg/L (Health Canada 2019a). As more than 70% of surface drinking water treatment plants in Canada use aluminum-based coagulants to remove contaminants, such as DOM and algae from source water supplies (Statistics Canada 2015), brownification of source waters and increasing occurrence of HABs will increase coagulant demand. A disregard for coagulation optimization or poor process control can result in high concentrations of aluminum (Al) and NOM in the treated water. As such, factors influencing their efficacy (e.g. coagulation pH and dose) should be well studied.

The observed changes in source water quality have caused some challenges in unconventional drinking water treatment plants (e.g. direct filtration, adsorption clarification) in Atlantic Canada. Some plants that were constructed prior to noticeable shifts in source water quality are operating near, or past, their design guidelines and are likely to require infrastructure upgrades for mitigation of future circumstances. However, the design and construction of plant upgrades is a prolonged endeavour, with design and implementation of capital improvements typically spanning years with detailed research needs for understanding climate and anthropogenic-driven source water changes. As such, immediate practices are needed while long-term solutions are developed.

Shorter-term strategies may include optimizing coagulation (e.g. type of chemicals, doses, and pH) and smaller-scaled infrastructure upgrades such as adjusting the filter media layout design. Optimizing coagulation and flocculation is an important first step, however, optimal operational parameters from a water quality perspective may not correspond to those of water production, so balancing efficacy and efficiency is crucial for adequate production of safe and clean drinking water. Adjusting post-coagulation treatment processes, such as the filter media layout, may assist in the balancing act, but vulnerable treatment plants are likely to ultimately require more significant process upgrades. Significant infrastructure upgrades should be robust and adaptable to changing source water quality. Furthermore, new designs should be easily retrofitted if further additions are later required, as climate and anthropogenic driven changes may not reach an equilibrium within the lifespan of the plant.

1.1 Objectives

The overarching goal of this thesis was to investigate the coagulation/flocculation of NOM and subsequent particulate removal processes in drinking water treatment plants that are vulnerable to changes in source water quality caused by lake recovery and climatic factors. This research fills a gap in literature pertaining to adaptive management strategies for drinking water treatment of source waters recovering from acidification or experiencing long-term changes due to climatic factors. Experiments were conducted to satisfy the following objectives:

1. Investigate immediate strategies to mitigate increasing source water NOM concentrations by evaluating the chemical coagulation conditions in two unconventional drinking water treatment plants. Strategies included:
    a. the use of cationic polyelectrolyte as a partial substitute for aluminum sulphate (alum) in a direct filtration plant and;
    b. adjustment of pH and coagulant dose for optimization of NOM removal and Al residual concentrations.
2. Investigate longer-term solutions through the evaluation of potential plant upgrades including:
    a. alternative filter media layouts used to offset the downstream effects of changing chemical dosing in response to increased concentrations of source water NOM and;

b. replacement of adsorption clarifiers with ballasted flocculation (BF) high-rate sedimentation for a treatment plant that is vulnerable to HABs.

1.2 Organization of thesis

The project rationale and relevant background information on the mechanisms and theory of NOM removal in drinking water treatment are presented in Chapter 2. Chapter 3 provides a detailed description of the materials and methods that are common among most of Chapter 4 through 6. Chapter 4 presents results from the combined use of cationic polyelectrolyte and alum for coagulation in a direct filtration pilot plant and discusses the impacts of filter media layout designs. In Chapter 5, the effects of pH and alum dose are determined on two low turbidity, low alkalinity source waters in Atlantic Canada. Chapter 6 outlines the potential impacts of upgrading an upflow adsorption clarification treatment plant with ballasted flocculation and high-rate clarification. Finally, Chapter 7 presents overarching conclusions from the work and suggests recommendations for future study of this topic.

CHAPTER 2: BACKGROUND

2.1 Project rationale

2.1.1 J.D. Kline Water Supply Plant

The J.D. Kline Water Supply Plant (JDKWSP) is Halifax Water's largest drinking water treatment plant, serving over 200 000 residents of the Halifax Regional Municipality in Nova Scotia (Halifax Water 2019). The dual-media, direct filtration plant operates at approximately 85 megalitres per day (MLD), one third of its capacity. Direct filtration plants are best suited for high quality stable source water, with average total organic carbon (TOC) less than 3 mg/L, colour less than 20 true color units (TCU), and turbidity of less than 5 nephelometric turbidity units (NTU) (Valade, Becker, and Edzwald 2009). Further, maximum alum doses between 10-15 mg/L are recommended for direct filtration (Hutchison 1976; Ratnayaka, Brandt, and Johnson 2009; Wagner and Hudson 1982). When built in 1977, the water quality of Pockwock Lake, the supply for JDKWSP, fell within these design guidelines; however, over the past few decades, there have been considerable changes to the source water quality as a result of lake recovery from acidification and climatic factors (Anderson et al. 2017).

From 1999 to 2015, the concentration of TOC in Pockwock Lake has increased from 2.4 mg/L to 3.4 ± 0.2mg/L (Anderson et al. 2017). Likewise, the color has increased from 12 to 21 TCU over the same period (Anderson et al. 2017). Both parameters now exceed the design guidelines for direct filtration. Furthermore, the changes in source water have had significant operational implications. In 2015, the alum dose at the JDKWSP was increased from 8 to 12 mg/L, marking the first time in 25 years the dosing had increased (Anderson et al. 2017), and approaching the maximum recommended alum dose for direction filtration plants.

The vulnerability of the JDKWSP to a changing source water was highlighted in March of 2016 when the plant experienced a significant upset due to increased raw water turbidity during a storm. Spikes in raw water turbidity from 0.3 to up to 0.7 NTU caused filter cycles to drop as much as 70%. With the likelihood of increased storms due to climate warming (Lal et al. 2012), it is anticipated that similar plant upsets may occur in the future.

Increasing levels pH in Pockwock Lake due to recovery from acidification has also caused several operational issues, largely due to the growth of algae that flourished in less acidic water. For example, in 2012, Halifax Water detected traces of geosmin, a taste and odor compound, in the treated water. The compound was ultimately linked to *Anabaena*, a cyanobacteria that grows around pH 6. Increased levels of geosmin have been reoccurring annually in late summer to early fall and although it does not have any health implications, it does cause earthy smells in the water. Another noticeable operational challenge was the presence of the filter clogging diatom, *Tabellaria fenestrata,* in 2018. The diatom caused significant reductions in filter run times, which were as low at 20 hours, compared to the typical 70-80 hour runs prior to the diatom bloom. The problem was partially handled with pre-chlorination, however it highlighted the vulnerability of the plant to changes in source water quality.

These recent events at the JDKWSP have disclosed the vulnerability of the treatment plant to changing source water quality and it is anticipated that, ultimately, significant plant upgrades will be required. However, the design and construction of these upgrades will require time for research, design, and construction. The following study, thus, investigated potential shorter-term strategies for mitigating the dynamic nature of source water quality in Pockwock Lake, particularly the increasing concentrations of NOM due to lake recovery from acidification. This research fills a gap in literature pertaining to adaptive management strategies for drinking water treatment of source waters recovering from acidification.

On top of the issues related to lake recovery, due to its direct filtration configuration, the JDKWSP is also susceptible to high concentrations of Al residual in the treated water when Al-based coagulant doses are increased, particularly in the colder, winter conditions. In anticipation of the proposed Health Canada aluminum OG of 50 μg/L and potentially higher alum demand due brownification, Halifax Water is seeking strategies to lower Al residual concentrations that can be immediately implemented.

2.1.2 Moncton Water Treatment Plant

The Moncton Water Treatment Plant (MWTP) serves over 110 000 residents of Moncton, Riverview, and Dieppe in New Brunswick (City of Moncton 2019). In 2019, the plant supplied an average of 42 MLD of treated water to its customers (City of Moncton 2019). Water from the Turtle Creek Reservoir is pre-oxidized with potassium permanganate prior to coagulation and flocculation. The flocculated water is then distributed between four up-flow adsorption clarifiers. Adsorption clarifiers are typically designed for high quality source water, with low turbidity (<10 NTU) and low coagulant demand (Becker et al. 2018; Logsdon et al. 2006). Although the source water quality and operational conditions remain within those design guidelines, the recent detection of algae in their supply has brought concerns to the utility.

In 2017, the Tower Road Reservoir, the secondary, upstream source to the primary Turtle Creek Reservoir, experienced a blue-green algae bloom. Small concentrations of cyanotoxins were detected in the secondary reservoir, but fortunately, neither cyanotoxins nor cyanobacteria entered the MWTP. Algae was detected again in both the Tower Road Reservoir and the Turtle Creek Reservoir in 2018 and 2019, however, no blooms were formed.

Nonetheless, these events have stressed the fragility of the MWTP to the occurrence of algae in the water supply. As adsorption clarifiers function more so like filters than conventional sedimentation clarification, they are prone to plugging in the presence of high algal counts (Marston et al. 2015; Ross, Baker, and Lucey 2019). As such, the City of Moncton expressed concerns regarding the hydraulic capacity of the plant in the event of a bloom. Further, as the current treatment process does not have the ability to sufficiently remove extracellular cyanotoxins, designs considered in plant upgrades must have this capacity. The work completed in partnership with the City of Moncton investigated upgrading the MWTP process to ballasted flocculation and high-rate sedimentation. Additionally, due to the nature of the adsorption clarifiers, jar tests are not regularly conducted at the MWTP, so an initial study was completed to determine the optimal coagulant doses and pH for treatment of the Turtle Creek Reservoir supply to optimize the treatment process prior to installation of any plant upgrades.

2.2 Natural organic matter

2.2.1 Sources of NOM

All natural waters contain natural NOM which consists of a wide variation of organic compounds and material (Zhang 2015; Matilanienen 2010). NOM is a pre-cursor for DBPs, carcinogenic compounds that are regulated by Health Canada (Health Canada 2019b). NOM is also the primary source of taste and odor compounds, which impact the aesthetic water quality parameters and can enhance bacterial growth in the distribution system (Zhang et al. 2015). Further, due to the reactive nature of their functional groups, many NOM compounds have strong adsorption and complexing capacity for trace inorganic (e.g. heavy metals) and organic pollutants. As such, the presence of NOM can facilitate their transport (Sillanpää et al. 2018; Zhang et al. 2015). For these reasons, the removal of NOM from source waters is highly important and has been a topic of study in drinking water treatment for decades.

The concentration, character, and properties of NOM in surface water are largely functions of the watershed ecosystem and environment, and depends on the geological, hydrological, and biological processes, as well as water chemistry, temperature, and pH (Matilainen, Vepsäläinen, and Sillanpää 2010; Sillanpää et al. 2018). NOM can be generated outside of the water body (e.g. substances stemmed from the breakdown of terrestrial organisms that are transported by runoff) or inside the water body (e.g. biological activity including algae and microorganisms) and the source of NOM often dictates its properties and subsequently, the treatment strategies for its removal (Sillanpää et al. 2018). Terrestrial sources of NOM are typically more humic and hydrophobic in nature, making their removal with coagulation easier than their counterparts (Sillanpää et al. 2018). On the other hand, NOM produced by biological activity inside the water body is often comprised of extracellular and intracellular macromolecules (i.e. carbohydrates, amino acids, peptides, toxins, etc.) which are more resistant to removal through coagulation (Sillanpää et al. 2018).

The degree of hydrophobic NOM in a water sample typically provides an adequate estimation of the expected efficacy of coagulation (Ghernaout 2014). A detailed account of the hydrophobicity and character of NOM can be measured with resin fractionation (Kent et al. 2014); however, this process is complex and thus not accessible for drinking water treatment operators. As such, the specific ultraviolet absorbance (SUVA) measurement has been long used as an indicator of the hydrophobicity of NOM in a source water (Edzwald 1993). SUVA is a measure of the UV absorbance at 254 nm (UV_{254}) (1/m) per mg/L of DOC (Edzwald 1993). Samples with high SUVA values (> 4 L/mg m) consist mainly of humic NOM that are relatively hydrophobic and aromatic in nature, with high molecular weights (MW) (Edzwald 1993). NOM in low SUVA samples (<2 L/mg m) is mainly non-humic, aliphatic, or low MW (Edzwald 1993) and samples with SUVA values between those thresholds (2-4 L/mg m) typically represent a mixture of humic and non-humic substances (AWWA and Edzwald 2011). However, the SUVA measurement does not always accurately represent the NOM in the water solution. For example, hydrophobic bases and neutrals have low SUVA values (<1 L/mg m) and hydrophilic neutrals have high values (3.5-4 L/mg m) (Edzwald 1993). If the source water is high in these fractions, then using SUVA as an estimation for the character of DOC may be misleading.

Previous work has also determined that character of NOM also impacts its reaction with disinfectants and thus the formation of DBPs. Despite some contradicting results (Kanokkantapong et al. 2006; Tubić et al. 2013), it is widely cited that the hydrophobic fraction is the largest contributor to DBP precursor material in raw waters (Bond et al. 2010, 2011; Chang et al. 2001; Li et al. 2017). As such, in water solutions where the majority of the NOM is humic (i.e. high SUVA measurements), UV_{254} can be a strong indicator of DBP formation. Carbon double bonds absorb UV light at 254 nm and are also highly reactive sites with oxidants, including chlorine, so high UV_{254} measurements often correlate with increased formation of DBPs (AWWA and Edzwald 2011; Chang et al. 2001). However, just as the humic, hydrophobic NOM is reactive with disinfectants, it is also reactive with coagulants, and thus is typically removed to a high degree in drinking water treatment. As such, it is often the fraction of NOM recalcitrant to coagulation that remains in the water matrix after treatment to form DBPs (Bond et al. 2010; Ghernaout 2014).

2.2.2 Impacts of lake recovery from acidification and climatic drivers on NOM

Over the last few decades, increasing concentrations of NOM, measured as DOC, have been recorded in many regions across Northern America and Europe (Garmo 2020; Garmo et al. 2014; Monteith et al. 2007). This trend has often been associated with ‘recovery from acidification’, a phenomenon defined as increasing acid neutralization capacity, alkalinity, or pH in response to reduced atmospheric acid deposition (Evans and Monteith 2001; Stoddard et al. 1999). Surface waters that were previously subject to chronic atmospheric sulfate deposition since the industrial revolution have, more recently, been recording decreased rates of deposition as a result of successful air pollution emission regulations enacted in the 1980s and 1990s (Monteith et al. 2007; Stoddard et al. 1999, 2002). These surface waters are now ‘recovering’ to either their pre-acidified or novel states (Meyer-Jacob et al. 2019), which often includes increased concentrations of DOC. Previous work has outlined the impacts of lake recovery in Atlantic Canada; Clair et al. (2011) analyzed water chemistry trends for 66 lakes over the period of 1984 to 2007 and observed a general negative trend in atmospheric sulfate deposition which corresponded to decreasing lake sulfate concentrations in all regions studied. Increasing trends in DOC were observed from 2000-2007. Likewise, Anderson et al. (2017) reported increasing pH, color, and DOC concentrations in two Nova Scotia Lakes since 1999.

However, it has been established that atmospheric sulfate deposition is not the sole influencing factor on key water quality parameters that define lake recovery from acidification. The increasing importance of climatic drivers on water chemistry, mainly temperature and precipitation, has been highlighted in more recent literature, as atmospheric acid deposition has begun to stabilize in some regions (Garmo 2020). Multiple studies have reported significant impact of climatic factors in temporal trends of DOC concentrations (Couture, Houle, and Gagnon 2012; Evans, Monteith, and Cooper 2005; Finstad et al. 2016; Imtiazy et al. 2020; Kopáček et al. 2019; Meyer-Jacob et al. 2020; Riise et al. 2018; De Wit et al. 2016) and DOC has increased in some lakes that were not acidified, indicating additional factors influenced the DOC concentrations besides reduced sulfate deposition (Evans et al. 2005; Gavin et al. 2018). In some regions, variations in climate was the dominant driver in controlling DOC concentrations since the 2000s

(Imtiazy et al. 2020; Riise et al. 2018). Moreover, climate has been proven to strongly impact catchment properties, which dictate many of the processes and mechanisms controlling the chemistry in the receiving water (Riise et al. 2018). The increase in DOM, causing increased color of surface waters, has been coined 'brownification' and is often linked to increased littoral DOM from increased run-off (Strock et al. 2016).

In addition to the brownification of surface waters observed in areas of the Northern Hemisphere, global increases in frequency, intensity, and duration of HABs have been reported over the last few decades (Huisman et al. 2018; Moore et al. 2008; O'Neil et al. 2012). The growth of cyanobacteria, or blue-green algae, is of particular concern due to their production of toxic, secondary metabolites, called cyanotoxins (Huisman et al. 2018; O'Neil et al. 2012). The increase in HABs have often associated to increased nutrient loading from surface run off but are also often linked to climatic drivers (e.g. precipitation and temperature) (Huisman et al. 2018). Warming atmospheric temperatures increases surface water temperatures, which favours the proliferation of cyanobacteria, as they typically reach their maximum growth rate at temperatures greater than 20 ºC (Huisman et al. 2018; O'Neil et al. 2012). Further, warming temperatures and brownification enhances lake stratification, reducing nutrient mixing in the water column and giving species that can control their buoyancy, such as cyanobacteria, a competitive advantage (Creed et al. 2018; Huisman et al. 2018; Moore et al. 2008; O'Neil et al. 2012; Urrutia-Cordero et al. 2016; Wagner and Adrian 2009).

Multiple studies have also shown that the phytoplankton communities have been impacted by decades of chronic acidification and the more recent increases in pH (Gray et al. 2012; Jeziorski et al. 2014; Stager et al. 2019), favouring cyanobacteria (Findlay et al. 1999; Keller, Heneberry, and Edwards 2019). An additional consequence of chronic acidification is the depletion of base cations pools in soils, specifically calcium (Ca^{2+}), and its subsequent reduced concentrations in receiving waters. Jeziorski et al. (2014) noted that this shift had led to the 'jellification' of species in surface waters, increasing the likelihood of filter clogging.

2.3 Aluminum

Aluminum in drinking water is derived from one of three sources: Al in the source water, residual Al added in treatment through Al-based coagulants, or Al leached from materials in the distribution systems (Snoeyink et al. 2003). In source waters, Al is mostly in the precipitated form and is bound to colloids or NOM (Snoeyink et al. 2003). The concentration of Al can be reduced in drinking water treatment through coagulation/flocculation, provided operational conditions are optimized. Otherwise, the addition of Al-based coagulants can result in higher concentrations of Al in the treated water (Health Canada 2019a; Snoeyink et al. 2003). Factors such as pH, flocculation efficacy, coagulant dose, NOM concentration, water quality, and temperature will all impact the concentration of Al in the finished water (Snoeyink et al. 2003). Factors influencing Al residuals are discussed further in Chapter 2.4.2.

If residual Al persists in the finished water, Al-based solids can form in the distribution system, causing scaling on plumbing material and increased turbidity at the tap (Kvech and Edwards 2001; Snoeyink et al. 2003). The development of scales increases the roughness of the internal surface of the piping, reducing the hydraulic pressure and ultimately leading to reduced carrying capacity or increased pumping costs (Snoeyink et al. 2003). Increased release of lead and copper in distribution systems through co-precipitation or adsorption has also been attributed to Al residual (Knowles et al. 2015; Kvech and Edwards 2001), and reduced efficacy of lead and copper corrosion inhibitors (Li et al. 2020). Further, Al has been associated to neurological diseases, such as Alzheimer's disease; however, there is a mixed consensus regarding the health impacts of Al from drinking water, as it represents a small fraction of the total daily consumption (Edzwald 2020; Flaten 2001; Health Canada 2019a). As such, low concentrations of Al in treated water is desirable.

2.4 Coagulation

2.4.1 Removal of NOM and algal organic matter

The concentration and character of NOM in a surface water often dictate the operational parameters in a drinking water treatment plant (Edzwald 1993; Pernitsky and Edzwald

2006). Furthermore, the variability of NOM, both spatially and temporally, present significant challenges to treatment design (Sillanpää et al. 2018). Within the range of pH found in natural waters, NOM holds a negative surface charge and thus, the repulsion potential of the electrical double layers of the colloids prohibits their agglomeration and keeps the contaminants in suspension (stabilized) (Sillanpää et al. 2018). Coagulation is the process of minimizing the repulsion forces between the colloids by reducing the electrical double layer potential (Sillanpää et al. 2018). The neutralized colloids can then agglomerate into larger particles called floc that can subsequently be removed with clarification or filtration (Sillanpää et al. 2018).

Destabilization of the NOM species is achieved with coagulants, most frequently metal salts, that are dissociated into trivalent ions when added to the water solution. At optimal coagulation pH, the trivalent ions then follow hydrolysis reactions to form positively charged dissolved species or amorphous hydroxide precipitates that are reactive with the negatively charged NOM species (Pernitsky and Edzwald 2006; Sillanpää et al. 2018). Due to complexity of NOM in the water matrix, it is difficult to determine the exact removal mechanisms, however, three mechanisms are predominant: (1) complexation of NOM by dissolved hydrolysis species that leads to precipitated metal-NOM solids; (2) complexation of NOM by dissolved hydrolysis species that are then adsorbed onto the surface of amorphous hydroxides or precipitated metal-NOM solids; (3) adsorption of NOM onto amorphous hydroxide solids (Pernitsky and Edzwald 2006). The hydrolysis species formed, and mechanism and efficiency of NOM destabilization, depends on a multitude of factors, including the raw water chemistry, coagulation pH and temperature.

The concentration and character of NOM in a source water will impact the efficiency of coagulation. Higher concentrations of NOM will require greater coagulant doses to satisfy the negative charge, and particle concentration will impact the frequency of collisions and thus flocculation kinetics (Shin, Spinette, and O'Melia 2008). Further, the character of NOM also influences its removal. Hydrophobic NOM has a higher negative charge density than its hydrophilic counterpart, mainly due to the increased presence of ionized carboxylic and phenolic functional groups (Matilainen et al. 2010; E. L. Sharp et al. 2006; Sillanpää et al. 2018). As such, the hydrophobic fraction often dictates coagulant demand for NOM removal and is more readily removed with coagulation (AWWA and Edzwald 2011). High SUVA source waters (>4 L/mg m) typically have DOC removal around 60-80%, where DOC removal between 20-40% are anticipated in low SUVA waters (<2 L/mg m) (AWWA and Edzwald 2011). Similarly, larger molecular weight compounds are typically more readily removed with coagulation than smaller MW (Matilainen et al. 2010; Nissinen et al. 2001; Sillanpää et al. 2018).

In the event of algae growth in the source water, coagulation and flocculation can be effective methods for removal of biomass and thus, intracellular toxins. However, algae organic matter (AOM) can be more challenging to coagulate than NOM compounds due to their morphological shape and low density (Ghernaout et al. 2010; He et al. 2016). Under typical operational parameters for drinking water treatment, cell lysis, and subsequent release of extra cellular toxins, is expected to be minimal (He et al 2016), but conventional coagulation/flocculation does not effectively remove extracellular cyanotoxins. Therefore, additional treatment barriers (e.g. ozonation, adsorption, etc.) may be needed for source waters experiencing a HAB (Noyma et al. 2017; Westrick et al. 2010). Further, the additional biomass from HABs can cause clogging of unit processes (e.g. adsorption clarification, filtration) (Ghernaout et al. 2010; Marston et al. 2015), requiring more frequent backwashes and higher operational costs.

2.4.2 Coagulation with Al-based coagulants

Aluminum sulphate. Alum is a common coagulant used in drinking water treatment due to its low cost and high availability (Sillanpää et al. 2018). When applied to raw water, the Al ion (Al^{3+}) dissociates and forms hydrolyses species that include charged, dissolved species, and precipitated Al hydroxide (Pernitsky and Edzwald 2006). The main factors influencing the efficacy of alum as a coagulant are the coagulation pH and the alum dose. In low alkalinity source waters, additional chemicals (e.g. lime) may be used to regulate the coagulation pH as the addition of alum, which is acidic, consumes alkalinity.

Controlling the pH is important as it determines the hydrolysis species formed during treatment. At pH <6, positive dissolved Al hydrolysis species are predominate and react with negatively charged NOM species in charge neutralization (Davis and Edwards 2014).

Lowering the pH not only increases the positive charge of the hydrolysis species, but also increases protonation of the carboxylic and phenolic groups in the NOM compounds, making them less negative (Davis and Edwards 2014; Shin et al. 2008). The combined effect results in a lower coagulant dose required for effective charge neutralization. Shin et al. (2008) reported a shift in optimal alum dosing from 0.47 mg Al/mg DOC at a pH of 7, to 0.3 mg Al/mg DOC at a pH of 6. Mesdaghinia et al. (2006) also reported lower coagulant doses, and thus reduced sludge production, at lower coagulation pH (<6).

On the other hand, increasing the coagulation pH (i.e. >6) shifts the hydrolysis species towards more amorphous Al hydroxide solids and, for pH>6.5, negatively charged dissolved Al species are predominate (Davis and Edwards 2014; Pernitsky and Edzwald 2006). The greater degree of hydroxide species and reduced presence of positive hydrolysis species will favour the adsorption of NOM onto the solid surfaces, however higher coagulant doses are often required to satisfy the negative charge of NOM (Davis and Edwards 2014). NOM molecules are adsorbed via ligand exchange or surface complexation with groups on the precipitated species (Davis and Edwards 2014; Shin et al. 2008).

Poor pH control and insufficient alum dosing during coagulation can result in poor treated water quality, in both NOM concentrations and residual Al. Coagulating near the pH of minimum solubility is a common strategy used to reduce the amount of residual Al (Health Canada 2019a). As the coagulation pH approaches the pH of minimum solubility, around 6.3 at 20 ºC and approximately 6.7 a 5 ºC, the amount of dissolved Al is reduced. The higher concentration of precipitated Al hydrolysis species usually results in lowered Al residual concentrations (Pernitsky and Edzwald 2006). On the other hand, if alum is underdosed, Al residual concentrations will be greatest when the alum dose satisfies the Al binding sites of NOM but is not great enough to cause flocculation (Gregor, Nokes, and Fenton 1997). The resulting organic-Al colloids can pass through clarification and filtration processes and remain in the treated water (Srinivasan, Viraraghavan, and Bergman 1999). Factors that cause poor flocculation (e.g. insufficient mixing, slower kinetics at colder temperatures) can also impact the removal of Al-NOM complexes, resulting in higher concentrations of Al in the finished water (Snoeyink et al. 2003).

Polyaluminum chloride. Aluminum chloride ($AlCl_3$) is partially neutralized to produce polyaluminum chloride (PACl), a coagulant that is often used in the treatment of low-alkalinity source waters due to its alkaline nature (Matilainen et al. 2010). PACl coagulants vary in basicity, defined as the ratio of the concentration of hydroxide ions to concentration of total Al (Pernitsky and Edzwald 2003). PACl with higher basicity will have more polymeric species and less alkalinity consumption (Pernitsky and Edzwald 2003).

In the neutralization of $AlCl_3$, polymeric Al species are formed, and $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{+7}$, abbreviated as Al_{13}^{+7} , is the predominate species at pH 5 to 7.5 for warmer waters and around 5.4 to 8 in colder temperatures (Pernitsky and Edzwald 2006). The preformed highly charged polymeric species in PACl are immediately accessible for coagulation reactions upon dosing and NOM removal mechanisms are analogous to those with alum. However, however a larger fraction of the Al-hydrolysis species will be the Al_{13}^{+7} polymer, thus mechanisms explained in Chapter 2.4.3 may also occur (Matilainen et al. 2010; Pernitsky and Edzwald 2003).

PACl offers many benefits as compared to alum. Lowered coagulant doses have been reported for PACl as compared to alum due to the higher charge of Al species and higher concentration of Al^{3+} for the same coagulant dose (He et al. 2019; Matilainen et al. 2010; Yang et al. 2010). Additionally, Yang et al. (2010)reported reduced concentrations of dissolved monomeric Al species, which were more toxic to humans than other forms of Al analyzed in the study, when using PACl as compared to alum. Coagulation with PACl is also less pH and temperature dependent than alum (Matilainen et al. 2010; Pernitsky and Edzwald 2006).

