# OPTIMIZING THE REMOVAL OF NATURAL ORGANIC MATTER IN DRINKING WATER WHILE AVOIDING UNINTENDED CONSEQUENCES FOLLOWING COAGULATION 

by

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## Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

at

Dalhousie University
Halifax, Nova Scotia
May 2011
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## DALHOUSIE UNIVERSITY

## DEPARTMENT OF CIVIL \& RESOURCE ENGINEERING

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## DEPARTMENT OR SCHOOL: Department of Civil \& Resource Engineering

DEGREE: PhD CONVOCATION: October YEAR: 2011

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## DEDICATION

I dedicate this thesis to my husband, Andy, for his continued patience, support, understanding and love along this journey.

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#### Abstract

Over the past decade, the objectives for coagulation based drinking water treatment processes have changed significantly. These changes are a result of stringent goals related to natural organic matter (NOM) removal to mitigate the formation of subsequent harmful and health-related disinfection by-products (DBPs) and the need to achieve adequate filtration performance to ensure sufficient particle removal for pathogen control. Another concern associated with coagulation optimization is the potential unintended consequences of a coagulant change on the distribution system, specifically related to lead release from lead pipe and solder materials. Optimizing these multi-objectives in a direct filtration treatment process presents significant challenges for source waters characterized by low levels of turbidity, alkalinity and organic matter content.

Bench and pilot-scale experiments were conducted to evaluate the performance of ferric sulfate, polyaluminum chloride ( PACl ) and aluminum chlorohydrate ( ACH ) against aluminum sulfate (alum) using variable coagulation dosage and pH conditions for a direct filtration facility. Bench-scale experiments were conducted to optimize NOM removal during coagulation using traditional organic matter surrogates coupled with molecular size characterization techniques. Pilot-scale studies provided a snapshot of feasibility in terms of filtration performance for favourable bench-scale conditions and also identified optimal conditions for filtration performance. Results from pilot testing demonstrated that favourable conditions identified for increased potential NOM removals during bench-scale testing were significantly different than optimal filtration conditions identified during pilot studies; and, in fact, severely compromised direct filtration performance due to increased solids loading to the filters.

Bench-scale experiments evaluated lead leaching from lead and lead:tin solder galvanically connected to copper under stagnant conditions using variable chloride-tosulfate mass ratio (CSMR) conditions for alum, ferric sulfate and PACl . Although recent research identifies high CSMRs ( $>0.5$ ) as the main mechanism of attack in distribution systems following coagulant changeovers, CSMR was not the primary catalyst for lead leaching following the coagulant changeover conditions evaluated in this study. Residual concentrations of iron and aluminum remaining following coagulation were the principal contributors. Positive correlations were revealed between particulate iron and particulate lead concentrations following stagnation demonstrating that the adsorption of lead to iron oxides is a viable hypothesis for lead release.


## LIST OF ABBREVIATIONS AND SYMBOLS USED

| Al | aluminum |
| :---: | :---: |
| Alum | aluminum sulfate |
| ACH | aluminum chlorohydrate |
| BCAA | bromochloroacetic acid |
| BCDM | bromodichloromethane |
| BDCAA | bromodichloroacetic acid |
| ${ }^{\circ} \mathrm{C}$ | degrees Celsius |
| $\mathrm{CaCO}_{3}$ | calcium carbonate |
| CDBAA | chlorodibromoacetic acid |
| CFD | Computational Fluid Dynamics |
| $\mathrm{Cl}^{-}$ | chloride |
| $\mathrm{CO}_{2}$ | Carbon dioxide |
| cm | centimeter |
| CSMR | chloride to sulfate mass ratio |
| Da | daltons |
| DBAA | dibromoacetic acid |
| DBCM | dibromochloromethane |
| DBP | disinfection by-product |
| DBPFP | disinfection by-product formation potential |
| DCAA | dichloroacetic acid |
| DO | dissolved oxygen |