The cost of PACl is typically greater than alum, however, it may be offset by the lower doses required for effective coagulation/flocculation and potential savings in pH controlling chemicals due to their higher alkalinity (Matilainen et al. 2010; Pernitsky and Edzwald 2006)

2.4.3 Coagulation with cationic polyelectrolyte

Due to their positive charge, cationic polyelectrolytes, have been used as both a primary coagulant and coagulant aid in drinking water treatment for effective NOM removal (Bolto and Gregory 2007). The main mechanisms of NOM removal with polyelectrolyte are charge neutralization and polymer bridging (Bolto and Gregory 2007). Both mechanisms, however, depend on polymer adsorption to contaminants in the water matrix. Cationic polyelectrolyte will adsorb onto particles of opposite charge due to electrostatic attraction and are likely to bind at multiple sites, called trains. The segments between trains are called loops, and the ends of the polymer that extend in the solution are called tails. The charge density of the polyelectrolyte will dictate its adsorption orientation, with higher charge density polyelectrolyte reaching a flatter configuration with minimal extension of tails and loops out of the electrical double layer, limiting the degree of bridging (Bolto and Gregory 2007).

In charge neutralization, the main objective is bringing the surface charge, or zeta potential, of the polymer-particle aggregate near zero (Bolto and Gregory 2007; Pernitsky et al. 2011). Similar to the coagulation mechanism with Al-based coagulants, this will eliminate the electrostatic repulsion forces between particles and allow closer particle contact and formation of larger flocs (Bolto and Gregory 2007). When high charge density cationic polyelectrolytes adsorb onto weakly negatively charged surfaces, electrostatic or patch flocculation can also occur (Bolto and Gregory 2007). This is when the overall particle is neutral in charge, but there exist patches of negatively and positively charged sites. Opposing sites from different particles exhibit attractive forces, and thus flocculation is induced. In the case of overdosing, the amount of adsorbed polymer on the particle surface will be too high such that a charge reversal can occur, and the particle is said to be restabilized. Restabilization often corresponds with high, positive zeta potential measurements and increased turbidity of the treated water (Bolto and Gregory 2007; Edzwald, Becker, and Tambini 1987).

High charge density cationic polyelectrolytes have been used in direct filtration as a primary coagulant as they provide charge neutralization capacity without the additional solid loading from a precipitating coagulant (Bolto and Gregory 2007). However, it has also been shown that polymers alone are not as effective in NOM coagulation as alum (Edzwald et al. 1987). Therefore, the partial substitution of alum with a cationic polyelectrolyte is a common practice, as the combined use offers benefits from both types of coagulants (Bolto et al. 2001; Edzwald et al. 1987; McCormick and King 1982). Filter run times can be extended due to the reduced volume of sludge from lower doses of alum and NOM removal is not compromised as sufficient charge neutralization capacity is applied through both alum and polyelectrolyte. Additionally, polyelectrolytes are pH independent, reducing chemical demand for pH control (Bolto and Gregory 2007; Chang et al. 2005; Nozaic, Freese, and Thompson 2001). This is especially beneficial for the treatment of low alkalinity source waters that have reported increased demand of carbon dioxide and lime for generation of alkalinity to maintain coagulation pH (e.g. Anderson et al. 2017). The use of high charge density cationic polyelectrolyte has seen successful application in full-scale and pilot-scale direct filtration plants as both the primary coagulant and as a coagulant aid with a metal salt (e.g. Bolto et al. 2001; Chang et al. 2005; Edzwald et al. 1987; Nozaic, Freese, and Thompson 2001; Pernitsky et al. 2011). Further, combinations of cationic polyelectrolyte and alum have shown to reduce effluent turbidity (Chang et al. 2005), increase UV_{254} removal (Bolto et al. 2001) and extend filter runs (McCormick and King 1982; Pernitsky et al. 2011).

However, there are multiple concerns regarding the use of polyelectrolytes in drinking water treatment. Firstly, polyelectrolytes, especially cationic polyelectrolytes, can be toxic to aquatic organisms (Bolto and Gregory 2007). As such, the National Sanitation Foundation has published recommended maximum doses for commercial polyelectrolytes often used in the United States (Bolto and Gregory 2007). These recommended doses vary for the type of polyelectrolyte used but are typically in the range of 1 to 50 mg/L (Bolto and Gregory 2007). Regarding their biodegradability, synthetic polyelectrolytes are fairly resistant, and as such degrade slowly in natural environments (Bolto and Gregory 2007). On the contrary, oxidants in pre-treatment can cause chain cleavage or reduced charge density, which can lower the treatment efficiency (Bolto and Gregory 2007). Further, residual polyelectrolytes can also cause formation of DBPs, however their formation are typically insignificant in the range of doses typically applied in drinking water treatment (Bolto and Gregory 2007).

2.5 Particulate removal

2.5.1 Direct Filtration

Direct filtration treatment plants do not have a clarification step following coagulation/flocculation; thus, solids removal occurs only through filtration. As such, direct filtration is typically limited to high quality source waters (Edzwald et al. 1987; Pernitsky and Edzwald 2006; Valade et al. 2009). Valade et al. (2009) recommended direct filtration be restricted to source waters with average TOC concentrations <3 mg/L and average turbidity <5 NTU. Further, maximum alum doses in the range of 10-15 mg/L are suggested for the process (Hutchison 1976; Ratnayaka et al. 2009; Wagner and Hudson 1982).

To reduce head loss development across the filter beds, small, ‘pin-point’ sized flocs (pin-floc) are desirable in direct filtration (Pernitsky and Edzwald 2006). This type of floc is best produced with charge neutralization under acidic conditions (pH<6) (Pernitsky and Edzwald 2006). The smaller floc can penetrate deeper into the filter bed, resulting in solids retention extended over larger depths of the filter and in turn, reduced rates of head loss development (Tobiason, Ph, and Cleasby 2010). As the coagulation pH approaches the pH of minimum solubility, the concentration of Al hydroxide precipitates increases (Pernitsky and Edzwald 2006) and sweep flocculation becomes more predominant (Duan and Gregory 2003; Kim, Moon, and Lee 2001). Flocs are formed in sweep floc as suspended particles are ‘swept’ out of suspension by precipitated species, most often the aluminum hydroxide (Duan and Gregory 2003; Kim et al. 2001). The resultant flocs are more dense, but greater in size, than flocs formed in charge neutralization (Duan and Gregory 2003; Kim et al. 2001). Larger floc often results in faster rates of head loss development and shorter filter cycles in direct filtration plants.

Direct filtration plants are also more sensitive to changes in source water quality, which can cause significant impacts on operational parameters (Zouboulis et al. 2007). For example, the presence of seasonal algae blooms or plankton can cause filter clogging (Ghernaout et al. 2010; Monscvitz et al. 1978). Further, increased concentrations of NOM or higher raw water turbidity demand greater coagulant doses, which increase solids loading on the filters and can reduce plant productivity (Anderson et al. 2017). As such, it is highly important to consider the downstream, operational impacts of coagulation chemistry in direct filtration plants.

Properties of the filter media layout will also impact the performance of direct filtration plants in terms of treated water quality and hydraulic capacity. Increasing the effective size (ES) of the filter media can extend filter runs and increase unit filter run volumes (UFRV). The coarser media allows for deeper penetration of incoming particulates into the filter bed, reducing rates of head loss development (Tobiason et al. 2010). However, increasing the ES of the media may also reduce the quality of the effluent, as smaller particles are more effectively removed with smaller filter media (Saltnes, Eikebrokk, and Ødegaard 2002). This effect can be offset by increasing the filter depth and maintaining the depth to size (L/d) ratio, where L is the bed depth and d is the media ES. Through increasing the ES of the media and expanding the depth of the filter bed, particle removal can be maintained while extending the filter runs (Monscvitz et al. 1978; Moran et al. 1993; Saltnes et al. 2002; Tchio et al. 2003).

2.5.2 Adsorption clarification

Adsorption clarification is a solid removal process that became more popular in the 1980s in ‘package’ treatment plants (Goodrich et al. 1992). Conventionally, the process combines flocculation and clarification into one step, where turbulence in the coagulated water caused by upwards flow through coarse clarification media (either buoyant or non-buoyant media) enhances particle collision and flocculation (Goodrich et al. 1992; Ross et al. 2019). The flocs are then removed through adsorption onto the clarifier media, and as such, smaller flocs are desirable (Ross et al. 2019). Nonetheless, turbidity removal of up to 95% can be achieved with adsorption clarifiers (Goodrich et al. 1992). Periodic flushing of the adsorption clarifier media is required to relieve pressure across the media (Ross et al. 2019).

Although there is very limited literature on drinking water treatment with adsorption clarifiers, the studies that do exist highlighted the sensitivity of the unit process to changes in influent water quality (Marston et al. 2015; Ross et al. 2019) and the treatment process is recommended for low-turbidity source waters with low coagulant demands (Logsdon et al. 2006; Valade et al. 2009). For example, Marston et al. (2015) reported that the presence of blue-green algae in a non-buoyant adsorption clarification plant caused severe plugging that resulted in shut down of the plant for several months.

2.5.3 Ballasted flocculation and high-rate clarification

Ballasted flocculation is the process of incorporating a high-density ballasting agent (BA) into the floc to increase their settling velocity. ACTIFLO® is a proprietary BF treatment technology introduced in the 1990s that uses microsand as a BA and high-rate sedimentation with lamella plate settlers (Desjardins, Koudjonou, and Desjardins 2002). The process has four steps: coagulation, injection, maturation, and settling (Desjardins et al. 2002; Plum et al. 1998). Coagulation and rapid mixing occur in the first basin and are followed by injection of the microsand and polyelectrolyte to facilitate the incorporation of BA into the flocs (Desjardins et al. 2002). Microsand doses reported in literature were within the range of 2-5 kg/m^3 (Desjardins et al. 2002; Young and Edwards 2003). Polyelectrolyte doses will depend on the dosing of primary coagulant and BA, with greater polyelectrolyte dosing required for increased BA and lower coagulant doses (Young and Edwards 2003). The addition of a BA does not typically impact the coagulation chemistry, as the surface charges of the BA are small in comparison to those of the colloids in suspension (He et al. 2019). After injection, a maturation period is allotted for growth of flocs which are then removed via sedimentation with high-rate lamella plate settlers (Desjardins et al. 2002). The sludge-BA mixture is then separated in a hydrocyclone and microsand is recycled in the ACTIFLO® process (Desjardins et al. 2002). The sludge flow from the hydrocyclone is typically around 6% of the total treated water flow (Desjardins et al. 2002).

Due to the incorporation of BA, flocs formed with BF have a higher density than those formed without BA (Young and Edwards 2003), and in turn, a faster settling (Watanabe

2017). Ballast flocs are also rounder and more compact, due to their tight bonding, making them stronger than those formed with conventional coagulation/flocculation (Ghanem, Young, and Edwards 2007; He et al. 2019; Young and Edwards 2003). Stronger flocs are desired in BF as more intense mixing is required to prohibit the BA from settling in the flocculation tank without being incorporated into the floc matrices (Young and Edwards 2003). Further, Ghanem et al. (2007) determined that BA takes the place of bound water in the floc, which reduces the water content of the sludge, a beneficial outcome for sludge dewatering.

The settling of ballasted flocs in ACTIFLO® treatment is not only accelerated with the incorporation of a BA, but also by the lamella plate settlers, which increase the area for sedimentation and results in higher apparent settling velocities (Guibelin, Desalle, and Binot 1994). The high rate clarification process allows for much smaller footprints as compared to conventional sedimentation. Turbidity removal from the raw to clarified water can be upwards of 80%, however, may be impacted by the polyelectrolyte, coagulant and BA dosing (Young and Edwards 2003). In bench-scale experiments, Young and Edwards (2003) determined that the remaining turbidity in settled water was mainly smaller microsand particles that were not successfully incorporated into the flocs.

In contrast to the other types of particulate removal studied in this thesis, the ACTIFLO® treatment process is not sensitive to changes in source water quality (Desjardins et al. 2002). The process is well suited for treatment of humic-rich or algae-laden source waters as these materials form low-density floc that are typically difficult to settle (Plum et al. 1998; Sieliechi et al. 2016). However, as the destabilization of NOM compounds is still achieved through coagulation, ACTIFLO® will not perform well with low SUVA source waters that contain NOM that is recalcitrant to treatment with coagulation (Desjardins et al. 2002).

Drinking water treatment with a BA also presents the opportunity for the addition of powdered activated carbon (PAC) into the treatment process. Plourde-Lescelleur et al. (2015) compared treatment with conventional coagulation/sedimentation to conventional treatment followed by ACTIFLO® CARB, which is identical to the conventional

ACTIFLO® process, but PAC is added in the BA mixture for adsorption of NOM. They found that the two treatment processes were complementary in their NOM removal, where conventional treatment removed high molecular weight compounds and ACTIFLO® CARB favoured the removal of lower MW compounds (Plourde-Lescelleur et al. 2015). Additional DOC removal (15-33%) and lowered DBPs were observed with the addition of ACTIFLO® CARB after conventional sedimentation (Plourde-Lescelleur et al. 2015). As conventional coagulation is ineffective in destabilizing cyanotoxins, PAC has also been used for treatment of algae-laden source waters (Ho et al. 2011; Newcombe and Nicholson 2004). Ho et al. (2011) observed nearly complete removal of cylindrospermopsins and microcystins in PAC jar tests spiked with the two cyanotoxins. Additionally, in reviewing literature on removal of cyanotoxins, Newcombe and Nicholson (2004) reported that PAC has the potential to remove microcystin, anatoxin-a, saxitoxin, and cylindrospermospsin, however their removal is dependent on the type of PAC selected and the water quality conditions.

2.6 Impacts of changing source water quality on drinking water treatment processes

Changing source water quality as a result of lake recovery from acidification or climate drivers can impact the operation of multiple unit processes drinking water treatment, affecting the overall efficiency and efficacy of the treatment plant. As the character and concentration of NOM largely dictate the coagulation operating parameters, shifts in these properties can cause significant treatment challenges (Edzwald 1993; Pernitsky and Edzwald 2006). For example, a shift towards more hydrophilic NOM may not be effectively removed with coagulation/flocculation, reducing the efficacy of the treatment plant and potentially leading to a greater concentration of DBPs in the treated water (Sharp et al. 2006). On the other hand, a shift towards more hydrophobic NOM may demand a greater coagulant dose, increasing the cost of treatment (Anderson et al. 2017).

Increased concentrations of NOM and subsequent chemical dosing contribute to increased solid loading on a treatment plant. Further, turbidity spikes from windstorms or heavy rainfall can also cause significant solid loading. In unconventional treatment plants (e.g.

direct filtration and adsorption clarification), the increased solid loading may lead to increased head loss development or plugging of unit processes (e.g. filters, adsorption clarifiers) (Anderson et al. 2017; Eikebrokk et al. 2004; Marston et al. 2015). This demands more frequent backwashes, reduced hydraulic capacity, and higher energy consumption (Anderson et al. 2017; Eikebrokk 2004). Additionally, a greater solid loading with effective treatment also produces more sludge, which demands greater energy consumption for its treatment (Eikebrook 2004).

Harmful algal blooms can have similar impacts on drinking water treatment as increasing concentrations of NOM, including increased chemical demand and solid loading. Algae biomass may also require increased chemical dosing, as they can be difficult to coagulate due to their morphological shape and low density (Ghernaout et al. 2010; He et al. 2016). Further, depletion of calcium ions in the watershed from chronic acid deposition can lead to the 'jellification' of surface waters (Jeziorski et al. 2014). This can be of particular concern in treatment units that are prone to plugging (e.g. filters, adsorption clarifiers), as hydraulic capacity can be substantially reduced due to the presence of filter clogging algae (Jeziorski et al. 2014; Marston et al. 2015). Cyanobacterial blooms in particular also present the concern of cyanotoxins, which can be effectively removed with coagulation when found inside the cell membrane, however, may require additional treatment barriers (e.g. oxidation, adsorption) if present as extracellular toxins (Ghernaout et al. 2010).

CHAPTER 3: MATERIALS AND METHODS

The experimental designs outlined in Chapter 4, 5, and 6 were conducted on raw source water from Pockwock Lake in Halifax, Nova Scotia and the Turtle Creek Reservoir in Moncton, New Brunswick. Both bench- and pilot-scale studies were completed to test changes to current full-scale plant (FSP) operations that may improve natural organic matter (NOM) removal and increase the plants' capacities to treat a changing source water quality.

The following chapter outlines the common materials and methods used in the experimental designs of Chapter 4, 5, and 6. Specific procedures for each experiment will be detailed in their respective chapters.

3.1 Halifax Water

Halifax Water operates two large drinking water treatment plants in the Halifax Regional Municipality, one of which is the JD Kline Water Supply Plant (JDKWSP). The JDKWSP is the main drinking water treatment plant for the city of Halifax.

3.1.1 Pockwock Lake

Pockwock Lake is the surface water from which Halifax Water draws source water for treatment at the JDKWSP. The lake drains a protected watershed; therefore, its water quality is not influenced by industrial or wastewater runoff. Additionally, anthropological activity has minimal influence on the source water.

Pockwock Lake is characterized as low-turbidity (<1 NTU), low alkalinity (<5 mg/L as $CaCO_3$) source water with moderate levels of NOM (3-5 mg/L of TOC). The pH is slightly acidic, averaging around 5.8 during the period of study. Additional raw water characteristics are presented in Table 3.1.

Table 3.1: Raw water (Pockwock Lake) characteristics (Feb 2019 to Jan 2020)

Analyte	Range	Average
pH	5.3-6.0	5.8
Turbidity – NTU	0.22-1.03	0.35
UV_{254} – 1/cm	0.084 – 0.134	0.105

Analyte	Range	Average
TOC – mg/L	2.82 – 4.62	3.34
DOC – mg/L	2.08 – 4.40	3.27
SUVA – 1/m per mg/L of DOC	2.5 – 5.8	3.3

3.1.2 J.D. Kline Water Supply Plant Overview

Commissioned in 1977, the JDKWSP is a direct filtration plant with an average daily flow of 85 megalitres per day (MLD) (Halifax Water 2019). Treatment steps that occur at the plant include pre-screening, oxidation, pre-chlorination, coagulation, flocculation, filtration, and chlorination.

Raw water drawn from Pockwock Lake subjected to a pre-screening process to remove heavy debris. It is then pumped to the first rapid mix tank, where lime ($Ca(OH)_2$) is added to increase the pH to approximately 10 for oxidation of iron (Fe) and manganese (Mn) with potassium permanganate ($KMnO_4$). The second rapid mix tank provides further mixing and contact time for oxidation. In the third rapid mix tank, carbon dioxide (CO_2) is added to maintain a coagulation pH of approximately 5.8. Alum is also added in the third pre-mix tank as the primary coagulant at a dose of 12 mg/L. A non-ionic polymer (MagnaFloc LT20, BASF) is dosed (~0.025-0.05 mg/L) in the third pre-mix tank as a flocculant aid. Lastly, pre-chlorination with chlorine gas (Cl_2) is achieved in the third pre-mix tank.

After coagulation, the water is flocculated into three flocculation trains, each following three-staged tapered flocculation. The JDKWSP has the capacity to operate four flocculation trains; however, one is kept offline to increase flow and improve hydraulic flocculation. The flocculated water is then passed through dual-media (anthracite and sand) filters. The finished water is dosed with Cl_2 and sodium hydroxide (NaOH) to maintain a residual of 0.2 mg/L of Cl_2 at the extremities of the distribution system and increase the pH to 7.4, respectively. Zinc orthophosphate blend and hydrofluosilicic acid are also added prior to distribution for corrosion control and to provide fluoride for dental health.

3.1.3 Pilot Plant Overview

The JDKWSP Pilot Plant (Intuitech, Inc., Salt Lake City, Utah) was commissioned in 2007 and is comprised of two identical and parallel treatment trains. The pilot plant is equipped for conventional treatment or direct filtration. To simulate the treatment process at the JDKWSP, the clarifiers are by-passed, and the pilot plant operates as a direct filtration plant. The effluent from both pilot plant trains was paired to that of the full-scale plant in 2008, meaning the pilot plant produces statistically equivalent water quality to the full-scale plant if operating under identical chemical dosing conditions (Knowles, Mackay, and Gagnon 2012).

An overview of the pilot plant treatment process is illustrated in Figure 3.1. Raw Pockwock Lake source water is supplied to the each pilot plant train at approximately 10 L/min. $Ca(OH)_2$ and $KMnO_4$ are added in the first of three 11.3-L rapid mix tanks, similar to the full-scale plant. The second pre-mix tank is used for additional mixing and contact time, and the third is used for application of CO_2, for pH control, and coagulants. Sodium hypochlorite (NaOCl) is added for chlorination in the third pre-mix tank. The doses of the applied chemicals are identical to those in the full-scale plant, unless alternative operating parameters are being investigated.

Water from the third rapid mix tank then flows to the first of three 189-L mechanical flocculation basins to begin three-stage, tapered flocculation. Flocculation with paddle mixers occurs at 30, 20, and 10 s^{-1}, respectively. The flocculated water then bypasses the sedimentation basin and is pumped to the filtration skid.

Each filtration skid consists of three 200-mm dual media (anthracite and sand) filter columns, through which the flow is evenly distributed. The first filter (F-FSP) simulates the full-scale plant filtration beds and is comprised of 61 cm of anthracite, with an effective size (ES) of 0.9 mm, and 30.5 cm of sand. The second filter media layout (F-ES0.9) has 91.5 cm of anthracite (ES 0.9 mm) and 30.5 cm of sand. The third filter column (F-ES1.3) has 91.5 cm of anthracite with a larger ES (1.3 mm), and 30.5 cm of sand. The pilot plant does not have the capacity to add chemicals to the finished water.

In-line water quality parameters (i.e. temperature, pH, turbidity) are measured at critical points throughout the treatment process. Additionally, filter hydraulic performance is evaluated with continuous head-loss development monitoring in each of the filter columns.

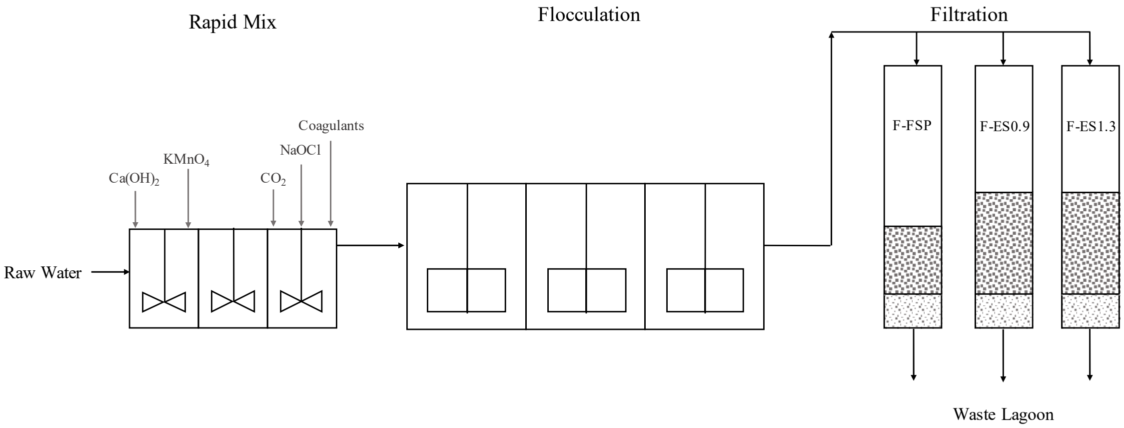

Figure 3.1 Overview of JDKWSP pilot plant treatment process

3.2 City of Moncton

The City of Moncton provides drinking water to Moncton, Dieppe, and Riverview through treatment of lake water at the Moncton Water Treatment Plant (MWTP) and a small well system with ultra-violet disinfection.

3.2.1 Turtle Creek and Tower Road Reservoirs

The Turtle Creek Reservoir is the primary source water for the MWTP. The reservoir also accepts flow indirectly from the Tower Creek Reservoir, a secondary reservoir that doubles the plant's reservoir capacity and could potentially be used as a direct source for the MWTP in the future. Both reservoirs drain the Turtle Creek Watershed, a designated watershed that is protected under the New Brunswick Clean Water Act.

The Turtle Creek Reservoir has low turbidity (typically <5 NTU) and low alkalinity (<10 mg/L as $CaCO_3$), with moderate concentrations of organics (<6 mg/L of TOC) (City of Moncton 2019). The pH of the lake remains around neutral (6.5-7.5) (City of Moncton, 2018). Raw water characteristic for Turtle Creek during the research period are presented in Table 3.2. Raw water in the context of the MWTP refers to the plant influent, where the source water from the Turtle Creek Reservoir had been oxidized with potassium permanganate.

Table 3.2 MWTP influent water characteristics (May 2019 to February 2020)

Analyte	Range	Average
pH	6.4 – 7.0	6.8
Turbidity – NTU	0.90 – 3.92	1.98
UV_{254} – 1/cm	0.119 – 0.227	0.144
TOC – mg/L	2.71 – 4.02	3.20
DOC – mg/L	2.14 – 4.18	3.10
SUVA – 1/m per mg/L of DOC	3.7 – 6.2	4.5

In September of 2017, an algae bloom occurred in the Tower Road Reservoir. The algae were identified as cyanobacteria, and small concentrations of cyanotoxins were detected in both the Tower Road Reservoir and near the spillway in the Turtle Creek Reservoir. Fortunately, the cyanotoxins did not enter the WTP. In 2018 and 2019, algae were again found in both reservoirs; however, no blooms occurred.

3.2.2 Moncton Water Treatment Plant

The MWTP, commissioned in 1999, averages a daily flow of 42 MLD (City of Moncton 2019). Water is treated with pre-screens, seasonal pre-oxidation, coagulation and flocculation, followed by adsorption clarification, filtration, and chlorination (Figure 3.2).

Water from the Turtle Creek Reservoir is passed through pre-screens and pumped from the low lift pump station, where potassium permanganate is added seasonally for oxidation of Mn and Fe. Contact time for oxidation is provided in the time required to pump the source water from the pump house to the MWTP. Once the water enters the MWTP, it is dosed in-line with lime to adjust the pH to approximately 8. The lime is mixed for one minute in an inlet chamber, then passed to a contact chamber for eight minutes. The water is passed to a mixing tank, where alum is used as the primary coagulant at an average concentration of approximately 25 mg/L. Mixing of the coagulant occurs for one minute before the water flows to the first of two flocculation tanks. In the first flocculation tank, a cationic polymer

(0.1 mg/L) is added as a flocculant aid. The retention time in both flocculation basins is eight minutes.

The flocculated water is then distributed between four up-flow adsorption clarifiers. The clarifiers contain 1.2 m of small plastic beads and remove the majority of the formed flocs. Clarified water is then gravity fed through multi-media filters: anthracite (458 mm), sand (229 mm), and garnet (76 mm). Finally, the finished water is dosed with Cl_2 for disinfection, NaOH to neutralize the pH, and poly-orthophosphate for corrosion control.

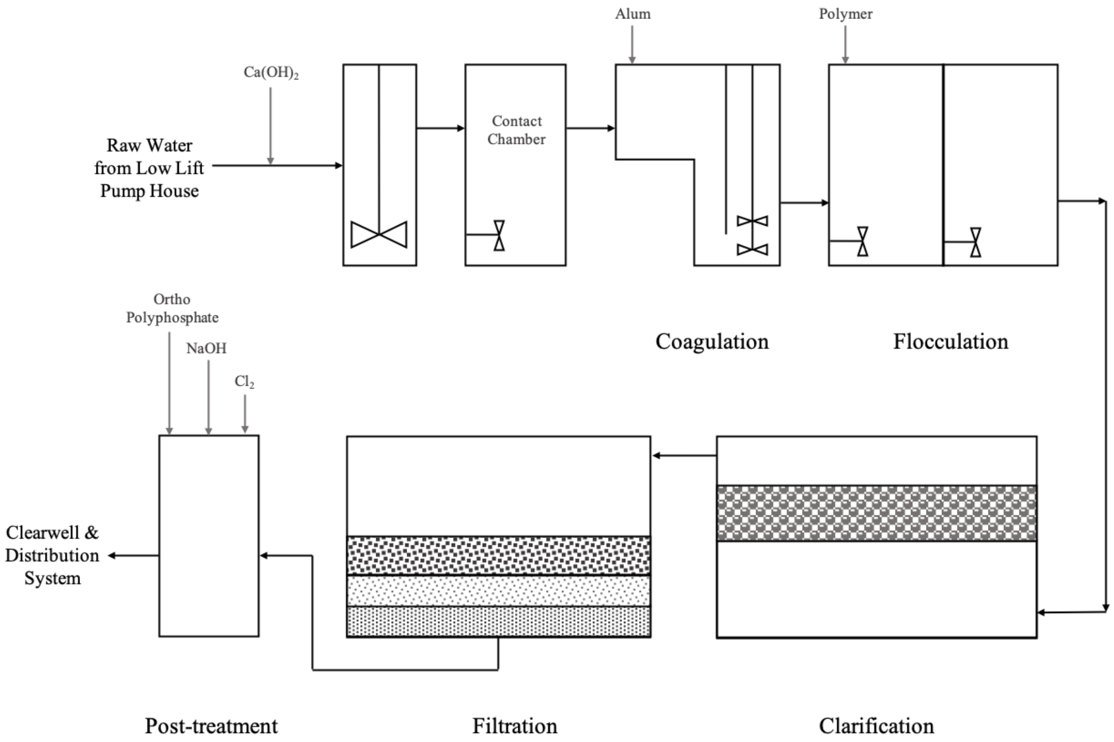

Figure 3.2 Overview of the MWTP treatment process

3.2.3 ACTIFLO® Pilot Plant

ACTIFLO® is a patented physio-chemical water treatment technology produced by Veolia Water Technologies (Paris, France). The process combines ballasted flocculation (BF) and clarification with lamella plate settlers (Figure 3.3).

A portion of the raw water entering the MWTP from the low lift pumping station was diverted into the ACTIFLO® pilot plant for the duration of its operation. The flow of raw water to the pilot plant was varied between 13 and 24 m^3/hr. Already oxidized with potassium permanganate from the pumping station, the raw water flowed into the coagulation tank (0.78 m^3) where lime was added for pH control and the primary coagulant was dosed. Next, an injection tank (0.78 m^3) was used for addition of the re-circulated micro-sand ballasting agent (BA). In the maturation tank (2.34 m^3), the mixing intensity was reduced for flocculation and cationic polyelectrolyte was employed to improve incorporation of the BA into the flocs, increasing their density, and thus, settling rate. The flocculated water then overflowed to a settling tank with lamella plate settlers (maximum surface area of 0.575 m^2) and the clarified water was pumped to the filtration skid. The surface area was adjusted to obtain different hydraulic loading rates.

The filtration skid consisted of two 200-mm diameter multi-media filter columns enclosed in a separate trailer. The filter media layout was identical to that in the full-scale plant, however, one column had old filter media that had been taken from the full-scale plant (FO), whereas the other had brand-new media (FN). There was no further chemical treatment after filtration.

In-line measurements in the ACTIFLO® pilot plant included: raw, clarified, and filtered water turbidity; raw and clarified water pH; and head-loss development across the filters.

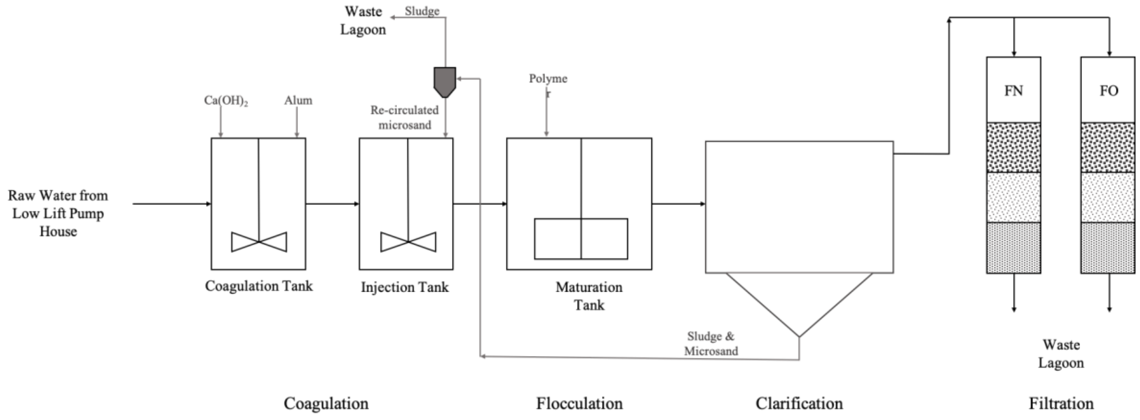

Figure 3.3 Overview of the ACTIFLO® pilot plant

3.2.4 Jar tests

A standard Phipps & Bird Jar Tester was used to for bench-scale analyses of the current treatment processes at the MWTP because there was no adsorption clarification pilot plant. The jar tests focused on the removal of dissolved contaminants (i.e. DOC, UV_{254}, dissolved Al), as adsorption clarification cannot easily be simulated in bench-scaled experiments.

Twenty-litre samples of the MWTP influent was collected and shipped, same day, to the clean water lab at Dalhousie University for testing. The MWTP oxidized their source water in the pumphouse, so the raw water received for this portion of the testing had already been dosed with potassium permanganate. Samples were stored at 4°C for up to two weeks prior to use.

The MWTP raw water was first brought to a temperature between 10 to 15°C, representative of shoulder season water temperatures, then titrations were performed to determine the required dose of lime for pH control during coagulation. One litre of sample was measured into each jar, and the pre-determined dose of lime was added during mixing at 50 rpm. Once the target pH was met, rapid mixing occurred at 100 rpm for 45 seconds, followed by an eight-minute period of mixing at 50 rpm. Next, the primary coagulant was added and mixed for one minute at 200 rpm. Polyelectrolyte, if required, was added immediately after the rapid mix. Flocculation began at 50 rpm for eight minutes, then transitioned to 25 rpm for an additional eight minutes. The mixing intensities and times were determined to simulate treatment at the full-scale plant. The flocculated samples were settled for 30 minutes, then filtered through a 0.45-µm polyethersulfone (PES) filter for analysis of dissolved contaminants.

3.3 Coagulants

The primary coagulant for the majority of the research was hydrated alum ($Al_2(SO_4)_3 \bullet 14H_2O$) supplied by Chemtrade. The polyelectrolytes were supplied by SNF Canada and Univar Solutions. Properties of the liquid coagulants are provided in Table 3.3 and powder flocculant properties are summarized in Table 3.4.

Table 3.3 Liquid Coagulant Properties

	Type of Coagulant	Provider	Charge Density	Specific Gravity	Supplied Concentration (w/w %)	pH (neat)
Liquid Alum	Aluminum sulphate	Chemtrade	n/a	1.3-1.35	48.5% $Al_2(SO_4)_3$	1.4-2.6
PAX-XL 6	Polyaluminum chloride (50% basicity)	Univar Solutions	n/a	1.18-1.28	5.1-5.7 % Al	2.1-3.1
FLOQUANT FL2449	Linear polyamine	SNF Canada	High	1.1-1.2	50% active content	4.0-6.0

Table 3.4 Power Flocculant Properties

	Type of Coagulant	Provider	Charge Density	Bulk Density (g/mL)	Molecular Weight
FloPAM FO 4190 PWG	Poly-methyl chloride ADAM	SNF Canada	Low	0.80	High

3.4 Analytical procedures

The water quality parameters outlined in this chapter were measured and evaluated throughout the course of the study. Any analytical procedures specific to an experiment are detailed further in respective chapters.

3.4.1 General Water Quality Parameters

When applicable, laboratory analysis and procedures were completed in accordance with *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA, and WEF 2017). Otherwise, analytical procedures followed the equipment manufacturer's directions. All glassware and apparatus were washed and rinsed three times with deionized (DI) water obtained from a Milli-Q® water purification system. Milli-Q® water was also used in preparation of stock chemical solutions.

Benchtop pH measurements were taken using Orion Ross Ultra pH/ATC Triode electrodes with a Thermo Scientific Orion Star A111 meter. A three-point calibration (pH 4, 7, 10) was conducted on each day of use. Turbidity was analysed on a calibrated HACH 2100AN

Turbidimeter or a calibrated HACH 2100Q Portable Turbidimeter. Zeta potential was measured on a Malvern Panalytical Zetasizer Nano ZS.

In both pilot plants, in-line turbidity measurements were collected on effluent from each filter column with HACH 1720E low range process turbidimeters. In-line pH measurements were taken on the raw water, in the flocculation basins, and on the finished water using Endress + Hauser Orbisint CPS11 analogue pH sensors.

3.4.2 Natural organic matter

NOM was characterised through measurement of TOC, DOC, UV_{254}, and SUVA. TOC and DOC were analyzed based on Standard Methods 5310 (APHA, 2012). Samples for TOC were collected, headspace free, in 40-mL glass vials and preserved to a pH <2 with phosphoric acid. Samples for DOC were first filtered through a 0.45-µm PES membrane (GVS Filter Technologies) that had been rinsed with 500 mL of DI water, and then preserved in the same manner as TOC samples. Organic carbon concentrations were measured with a TOC analyzer (Shimadzu TOC-V_{CPH}).

UV_{254} (Standard Methods 5910) was measured on samples filtered through a 0.45-µm PES filter (GVS Filter Technologies) that had been rinsed with 500 mL of DI water. Samples were analyzed using a HACH DR5000 UV-Vis spectrophotometer at a wavelength of 254 nm.

SUVA is the ratio of UV_{254} absorbance (in m^{-1}) to DOC (mg/L). The calculation is frequently used as an indicator of the character of NOM in a sample. High SUVA values (>4 L/mg m) indicate that NOM is largely composed of hydrophobic humic matter, with high molecular weights (Edzwald 1993). Lower SUVA values (<2 L/mg m) suggest mostly non-humic, low hydrophobicity NOM, with low molecular weights (Edzwald 1993).

SUVA is calculated with the following equation:

$$\text{SUVA}\left(\frac{\text{L}}{\text{mg m}}\right)=\frac{\text{UV}_{254}\,(\frac{1}{\text{cm}})}{\text{DOC}\,\left(\frac{\text{mg}}{\text{L}}\right)}*\ \frac{100\text{ cm}}{1\text{ m}}$$

3.4.3 Disinfection by-product formation potential

Disinfection by-product formation potential (DBPfp) were analyzed using a modified version of Standard Methods 5710 (APHA et al. 2017). DBPfp analysis included trihalomethane formation potential (THMfp) and haloacetic acid formation potential (HAAfp). Samples were buffered with borate, then pH adjusted to 8 ± 0.2 with sulphuric acid (H_2SO_4) or NaOH. Buffered samples were then chlorinated with a pH 8-buffered NaOCl solution to obtain a residual chlorine concentration of 1.0 ± 0.4 mg/L after a 24-hour incubation period. Samples were incubated headspace free in chlorine demand free glass amber bottles at 20°C.

After incubation, samples were preserved in clear 20-mL glass vials. Preserved samples were prepped for analysis by liquid-liquid extraction with pentane (THMfp) or methyl tert-butyl ether (HAAfp). One microlitre of extract was separated and analyzed via gas chromatography with an electron capture detector (GC-ECD – Thermo Scientific Trace 1300 Series). Samples were integrated using Chromeleon 7 Interactive Graphics software.

Samples were analyzed for four THM compounds (chloroform, bromodichloroform, chlorodibromoform, and bromoform) and nine HAA compounds (chloroacetic acid, bromoacetic acid, dichloroacetic acid, trichloroacteic acid, bromochloroacetic acid, dibromoacetic acid, bomodichloroacetic acid, chlorodibromoacetic acid, and tribromoacetic acid). THM and HAA measurements are the sum of the all the respective compounds.

3.4.4 Metals

Concentration of elements (Al and Mn) were analyzed with inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific X-Series 2) following Standard Methods 3125 (APHA et al. 2017). Samples (10 mL) were collected in 15-mL collection bottles then acidified to pH<2 with trace metal grade concentrated nitric acid (HNO_3). Bottles and caps were soaked in a 10% nitric acid solution for at least 24 hours prior to use, then rinsed with DI water. Samples with high anticipated concentrations of Mn or Al were diluted prior to acidification.

3.4.5 Statistical analysis

All statistical analysis was conducted using R (R Core Team 2020; Wickham et al. 2019) and Excel. T-tests, analysis of variance, and linear regression were among the most common methods of data analysis and specific tests conducted for each study are described in their respective chapters. The level of significance for all statistical tests was 0.05.

CHAPTER 4: MITIGATING CHANGING SOURCE WATER QUALITY IN DIRECT FILTRATION PLANT

4.1 Introduction

Over the last few decades, increasing concentrations of natural organic matter (NOM), measured as dissolved organic carbon (DOC), have been recorded in many regions across Northern America and Europe (Garmo 2020; Garmo et al. 2014; Monteith et al. 2007). This trend has often been associated with 'recovery from acidification', a phenomenon defined as increasing acid neutralization capacity, alkalinity, or pH in response to reduced atmospheric acid deposition (Evans and Monteith 2001; Stoddard et al. 1999). The composition and character of NOM in surface waters is also impacted by climatic factors, including precipitation events (e.g. increased rainfall and droughts) and warming temperatures, which often lead to increased seasonal fluctuation in surface water quality (Imtiazy et al. 2020; Meyer-Jacob et al. 2020; Strock et al. 2016; De Wit et al. 2016; Xiao et al. 2020).

Increasing concentration of DOC in water supplies has multiple design implications for drinking water treatment. As the primary precursor for disinfection by-products (DBPs), higher concentrations of organic material in the supply can result in higher concentrations of DBPs in the treated water if the plant is unable to effectively withstand the increasing organic load. Drinking water treatment plants have reported concomitant increases in dosing of chemicals, including coagulants, chemicals used in pH control (e.g. lime, CO_2), and disinfectants, to address increasing trends in raw water DOC (Anderson et al. 2017; Eikebrokk, Vogt, and Liltved 2004; Emma L. Sharp, Parsons, and Jefferson 2006).

The mechanism of removal depends on the properties of NOM and the aluminum hydrolysis species formed upon dosing of aluminum sulphate (alum); however, increased alum doses applied to mitigate higher DOC concentrations will result in greater concentrations of metal hydroxide precipitates and larger volumes of sludge produced in the treatment process. This often leads to shorter filter runs, more frequent backwashing, and reduced productivity. For this reason, direct filtration plants are often designed for low-turbidity, low organic content source waters, and they are particularly vulnerable to changes in source water quality, such as the increasing trend in DOC concentrations (Valade et al. 2009).

The partial substitution of alum with a high charge density cationic polyelectrolyte is a common practice in direct filtration, as it offers the benefit of charge neutralization capacity without the additional solid loading from a precipitating coagulant (Bolto et al. 2001; Edzwald et al. 1987; McCormick and King 1982). As such, unit filter run volumes (UFRV) can be increased due to the reduced volume of sludge from lowered alum doses (Bolto and Gregory 2007; Chang et al. 2005; Nozaic et al. 2001). The combination of high charge density cationic polyelectrolyte with alum has been successful in full-scale and pilot-scale direct filtration applications where reduced effluent turbidity (Chang et al. 2005), increased UV_{254} removal (Bolto et al. 2001) and extend filter runs (McCormick and King 1982; Pernitsky et al. 2011) have all been achieved. Another strategy used to extend filter cycles is to increase the effective size (ES) of the filter media. A coarser media allows for deeper penetration of incoming particulates into the filter bed, resulting in solids retention extended over larger depths of the filter and in turn, reduced rates of head loss development (Tobiason et al. 2010).

Nearly all the direct filtration plants in North America were built prior to the 1990s (Pernitsky et al. 2011; Valade et al. 2009), before noticeable shifts in source water quality (Clair et al. 2011; Evans and Monteith 2001; Garmo et al. 2014; Monteith et al. 2007; Stoddard et al. 1999). Some of these plants were designed based on acidified water quality conditions, and are currently operating at, or have passed, the threshold of their design guidelines (Pernitsky et al 2011; Anderson et al 2017). Given that treatment plant upgrades can be a timely process, there is a need for immediate, but perhaps less sustainable, strategies to account for the changing source water quality while more significant upgrades are considered. As such, the presented work investigated strategies to improve the efficacy and efficiency of direct filtration while facing the stress of increasing concentrations of DOC. First, combinations of cationic polyelectrolyte and alum for coagulation were studied as means to increase NOM removal, and subsequent DBP concentrations in the treated water, without compromising drinking water productivity. Second, the effects of increased

ES of filter media and extended filter bed depths on the responses of effluent water quality and UFRV were determined.

4.2 Materials and methods

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

The J.D. Kline Water Supply Plant (JDKWSP) is a direct filtration drinking water treatment plant in the Halifax Regional Municipality of Nova Scotia, Canada and consists of pre-screening, oxidation, pre-chlorination, coagulation, flocculation, dual-media filtration, and chlorination. It is operated by Halifax Water at an average of 85 megalitres per day (MLD). The source water for the JDKWSP is Pockwock Lake, a low-turbidity (< 1 NTU), low-alkalinity (<5 mg/L as $CaCO_3$) lake which drains a protected watershed. Raw water characteristics for the period of study are presented in Table 4.1.

Table 4.1 Raw water (Pockwock Lake) characteristics during period of study (April to July 2019)

Analyte	Range	Average	SD
pH	5.6-5.9	5.7	0.1
Turbidity – NTU	0.28-1.03	0.39	0.10
UV_{254} – 1/cm	0.127 – 0.109	0.117	0.006
TOC – mg/L	3.08 – 4.34	3.52	0.36
DOC – mg/L	3.05 – 4.40	3.62	0.39
SUVA – 1/m per mg/L of DOC	2.6 – 5.8	3.4	0.8
THMfp – µg/L	111 – 234	192	29
HAAfp – µg/L	158 – 422	221	79

The water quality of Pockwock Lake is approaching the upper thresholds of design guidelines for direct filtration plants. Valade et al. (2009) recommended water drawn for treatment with direct filtration have average annual total organic carbon (TOC) concentrations <3 mg/L, a value that Pockwock Lake has surpassed since the commission of JDKWSP in 1977. As such, the alum dose recently increased from 8 to 12 mg/L. Although this is within the range of maximum doses recommended for direct filtration plants (10-15 mg/L) (Hutchison 1976; Ratnayaka et al. 2009; Wagner and Hudson 1982), it leaves little buffer room for adjustment in response to increasing DOC concentrations. Additional treatment challenges at JDKWSP include reduced filter run times and increased formation of DBPs.

4.2.2 JDKWSP Pilot Plant

The JDKWSP is equipped with a research pilot plant (Intuitech, Inc) comprised of two identical and parallel direct filtration treatment trains that simulate the treatment process at the full-scale plant (Knowles et al. 2012). For the duration of the study, one of the trains was continuously operated under 'baseline conditions' that represented the chemical dosing applied at the full-scale plant. This dosing was consistent at 12 mg/L of alum.

Raw Pockwock Lake water was supplied to the pilot plant (Figure 3.1) at an average flow rate of 10 L/min. In the pre-mix tanks, potassium permanganate ($KMnO_4$) was added for oxidation of Fe and Mn and sodium hypochlorite (NaOCl) was applied for pre-chlorination. Lime ($Ca(OH)_2$) and carbon dioxide (CO_2) were used to maintain a coagulation pH of 5.8. Three-stage, tapered flocculation (30, 20, and 10 s^{-1}) followed pre-mixing. The flocculated water was then pumped to the filtration skid. Each filtration skid consisted of three 200 mm dual media (anthracite and sand) filter columns, through which the flow was evenly distributed at a constant loading rate around 4.5 m/hr. The first filter (F-FSP, or 'baseline') simulated the full-scale plant filtration beds and was comprised of 61 cm of anthracite (ES of 0.9 mm) and 30.5 cm of silica sand. The second filter media layout (F-ES0.9) has 91.5 cm of anthracite (ES 0.9 mm) and 30.5 cm of sand. The third filter column (F-ES1.3) has 91.5 cm of anthracite (ES 1.3 mm) and 30.5 cm of sand. Filter runs were terminated when the effluent turbidity exceeded 0.2 NTU, the head loss across the filter was greater than 2.15 m, or the filter run was longer than 80 hours. No additional chemical treatment on the filtrate was possible in the pilot plant.

4.2.3 Chemical reagents

The primary coagulant used was liquid aluminum sulphate ($Al_2(SO_4)_3 \bullet 14H_2O$) (Chemtrade) and the cationic polyelectrolyte was FLOQUANT FL 2449 (SNF Canada).

FL 2449 is a high charge density, linear polyamine with approximately 50% active content. It was selected based on its physical and chemical properties.

4.2.4 Experimental procedures

Investigation of the impact of cationic polyelectrolyte used in conjunction with alum was completed by comparing alum doses of 10 and 12 mg/L with polyelectrolyte doses of 0.5 and 1 mg/L, to baseline conditions of 12 mg/L of alum with no polyelectrolyte. Each dosing condition was tested in duplicate, for each filter media layout. One complete filter run represented one test. Grab samples were collected on the raw water and filter effluents 24 hours into the filter run and analysed for TOC, DOC, ultraviolet absorbance at 254 nm (UV_{254}), and disinfection by-product formation potential (DBPfp). Flocculated water samples were also collected for zeta potential analysis. Filter hydraulic performance was evaluated based on the UFRV, and turbidity and head loss profiles.

To determine the impacts of increasing the ES of the filter media and extending the depth of the filter, comparison of filter hydraulic performance between F-FSP and F-ES1.3 was conducted under identical chemical dosing, described previously. Effluent TOC, UFRV, and head loss and turbidity profiles were used as response parameters.

The aforementioned experiments were conducted from April 2019 to July 2019; therefore, the results have limited seasonal variation.

4.2.5 Analytical procedures

When applicable, laboratory analysis and procedures were completed in accordance with *Standard Methods for the Examination of Water and Wastewater* (APHA et al. 2017). TOC and DOC samples were prepared following Standard Methods (5310) and measured with a TOC analyzer (Shimadzu TOC-V_{CPH}). UV_{254} was measured on a HACH DR5000 UV-Vis spectrophotometer at a wavelength of 254 nm and used for calculation of specific UV absorbance (SUVA). Samples were prepped for DBPfp, namely trihalomethane formation potential (THMfp) and haloacetic acid formation potential (HAAfp), following a modified version of Standard Methods (5710). The samples were buffer to pH 8, and chlorine was dosed such that free chlorine residual was 1.0 ± 0.4 mg/L after a 24-hour incubation period.

Measurement of HAAs and THMs in the incubated samples was done using gas chromatography with electron capture (US Environmental Protection Agency methods 552.2 and 551.1, respectively). Zeta potential was measured on a Malvern Panalytical Zetasizer Nano ZS. In-line water quality parameters (temperature, pH, turbidity) were measured at critical points throughout the treatment process and filter hydraulic performance was evaluated with continuous head-loss and flow monitoring across each filter bed.

4.2.6 Statistical analysis

Statistical analysis was conducted with R (R Core Team 2020; Wickham et al. 2019). Paired t-tests were used to compare the response of alternative coagulation conditions to baseline conditions. Analysis of variance (ANOVA) was used to determine if differences in results existed between the filter media layouts. Tests for normality were conducted with the Shapiro-Wilks test and Kendall's tau correlations were applied to understand relationships between treated water quality parameters. The level of significance for all statistical tests was 0.05.

4.3 Results

4.3.1 Combined use of cationic polyelectrolyte and alum

As the majority of TOC in both the raw (102 ± 4.6%) and treated (99 ± 8%) water was in the dissolved form, TOC measurements were used to represent NOM in analysis. In comparing residual TOC concentrations (Figure A.1) and TOC removal (Figure A.2) in the three filter media layouts with ANOVA, effluent water quality was equivalent and as such, the results were summarized (Figure 4.1). TOC removal ranged from a minimum of 31% to a maximum of 44% for all four dosing combinations applied in Figure 4.1. At a constant alum dose of 12 mg/L, the average residual TOC concentration decreased from 2.20 mg/L to 2.10 mg/L with the addition of 0.5 mg/L of polyelectrolyte, however, there was no statistically significant difference in the means of the two samples. Likewise, TOC removal was consistent (~38%) with alum doses of 12 mg/L, with or without the addition of polyelectrolyte. When alum was partially substituted with polyelectrolyte (i.e. comparing

12 mg/L of alum to 10 mg/L of alum with 0.5 and 1 mg/L of polyelectrolyte), there was again, no significant improvement or reduction in TOC removal. Overall, results suggested that partial substitution of alum with a high charge density, cationic polyelectrolyte would maintain NOM removal, but not improve it.

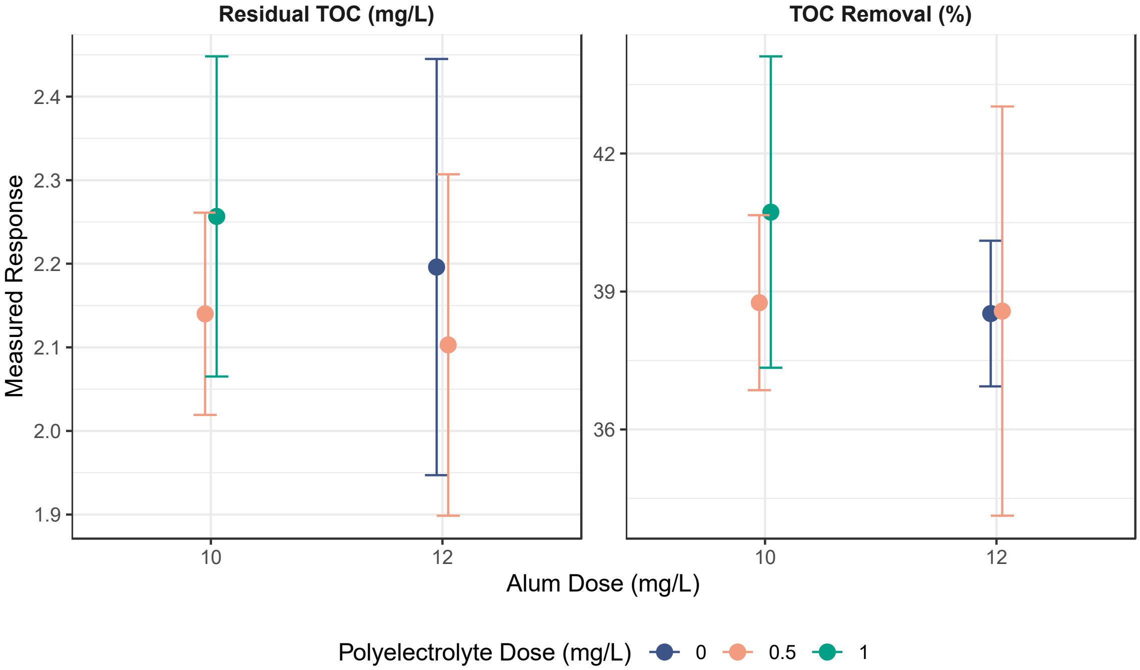

Figure 4.1 Average residual TOC concentrations and TOC removal for combinations of alum and polyelectrolyte doses tested in pilot-scaled direct filtration trials. Error bars represent the standard deviation about the mean (n=6 for all dosing except 12 mg/L alum and 0 mg/L polyelectrolyte where n=15)

HAAfp and THMfp in the treated water ranged from 44 to 107 µg/L and 24 to 97 µg/L, respectively, for all dosing conditions applied (Figure 4.2). Kendall's rank correlation tests found no relationship between residual TOC concentration and HAAfp (p=0.2518), however, a weak, positive correlation was identified with THMfp (τ=0.26; p=0.0186). This suggests that as residual TOC concentrations increased, slight increases in THMfp were also recorded. However, when the entire dataset was considered (i.e. raw and treated water), significant positive correlations were observed between residual TOC concentrations and HAAfp and THMfp (τ=0.34 and τ=0.53, respectively).