| DOC | Dissolved organic carbon |
| :---: | :---: |
| ETSW | Extended Terminal Sub-fluidization Wash |
| Fil | filter |
| Floc3 | post-flocculation |
| FRL | Filter Run Length |
| FRV | Filter Ripening Volume |
| FSP | Full scale plant |
| Fe | iron |
| ft | foot |
| h | hour |
| HAA | haloacetic acid |
| HAAFP | haloacetic acid formation potential |
| HBNS | high basicity non-sulfated |
| HPSEC | high pressure size exclusion chromatography |
| HW | Halifax Water |
| in | inch |
| JDKWSP | JD Kline Water Supply Plant |
| $\mathrm{KMnO}_{4}$ | Potassium Permanganate |
| L | liter |
| $\mathrm{L} / \mathrm{min}$ | liters per minute |
| m | meter |
| $\mathrm{m}^{2}$ | square meter |
| $\mathrm{m}^{3} / \mathrm{m}^{2}$ | square meters/ cubic meters |


| $\mu \mathrm{m}$ | micrometer |
| :---: | :---: |
| MBAA | monobromoacetic acid |
| MBNS | medium basicity non-sulfated |
| MCAA | monochloroacetic acid |
| $\mu \mathrm{g} / \mathrm{L}$ | micrograms per liter |
| $\mathrm{mg} / \mathrm{L}$ | milligrams per liter |
| min | minute |
| mm | millimeter |
| $\mu \mathrm{L}$ | micro liter |
| ML/d | million liters per day |
| $\mathrm{mL} / \mathrm{min}$ | milliliters per minute |
| $\mathrm{ML} / \mathrm{m}^{2}$ | million liters of water per square meter |
| mV | millivolt |
| MW | molecular weight |
| NOM | natural organic matter |
| NTU | nephelometric turbidity units |
| ORP | oxidation reduction potential |
| PACl | Polyaluminum chloride |
| PI | performance indicator |
| PM3 | post-coagulation |
| PP1 | Pilot plant train 1 |
| PP2 | Pilot plant train 2 |
| QC | quality control |


| $\mathrm{R}^{2}$ | coefficient of determination |
| :--- | :--- |
| RO | reverse osmosis |
| RW | raw water |
| SEC | size exclusion chromatography |
| SO $_{4}{ }^{2-}$ | sulfate |
| SUVA | specific UV ${ }_{254}$ absorbance |
| TBAA | tribromoacetic acid |
| TCAA | trichloroacetic acid |
| THM | trihalomethane |
| THMFP | trihalomethane formation potential |
| TOC | Total organic carbon |
| UFRV | Unit Filter Run Volume |
| UV 254 | Ultra violet absorbance at 254nm |
| WQMP | Water Quality Master Plan |

## ACKNOWLEDGMENTS

First and foremost, I would like to thank my supervisor, Dr. Graham Gagnon, for his technical advice and guidance throughout my graduate studies. Your continued support, enthusiasm and optimism both academically and professionally are much appreciated. I can't thank you enough for the opportunity to attend and present at countless conferences and to be involved in such practically oriented research. Both have proven to be invaluable contributions to my professional development. Conducting research within your water quality group has been a great experience and I am honoured to have worked with you over the past 5 years.

Thank you to the Natural Science and Engineering Research Council of Canada (NSERC) who funded my graduate studies under both a NSERC Industrial Postgraduate Scholarship (IPS) and a NSERC Postgraduate Studies Doctoral award (NSERC PGS-D). I would like to acknowledge and thank the NSERC for funding the research conducted in this thesis under the NSERC/Halifax Water Industrial Research Chair.

I would like to thank Dr. Margaret Walsh, Dr. Amyl Ghanem, and Dr. Jennie Rand for not only taking the time to be a part of my committee, but for your guidance and support along the way. Also, many thanks to my external examiner Raymond Hozalski from the University of Minnesota.

I would like to acknowledge the contributions of research support staff in Dr.Gagnon's research group including Amina Stoddart, John Bergese, Matt Follet, Krysta Montreuil, Franziska Grahl, and Chad Furey. In particular I would like to thank Heather Daurie and Jessica Mackay for their immeasurable assistance both experimentally and in the laboratory with many aspects of this thesis. Your patience, time and positive attitudes are much appreciated. I would also like to acknowledge Dr. Gagnon's research group as a whole for their support and friendship. In particular, I would like to recognize Wendy Krkosek. I have leaned on Wendy throughout my graduate studies, as both a friend and a mentor. I will be forever grateful for your open ear and kind words of encouragement throughout this process.