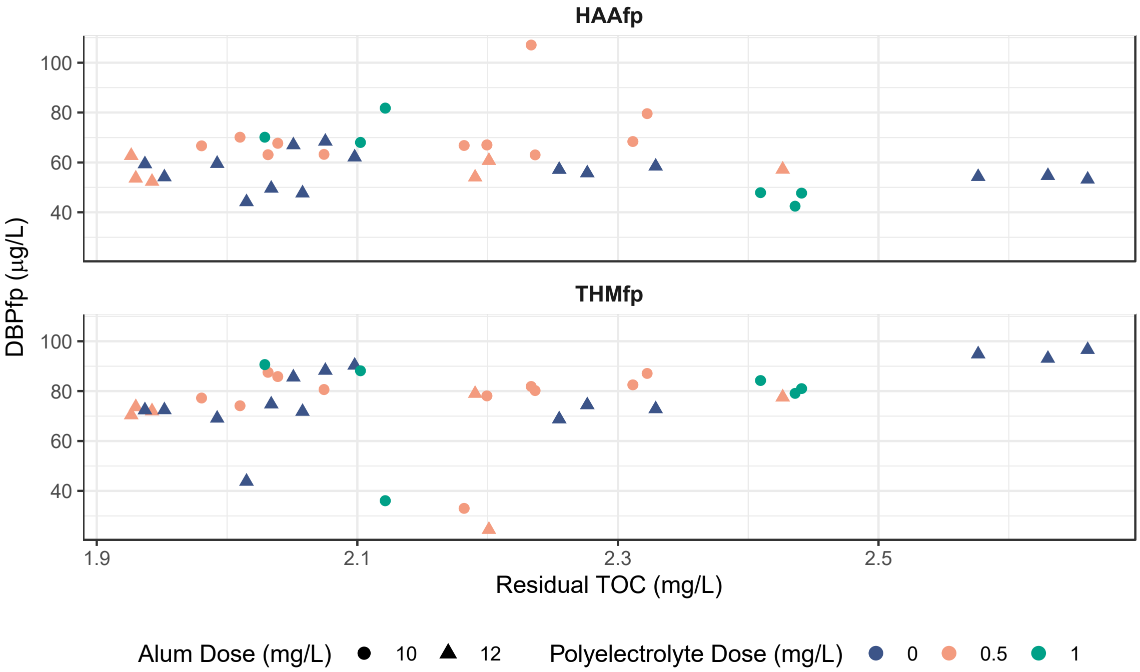

Figure 4.2 HAAfp/THMfp and residual TOC concentrations of treated water samples coagulated under a variety of combinations of coagulants in pilot-scaled direct filtration trials.

Figure 4.3 shows the impacts of alternative coagulant dosages on the UFRV. A negative value represented a decrease in the UFRV as compared to the baseline conditions. Pilot plant baseline runs for this study averaged 270 ± 75 m^3/m^2 and typical UFRVs in the full-scale plant were 250 ± 50 m^3/m^2. Results showed that the addition of 0.5 mg/L polyelectrolyte while maintaining an alum dose of 12 mg/L did not impact the UFRV. Similarly, supplementing a lowered alum dose (10 mg/L) with 0.5 mg/L of polyelectrolyte also resulted in consistent UFRV as compared to the baseline. However, when 1 mg/L of polyelectrolyte was applied with a lowered alum dose, there was a significant decrease in the URFV.

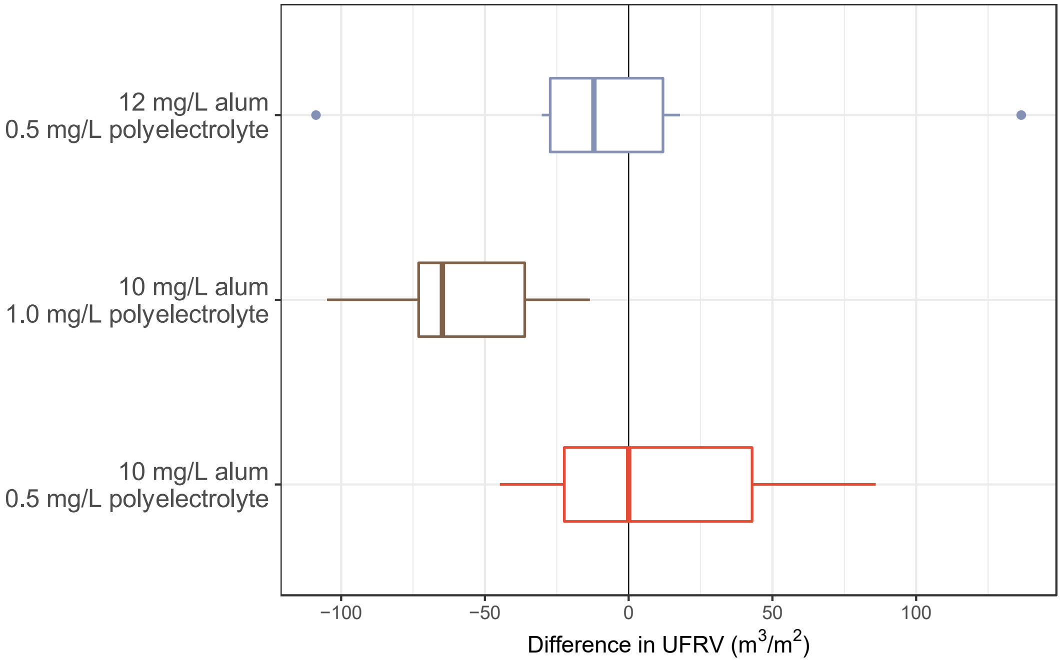

Figure 4.3 Difference in pilot-scaled UFRV with alternative coagulant dosing as compared to the baseline (12 mg/L of alum) (n=6 for all dosing). Negative values indicate reductions in UFRV as a result of the switch to alternative dosing.

Analysis of simplified head loss profiles for all trials (Figure 4.4) indicated increased rates of head loss development with the addition of polyelectrolyte as compared to baseline conditions. However, simplified turbidity profiles (Figure 4.4) showed improved effluent turbidity, with the exception of Trial 1, when comparing runs with polyelectrolyte to baseline conditions. During Trial 2, spikes in effluent turbidity were observed under baseline conditions, but were minimized when polyelectrolyte was used as a coagulant aid (Figure A.3). Improved effluent turbidity was also recorded in preliminary trials, where a lowered alum dose (10 mg/L) without polyelectrolyte resulted in high effluent turbidity, such that the filters were unable to ripen (Figure A.4). The addition of polyelectrolyte (0.5 mg/L) at the same alum dose improved filter runs up to the maximum of 80 hours (Figure A.4) The mechanisms for termination of filter runs in the study were variable, however in trials with higher coagulant doses (i.e. 12 mg/L alum with 0.5 mg/L polyelectrolyte, and 10 mg/L alum and 1 mg/L polyelectrolyte), turbidity breakthrough was most common.

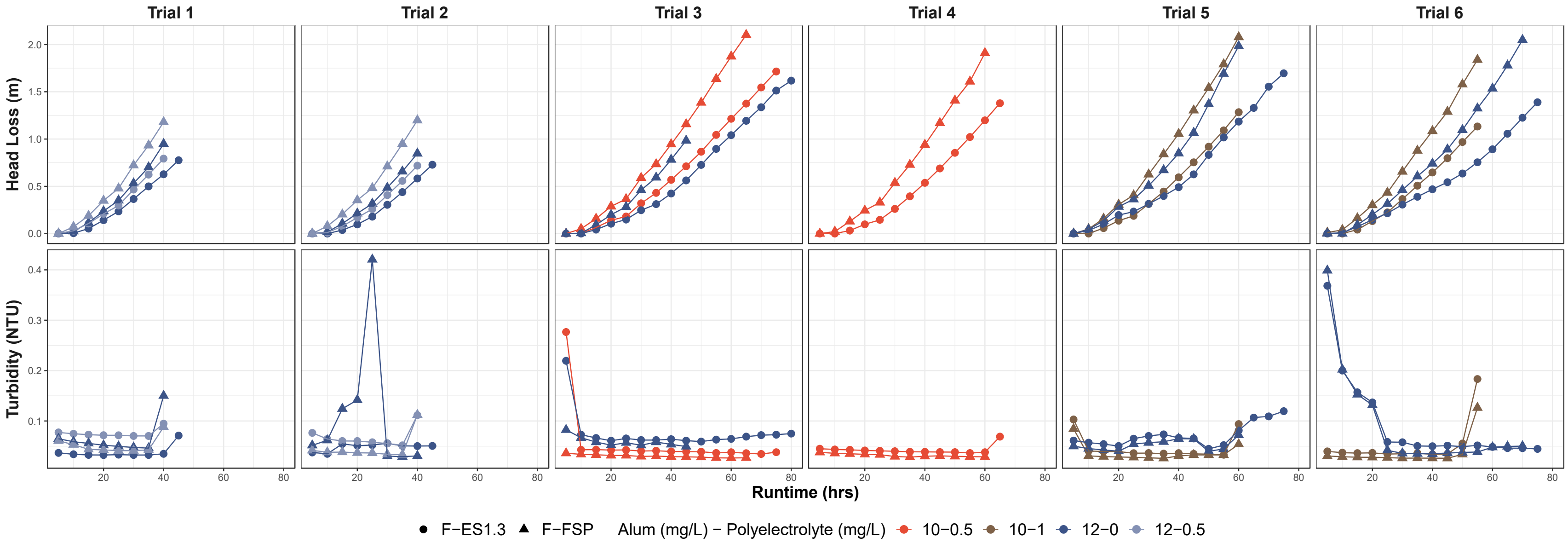

Figure 4.4 Simplified head loss and turbidity profiles for all coagulant dosing conditions through F-FSP (mimicking the full-scale plant filter media layout) and F-ES1.3 (increased effective size while maintaining the effective size to bed depth or *L/d* ratio) in pilot-scaled trials. Profiles were simplified by averaging the measurement for each hour, every five hours.

4.3.2 Increased effective size of filter media and extended filter bed depth

Results from a paired t-test comparing filters F-FSP and F-ES1.3 indicated that switching the filter media layout did not impact the TOC removal (95% CI for the difference in means was -1.173 to 0.223%). However, UFRVs improved by 3.16 to 16.19 m^3/m^2 when the ES and bed depth were increased.

Head loss and effluent turbidity profiles for F-FSP and F-ES1.3 are compared for identical dosing conditions in Figure 4.4. Results demonstrated a clear reduction in the rate of head loss development with the higher ES media and extended filter bed depth. Furthermore, the alternative filter media layout produced equivalent turbidity profiles to the baseline. Filter runs in F-ES1.3 did not terminate due to head loss, which was the cause of termination for five of the 11 runs in F-FSP. Most trials in F-ES1.3 were ended due to effluent turbidity exceeding the limit of 0.2 NTU, and four reached the maximum run time.

4.4 Discussion

4.4.1 Combined use of cationic polyelectrolyte and alum

TOC removal and residual TOC concentrations were consistent for all alternative doses investigated (Figure 4.1). This was contradictory to previous findings that reported improved removal of organic matter and filtered water quality with the addition of cationic polyelectrolyte (Bolto et al. 2001; Chang et al. 2005; Pernitsky et al. 2011). However, the TOC removal percentages measured in this study were consistent with expected values based on the nature of DOC in the raw water.

Raw water SUVA values for the period of study averaged 3.4 L/mg m, but values as low as 2.6 L/mg m were recorded. For SUVA values between 3-4 L/mg m, organic material is likely a mixture of hydrophobic (HPO) and hydrophilic (HPI) compounds and DOC removal is expected to be between 40-60% (AWWA and Edzwald 2011; Edzwald 1993). The TOC removal recorded in this study ranged from 31 to 44%, on the lower end of the spectrum reported by AWWA (2011). However, fractionation work completed by Anderson (2019) at the same time as this study indicated that hydrophobic neutrals (HON) represented the largest fraction of DOC (~55%) in Pockwock Lake. HONs can be resistant towards coagulation and removal around 10% have been reported for this fraction (Edzwald 1993). Further, a previous study at the JDKWSP compared DOC fractions before and after treatment and reported that the HON fraction, along with hydrophilic acid (HIA) and hydrophilic base (HIB) fractions, were unchanged in the summer months (Montreuil 2011). These three fractions represented approximately 62% of the raw water DOC in July 2019 (Anderson 2019). Additionally, the hydrophilic neutral fraction (HIN), which was ~20% of the untreated DOC at the time of this study (Anderson 2019), can have SUVA values between 3.5-4 L/mg m, causing a shift towards higher measurements and potential misinterpretation of expected DOC removal because this fraction is not readily removed with coagulation (AWWA and Edzwald 2011; Edzwald 1993). Therefore, despite a high portion of hydrophobic NOM in the raw water, TOC removal was expected to be on the lower end of the 40-60% range typical of supplies with SUVA values between 3 and 4 L/mg m.

Additional tests at 14 and 16 mg/L of alum and no polyelectrolyte showed minimal improvement (~5%) in TOC removal when compared to the initial tests conducted in this study (Table A.1), and removal was not improved by increasing the alum dose from 14 to 16 mg/L. Additionally, the zeta potential measurements taken on flocculated water (Figure 4.5) were within the recommended -10 to +5 mV range for effective charge neutralization (Pernitsky et al. 2011). As such, it is suggested TOC removal is near optimal values for the current concentration and character of NOM in the surface water so increasing the coagulant dose will have minimal impact on the quality of the treated water.

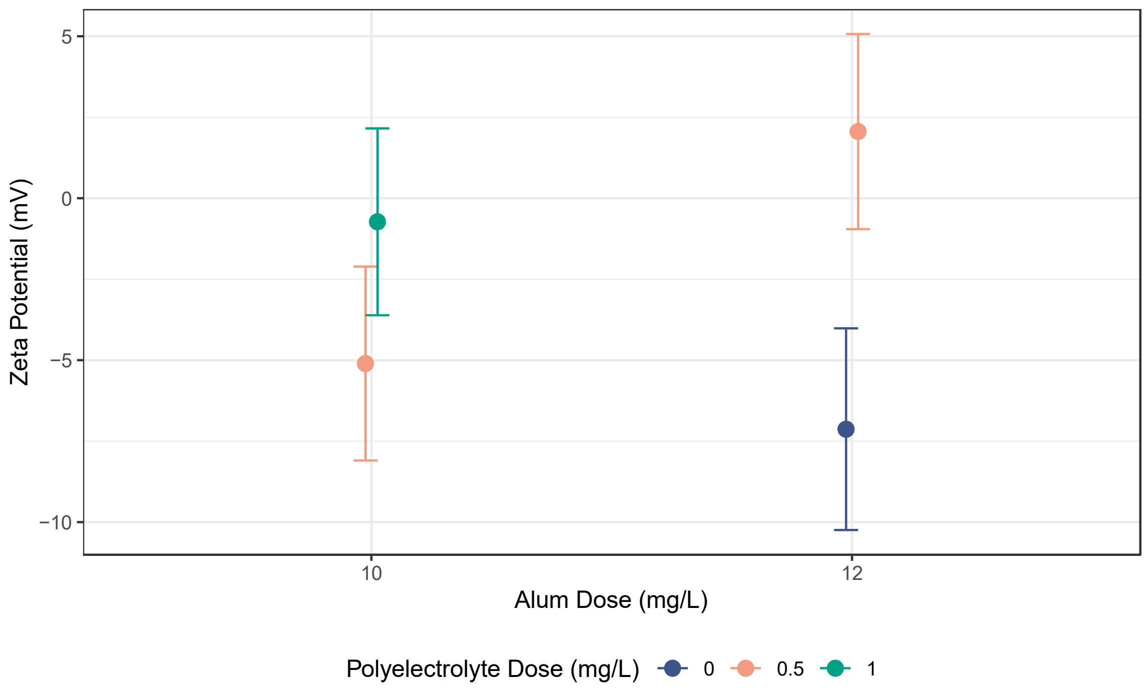

Figure 4.5 Zeta potential measured on flocculated water under alternative and baseline coagulation dosing in pilot-scaled trials. Error bars represent the pooled standard deviation (from two samples) about the mean.

Despite some contradicting results (Kanokkantapong et al. 2006; Tubić et al. 2013), it is widely cited that the hydrophobic fraction is the largest contributor to DBP precursor material in raw waters (Bond et al. 2010, 2011; Chang et al. 2001; Li et al. 2017). However, this is also the fraction that is most readily removed with coagulation. Therefore, it is typically the fraction that is recalcitrant to coagulation that controls post-coagulation NOM concentrations (E. L. Sharp et al. 2006), and in turn, DBP formation (Bond et al. 2010). Additionally, small, low molecular weight (MW) compounds have also been noted to be significant contributors to DBP precursor material (Chang et al. 2001) and are often not sufficiently removed with coagulation (Nissinen et al. 2001). In the current study, it is hypothesized that the DBP precursor material remaining post-coagulation was of this nature because DBPfp was not improved with lower residual TOC concentrations. This theory was supported by the SUVA values of the treated water, which were all <2, implying mainly hydrophilic NOM (Edzwald 1993). Additionally, Montreuil (2011) found similar results for treatment at the JDKWSP, where the hydrophilic fraction had a large contribution to the DBPfp in the treated water, but the raw water was dominated by hydrophobic DBP precursors. Further, DBPs formed from pre-chlorination were <7% of the final DBPfp values, so this was not a significant source of DBP formation. Increased removal of NOM should, therefore, be targeting the DBP precursors that remain after coagulation under the current treatment conditions. This targeted treatment may require additional plant upgrades, as discussed in Chapter 4.5.3.

It was hypothesized that partial substitution of alum with cationic polyelectrolyte would result in reduced sludge volumes and longer filter runs. This theory was supported in the literature, where the combination cationic polyelectrolytes used in conjunction with alum increased UFRV up to 50% (Pernitsky et al. 2011), and extended filter runs when compared to coagulation with just alum (McCormick and King 1982). However, such an effect was not observed in the presented work. The lack of improvement in UFRV was likely due to the increased rate of head loss development observed with the addition of polyelectrolyte (Figure 4.4). One proposed mechanism for the increased rate of head loss is an increase in floc size when polyelectrolyte was used as a coagulant aid. The addition of polyelectrolyte may have caused a degree of bridging between flocculated particles, despite the main mechanism being charge neutralization (Bolto and Gregory 2007). Bridged flocs are typically larger than those produced with charge neutralization, as they are stronger and can resist breakage at higher shears (Bolto and Gregory 2007; Fabrizi et al. 2010; McCormick and King 1982). The larger flocs are less likely to have deep penetration into the filter bed, increasing the rate of head loss development resulting in shorter filter runs (Tobiason et al. 2010).

Another possible mechanism for the reductions in UFRV is polymer carryover. This occurs when polyelectrolyte is overdosed in coagulation and binds to the filter media. However, carryover would be represented by high, positive zeta potentials, indicating that the desired neutral surface charge of particles in the raw water has been achieved and polyelectrolyte was applied in excess, and increased filtrate turbidity (Bolto and Gregory 2007). As per Figure 4.5, zeta potential measurements were near zero, or negative, suggesting that polymer carryover was not a significant cause for the increased head loss.

Further investigation into the volume of sludge produced (e.g. mass balance calculations), floc penetration into the filter bed (e.g. filter surveillance) and the size of flocs (e.g. image analysis, laser diffraction) formed under different coagulant dosing would give additional insight into the mechanisms affecting the filter hydraulic performance.

4.4.2 Increased effective size of filter media and extended bed depth

Previous reports have found that the decline in filtrate water quality anticipated with a coarser media can be offset by extending the bed depth and maintaining the length to depth ratio (*L/d*) (Moran et al. 1993; Saltnes et al. 2002). The *L/d* ratios in the two filter media layouts tested in the study were 1288 and 1315 for the F-FSP (mimicking the full-scale plant) and F-ES1.3 (increased ES and bed depth), respectively. Therefore, filtered water quality should be maintained, as was observed through recorded TOC removal and effluent turbidity profiles.

The extended filter run times and subsequent increase in UFRV in F-ES1.3 as compared to F-FSP were associated to the slower rates of head loss development observed in F-ES1.3. With coarser media, flocs penetrate deeper into the filter bed and the captured solids are spread over a larger volume of media, reducing the head loss (Moran et al. 1993; Tobiason et al. 2010). This strategy has been successfully used in practice to reduce rates of filter clogging (Monscvitz et al. 1978). Further, Tchio et al. (2003) reported that coarse media (2 mm) was more suitable, as compared to fine media (0.4 mm), for deep beds at lower filtration rates (<5 m/hr). The filter loading rates used in this study (~4.5 m/hr) were comparable to those in (Tchio et al. 2003)

Despite the advantages of coarser media, greater passage of flocs has also been reported with increased ES of media, potentially leading to turbidity breakthrough (Hutchison 1976; Tchio et al. 2003). Coarser anthracite also leads to higher deposit of solids in the sand layer of the dual media filter and ultimately resulted in saturation of the media and turbidity breakthrough (McCormick and King 1982). It is likely that this mechanism was reflected in the findings, as seven of the 11 trials in F-ES1.3 were terminated due to abrupt increases in effluent turbidity after extended periods of constant readings. As such, when switching to coarser filter media as a strategy to increase productivity of direct filtration plants, investigation of the potential changes in effluent water quality and turbidity breakthrough should be completed prior to full-scale implementation.

4.5 Implications of findings

4.5.1 Shift from Al-based coagulants

It was determined that residual TOC concentrations could be maintained when partially substituting alum with a cationic polyelectrolyte. This has beneficial implications for drinking water utilities seeking to reduce their dependence on Al-based coagulations. Low doses of alum are desired because Al has been cited as a hazard to human health (Bondy 2016; Flaten 2001) and some studies link the metal to early onset of Alzheimer’s disease (AD) (Exley 2017). However, only a very small portion of daily Al intake is from drinking water (Van Dyke et al. 2020; Flaten 2001) and there is not enough evidence to prove a causal link between Al in drinking water and AD (Health Canada 2019a). As such, the non-health related impacts of may be more important than the health impacts (Edzwald 2020). For example, turbidity produced from precipitated Al species may interfere with chemical disinfection, and Al deposition on pipes in the distribution system can lead to reduced internal diameters and increased surface roughness causing lower hydraulic pressure (Edzwald 2020). Additionally, recent work found that the presence of Al hindered the ability of orthophosphate to act as a lead corrosion inhibitor (Li et al. 2020). Therefore, utilities seeking to shift from Al-based coagulants to mitigate residual Al concentrations in treated water should consider cationic polyelectrolyte.

4.5.2 Turbidity control with polyelectrolyte

Direct filtration plants are more sensitive to changes in raw water than conventional treatment processes due to the lack of clarification. This has been highlighted at the JDKWSP, which experienced a significant operational upset in March 2016 due to increased raw water turbidity during a storm. A spike in raw water turbidity from ~0.3 to a maximum of 0.7 NTU caused full-scale plant filter runs to drop as much as 70%. The use of polyelectrolyte may be a practical strategy for turbidity control when baseline alum doses are insufficient. The use of polyelectrolyte instead of alum to control spikes in raw water turbidity could result in significantly lower sludge volumes and increased water productivity. This may have beneficial implications as increased frequency of climatic events (e.g. heavy precipitation, which may lead to sudden spikes in turbidity) is anticipated with climate warming (Lal et al. 2012). .

4.5.3 Shifts in NOM and mitigating DBPs

Shifts in concentration and character of DBP precursor material have resulted increased DBPfp at the JDKWSP over the past decade, especially the HAAfp, which was <40 μg/L in 2010 (Montreuil 2011) and ranged between 40 to 107 μg/L in this study. Furthermore, it was concluded that DBP precursor material recalcitrant to coagulation was not readily removed with the current treatment and additional processes may be required for improved treated water quality. Application of technologies such as biofiltration (Stoddart and Gagnon 2015), membrane filtration (Bond et al. 2010; Teixeira, Rosa, and Sousa 2011), adsorption with granular activated carbon (Badawy et al. 2012), and magnetic ion exchange resin (Bond et al. 2011; Fearing et al. 2004) have all previously been used to remove more persistent DBP precursors.

To achieve longevity in treatment plant design, understanding the network of factors (e.g. lake recovery from acidification, changing climate, land use, etc.) that impact the concentration and character of NOM, and its reactivity with disinfectants, is critical. Treatment strategies should be selected based long-term and seasonal trends in the amount and nature of NOM identified through high-resolution monitoring. Further, utilities observing shifts in the water quality of their supply should consider upgrading to adaptable processes (e.g. modular units that can be temporally brought online) to mitigate seasonal or unexpected shifts in source water quality.

4.6 Conclusions

In attempts to mitigate the impacts of changing source water quality prior to plant upgrades, the combined used of cationic polyelectrolyte and alum was compared to coagulation with only alum in a direct filtration pilot plant. The application of polyelectrolyte did not improve NOM removal, likely because chemical dosing was already near optimal conditions for the nature of the NOM in the source water. However, the addition of polyelectrolyte did show the potential for mitigation of spikes in raw water turbidity and could lower the utility's dependency on Al-based coagulants, with no impact to treated water quality or productivity.

The partial substitution of alum with cationic polyelectrolyte did not improve UFRV, as was hypothesized. On the other hand, increasing the ES of filter media and expanding the depth of the filter bed did improve UFRV without compromising the quality of the treated water. This strategy could be applied to increase productivity under current chemical doses or maintain productivity if increased coagulant doses are required in the future.

An additional finding of this research was the lack of improved DBPfp with lower residual TOC concentrations in the treated water. It was proposed that DBP precursor material remaining in the filtrate was resistant to coagulation, and as such, additional treatment processes are recommended to mitigate their removal. This highlighted the importance of understanding trends in the concentration and character of source water NOM and DBP precursor material caused by factors such as lake recovery and climate change prior to plant upgrades, as these drivers will ultimately determine future treatment needs.

CHAPTER 5: INVESTIGATING THE IMPACTS OF COAGULANT DOSING AND PH ON TREATMENT EFFICACY AND EFFICIENCY

5.1 Introduction

More than 70% of surface water treatment plants in Canada use aluminum-based coagulants (Statistics Canada 2015). These coagulants are used to remove both organic and inorganic contaminants from source water and their effectiveness is dependent on proper coagulation conditions. The two most significant factors influencing their efficacy are coagulation pH and dose (Sillanpää et al. 2018).

A disregard for coagulation optimization resulting from poor pH control and alum dosing can result in high concentrations of NOM and Al in treated water. The removal of natural organic matter (NOM) is important as NOM is the main precursor for disinfection by-products (DBPs), which are cancerous compounds that are regulated by Health Canada (2019b). High levels of NOM can also discolor the water and contribute to taste and odor compounds (Sillanpää et al. 2018). Although these compounds may not have direct health implications, they can lead to drinking water that is not pleasing from an aesthetic perspective.

Low Al concentration in treated drinking water is desired because Al has been associated to neurological diseases, such as Alzheimer's disease (Health Canada 2019a); however, there is a mixed consensus regarding the health impacts of Al from drinking water, as it represents a small fraction of the total daily consumption (Edzwald 2020; Flaten 2001; Health Canada 2019a). Increased Al concentrations in treated water has also led to the development of scales in the distribution system, increasing the roughness of the internal surface of the piping, reducing the hydraulic pressure and ultimately leading to lower carrying capacity or increased pumping costs (Snoeyink et al. 2003). Additionally, Al in the distribution system has also been associated with increased release of lead and copper through co-precipitation or adsorption (Knowles et al. 2015; Kvech and Edwards 2001), and reduced efficacy of lead and copper corrosion inhibitors (Li et al. 2020). As such, Health Canada (2019a) has proposed updated Al guidelines of a MAC guideline of 2.9 mg/L, and an OG of 0.05 mg/L.

This work was completed in light of recent shifts in source water quality as a result of recovery from acidification and climatic drivers. The observed increasing concentrations of NOM demand higher alum doses for effective removal (Anderson et al. 2017; Ghernaout et al. 2010), which may result in higher concentrations of Al in treated drinking water if coagulation is not optimized (Health Canada 2019a). Furthermore, the factors affecting NOM and Al removal can vary by source. It is, therefore, important to conduct site-specific studies to determine the optimal operational parameters for drinking water treatment. The objective of this study was to determine the impact of pH and coagulant doses on concentrations of treated water NOM and Al in treatment of low turbidity, low alkalinity, and moderately coloured source waters.

5.2 Materials and methods

Treatment of two low-turbidity, low-alkalinity drinking water treatment plant source waters were considered for the analysis. The first water studied was the source water for the J.D. Kline Water Supply Plant (JDKWSP) in Halifax, Nova Scotia, a plant that has observed increasing trends in DBP formation and has, historically, had difficulty meeting the current 0.1 mg/L Al operational guideline (OG) under cold water conditions. Secondly, coagulation of source water from the Moncton Water Treatment Plant (MWTP) in Moncton, New Brunswick was investigated.

5.2.1 J.D. Kline Water Supply Plant

The JDKWSP is a direct filtration drinking water treatment plant in the Halifax Regional Municipality of Nova Scotia, Canada and is operated by Halifax Water at an average of 85 megalitres per day (MLD). Treatment at JDKWSP consists of pre-screening, oxidation, pre-chlorination, coagulation, flocculation, dual-media filtration, and chlorination. Current coagulation conditions (referred to as the ‘baseline’) are 12 mg/L of alum at a pH of 5.8. A more detailed description of the JDKWSP and its pilot plant is presented in Chapter 3.

The source water for the JDKWSP is Pockwock Lake, a low-turbidity (< 1 NTU), low-alkalinity (<5 mg/L as $CaCO_3$) lake which drains a protected watershed. Raw water characteristics for the period of study are presented in Table 5.1.

Table 5.1 Raw water (Pockwock Lake) characteristics during the period of study (Jan 2020).

Analyte	Range	Average	SD
pH	5.68-5.96	5.80	0.05
Turbidity – NTU	0.28-0.70	0.37	0.09
UV_{254} – 1/cm	0.083-0.140	0.109	0.011
TOC – mg/L	2.850-3.702	3.281	0.363
DOC – mg/L	2.703-3.608	3.141	0.424
SUVA – 1/m per mg/L of DOC	3.18-3.51	3.29	0.13
Aluminum - µg/L	76.79-107.30	90.46	13.63

Water quality data collected on raw and filtered water at the JDKWSP over the past year indicated seasonal fluctuations in Al concentrations (Figure 5.1). It is not uncommon for Al concentrations to be greater in treated than in the raw water. This is most frequently caused by improper coagulation of contaminants and the addition of Al-based coagulants (Health Canada 2019a) and is especially noticeable in the winter, when colder temperatures cause an increase in the pH of minimum solubility (Pernitsky and Edzwald 2006). Without corresponding adjustment in pH, coagulation occurs farther from the pH of minimum solubility, resulting in more dissolved Al (Pernitsky and Edzwald 2006). The current Health Canada OG (100 µg/L) and new, proposed OG (50 µg/L) are indicated by the red, dashed lines (Figure 5.1). From the data presented, the filtered water has not met the proposed guideline in the past year.

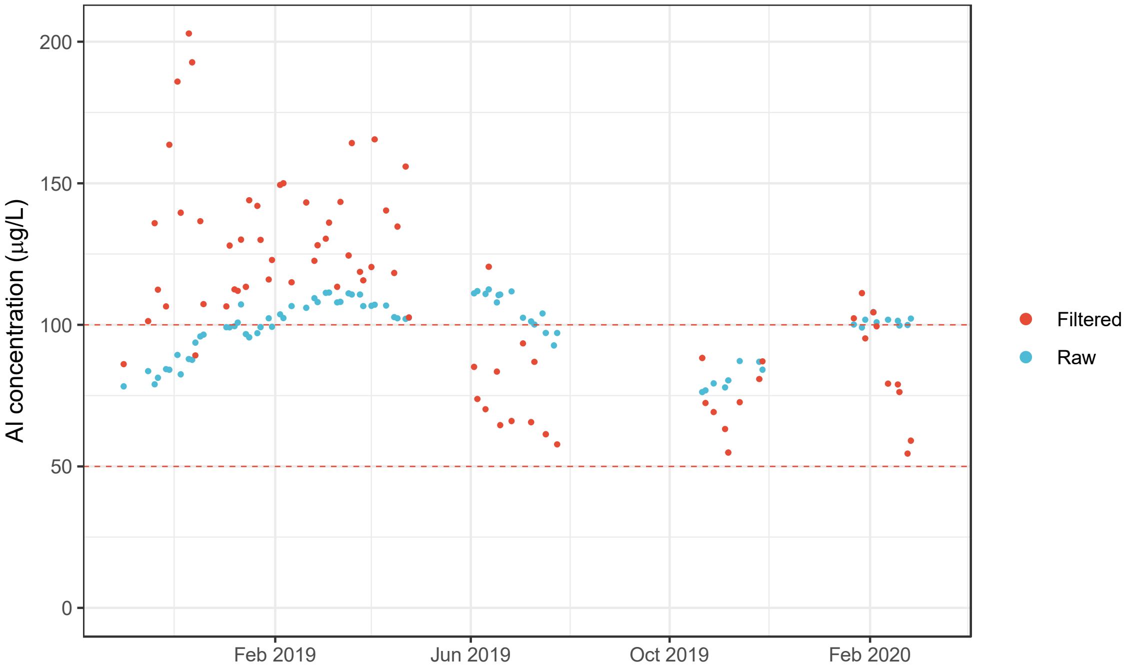

Figure 5.1 Raw and treated (filtered) Al concentrations at the JDKWSP full-scale plant. The red dotted lines represent the current (100 µg/L) and proposed (50 µg/L) finished water Al operational guideline by Health Canada (2019a).

5.2.2 Moncton Water Treatment Plant

The MWTP serves the cities of Moncton, Riverview, and Dieppe in New Brunswick at an average flow of 42 MLD. Raw water is pumped from Turtle Creek Reservoir and treatment consists of pre-screening, oxidation, coagulation and flocculation, adsorption clarification, multi-media filtration, and chlorination. The average alum dose at the MWTP is around 23.5 mg/L and coagulation occurs at a pH of 6.5. A more detailed description of the MWTP is presented in Chapter 3. Influent water characteristics for the period of study are presented in Table 5.2.

Table 5.2 MWTP influent characteristics during the period of study (May to Aug 2019)

Analyte	Range	Average	SD
pH	6.66-6.98	6.79	0.09
Turbidity – NTU	1.00-2.51	1.60	0.59
UV_{254} – 1/cm	0.119-0.145	0.132	0.010

Analyte	Range	Average	SD
TOC – mg/L	2.755-4.019	3.451	0.520
DOC – mg/L	2.727-3.453	3.060	0.239
SUVA – 1/m per mg/L of DOC	3.71-5.05	4.32	0.46
Dissolved Aluminum - µg/L	32.41-102.2	48.73	23.50

The source water is a low turbidity (<5 NTU), low alkalinity (<20 mg/L as $CaCO_3$) lake with moderate concentrations of total organic carbon (TOC) (3-5 mg/L) (Table 2). In 2017, an algae bloom occurred in the secondary reservoir (Tower Road Reservoir), and cyanotoxins were detected in small concentrations, although they did not enter the treatment plant.

The current coagulant dosing at the MWTP is based on feedback from an online streaming current analyzer and operator judgement. As adsorption clarification is difficult to mimic in jar tests, they are not conducted at the MWTP and it is unknown if the pH and coagulant dose are optimized for organic removal.

5.2.3 Experimental procedure

The JDKWSP direct filtration pilot plant was used to investigate the impact of pH on residual Al concentrations. Two coagulation conditions were compared: (1) alum dose of 12 mg/L at a pH of 5.8 (baseline), and (2) alum dose of 22 mg/L and pH of 6.4 (high pH-high alum). The coagulation pH for the high pH-high alum pH trials was selected to be approximate to the pH of minimum solubility under cold water conditions (Pernitsky and Edzwald 2006). The alum dose of 22 mg/L was selected based on dosing required to obtain acceptable effluent turbidity (<0.1 NTU) in preliminary experiments. Each condition was tested in triplicate, and one filter run represented one test. Tests were completed from December 2019 to January 2020, as residual Al concentrations were historically greatest during the winters. Grab samples were taken on raw and filtered water 24 hours after the start of each filter run and were measured for the following response parameters: TOC, dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV_{254}), and total Al. In-line measurement of turbidity, flow rate, and head loss across the filters was used for analysis of filter hydraulic performance along with unit filter run volume (UFRV).

As the MWTP is not equipped with a pilot plant, jar tests were conducted for analysis of their source water. The jar test procedure was developed to simulate the coagulation and flocculation stages at the MWTP, including pH adjustment. This procedure is outlined in Chapter 3.2.4. Alum doses for the jar test experiments ranged from 20 to 35 mg/L and tests were conducted at a pH of 6 and 6.5. As the adsorption clarifiers could not be simulated at the bench-scale, analysis emphasized dissolved constituents, including DOC, UV_{254}, and dissolved Al. However, additional parameters, such as turbidity, were measured on the settled water and zeta potential measurements were taken on flocculated water samples.

5.2.4 Analytical procedures

Laboratory analysis and procedures were conducted in accordance with *Standard Methods for the Examination of Water and Wastewater* (APHA et al. 2017). Samples were prepped for measurement of TOC and DOC following Standard Methods (5310) and organic carbon concentrations were measured with a TOC analyzer (Shimadzu TOC-V_{CPH}). UV_{254} absorbance was measured on filtered samples (0.45 µm polyethersulfone (PES) filters) using a HACH DR5000 UV-Vis spectrophotometer at a wavelength of 254 nm and was used for calculation of specific UV absorbance (SUVA). Dissolved and total Al was analyzed with inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific X-Series 2) following Standard Methods (3125). Zeta potentials were measured on flocculated water using a Malvern Panalytical Zetasizer Nano ZS. In-line measurements (i.e. temperature, turbidity, pH) were taken at critical treatment points in the pilot plant, and head loss and flow rate were continuously measured across the filters.

5.2.5 Statistical analysis

Statistical analysis was conducted using R (R Core Team 2020; Wickham et al. 2019) and Excel. One-way analysis of variance (ANOVA) was used to compare differences in means of response parameters across the three filter media columns at the JDKWSP and across different alum doses at the MWTP. T-tests were conducted when only two levels of a single factor were considered. Linear regression analysis was used to determine the significance of the impacts of pH and alum dose on response parameters at the MWTP. The level of significance for all statistical tests was 0.05.

5.3 Results

5.3.1 Impact of alum dose and coagulation pH on direct filtration

To reduce the Al residual concentration in the treated drinking water, coagulation pH at the JDKWSP was increased to 6.4, near the pH of minimum solubility. Initial trials incrementally increased the pH while maintaining the baseline coagulant dose (12 mg/L); however, a change of +0.1 in the pH (to 5.9) caused significant increases in effluent turbidity, to the extent where the filters did not ripen (effluent turbidity >0.2NTU). As such, a concomitant increase in alum dose was required for filter ripening and to obtain acceptable effluent turbidity (<0.1 NTU). Increasing the pH further, to 6.0, demanded an alum dose of 17 mg/L for acceptable effluent turbidity and at the target pH of 6.4, a dose of 22 mg/L was needed. In turn, results presented compare baseline conditions (pH 5.8, 12 mg/L alum) to coagulation with high pH-high alum conditions (pH 6.4, 22 mg/L alum) (Figure 5.2 to Figure 5.5).

The residual TOC and DOC concentrations from each of the three filter media layouts, under both baseline and high pH-high alum coagulation conditions, were compared with ANOVA and equivalency was proved between the three layouts. As such, results were combined and summarized (Figure 5.2 and Figure 5.3). In comparing the two coagulation conditions tested, there was no significant difference in either the residual TOC and DOC concentrations and nearly all the residual organic carbon was in the dissolved form. In increasing the alum dose and pH, TOC removal improved from approximately 35% to 45% (Figure 5.3). However, the higher removal was due to increased raw water TOC concentrations during the high pH-high alum trials. Significant decreases were observed in the UV_{254} measurements on the filtered water at higher pH and alum doses, despite a higher UV_{254} absorbance measurement on the raw water (Figure 5.2). Subsequently, this resulted in calculated SUVA values decreasing from ~1.65 to ~1.3 L/mg m from baseline to high pH-high alum conditions.

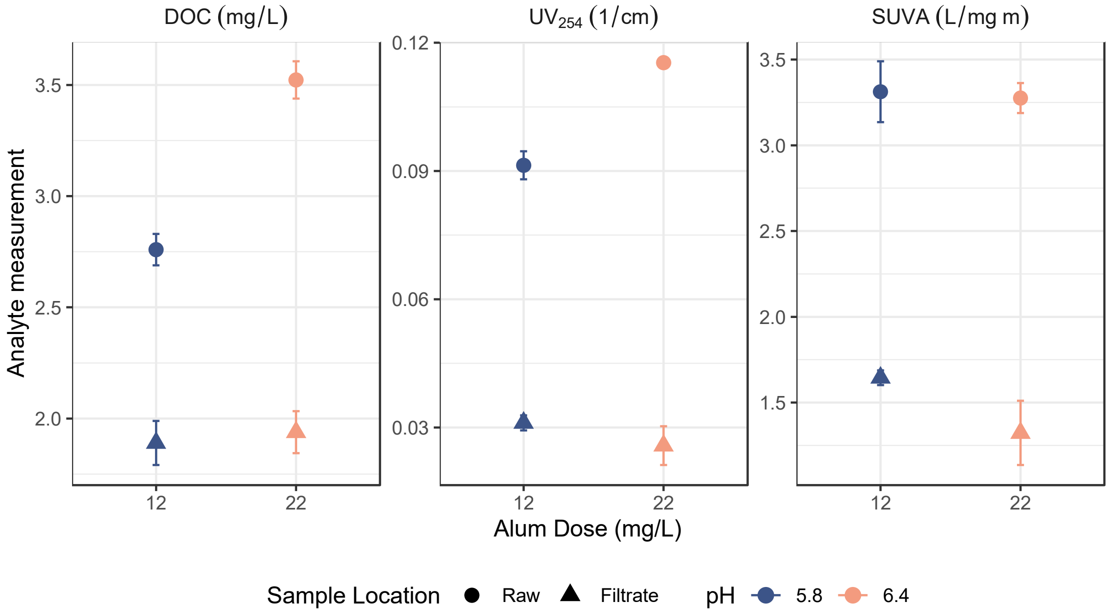

Figure 5.2 Raw and average filtrate DOC concentrations, UV$_{254}$ measurements, and SUVA values for baseline and high pH-high alum conditions at the JDKWSP pilot plant. Error bars represent the standard deviation about the mean.

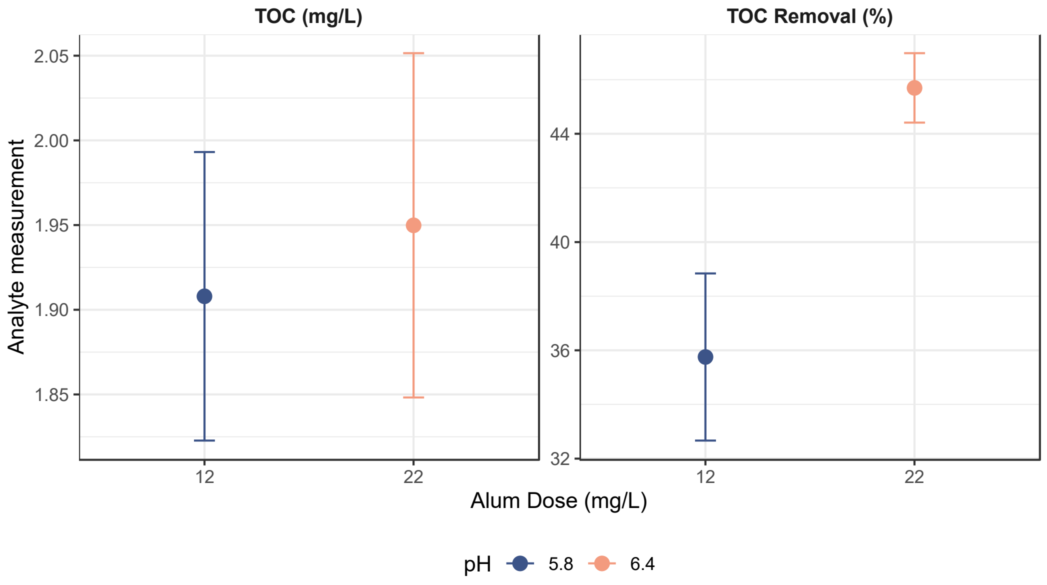

Figure 5.3 Average filtrate TOC concentrations and TOC removal for baseline and high pH-high alum conditions at the JDKWSP pilot plant. Error bars represent the standard deviation about the mean.

At a coagulation pH of 6.4, residual total Al concentrations were significantly less the baseline, despite more Al added to the solution from the higher alum dose (Figure 5.4). Total Al baseline concentrations were ~91 µg/L, compared to ~28 µg/L under the high alum-high pH condition. Raw water Al concentrations were greater during the high alum-high pH trials, averaging 105 µg/L, where concentrations in the baseline condition averaged 80 µg/L.

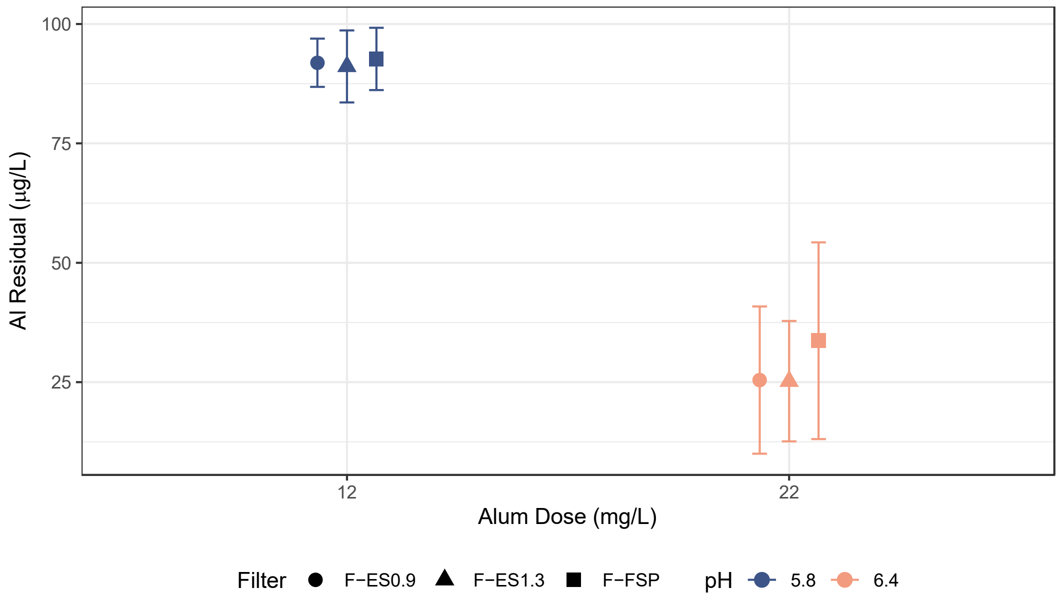

Figure 5.4 Baseline and high pH-high alum Al residual concentrations at the JDKWSP pilot plant through each filter media layout. Error bars represent the standard deviation about the mean.

Turbidity and head loss profiles for all six runs are displayed in Figure 5.5. Results clearly indicate significantly shorter filter runs under high alum-high pH conditions. Further, the rate of head loss development was greater with increased alum doses and coagulation pH, however effluent turbidity was reduced. Filter runs under high alum-high pH conditions were all terminated as a result of turbidity breakthrough, where head loss or maximum filter run times were the causes of termination under baseline conditions.

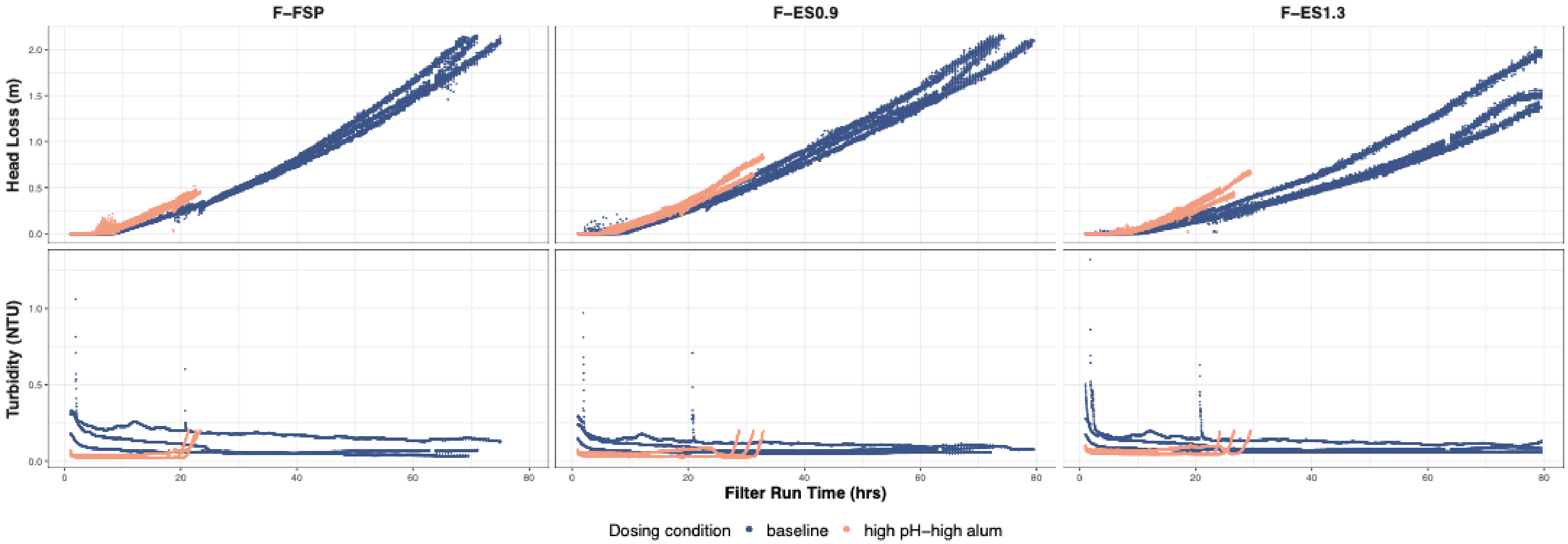

Figure 5.5 Head loss and turbidity profiles through each filter media layout for high pH-high alum and baseline trials in the JDKWSP pilot plant.

5.3.2 Impact of alum dose and coagulation pH in jar testing

For analysis of coagulation pH and alum dose at the MWTP, jar tests were completed as the plant does not have an adsorption clarification pilot plant. Two coagulation pHs were tested (6 and 6.5) at varying alum doses (20 to 35 mg/L). The quality of the raw water used for jar tests at each coagulation pH did differ (Table 5.3), where tests completed at a coagulation pH of 6.5 had higher raw water UV_{254}, but a slightly lower DOC concerned, resulting in a lower SUVA value. As such, results are presented as the amount of analyte removed during treatment (i.e. X_{raw}-$X_{treated}$) (Figure 5.6).

Table 5.3 MWTP influent characteristics for trials conducted at pH 6 and 6.5

	DOC *(mg/L)*	**UV_{254}** *(1/cm)*	**SUVA** *(L/mg m)*	**Dissolved Al** *(µg/L)*	**Turbidity** *(NTU)*
pH 6.0	2.98 ± 0.16	0.140 ±0.007	4.7 ± 0.3	37 ± 4	1.1 ±0.1
pH 6.5	3.10 ± 0.36	0.125 ±0.005	4.0 ± 0.3	46 ± 14	2.0 ±0.1

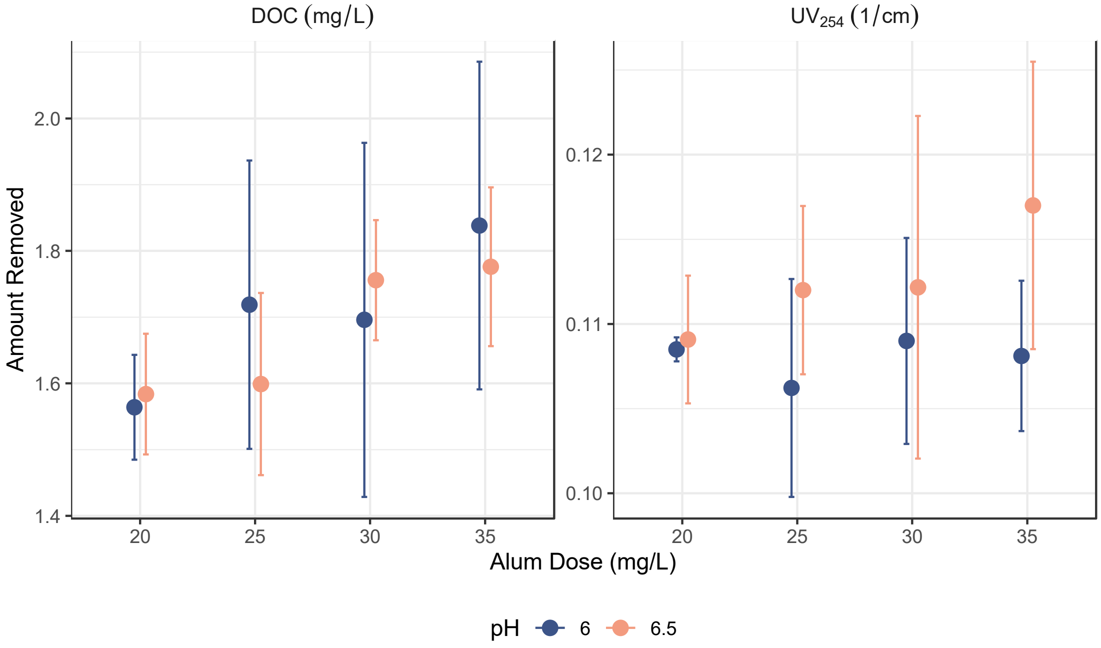

Figure 5.6 Amount of DOC and UV_{254} removed during jar testing of MWTP influent with various alum doses and coagulation pH. Error bars represent the standard deviation about the mean.

Linear regression analysis was conducted with the alum dose and pH as two, independent factors, and removed DOC and UV_{254} as response parameters. The findings indicated that, within the range of pHs tested, the alum dose was a significant predictor of removed DOC but not of removed UV_{254}. Conversely, for the range of alum doses tested, pH was a significant predictor of removed UV_{254} but not removed DOC. As such, removed DOC concentrations increased with increasing alum doses, but not pH. A one-way ANOVA test conducted on removed DOC concentrations for alum doses of 25 mg/L or greater indicated no significant difference between the samples, regardless of pH. The amount of UV_{254} absorbing material removed through treatment increased with increasing pH, but not alum dose. The higher values of removed UV_{254} resulted in lowered SUVA at the lower coagulation pH (Figure 5.7).