Many thanks to the folks at Halifax Water, in particular Reid Campbell, Peter Flinn and all of the operators at the JD Kline Water Treatment Plant. Your patience, hospitality, practical insight and field support were invaluable to the outcomes and success of this research program. I would also like to thank and acknowledge Dr. Marc Edwards and Caroline Nguyen at Virginia Tech for their technical support and guidance with the lead research components of this thesis.

Last, but certainly not least, I would like to express my sincere gratitude to my family and friends, especially my husband, Andy, my parents, Roger and Linda, and my brother, Roger. I really can't thank you enough for your kind words, support and encouragement throughout this whole process. I wouldn't be where I am today without your love and support.

## CHAPTER 1 INTRODUCTION

Over the past decade, the objectives for coagulation based drinking water treatment processes have changed significantly as a result of stringent goals related to natural organic matter (NOM) removal to meet disinfection by-product (DBP) regulations and the need to achieve adequate filtration performance to ensure adequate particle removal for pathogen control. Resulting from the reaction of organic matter and chlorine in subsequent disinfection processes, DBPs are regulated because certain species have been classified as carcinogenic, mutagens and toxicants and pose a significant health risk to humans when ingested through drinking water over an extended period of time (Health Canada, 2006). Balancing the optimization of these multi-objective goals in a direct filtration treatment process presents significant challenges in source waters characterized by low turbidity, low alkalinity and low organic matter content.

The optimization of both organic matter and particle removal for a direct filtration plant with low-level turbidity in the source water is challenging because of its limited treatment barriers. Direct filtration facilities are typically used to treat low turbidity ( $<10-\mathrm{NTU}$ ) source waters and coagulation processes within these facilities were historically optimized primarily with turbidity removal objectives in mind. Since a clarification stage does not exist between the coagulation and filtration stage, direct filtration requires effective charge neutralization and very small "pin" floc to ensure acceptable filtration performance is achieved in terms of filter headloss, particle removal and filter run times (Pernitsky and Edzwald, 2006).

Optimal conditions for turbidity removal are not always the same as those for NOM removal; in fact, the coagulant demand is usually governed by the concentration of NOM for low turbidity waters (Gregor et al., 1997 and Pernitsky and Edzwald, 2006). The coagulation pH and dosage required for organic matter removal does not only depend on the concentration of organic matter in the source water; recent researchers have reported that specific physical and chemical properties of NOM impact the removal of NOM during coagulation and the DBP formation potential of the treated water (Croue et al., 2000; Pernitsky and Edzwald, 2006; Ates et al., 2007). The negtive charge of NOM in surface waters is generally greater than that of particulate matter and, in turn, is associated with much higher coagulant demands for effective removal (Pernitsky and Edzwald, 2006).

In a direct filtration treatment plant, optimizing coagulation processes based solely on the removal of organic matter may cause significant problems with filtration performance and overall particle removals. Dosing to meet NOM removal goals in these facilities leads to high solids loading to the filters and results in early breakthrough, increased head loss rates and, therefore, shorter filter run times (Eikebrokk et al., 2007). In a direct filtration process, coagulation optimization is the primary means of ensuring optimal filtration performance is achieved and the stringent filtration goals of today's regulatory regime are achieved. In addition, the removal of soluble NOM from low-level turbidity source water presents another practical challenge related to the low concentrations of stable particles available to form acceptable floc (Gregor et al., 1997; Eikebrokk et al., 2007). In direct filtration facilities, coagulation processes must be optimized with
multiple performance objectives in mind. There are noticeable gaps in literature pertaining to coagulation optimization of source waters characterized by low levels of turbidity, alkalinity, and organic matter, which is a problem inherent throughout Nova Scotia, and several other provinces across Canada.

Another potential concern associated with coagulation optimization is the potential unintended consequences of a coagulant change on the distribution system, specifically related to lead release from lead pipe and solder materials. Previous studies have reported that coagulant changeovers were a key factor in unexpected high lead concentrations in distribution systems (Dodrill and Edwards, 1995; Edwards et al., 1999). Evidence obtained through lead release data resulting from practical case studies and laboratory-based studies have demonstrated that a high chloride $\left(\mathrm{Cl}^{-}\right)$to sulfate $\left(\mathrm{SO}_{4}{ }^{2+}\right)$ mass ratio (CSMR) induces high galvanic currents and governs lead leaching incidences in distribution systems following coagulant changeovers (Dodrill and Edwards, 1995; Edwards et al., 1999; Dudi, 2004; Edwards and Triantafyllidou, 2007, Nguyen et al., 2010a; Nguyen et al., 2010c). Additionally, due to the limited database of lead release occurrences from these utilities, supporting data relating CSMR and lead leaching in systems with water sources characterized by low alkalinity and turbidity is limited and more research is required to validate this theory (EPA and AwwaRF, 2007).