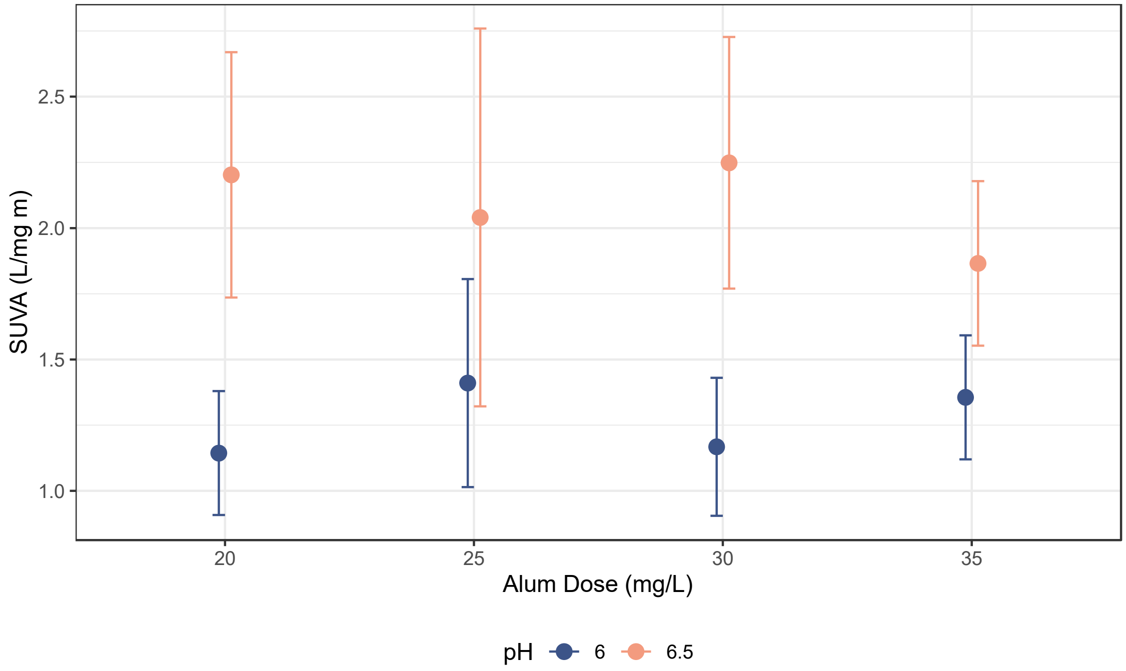

Figure 5.7 SUVA values for MWTP jar tests at various alum doses and coagulation pH of 6 and 6.5. Error bars represent the standard deviation about the mean.

Dissolved Al concentrations in treated water samples were greater at higher pH, for all alum doses except 35 mg/L, where they were equal (Figure 5.8). Nonetheless, all samples had dissolved Al concentrations less than 56 µg/L. Linear regression analysis indicated that pH was a significant predictor in dissolved Al, where the lower coagulation pH resulted in lowered residuals.

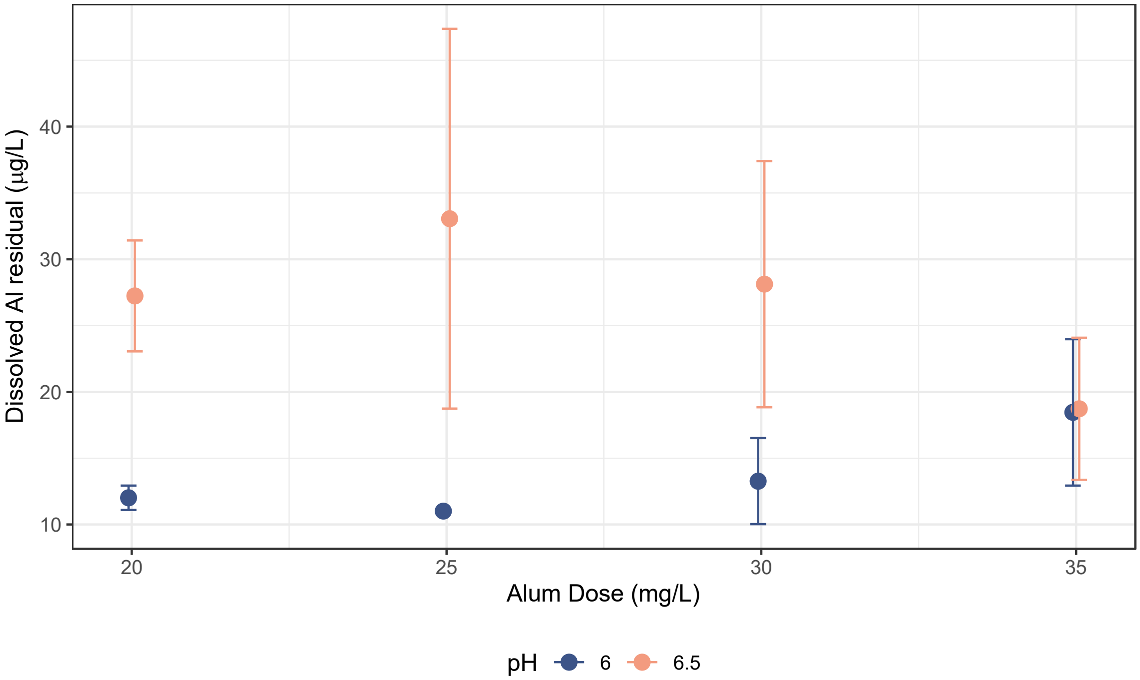

Figure 5.8 Dissolved Al residual concentrations for MWTP jar tests at various alum doses and coagulation pH. Error bars represent the standard deviation about the mean.

In attempts to provide insight into the potential impacts on filer hydraulic performance, turbidity was measured on the settled water for each trial (Figure 5.9). T-tests comparing high and low pH values at each alum dose indicated that turbidity was equivalent for pH 6 and 6.5 at the two lowest alum doses (20 and 25 mg/L), however at the two higher alum doses (30 and 25 mg/L), a coagulation pH of 6.5 resulted in significantly lower settled water turbidity.

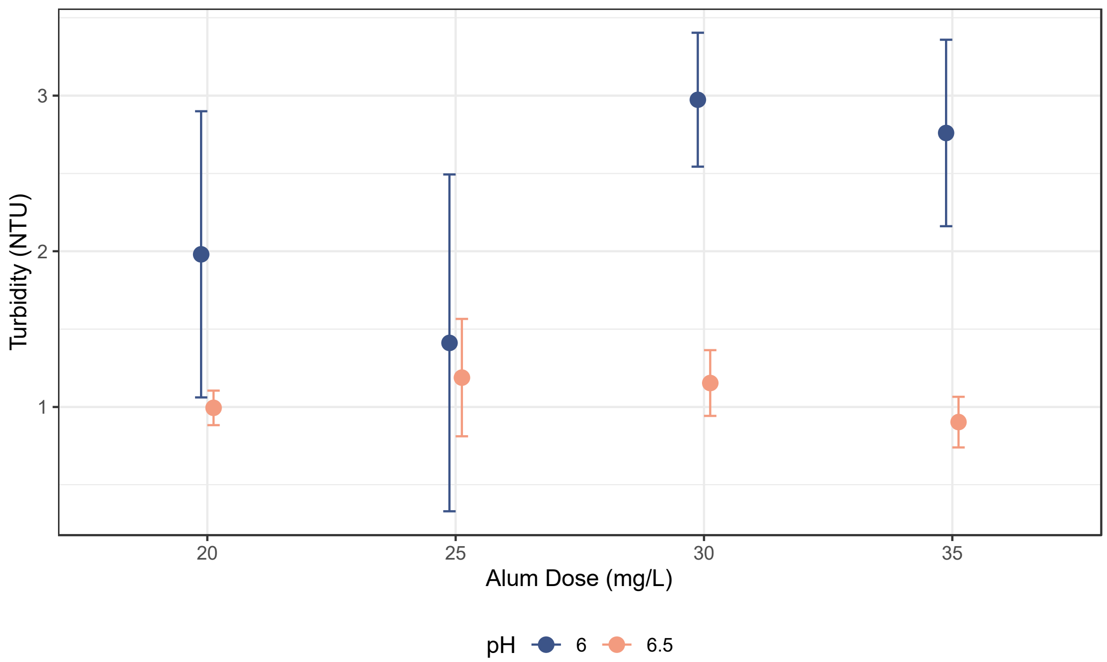

Figure 5.9 Turbidity of settled water from MWTP jar tests at various alum doses and coagulation pH. Error bars represent the standard deviation about the mean.

5.4 Discussion

5.4.1 Impact of alum dose and coagulation pH on direct filtration

Preliminary trials conducted in attempt to increase the pH of coagulation at the JDKWSP pilot plant without increasing the alum dose resulted in effluent turbidity exceeding the allowable threshold of 0.2 NTU. The increased turbidity was likely a result of underdosed alum, as shifts towards higher coagulation pH have shown to increase coagulant demand in past work (Bell-Ajy et al. 2000; Davis and Edwards 2014; Mesdaghinia et al. 2006; Shin et al. 2008). As the coagulation pH was increased from the baseline, the deprotonation of NOM resulted in more negatively charged compounds. Likewise, the charge of the Al hydrolysis species from coagulation became less positive as the pH increased. The combined effect of these two mechanisms resulted in a higher coagulant demand for increasing coagulant pH (Bell-Ajy et al. 2000; Mesdaghinia et al. 2006; Shin et al. 2008; Yang et al. 2010). Where the coagulant demand was not sufficient to effectively neutralize the charge of the dissolved organic matter (DOM), formed metal hydroxide precipitates and Al-NOM complexes didn’t effectively agglomerate and remained as colloids, passing through the filters and resulting in increased effluent turbidity, DOC concentrations, and Al residuals (AWWA and Edzwald 2011; Gregor et al. 1997; Health Canada 2019a; Mesdaghinia et al. 2006; Srinivasan et al. 1999)

Once the effluent turbidity was controlled with higher alum doses, comparison between baseline and high alum-high pH trials was conducted. The increased TOC removal with the high alum-high pH condition was due to increased TOC in the raw water, as the residual TOC concentrations were unchanged for the two conditions. Further, the additional raw water TOC was concurrent with an increase in raw water UV_{254} absorbance, so the SUVA value was unchanged, and the additional TOC was assumed to be of mainly hydrophobic nature. As such, it is likely that the consistent residual TOC concentrations under both coagulation conditions represented a fraction of TOC that is recalcitrant to coagulation. It was determined that higher coagulant doses will be able to mitigate increased TOC concentrations in Pockwock Lake, if the shift is a result of additionally hydrophobic DOM (i.e. humic matter). However, the increased alum dose resulted in significant reductions in UFRV, as discussed later in this chapter. If increasing raw water NOM concentrations are due to more hydrophilic DOM, however, corresponding increasing in residual TOC concentrations are anticipated, as this fraction is more recalcitrant to coagulation. This may have consequential impacts on DBP formation and may require additional treatment barriers.

In comparing the UV_{254} residuals for the two conditions (Figure 5.2), the high alum-high pH condition had lower effluent UV_{254} absorbances than the baseline, despite also having higher measurements in the raw influent. The consequential reduction in SUVA indicated a greater removal of hydrophobic NOM under the high alum-high pH conditions. Removal of UV_{254} absorbing organic matter is usually improved at lower pH due to the weakened negative charge of the NOM compounds, allowing removal of species that may not typically be influenced by coagulation (Bell-Ajy et al. 2000; Mesdaghinia et al. 2006; Shin et al. 2008; Yang et al. 2010). However, the increased removal of UV-absorbing compounds in this study was associated to the increased alum dose, which at higher pH, likely produced a larger concentration of Al hydroxides that acted as adsorption sites for

NOM. As adsorption a) favours hydrophobic, high SUVA NOM (Davis and Edwards 2014), and b) increases in importance as a NOM removal mechanism as pH increases (Archer and Singer 2006; Davis and Edwards 2014; Qin et al. 2006), it is likely that the decrease in UV_{254} absorbance under the high alum-high pH conditions was a result of increased adsorption of NOM onto amorphous Al hydroxide precipitates. Reduced effluent SUVA is desirable in drinking water treatment, as the SUVA value is often positively correlated with formation of DBPs. Reactive compounds with conjugated double bonds often have high UV_{254} absorbance, so increased removal of UV_{254} absorbing material per mg/L of DOC reduces the concentration of reactive compounds, and thus, DBP formation, in the treated water (AWWA and Edzwald 2011; Weishaar et al. 2003).

The reduction in Al residuals under the high alum-high pH condition was presumed to be a result of the decreased solubility of Al, as the coagulation pH was closer to the pH of minimum solubility of Al for coagulation with alum (Pernitsky and Edzwald 2006). As such, more Al in the solution was incorporated into flocs, as either Al hydroxides, or Al-NOM complexes, and less Al remained in the soluble, dissolved form, where it can pass through the filters and persist in the effluent. The results are in agreement with past work (Bérubé and Dorea 2008), where the coagulation pH was adjusted from 5.9 to 6.4 and dissolved Al in samples treated with alum were lower under less acidic conditions. The efficacy of coagulation can also impact the residual Al concentration. If proper flocculation does not occur, there will be a higher concentration of colloidal organic-Al in particulate form in the treated water (Gregor et al. 1997; Health Canada 2019a; Srinivasan et al. 1999). In increasing alum dose during the study, there were likely higher concentrations of Al hydroxide precipitates and Al-NOM complexes, resulting in more frequent collisions and better flocculation. Thus, the combination of less soluble Al and increased flocculation was proposed as the cause of reduced effluent Al concentrations at the JDKWSP under the high pH-high alum conditions.

Despite improved effluent quality under the high alum-high pH coagulation condition, the downstream effects on the filter hydraulic performance were unfavourable (Figure 5.5). The significantly reduced filter run cycles, and thus UFRVs, were likely a result of increased solids loading on the filters, due to both increased removal of organic matter and turbidity, and a greater formation of precipitated Al hydrolysis species. The greater volume of sludge held in the filters were a probable cause for the increased rate of head loss development observed for the high alum-high pH trials. However, all of the trials under the high alum-high pH condition were terminated due to turbidity breakthrough. As the head loss measurements were relatively low at the end of these runs, the expected cause of turbidity breakthrough was the saturation of the filter media. It is anticipated that saturation occurred in the sand layer, where the smaller ES of the media would result in the greatest particulate removal and thus be the first to fill its adsorption sites (French 2012). Results from a filter surveillance test could confirm this hypothesis, however this was outside the scope of the presented work.

5.4.2 Impact of alum dose and coagulation pH in jar testing

Upon analysis of data from the MWTP jar tests, it was determined that overall, the alum dose impacted the concentration of removed DOC, but pH did not. Further, there was no significant improvement in removed DOC with alum doses greater than 25 mg/L for either pH, suggesting that the point of diminishing returns had been met and the MWTP is, in fact, currently operating near the optimal alum dose for DOC removal. The coagulation pH did not impact the amount of organic matter removed, however, lowering the pH did result in a reduction in UV_{254}-absorbing material in the treated samples. Contrary to the JDKWSP, where improved UV_{254} was associated with higher alum doses, the improvement at the MWTP was likely due to weakened negative charges of NOM and increased positive charges of Al hydrolysis species at lower pH. Linear regression performed on the zeta potentials of flocculated water confirmed that both pH and alum dose significantly increased the surface charges of particulate in the water (Figure 5.10). This effect has been widely identified as the cause for increased organic removal in literature (AWWA and Edzwald 2011; Bell-Ajy et al. 2000; Yang et al. 2010). Although removal of DOC was not improved at the lower coagulation pH, there was a shift in the character of DOC removed as indicated by the effluent SUVA values (Figure 5.7). As UV_{254} absorbing material is often highly reactive with chlorine, a coagulation pH of 6 is recommended at the MWTP to reduce formation of DBPs.

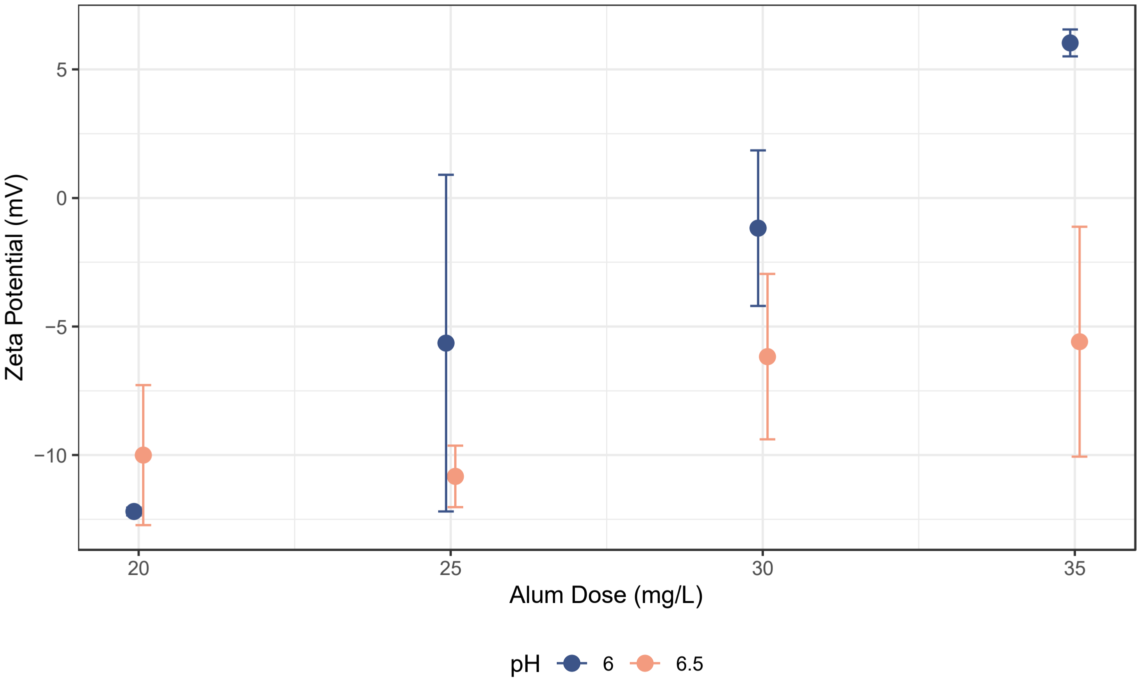

Figure 5.10 Zeta potentials of flocculated water in MWTP jar tests for various alum doses and coagulation pH. Error bars represent the standard deviation about the mean.

The increased dissolved Al concentrations in the samples treated at pH 6.5 compared to 6.0 contradicted previous findings in the literature. Jar tests were conducted at a temperature of approximately 13-14ºC, thus the pH of minimum solubility of Al is expected to be between 6.3 and 6.7 (Pernitsky and Edzwald 2006). As such, coagulation at a pH of 6.5 should have resulted in lower dissolved Al residuals, provided that sufficient coagulation and flocculation was achieved, because the concentration of insoluble Al hydrolysis species was expected to decrease around the pH of minimum solubility. It is unlikely that insufficient flocculation occurred, as the presence of colloidal Al-NOM complexes in the treated sample would have resulted in increased turbidity of the settled water (Figure 5.9) (AWWA and Edzwald 2011). Further, zeta potentials were within the recommended range of -10 to +5 mV for effective coagulation (Figure 5.10) (Pernitsky et al. 2011). One partial explanation for the increase residual Al may be the greater addition of calcium hydroxide for pH control. Traces of Al have been found in commercial lime products, resulting in up to an additional 8 µg/L of Al at the tap (Health Canada, 2019). As the difference in Al concentrations of the samples found in this study were mostly greater than 8 μg/L, this is hypothesis would be responsible for only a fraction of the difference. Additional sources of the increase may be linked to contamination of samples during filtering or poor temperature control of the small, 1-L sample. The specific character of NOM will also impact the Al-NOM complexes and subsequentially Al residual concentrations (Davis and Edwards 2014; Pernitsky and Edzwald 2006). While SUVA is an indicator of NOM character, a measurement of character (e.g. resin fractionation) would provide further understanding into potential complexation reactions between Al and NOM that impact Al residual concentrations.

To gain insight into the potential downstream effects of the different coagulation conditions tested at the bench-scale, turbidity measurements were taken on water that had been settled for 30 minutes. The higher settled water turbidity at the lower coagulation pH, for all alum doses, was likely a result of larger and denser flocs formed at the higher coagulation pH. Increased concentration precipitated hydrolysis species at the higher pH encourages the formation of sweep floc. This type of floc has been shown to be larger and denser than flocs formed through charge neutralization, resulting in an increased settling rate (Kim et al. 2001). Although this does provide beneficial result for sedimentation clarification, in adsorption clarification, the formation of smaller flocs is desired as the process is more similar to filtration than conventional clarification (Ross et al. 2019). For this reason, the lower coagulation pH is recommended for treatment at the MWTP, however, pilot-scaled trials are recommended prior to implementation at the full-scale.

The inability to analyze the impacts of coagulation pH and alum doses on the adsorption clarification and filtration processes is a limitation of this study. A pilot plant would be required to adequately determine the downstream impacts of altering the coagulation pH and alum dose.

5.5 Conclusion

The presented findings studied the impacts of coagulation pH and alum dose on the concentrations of NOM (TOC/DOC) and Al (total and dissolved). Treated water TOC/DOC concentrations were consistent for high alum-high pH and baseline conditions in direct filtration treatment, however a higher alum dosing was required to for effective coagulation/flocculation as the coagulation pH increased. For treatment using jar tests, the coagulation pH did not significantly impact the treated water DOC concentrations, which reached the point of diminishing returns at 25 mg/L of alum, regardless of pH. Improved removal of UV_{254} absorbing organic matter in direction filtration under high alum-high pH coagulation was believed to be as a result of increased adsorption sites from the higher alum dose. In the jar tests, the improved UV_{254} removal was associated with weakened negative charge of NOM and strengthened positive charge of Al hydrolysis species as the pH decreased from 6.5 to 6.

A significant decrease in effluent Al concentrations was observed at the direct filtration treatment plant when coagulation pH was adjusted from 5.8 to 6.4, near the pH of minimum solubility of Al with alum coagulation. On the other hand, reducing the coagulation pH for treatment in jar tests for the adsorption clarification plant resulted in lower concentrations of dissolved Al in the treated samples. This highlighted the importance of site-specific optimization strategies, as water chemistry and quality impact the efficacy of coagulation.

In evaluating the downstream effects of shifts in coagulation pH and chemical dosing in direct filtration, significant decreased in filter cycles occurred due to increased pH and alum dose. Lowering the coagulation pH to 6 at the bench-scale produced slower settling flocs than at pH 6.5. The smaller, less dense flocs are more desirable for treatment with adsorption clarification, as their removal mechanisms are more similar to filtration than conventional sedimentation (Ross et al. 2019).

Overall, it was determined that the optimal coagulation conditions can vary significantly from source water to source water. This highlights the importance of conducting regular experiments to ensure the highest possible water quality within the operational limits of the plant design. Further, the contrast in optimal coagulation conditions from a water quality and productivity perspective at the direct filtration plant indicated the need for pilot-scaled tested prior to significant changes in treatment processes. Pilot work can be used to determine a balanced treatment strategy that considers both efficacy and efficiency.

CHAPTER 6: ASSESSING THE IMPACTS OF UPGRADING A DRINKING WATER TREATMENT PLANT FROM ADSORPTION CLARIFICATION TO ACTIFLO®

6.1 Introduction

Global increases in frequency, intensity, and duration of harmful algae blooms (HABs) have been reported over the last few decades (Huisman et al. 2018; Moore et al. 2008; O'Neil et al. 2012). Blooms of blue-green algae, or cyanobacteria, are of particular concern due to their production of toxic, secondary metabolites, called cyanotoxins (Huisman et al. 2018; O'Neil et al. 2012). The drivers behind the proliferation of cyanobacteria are vast and diverse, making it difficult to pin-point the individual impact of the various factors (O'Neil et al. 2012; Wagner and Adrian 2009). However, factors such as increasing temperatures due to climate warming and brownification have proven to stimulate their growth (Huisman et al. 2018; Moore et al. 2008; O'Neil et al. 2012; Wagner and Adrian 2009).

The presence of HABs in drinking water sources not only presents the concern of cyanotoxins (Noyma et al. 2017), but also increases the solids loading on treatment plants (Ghernaout et al. 2010). Although coagulation/flocculation can remove solids caused by HABs, it does not effectively remove extracellular cyanotoxins. As such, additional treatment barriers (e.g. ozonation, adsorption) may be needed for treatment of source waters experiencing a HAB (Noyma et al. 2017; Westrick et al. 2010). The additional biomass from HABs can cause clogging of unit processes (e.g. adsorption clarification, filtration) (Ghernaout et al. 2010; Marston et al. 2015), requiring more frequent backwashes and higher operational costs. Further, low density algal material is more difficult to settle than inorganic suspended particles with conventional treatment; as such, greater coagulant doses may be required for effective removal (Ghernaout et al. 2010; He et al. 2016).

ACTIFLO® is a proprietary treatment technology that consists of coagulation, ballasted flocculation (BF), and high-rate clarification with lamella plate settlers (Desjardins et al. 2002). In ballasted flocculation, the settling rates of flocs are increased through incorporation of a high-density ballasting agent (BA) (Watanabe 2017). This treatment technology is particularly beneficial for humic-rich waters, in which formed flocs typically have slower settling rates due to the low-density nature of their aggregates (Sieliechi et al. 2016). The ACTIFLO® treatment process has also been cited to effectively remove algae (Plum et al. 1998) and powered activated carbon (PAC) can be incorporated into the BA mixture for adsorption of extracellular cyanotoxins (Ho et al. 2011).

Although ACTIFLO® is often used with alum, alternative coagulants, such as polyaluminum chloride (PACl) can also be applied. The benefits of using PACl for drinking water treatment include reduced dependence on pH, and temperature, lower alkalinity consumption, aluminum residual concentrations, and sludge volumes (Matilainen et al. 2010; Zhang et al. 2015). Further, past work has demonstrated that PACl is more efficient in removal of algae (Wang et al. 2011) and removes a lower molecular weight fraction of algal organic matter than alum (Naceradska et al. 2019). PACl has also successfully been used in BF for control of in situ HABs. For example, Noyma et al. (2017) determined that up to 99.7% of flocculated cyanobacteria in bench-scaled experiments could be removed with low doses of PACl (0-8 mg/L as Al) and a BA (<400 mg/L). Further, Miranda et al. (2017) reported that low doses of PACl (<4 mg/L as Al) with a BA would successfully flocculate and sink cyanobacteria without causing immediate cell lysis and subsequent release of cyanotoxins in lakes.

The Moncton Water Treatment Plant (MWTP) (New Brunswick, CA) is a drinking water treatment plant that is vulnerable to HABs. The use of adsorption clarifiers at the MWTP makes the plant sensitive to changes in source water quality that are likely to occur during a bloom, particularly plugging of clarifier and filter media. Further, the plant currently lacks the ability to effectively remove extracellular cyanotoxins. In September of 2017, a bloom was recorded in the plant's secondary reservoir with low concentrations of cyanotoxins. Fortunately, no cyanobacteria nor cyanotoxins entered the treatment plant. However, the event instigated plans for plant upgrades to BF and sedimentation. These upgrades would increase the hydraulic capacity of the plant in the event of a bloom and provide the opportunity for cyanotoxin removal with PAC in the BA. As there was no bloom in the MWTP source water at the time of study, the objective of this work was to investigate the impacts on water quality (i.e. TOC, UV_{254}, Al, Mn, turbidity) if treatment processes were upgraded to ACTIFLO®. Secondly, it investigated the potential benefits of switching from coagulation with alum to PACl in the ACTIFLO® pilot plant.

6.2 Materials and methods

6.2.1 Overview of treatment process

Both the full-scale and pilot-scale treatment processes consisted of oxidation, pre-treatment (coagulation and flocculation), clarification, and filtration (Figure 6.1). Raw water was drawn from the Turtle Creek Reservoir and oxidized with potassium permanganate at the pumping station. Upon entering the full-scale plant, a portion of the raw water was diverted to the pilot plant, where it was further treated with ACTIFLO® technology and the dosing and operational parameter associated with the process. Key differences in chemical dosing of the two treatment technologies include the location of polymer dosing and the alum and lime dosing applied. Additional details on the full-scale plant and pilot plant processes are explained in Chapter 3. Raw water characteristics over the period of study are presented in Table 6.1.