### 1.1. RESEARCH QUESTIONS AND OBJECTIVES

The main objective of this thesis was to optimize the removal of organic matter DBP precursors in a direct filtration facility treating surface water with low levels of turbidity, alkalinity and organic matter while ensuring filtration performance is not compromised
and significant or harmful effects with respect to lead leaching in the distribution system are not triggered. Bench-scale and pilot-scale experiments were designed to satisfy the following research sub-objectives:

Objective 1. Determine favourable coagulation conditions for the removal of organic matter from a low turbidity, low alkalinity, and low organic matter source water through bench-scale alternate coagulant studies using ferric sulfate, polyaluminum chloride $(\mathrm{PACl})$, aluminum chlorohydrate $(\mathrm{ACH})$ and alumunim sulfate (alum) at variable coagulant dosage and pH conditions.

Objective 2. Evaluate particle removal and filtration performance using a direct filtration pilot plant for the favourable coagulation conditions determined for NOM removal using ferric sulfate, $\mathrm{PACl}, \mathrm{ACH}$ and alum. If these conditions are significantly different from the conditions identified in Objective 1, determine if balanced conditions to meet performance goals can be achieved.

Objective 3. Evaluate potential "unintended consequences" of chemical changeovers on finished water quality and distribution systems related to lead release.

Objective 4. Develop a framework for implementing and evaluating coagulation optimization studies to be used by other utilities.

### 1.2. ORGANIZATION OF THESIS

The main chapters in this thesis were organized and formatted with the intention of being
submitted for publication; therefore, each contains an abstract, introduction, materials and methods, results and discussion, and conclusions section. Raw and supplemental data for Chapters 4 through 7 are provided in Appendices A through D, respectively.

Chapter 2 outlines the rationale behind this research project and presents general background information on NOM occurrence, coagulation mechanisms, coagulation optimization with alternate coagulants and lead release consequences associated with galvanic corrosion and coagulant changeovers.

Chapter 3 describes raw water sampling and collection, equipment and analytical procedures that are common to the experimental designs presented in Chapters 4, 5, $\mathbf{6}$ and 7. For clarity, materials and methods that are chapter specific are described within that particular chapter.

Chapter 4 presents findings from the experimental and statistical validation procedures used to verify that the pilot treatment process, used for coagulation optimization trials in Chapter 5, replicates the corresponding full-scale direction filtration plant and that the two pilot treatment trains produced equivalent water quality.

Chapter 5 presents results of the bench-scale and pilot-scale experiments conducted to optimize organic matter and particle removal for a direct filtration plant through evaluating the performance of ferric sulfate, polyaluminum chloride ( PACl ) and
aluminum chlorohydrate ( ACH ) against aluminum sulfate (alum) using variable coagulant dosage and pH conditions.

Chapters 6 and 7 report on the results of experiments designed to evaluate the role of a coagulant change in causing lead leaching in lead-to-copper galvanic connections. The coagulants studied include alum, PACl and ferric sulfate and the two lead bearing plumbing materials studied were lead:tin solder and passivated lead pipe, both in connection with copper pipe. This work contributes to the established data set for coagulant changeover studies with a particular emphasis on very low alkalinity water (less than $10 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ ) and high CSMR values.

Finally, Chapter 8 provides a summary and conclusions of all individual research projects presented in this thesis and Chapter 9 offers recommendations and opportunities for future research projects that were beyond the scope of this thesis, but merit additional investigation.

## CHAPTER 2 BACKGROUND

### 2.1. PROJECT RATIONALE

This research project was carried out as part of a much larger 5-year collaborative project between Halifax Water (HW) and Dalhousie University. HW is the municipal water, wastewater and stormwater utility serving the residents of the Halifax Regional Municipality in Nova Scotia, Canada. In 2005, HW completed its first formal Water Quality Master Plan (WQMP) document to be used as a roadmap to ensure safe, high quality water is delivered to consumers for the foreseeable future. Water quality master planning examines water quality regulations and trends, and makes reasonable estimations of what future regulations will be, and therefore allows the utility to set long term water quality goals. Master planning also affords the utility time to select the most cost effective response to future regulations and to plan for the required capital expenditures. Dalhousie University, HW and the NSERC collaborated to execute this water quality research program.

The focus of the WQMP has largely been on upgrades and investigations concerning the JD Kline Water Supply Plant (JDKWSP); HW's most mature treatment facility. This plan focused on addressing research needs at this facility to ensure that the JDKWSP will be able to maintain treatment performance in an increasingly volatile regulatory regime, despite the advancing age of this facility. Carefully planning for future demands and regulatory changes ensures the facility is maintained and upgraded in a sustainable manner.

The JDKWSP, commissioned in 1977, is HW's largest drinking water plant. The JDKWSP is a direct filtration surface water treatment plant with a capacity of 220 ML/day (currently supplies $\sim 98 \mathrm{ML} /$ day ) and is located on Pockwock Lake. In general, Pockwock Lake is characterized by low alkalinity ( $<1-\mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ ), pH (4.9 to 5.4) and turbidity ( 0.28 to 0.49 ), with low organic carbon concentrations ( 1.4 to $3.3 \mathrm{mg} / \mathrm{L}$ ). These conditions pose several significant challenges when developing drinking water treatment solutions and optimizing current facilities to meet more stringent regulations. The optimization of coagulation processes, backwash procedures, mixing conditions, and disinfection practices were all key issues that HW targeted for this facility.

To aid in addressing these research needs, a direct filtration pilot-scale treatment plant was commissioned in 2007 at the JDKWSP to be used as an investigative tool in the implementation of this research plan. Since many of the research tasks were directly related to process improvements, in order to be fully evaluated, they must be executed at either pilot-scale or full-scale. Full-scale research entails unacceptable risks to public health, therefore the pilot plant would close the gap between bench-scale and full-scale research and provide a means of fully evaluating the proposed process modifications without posing a public health risk.

One of the key water quality objectives identified in the WQMP was the reduction of DBPs. Given that DBPs are of concern to water consumers and that they are a suspected carcinogen, HW directed efforts towards DBP reduction. Although, at the time, the trihalomethane (THM) levels measured in HW's distribution systems met current regulatory requirements $(100-\mu \mathrm{g} / \mathrm{L})$, there was much room for improved performance based on what others in the industry were achieving. There was also some concern about whether the plant could maintain compliance under more stringent regulations, specifically the $80-\mu \mathrm{g} / \mathrm{L}$ regulatory requirements currently in force in the United States. At the time, haloacetic acids $\left(\mathrm{HAA}_{5}\right)$ were not regulated in Canada, but were regulated to a maximum contaminant level of $60-\mu \mathrm{g} / \mathrm{L}$ in the United States. Therefore, HW set aggressive THM and HAA objectives in the WQMP of $80 \mu \mathrm{~g} / \mathrm{L}$ and $60 \mu \mathrm{~g} / \mathrm{L}$, respectively, for this facility.

As a piece of this large research program, this thesis research was intended to optimize chemical coagulation processes for the removal of NOM to minimize DBPFP without compromising particle removals in a direct filtration water treatment system. As a secondary objective, HW was interested in investigating unintended consequences associated with coagulant changeovers on lead release in the distribution system. To that end, HW was a participating utility in Water Research Foundation Project \#4088, investigating the potential effects of a coagulant changeover on lead release from lead plumbing components (Nguyen et al., 2010a).

There are noticeable gaps in literature pertaining to coagulation optimization of surface water characterized by low alkalinity and turbidity. In addition, there is a lack of research pertaining to the optimization of direct filtration treatment processes to meet increasingly stringent NOM and turbidity removal requirements. Additionally, due to the limited database of lead release occurrences resulting from coagulant changeovers, supporting data relating lead leaching and coagulant changeovers in systems with water sources characterized with low alkalinity and turbidity was limited (EPA and AwwaRF, 2007). Accordingly, the results of this research will be useful to both water utilities and regulatory applications within the water treatment industry.