Table 6.1 MWTP influent characteristics as measured in the pilot plant and the full-scale plant (Jan to Feb 2020)

Analyte	**Full-scale Plant**		**Pilot Plant**	
	Average	*SD*	*Average*	*SD*
DOC – mg/L	2.92	0.01	2.87	0.06
TOC – mg/L	2.95	0.13	2.96	0.12
UV_{254} – 1/cm	0.141	0.012	0.136	0.007
SUVA – L/mg m	4.8	0.3	4.8	0.2
Total aluminum – µg/L	68	3	71	2
Total manganese – µg/L	230	32	238	40
Turbidity - NTU	1.87	0.02	3.00	0.45

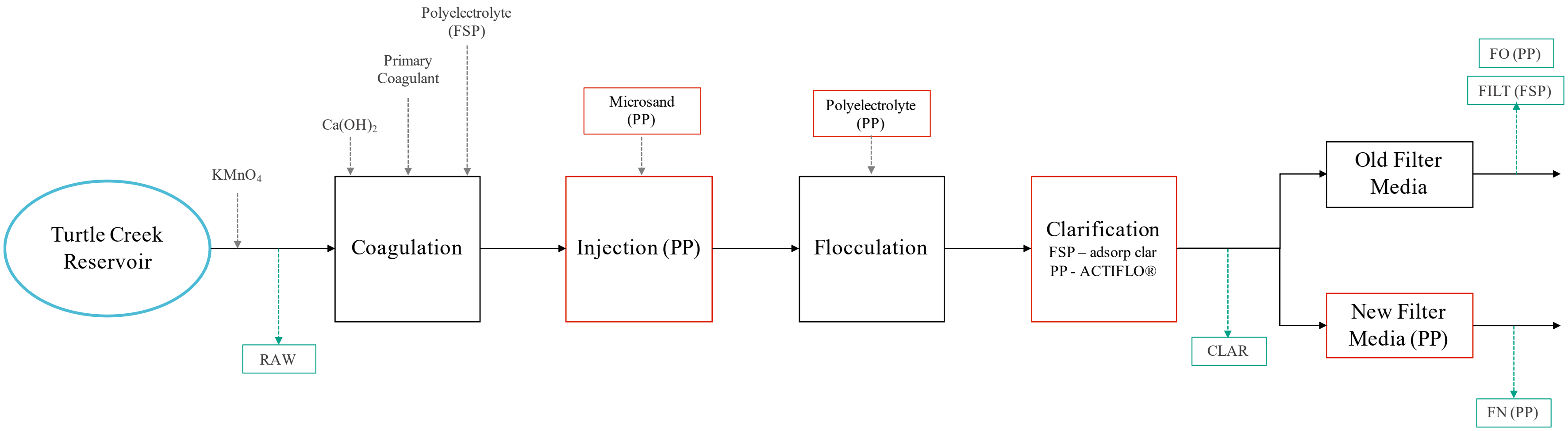

Figure 6.1 Overview of treatment processes in the full-scale plant (FSP) and pilot plant (PP) at the MWTP. Key differences are highlighted in red and sampling locations are shown in green.

6.2.2 *Experimental procedure*

The pilot plant was commissioned for validation of the ACTIFLO® technology prior to upgrading the full-scale plant clarifiers from January 20 to February 14, 2020. The goal was to prove that ACTIFLO® clarification technology could meet the treatment objectives outlined in Table 6.2. As such, the operating conditions (Table 6.3) were determined externally by Veolia Technology operators. Full-scale plant operational parameters were determined by MWTP operators.

Table 6.2 Treatment objectives for the ACTIFLO® pilot validation study as per Veolia Water Technologies

Parameter	**Goal**
Clarified turbidity - NTU	< 1
Clarified DOC - mg/L	< 2
Filtered total aluminum - mg/L	< 0.075
Filtered total manganese - mg/L	< 0.1
Filtered turbidity - NTU	< 0.1

Table 6.3 Chemical dosing and operating parameters in the full-scale plant and pilot plant during the three phases of study

	Phase 1 ***Design Flow***	**Phase 2** ***Low Flow***	**Phase 3** ***PACl***	**Full-scale Plant**
Potassium Permanganate Dose – mg/L	0.6	0.6	0.6	0.6
Lime Dose – mg/L	10.2	8.2	1.3	5.5
Alum dose – mg/L	33	24.1	NA	19
PACl Dose – mg/L	NA	NA	36.6	NA
Coagulant dose – mg/L as Al	1.45	1.06	1.97	0.836
Polymer Dose – mg/L	0.13	0.15	0.14	0.11
Coagulant pH	7	6.9	6.87	6.56-6.60
Actiflo flow rate – m^3/h	23.4	13.4	23.4	NA
Actiflo rise rate – m/h	80	46	80	NA
Ballasted agent dose – g/L	16-25	17-25	15-25	NA

Three study phases were conducted with different chemical dosing and operational parameters in the pilot plant, but consistent treatment in the full-scale plant. In Phases I and

II, the pilot plant operated at design flow and low flow, respectively. After a short optimization period (at most a few days), chemical dosing in the pilot plant was adjusted for the varying flow rate and differed from full-scale plant doses. The final phase (Phase III) studied the use of PACl instead of alum as the primary coagulant. Chemical doses were again, adjusted to optimize treatment at the discretion of the pilot plant operators.

The pilot plant was in commission for one month and the duration of each phase was one week. After pilot plant and full-scale plant operators had ensured stable effluent water quality, two grab samples were collected one hour apart at key locations throughout the two treatment processes (Figure 6.1). Due to the short time frame of the validation study and the travel distance from Halifax, each phase was sampled only once. Samples were then analyzed for organic analytes (TOC, DOC, and UV_{254}) and inorganic analytes (Al, Mn, turbidity). Comparison of the two treatment technologies was done through evaluation of organic and inorganic matter removal or concentrations through subsequent treatment steps.

Due to the condensed timeline of the validation pilot commissioning, filter hydraulic performance (e.g. run times, unit filter run volume (URFV)) were unable to be properly evaluated. Instead emphasis was placed on clarified and effluent water turbidity, and how changes to this parameter would impact filter hydraulic performance.

6.2.3 Chemical reagents

The primary coagulant for the majority of the study was alum ($Al_2(SO_4)_3 \bullet 14H_2O$) supplied by Chemtrade. The medium charge density cationic polyelectrolyte used in both the full-scale plant and pilot plant was FloPAM FO 4190 PWG supplied by SNF Canada. PAX-XL 6 (Univar Solutions) was the PACl used during Phase III in the ACTIFLO® pilot plant.

6.2.4 Analytical procedures

Samples were prepped for analysis of TOC and DOC following Standard Methods (5310) (APHA AWWA 2017) and organic carbon concentrations were measured with a TOC analyzer (Shimadzu TOC-V_{CPH}). UV_{254} absorbance was measured on a HACH DR5000 UV-Vis spectrophotometer and used for calculation of SUVA. Total concentrations of Al and Mn were analyzed with inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific X-Series 2) following Standard Methods (3125). Turbidity was measured with a HACH 2100N Turbidimeter.

6.2.5 Statistical methods

All statistical analysis was completed with R (R Core Team 2020; Wickham et al. 2019). However, due to the limited frequency of sampling, statistical analysis was limited to the comparison of water quality parameters between the pilot plant and the full-scale plant with t-tests. Significance levels for these tests were set to 0.05.

6.3 Results

6.3.1 Comparing effluent water quality with treatment through ACTIFLO® and adsorption clarification

To compare the organic removal with adsorption clarification and ACTIFLO® treatment processes, TOC and UV_{254} removal was calculated through subsequent treatment steps. Results are presented in Figure 6.2 for both the full-scale plant and the pilot plant. TOC removal in the pilot plant was equivalent to that of the full-scale plant all treatment steps. The majority of TOC was removed during clarification (~58% in both the pilot plant and full-scale plant) and the filters removed between 2 and 20% of TOC from the clarified water. The sample size of the UV_{254} measurements was not large enough for sound statistical analysis. However, minimal differences in treatment efficacy were observed, as removal through the clarification step was 86 ± 1% for both clarification technologies. There was slightly greater variance in removal through the filters, which varied between -5 to 5% in FN and -5 to 14% in FO. Negative values indicated an increase in UV_{254} measurements across the filters. Absolute differences in UV_{254} measurements of the full-scale plant and pilot plant were less than 0.03 cm^{-1} and thus were not expected to impact finished water quality.

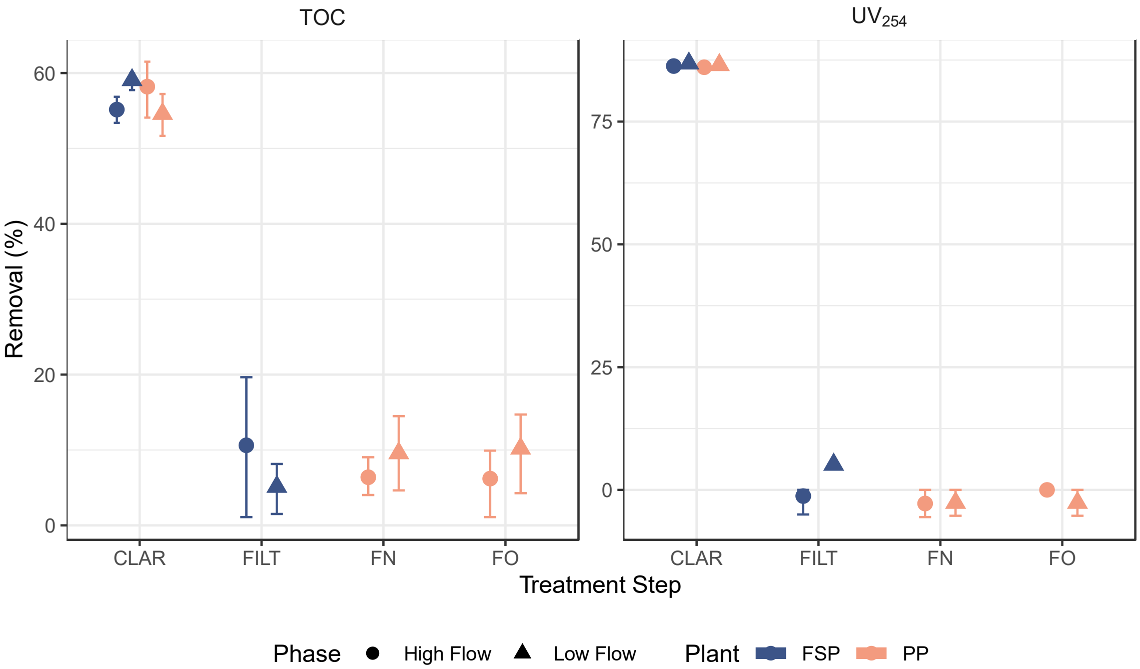

Figure 6.2 Removal of TOC and UV_{254} through subsequent treatment steps (see Figure 6.1) in the full-scale plant and pilot plant for Phases I and II. Error bars on TOC measurements are representative of the standard deviation about the mean, error bars on UV_{254} measurements are the maximum and minimim measurements.

Concentration of metals (Al and Mn) after clarification and filtration are shown in Figure 6.3. Higher concentrations of Al were recorded in the clarified water in the pilot plant as compared to the full-scale plant. However, effluent concentrations were all within the range of 7.8 to 17.7 µg/L. Conversely, Mn concentrations were consistently greater in the pilot plant than in the full-scale plant. Filtered water concentration averaged between 14.0-16.2 and 20.8-29.5 µg/L in the full-scale plant and pilot plant, respectively.

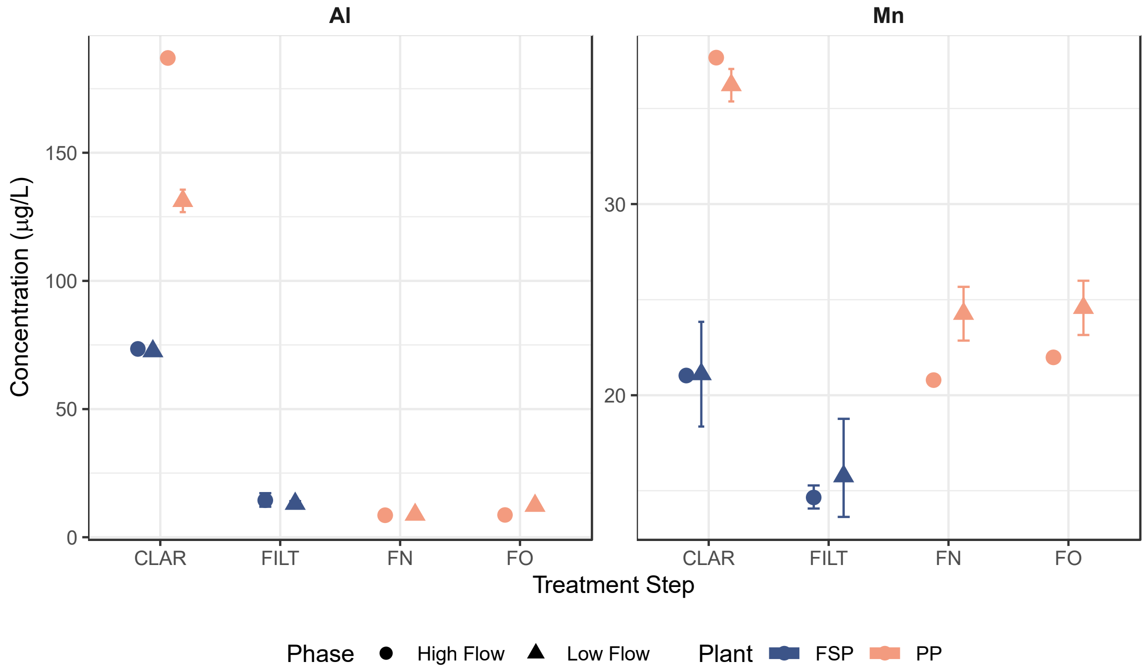

Figure 6.3 Total Al and Mn concentrations at various treatment steps (see Figure 6.1) in the full-scale plant and pilot plant for Phases I and II. Error bars represent the maximum and minimum values.

Clarified water was more turbid with treatment using ACTIFLO® clarification as compared to adsorption clarification (Figure 6.4). Nonetheless, both treatment processes produced low turbidity waters (<0.1 NTU). The turbidity measurements from the full-scale plant were collected, in retrospect from the plant operator and as such, measurements were only available on older filter media.

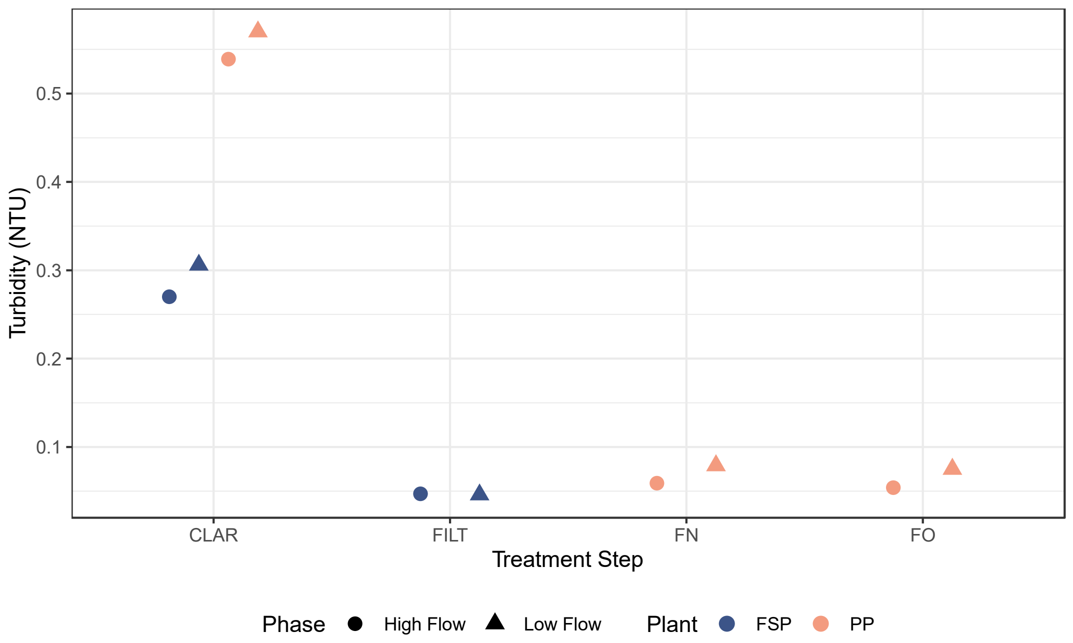

Figure 6.4 Turbidity after various treatment steps (see Figure 6.1) in the full-scale plant and pilot plant during Phases I and II.

There were no substantial differences in organic matter removal, filtrate metals concentrations, or filtrate turbidity in comparing the design flow and low flow Phases in the pilot plant.

6.3.2 Impact of conversion from alum to PACl in the ACTIFLO® process

To assess the use of PACl as a primary coagulant in the ACTIFLO® treatment process, the PACl and Design Flow trials in the pilot plant were compared (Figure 6.5 to Figure 6.7). Organic matter removal, as measured by TOC and UV_{254}, through the clarification step was consistent for both coagulants, around 55-60% (Figure 6.5). Similarly, there was minimal difference in removal of UV_{254}-material through the filters when comparing the two coagulants. TOC removal, however, was significantly improved through both filters with PACl coagulation.

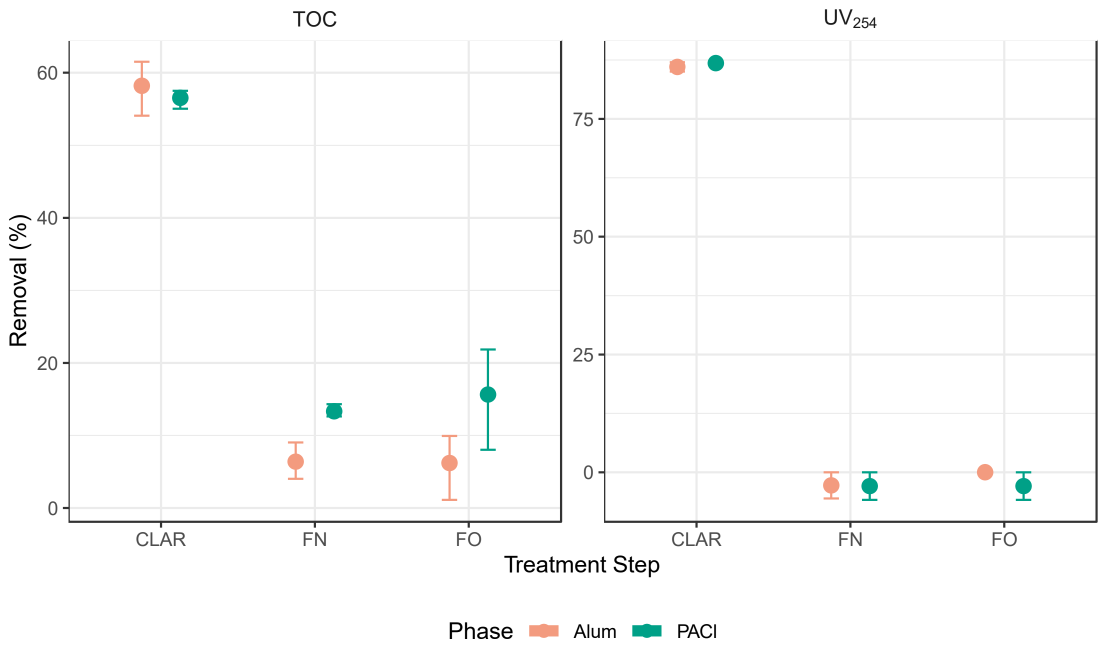

Figure 6.5 TOC and UV$_{254}$ removal through subsequent treatment steps (see Figure 6.1) for coagulation with PACl and alum in the ACTIFLO® pilot plant. Error bars on TOC represent the standard deviation about the mean, error bars on UV$_{254}$ measurements show the maximum and minimum recorded values.

The concentration of total Al was slightly reduced after clarification with PACl instead of alum (Figure 6.6). However, effluent concentrations were between 7 to 12 µg/L for both types of coagulants. On the other hand, Mn concentrations were consistently greater when coagulating with PACl as compared to alum. Concentrations for the PACl trial were ~20 µg/L greater in the clarified water and 10 to 17 µg/L greater in filtered water.

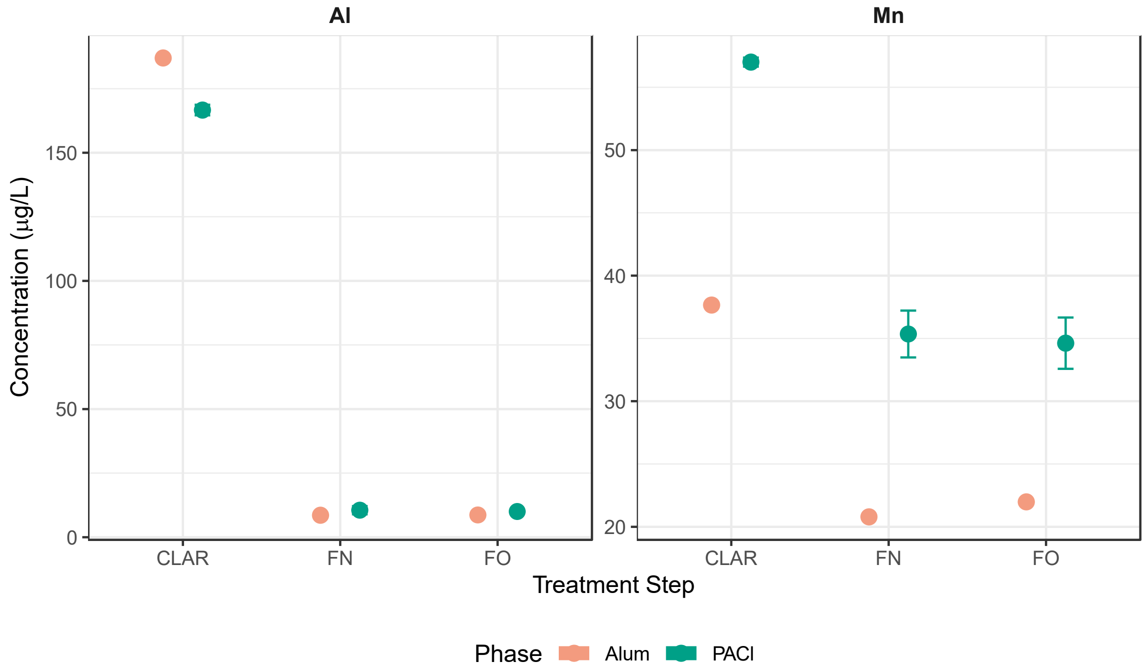

Figure 6.6 Total Al and Mn concentrations at various treatment steps (see Figure 6.1) in the ACTIFLO® pilot plant for coagulation with PACl and alum. Error bars represent the maximum and minimum measurements.

A decrease of approximately 0.2 NTU was observed in clarified water turbidity when the primary coagulant was switched from alum to PACl (Figure 6.7); however, the clarified water for both trials was still less than 0.6 NTU. The type of coagulant did not impact the filtered water turbidity, as both trials were within the range of 0.05 to 0.07 NTU.

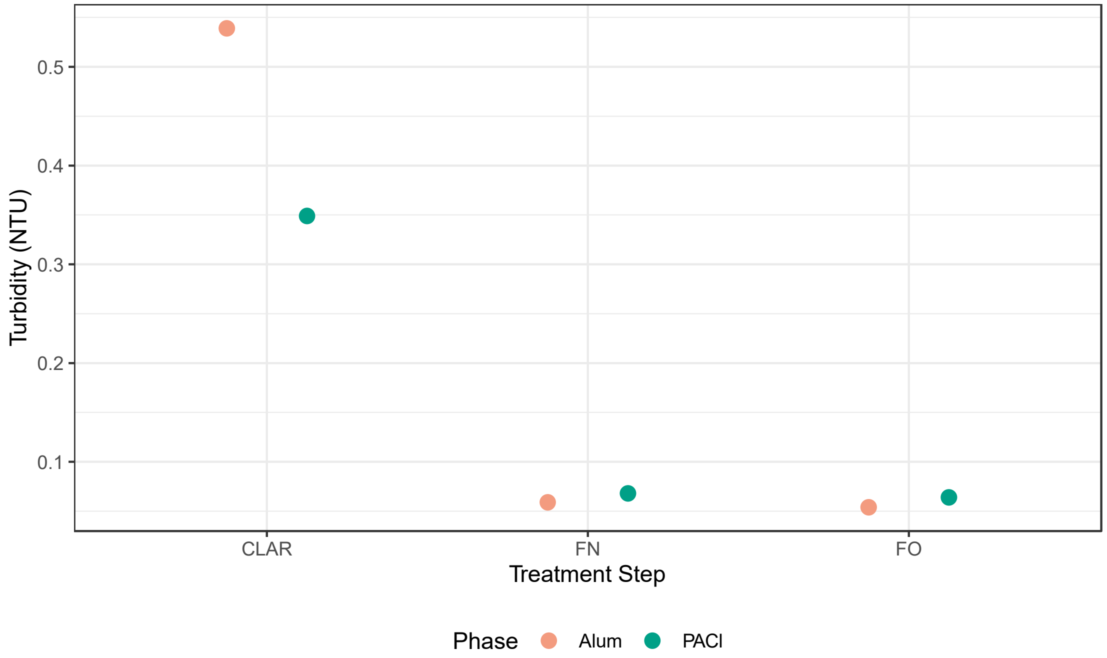

Figure 6.7 Turbidity recorded after various treatment steps (see Figure 6.1) for coagulation with PACl and alum in the ACTIFLO® pilot plant (Phase III).

6.4 Discussion

6.4.1 *Comparing effluent water quality with treatment through ACTIFLO® and adsorption clarification*

Overall removal of organic matter, as measured by TOC, was not impacted by the changes in clarification process. This was anticipated as previous work had determined that the addition of a BA does not impact the coagulation chemistry due to its low surface charge density in comparison to colloids in the water matrix (He et al. 2019; Young and Edwards 2003). As such, if the chemical dosing was sufficient to destabilize organic compounds during coagulation, the addition of a BA should not impact their removal. Both the alum dose and coagulation pH were greater in the pilot plant (24-33 mg/L of alum and pH of 7) as compared to the full-scale plant (19 mg/L of alum and pH of 6.5) during Phases I and II. As determined in Chapter 5, the coagulation pH and alum dose did impact the treatment of NOM. However, slight increases in pH did not mandate higher alum doses in the jar tests conducted on this source water. Therefore, the shifts in coagulation chemistry observed in this study were not expected to have a significant impact on the destabilization and subsequent removal of organic matter.

TOC removal for all trials, in both the ACTIFLO® pilot plant and the full-scale plant were between 55 and 65%. This is within the expected range as raw waters with SUVA values greater than 4 L/mg m are anticipated to have removal upwards of 50% (Edzwald 1993). The SUVA values of the clarified and treated water were between 1.45 and 1.6 L/mg m for all trials, suggesting the remaining fraction of organic matter is, for the most part, recalcitrant to coagulation (Edzwald 1993). Additionally, where equivalent TOC removal was observed through both clarification options, it is likely that the ACTIFLO® process sufficiently incorporated the BA and destabilized organic matter into the floc.

The higher Al concentrations in the pilot plant clarified water was likely due to the increased alum dose as compared to the full-scale plant. Further, the full-scale plant operated at a lower coagulation pH that was closer to the pH of minimum solubility, resulting in lower concentrations of negatively-charged dissolved Al hydrolysis species (Pernitsky and Edzwald 2006). These negatively-charged species present outside the range of minimum solubility are less likely to form floc through charge neutralization of NOM and may remain stabilized in the water matrix after clarification (Davis and Edwards 2014; Pernitsky and Edzwald 2006).