### 2.2. COAGULATION OPTIMIZAITON

NOM in Drinking Water. All drinking water supplies contain organic matter. NOM refers to the organic complexes in water bodies that result from natural sources through the chemical and microbial breakdown of vegetation and soil-based materials (MWH, 2005). Typically, NOM exists in surface water at concentrations ranging from 1 to 20 $\mathrm{mg} / \mathrm{L}$, but the quality and quantity is source specific (MWH, 2005). The presence of NOM, no matter what the concentration, impacts several water quality parameters and processes in water treatment. NOM is a major cause of aesthetic quality problems such as yellow colouring, taste and odour (MWH, 2005). NOM in drinking water has no apparent harmful effect to humans, however, in combination with chlorine, NOM can result in the formation of DBPs such as THMs and HAAs. Many of these DBPs are carcinogenic when ingested through drinking water over an extended period of time (Health Canada, 2006; Health Canada, 2008). Due to aggressive THM and HAA
regulations, water treatment facilities have been faced with developing new strategies to achieve increased organic matter removal to mitigate the formation of such DBPs.

The optimization of coagulation processes for the removal of NOM is not a new idea in the water industry. For drinking water research, NOM has traditionally been optimized through the evaluation of NOM surrogate parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), ultra-violet light absrobance at $254 \mathrm{~nm}\left(\mathrm{UV}_{254}\right)$ and specific $U_{254}$ absorbance (SUVA). More advanced NOM characterization techniques to determine optimal coagulation conditions is only recently gathering attention. A number of researchers have reported that specific physical and chemical properties of NOM, including the molecular weight of organic constituents, all impact the removal of NOM during coagulation (Croue et al., 2000; Liang and Singer, 2003; Ates et al., 2007). Therefore, characterizing the organic matter content in the both raw and treated water has become a useful tool for evaluating the efficiency of coagulation processes and for optimizing organic matter removal.

The specific physical and chemical properties of NOM can be established through the use of high-performance size exclusion chromatography (HPSEC) and resin fractionation techniques, respectively. NOM molecules are all unique but share similar characteristics. Fractionation selects a sub-group of these molecules from the mixture that share a narrower range of common properties than the entire aggregate (Croue et al., 2000). Resin fractionation is a technique using ion-exchange resins to absorb specific organic compounds out of solution and essentially separates the water samples into specific
organic fractions, which include both hydrophobic and hydrophilic neutrals, bases and acids (Croue et al., 2000). HPSEC separates the NOM molecules based on molecular size, so that the molecular weight distribution can be determined. Large molecules move through the gel column faster than smaller ones. For this research, the column is interfaced with a $\mathrm{UV}_{254}$ detector and the molecular weight distribution is obtained by comparing the response of the NOM sample with that of standard molecules (usually proteins) of known molecular weight.

Organic matter is often described in terms of hydrophobic and hydrophilic fractions and there is conflicting literature regarding which NOM types are predominant as precursors of THMs and HAAs. The THM formation potential (THMFP) and HAA formation potential (HAAFP) is affected by the type and concentration of NOM and the chlorination pH , temperature, dosage and contact time (Liang and Singer, 2003). Recently, research efforts have attempted to correlate DBPFP with fundamental characteristics of organic matter (i.e., molecular weight, structure, aromaticity, etc.) and with NOM surrogate parameters such as DOC, UV 254 and SUVA (Croue et al., 2000; Liang and Singer, 2003 and Ates et al., 2007). Several researchers have reported that the hydrophobic, aromatic NOM fractions and humic substances are the principal DBP precursors and, therefore DBPFP correlates with $\mathrm{UV}_{254}$ and SUVA levels in the raw water (Croue et al., 2000; Liang and Singer, 2003 and Ates et al., 2007). However, recent research highlights the contributions of the non-aromatic, hydrophilic organic fraction as being an important precursor to DBPFP and, therefore, these raw water $\mathrm{UV}_{254}$ and SUVA values exhibit weak correlations with DBPFP. (Ates et al., 2007).

Generally, research agrees that highly aromatic and high molecular weight (MW) organic compounds are associated with hydrophobic NOM and have been shown to be more amenable to removal by coagulation than hydrophilic NOM (Liang and Singer, 2003; Pernitsky and Edzwald, 2006). Hydrophilic organic matter typically encompass nonaromatic, low MW compounds with a significantly lower charge density than hydrophobic organic matters and are less amenable to removal by coagulation (Liang and Singer, 2003; Pernitsky and Edzwald, 2006).