The cause of the increased concentrations of Mn in all stages of treatment in the pilot plant is less understood. As potassium permanganate doses were consistent in both treatment processes and oxidation occurred prior to entrance of both the full-scale plant and pilot plant, dosing conditions were not likely the cause for the alternative outcome. If permanganate doses were sufficient to precipitate dissolved Mn, and it is suggested that it was based on the stoichiometric relationship of 1.92 mg/L of permanganate per mg/L of Mn^{2+} (Tobiason et al. 2016), the precipitated species, which are typically colloids, need to be destabilized for effective removal. It is likely that this removal was enhanced in the adsorption clarifiers, as full-scale plant clarified Mn concentrations were significantly lower than those in ACTIFLO® clarified water (Figure 6.3). With ACTIFLO® treatment, it is possible that insoluble Mn was not successfully incorporated into the ballasted floc, remaining in suspension as colloids. Additionally, where the MWTP does not pre-chlorinate, there was potential for biological growth on the clarifier and filter media in the full-scale plant. This may result in Mn removal, as biofiltration is used as a strategy for Mn removal in drinking water plants (Tobiason et al. 2016). Biological sampling (e.g. adenosine triphosphate) could provide further insight into the potential of biological removal of Mn. Further, a more extensive optimization period could improve Mn removal through the ACTIFLO® process, as the time-sensitive optimization for this study focused mainly on effluent turbidity.

With respect to turbidity measurements through the two treatment processes, higher clarified water turbidity was recorded after treatment with the ACTIFLO® process than the adsorption clarifiers. This increase is likely attributed to both higher turbidity of the raw water in the pilot plant (2.68 ± 0.37 NTU in pilot plant versus 1.89 ± 0.02 NTU in full-scale plant) and slightly reduced turbidity removal with ACTIFLO® clarification (84 ± 6%) as compared to adsorption clarification (87 ± 1%). Past work has found similar findings, proposing turbidity removal of 95% or greater with adsorption clarification (Goodrich et al. 1992) and upward of 80% for ballasted media clarification (Young and Edwards 2003). Further, residual BA could also be a source of turbidity in the ACTIFLO ® clarified water. Microsand doses applied during the study ranged from 16 to 25 g/L, almost four times greater than doses suggested in the literature (Desjardins et al. 2002; Young and Edwards 2003). If the coagulant and polymer doses were insufficient and all binding sites are occupied, additional BA will not be incorporated into the floc (Ghanem et al. 2007; He et al. 2019; Young and Edwards 2003). This can impact the settled water turbidity. For example, Edwards and Young (2003) reported that residual turbidity in bench-scale BF tests with alum was mostly due to smaller microsand that had not been incorporated into the floc and remained in suspension. There is potential to improve clarified water turbidity with ACTIFLO® treatment by altering BA, coagulant and polymer doses in an extended optimization period.

The slight increase in clarified water turbidity (approximately +0.2 NTU), but consistent effluent turbidity, may cause greater solids loading on the filters, potentially resulting in more frequent backwashes if ACTIFLO® were to be implemented in the full-scale plant. However, the adsorption clarifiers at the MWTP are typically flushed every 5 to 6 hours, consuming approximately 20% the water treated with alum, polymer, and potassium permanganate. As such, replacing the adsorption clarifiers with ACTIFLO® and eliminating the flushing requirement of the adsorption clarifiers may improve overall production and efficiency, despite the potential reduction of filter cycles.

6.4.2 Impact of conversion from alum to PACl in the ACTIFLO® process

TOC removal through clarification and the entire pilot plant treatment process were not significantly impacted by the type of coagulant. Thus, consistent removal of organic matter could be achieved by switching from alum to PACl. Additionally, the dose (in mg/L as Al) in Phase III was greater than that of Phase I without additional TOC removal. As such, it is likely that the PACl dose could be reduced to be equivalent to that of alum in Phase I, without compromising the effluent water quality. The prehydrolyzation of $AlCl_3$ to form PACl also enhances the amount of $AlO_4Al_{12}(OH)_{24}^{7+}$ (or Al_{13}) formed, a Al-hydrolysis species that has been noted as highly efficient for NOM removal due to its high positive charge and large size (Matilainen et al. 2010). Thus, PACl can often be applied in lower doses than alum (Matilainen et al. 2010) and a switch to PACl from alum may result in even lower coagulant doses.

Slightly lower Al concentrations were observed in the clarified water when coagulating with PACl than with of alum. This small shift was attributed to the differences in pH of minimum solubility for the two coagulants, which is ~6.7 for alum at 5°C and ~6.9 for PACl at the same temperature (Pernitsky and Edzwald 2006). As the coagulation pH was approximately 7 for both trials, there was likely less soluble Al species with PACl. Further, Yang et al. (2010) reported decreased concentrations of dissolved monomeric Al with PACl as compared to alum at identical doses and pH. However, effluent concentrations were similar for the two coagulants, suggesting that the additional Al in the water clarified with alum was not dissolved, but instead in a precipitated form that had not been incorporated into the ballasted flocs. Mn concentrations were higher after each treatment step when PACl was used for coagulation instead of alum. The mechanism for this increase is unknown and may require further investigation if PACl were to be used at the full-scale plant. Nonetheless, the filtered water Mn concentrations remained between the 50 µg/L aesthetic objective (AO) outlined by Health Canada (2019a) and the 100 µg/L utility objective outlined in Table 6.2.

Settled water turbidity was lower for coagulation with PACl than with alum and comparable to clarified water turbidity in the full-scale plant. One potential explanation for this finding could be reduced breakage of flocs due to their increased strength when coagulated with PACl versus alum. He et al. (2019) found that ballasted flocs formed with PACl were much stronger and more compact than those formed with alum under the same dose. The stronger flocs were less susceptible to breakage, which leads to smaller and lighter fragmented particles that may not sufficiently settle, increasing clarified water turbidity (He et al. 2019). On the other hand, the lower turbidity may have been a result of greater incorporation of BA into the floc, which could have been achieved by the greater degree of polymeric Al hydrolysis and increased coagulant dose (in mg/L as Al) with PACl as compared to alum. Higher coagulant doses have been shown to allow for greater incorporation of BA into floc, increasing the settling rate and improving the clarified turbidity (Young and Edwards 2003).

6.5 Implications of findings

6.5.1 Reduced sensitivity to changes in raw water quality

Treatment through the ACTIFLO® process did not present any significant concerns regarding quality of drinking water produced in comparison to that of the full-scale plant. However, replacing the adsorption clarifiers at the MWTP with ACTIFLO® will reduce the sensitivity of the plant to changes in source water quality, including HABs. Adsorption clarifiers are best suited for low turbidity, high quality source waters with low coagulant demands, making them particularly vulnerable to changes in source water quality (Becker et al. 2018; Logsdon et al. 2006). Where adsorption clarifiers store the flocculated particles in the pores between media, they act similarly to a filtration system and are impacted by the solids loading (Ross et al. 2019). Algae has previously caused plugging of adsorption clarifiers, and ultimately caused a treatment plant in New England to shut down for several months (Marston et al. 2015). The City of Moncton has expressed concerns regarding the potential impacts of HABs on hydraulic capacity of the plant and the switch to ACTIFLO® would likely relieve this concern (City of Moncton 2019).

6.5.2 Adsorption of cyanotoxins

The removal of algae and cyanotoxins was not included in the scope of this study as there was no detection of algae in the Turtle Creek Reservoir at the time of the research. However, the addition of weighted sedimentation allows for the addition of PAC in the treatment process. PAC has been shown to improve removal of lower molecular weight compounds that are typically recalcitrant to coagulation (Plourde-Lescelleur et al. 2015), potentially reducing the formation of DBPs. Further, PAC can remove extracellular cyanotoxins that may be present during HABs (Ho et al. 2011; Newcombe and Nicholson 2004). This offers a beneficial treatment barrier that can be implemented intermittently, when HABs occur, but need not be used year-round as blooms are typically seasonal events.

6.6 Conclusion

It was demonstrated that ACTIFLO® clarification can replace adsorption clarification at the MWTP with minimal impacts on effluent water quality. TOC removal through both clarification processes were similar (~58%) and minimal differences in effluent water quality were observed between the two treatment technologies. Clarified water turbidity was slightly higher in the ACTIFLO® process as compared to the full-scale plant, however the difference was small (~0.2 NTU) and may be reduced with a more extensive optimization study. Filtered water metal concentrations (Al and Mn) were consistent for both treatment trains.

Overall TOC removal was consistent when PACl was used as the primary coagulant instead of alum in the ACTIFLO® pilot plant. The use of PACl did, however, lower the clarified water turbidity ~0.2 NTU, which may enhance filter hydraulic performance, although further work is needed to confirm this potential impact. Al residual concentrations were consistent with the two coagulants, and Mn concentrations were higher with PACl as compared to alum.

A switch to a BF and sedimentation clarification process would reduce the sensitivity of the MWTP treatment plant to changes in source water quality (Plum 1998), a beneficial outcome with anticipated occurrence of HABs in the source water. Further work should be conducted to better understand the treatment mechanisms of ballasted settling in the MWTP, and a more detailed analysis over a longer time period would be beneficial to ensure treatment capacity for all seasonal trends. Nonetheless, the study provided a baseline for the use of ACTIFLO® in low-turbidity, low-alkalinity, moderately coloured source waters.

CHAPTER 7: RECOMMENDATIONS AND CONCLUSION

7.1 Conclusion

Changes in source water quality caused by both lake recovery and climatic drivers have recently been observed in Atlantic Canada. These changes include shifts in water chemistry (e.g. pH, alkalinity), increasing concentrations of natural organic matter (NOM), and increased occurrence of harmful algae blooms (HABs). The dynamic nature of source water quality has multiple design implications for drinking water treatment, especially for unconventional treatment processes (e.g. direct filtration, adsorption clarification). The overall objective of this thesis was to investigate potential solutions, both short- and long-term, to mitigate the changing source water quality caused by lake recovery or climatic drivers in vulnerable drinking water treatment plants. Both pilot- and bench-scaled experiments were designed to determine the impact of alternative treatment strategies in three different studies.

Chapter 4 investigated the impacts of partially substituting alum with a cationic polyelectrolyte for removal of disinfection by-product (DBP) precursor material. Results indicated that the application of polyelectrolyte did not reduce the amount of DBPs formed in the filtered water, likely because chemical dosing was already near optimal conditions for coagulation of NOM in the source water. However, the addition of polyelectrolyte did improve filtered water turbidity when underdosing alum, a finding that may be beneficial for mitigation of spikes in raw water turbidity. This study also investigated the effects of increasing the effective size of the filter media and extending the depth of the filter bed to improve filter cycles and increased plant productivity. It was determined that this strategy could be successfully applied without undesirable consequences on filtered water quality.

In Chapter 5, the effects of pH and alum dose on removal of NOM and residual Al concentrations were investigated. It was determined that optimal conditions for NOM removal may not be consistent with optimal conditions for minimizing Al residual concentrations in the finished water. Further, the downstream effects of altering coagulation parameters were highlighted, emphasizing the importance of pilot-scaled work in unconventional treatment processes that are not easily simulated at the bench-scale.

Further, the impacts of pH and alum dose differed for the two source waters considered, stressing the importance of regular optimization studies for each site.

Finally, results from Chapter 6 suggested that there would be minimal impacts on the quality of drinking water produced from low-alkalinity, low-turbidity source water in switching the flocculation/clarification process from adsorption clarifiers to ballasted flocculation and high-rate clarification (ACTIFLO®). Further, the switch to ACTIFLO® would likely reduce the sensitivity of the treatment plant to changing source water quality (e.g. algae blooms) and allows the opportunity for intermittent treatment with powdered activated carbon to remove cyanotoxins during algae blooms.

Overall, the work conducted in this thesis highlighted a few overarching findings. Firstly, the importance of pilot-scaled experiments was stressed. The need for pilot-scale evaluation is especially important in unconventional treatment processes that cannot be easily replicated at the bench scale. In Chapters 4 and 5, significant changes on the filter hydraulic performance were observed at the JDKWSP after variations in the type of coagulants, their doses, and the coagulation pH. It is important to determine how changes in coagulation, flocculation, and clarification (if applicable) may impact the filtration process, and ultimately, the plant productivity. Further, balancing water quality and quantity is a difficult task that is best suited for pilot-scaled experiments, as it is unlikely that optimal conditions for NOM removal, Al residual concentrations, and filter hydraulic performance will be consistent.

Secondly, findings from the work completed suggested that upgrades to the two drinking water treatment plants studied will likely be necessary in the near future with the anticipated changes in source water quality. The City of Moncton has already taken the initial steps towards retrofitting the MWTP with the ACTIFLO® process in anticipation of future cyanobacteria blooms. The sensitivity of the direct filtration process to changes in coagulation parameters (e.g. increased alum dose) was highlighted at the JDKWSP. With the increasing trend in DOC concentrations in its supply, higher alum doses are anticipated, which were found to lead to significant decreases in productivity with the current treatment process (Chapter 5). Further, a significant fraction of raw water NOM that was found to be recalcitrant to coagulation, thus additional treatment strategies may be required to target the remaining DBP pre-cursors after coagulation (Chapter 4).

7.2 Recommendations

Multiple recommendations for future research were identified through the work conducted in this thesis. A recommendation that applies to all of the experiments conducted would be to extend the timeline of the studies. Due to the shorter timeframe of the MASc program, the work completed was not able to be repeated over multiple seasons. Further as the work was completed entirely in partnership with utilities, there were often times where scheduling was dictated by their needs. Extending the work into multiple seasons would be beneficial to determine the impacts of temperature, seasonal shifts in NOM, etc. on the presented results.

The work completed also emphasized the need for detailed, high-resolution monitoring for sustainable drinking water treatment plant design. To design the best process for treatment of a source water, it is important to have a complete understanding of what needs to be treated. As observed in Chapter 4, formation of DBPs were not reduced with lowered residual TOC concentrations, suggesting that the remaining DBP pre-cursor material was recalcitrant to coagulation and would require additional treatment barriers and plant upgrades for its removal. A greater understanding of the character and reactivity of NOM remaining after coagulation and its contribution to DBP formation could allow for such targeted treatment. Further, high resolution monitoring (e.g. resin fractionation, cyanobacteria/cyanotoxins) would give an understanding of the seasonal and long-term trends in water quality as a result of recovery from acidification and climatic drivers. Treatment technologies could then be designed and implemented to be adaptable to the anticipated changes and target the contaminants of concern. These technologies should also consider the entire treatment train, as it was often observed in the completed work that changes in coagulation operating conditions resulted in unintended consequences downstream.

Secondly, it was observed in Chapter 5 that increasing the coagulation pH at the JDKWSP increased coagulant demand. This resulted in negative downstream impacts on the filter hydraulic performance and the filter run cycles were significantly reduced as compared to baseline conditions. In Chapter 4, it was identified that cationic polyelectrolyte provided sufficient charge neutralization to reduce the effluent turbidity when alum was underdosed. As such, future work should be conducted to determine if the application of polyelectrolyte could adequately reduce the effluent turbidity at higher coagulation pH while maintaining NOM removal and causing minimal impact to the filter hydraulic performance. If successful, this solution could offer the benefit of reduced Al residual concentrations with consistent NOM removal and subsequently, formation of DBPs.

Although the work completed in Chapter 6 did indicate that drinking water quality would likely not be compromised when switching from adsorption clarification to ACTIFLO® at the MWTP, additional process optimization is recommended prior to implementation at the full-scale plant. Due to the short duration of the validation study, it is likely that the 'optimal' conditions selected for each Phase were not the optimal conditions for full-scaled implementation. Changes in microsand, coagulant, and polymer doses, as well as coagulation pH, were all reported to significantly impact NOM removal with ballasted flocculation (Desjardins et al. 2002; He et al. 2019), and operational parameters such as mixing intensities, flocculation times, and settling rates can also impact effluent water quality (Young and Edwards 2003). These parameters, and their impacts on treated water, filter hydraulic performance, and sludge production, should all be sufficiently studied at the pilot-scale prior to full-scale implementation to ensure the highest quality of effluent water is being provided to the consumers and to enhance cost and energy savings.

Additionally, studying the treatment of algae-laden source water with ACTIFLO® is recommended in preparation for future blooms at the MWTP. This work should begin with bench-scaled jar ACTIFLO® jar tests using raw water samples spiked with cyanotoxins or cyanobacteria, and phase into pilot-scaled tests of a similar nature. Intermittent treatment with powdered activated carbon should be studied to determine the efficacy of powdered activated carbon in removing cyanotoxins with ballasted flocculation and to identify other factors that will influence their removal. Essentially, a detailed guideline for treatment of cyanobacteria and cyanotoxins should be created such that the City of Moncton is well prepared in the event of an HAB.

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APPENDIX A

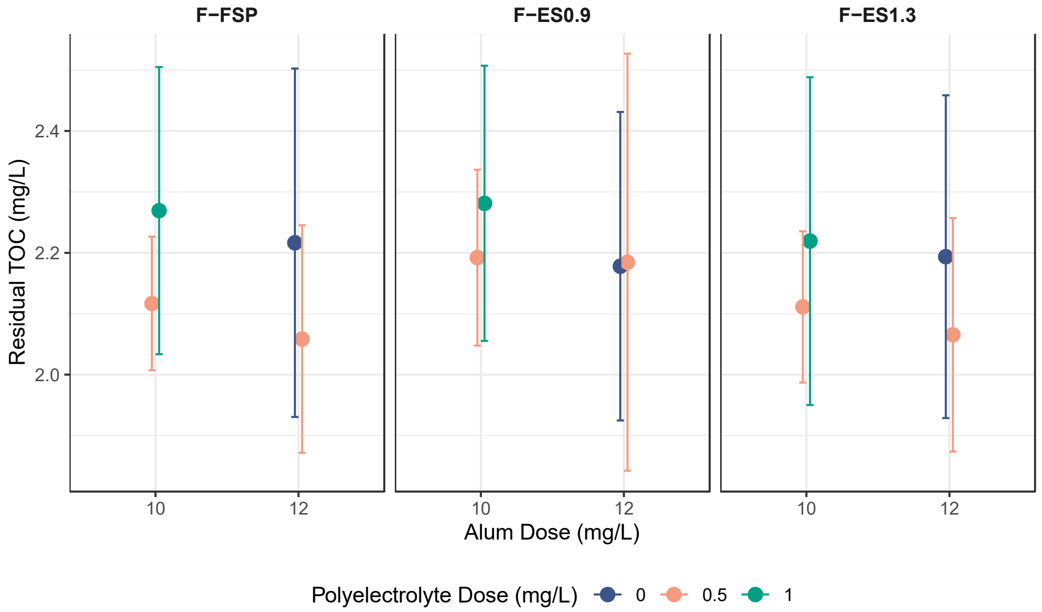

Figure A.1. Residual TOC concentrations for all combinations of coagulant dosing through each filter media layout in a direct filtration pilot plant. Error bars represent the standard deviation about the mean.

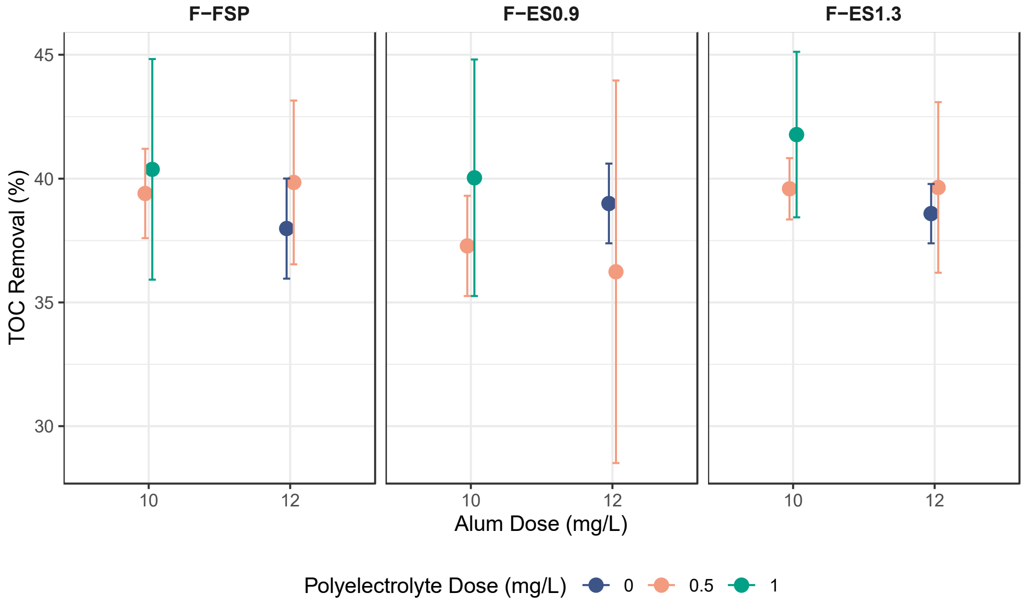

Figure A.2 TOC removal for all combinations of coagulant dosing through each filter medial layout in a direct filtration pilot plant. Error bars represent the standard deviation about the mean.

Table A.1 TOC removal in a direct filtration pilot plant for all combinations of coagulant dosing and additional trials at 14 and 16 mg/L of alum

Alum Dose (mg/L)	Polyelectrolyte Dose (mg/L)	TOC Removal (%)			Sample Size
		Range	*Average*	*SD*	
12	0.5	30.1-42.2	38.6	4.4	6
10	0.5	35.2-39.4	37.6	1.5	6
10	1	36.6-44.1	40.7	3.4	6
14	0	42.9-49.3	46.4	2.5	5
16	0	43.0-46.7	45.7	1.4	6

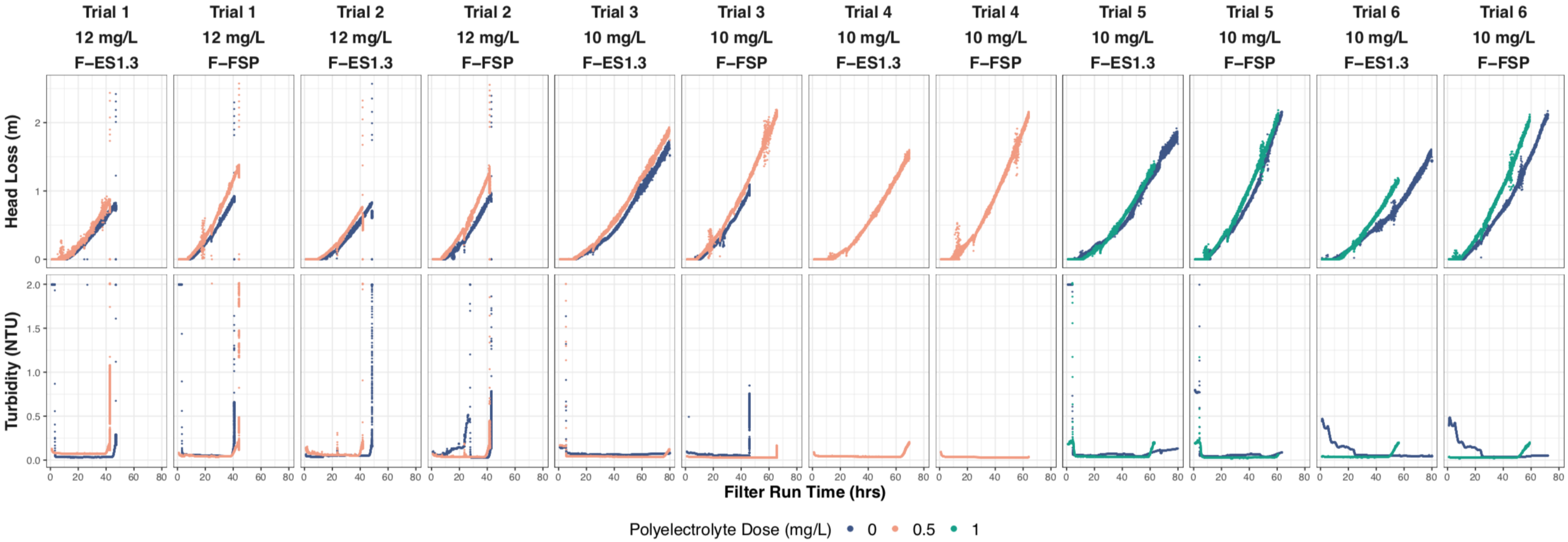

Figure A.3 Raw head loss and turbidity profiles for all trials in the direct filtration pilot plant through filters F-FSP (simulating the full-scale plant, anthracite effective size of 0.9 mm and sand) and F-ES1.3 (increased effective size of anthracite to 1.3 mm and extended depth of anthracite layer).

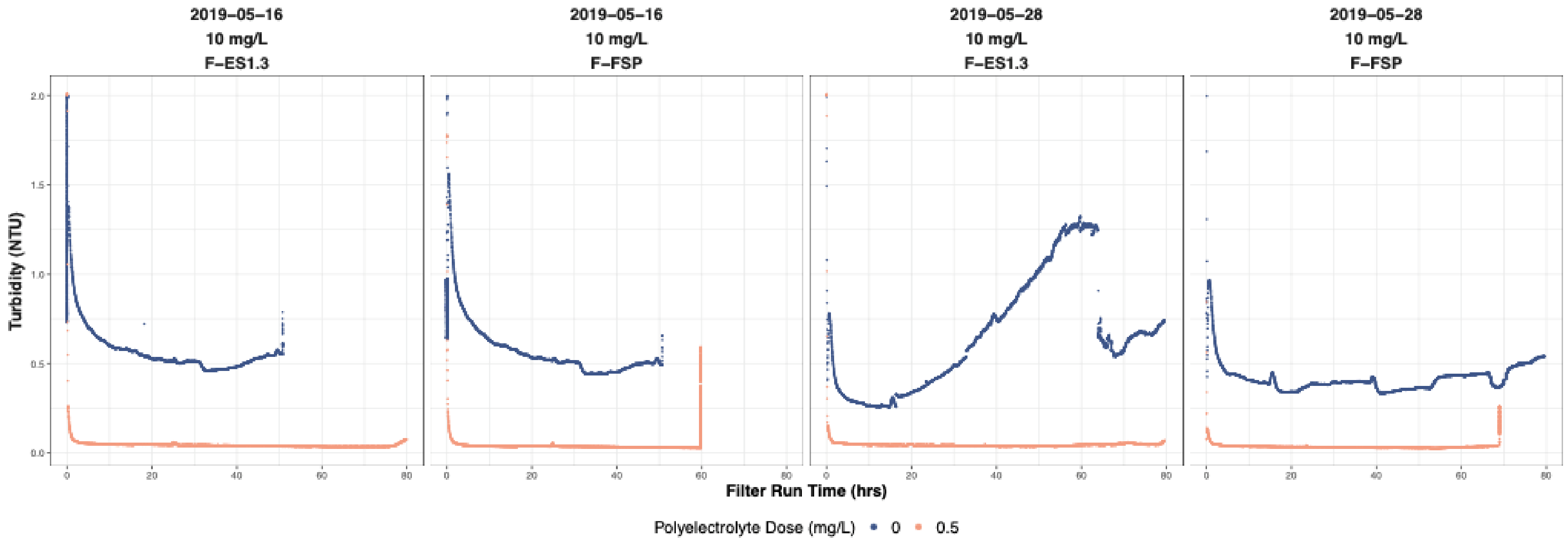

Figure A.4 Turbidity profiles for additional trials at 10 mg/L of alum and 0 and 0.5 mg/L of polyelectrolyte in the direct filtration pilot plant. Profiles are shown for filters F-FSP (simulating the full-scale plant, anthracite effective size of 0.9 mm and sand) and F-ES1.3 (increased effective size of anthracite to 1.3 and extended filter bed depth).