Coagulation. In drinking water treatment, coagulation is a process in which a chemical coagulant is added to destabilize particles and remove dissolved organic matter through complexation reactions followed by a phase change (Pernitsky, 2003; Pernitsky and Edzwald, 2006). Coagulation processes are followed by a flocculation, or slow mixing, stage that promotes the aggregation of these destabilized particles and precipitation/adsorption of products into larger "floc" particles that are subsequently removed by clarification and/or filtration processes (MWH, 2005). The overall size and density of the floc formed is dependent on the subsequent processes used to remove the flocculated particles. Mixing is also a very important aspect of coagulation and flocculation processes; it is central to (1) the adequate dispersion of the chemical coagulant (rapid mixing during coagulation) and (2) the promotion of contact between particles and the rate of the destabilization and complexation reactions (slow mixing or flocculation) (MWH, 2005).

The four key mechanisms associated with the removal of dissolved NOM and particles
during coagulation processes are enmeshment, adsorption, charge neutralization/destabilization and complexation/precipitation (Pernitsky, 2003). The mechanisms associated with the removal of NOM and particles are very different, therefore, the relative concentrations of these contaminants greatly affect the chemistry of coagulation. As described by Pernitsky and Edzwald (2006), when considering the removal of particles alone, the two primary coagulation mechanisms are (1) charge neutralization of the negatively charged particles by positively charged dissolved metal species and (2) enmeshment of colloids in precipitated metal hydroxide solids. The coagulation mechanisms involved in NOM removal are (1) complexation of NOM with the dissolved metal species that leads to precipitation of NOM-metal complexes, (2) the complexation of NOM with dissolved metal species that is subsequently adsorbed to precipitated metal hydroxide solids and (3) the direct adsorption of NOM onto precipitated metal hydroxide solids (Pernitsky and Edzwald, 2006).

There are many important factors affecting the coagulation of NOM and particles including the overall concentrations of both dissolved metal species and precipitated metal hydroxide solids, the raw water NOM and particle levels, the physical and chemical properties of NOM and particles (particularly the overall charge density of these contaminants) and the pH of coagulation (Pernitsky and Edzwald, 2006). With respect to process control, coagulation dosage and pH are the most important operational parameters for optimizing the overall removal of NOM and particles. However, optimal conditions for turbidity removal are rarely the same as those for NOM removal; in fact, the coagulant demand is usually governed by the concentration of NOM for low turbidity
waters (Gregor et al., 1997; Pernitsky and Edzwald, 2006).

When coagulation occurs, NOM reacts and binds with metal ions and it has been shown by many researchers that the coagulant demand is normally controlled by NOM-metal interactions and not particle-metal interactions (Edzwald, 1993; MWH, 2005; Pernitsky and Edzwald 2006). The negative of NOM in surface waters is generally higher than that of particulate matter and, in turn, is associated with much higher coagulant demands for effective removal (Pernitsky and Edzwald, 2006). For example, Pernitsky and Edzwald (2006) report total negative charge densities for aquatic fulvic acid at 5 to $15 \mu \mathrm{~g} / \mathrm{L}$. The higher the pH , the higher the negative charge due to ionization of carboxyl and phenolic functional groups. The magnitude of negative charge is specific to each organic fraction in the water (hydrophilic versus hydrophobic and the solute classes within each such as humic and fulvic acids). Whereas, for a clay suspension, the total negative charge density ranges from 0.05 to $0.5 \mu \mathrm{~g} / \mathrm{L}$, which are substantially lower than NOM. The higher the pH , the higher the negative charge due to ionization of the metal oxide or hydroxyl group on the surface of the particle (Pernitsky and Edzwald, 2006). In addition, NOM can adsorb on particles and control their particle stability, increasing the negative charge of the particle and requiring higher coagulant dosages to remove them from the water (Pernitsky and Edzwald, 2006). Therefore, the concentration and nature of NOM controls coagulant dosages and overall organic matter removals. This is the case for most raw water combinations, except for very low TOC water and high turbidity water.

Coagulation pH affects the charge density of the dissolved organic matter and particles
and also affects the distribution of the metal species during coagulation. At the pH of minimum solubility, the maximum amount of coagulant is converted to solid phase-floc particles (Pernitsky, 2003). For low pH values, highly charged dissolved metal species are dominant and, as pH values increase, the charge of the dissolved metal species decreases. At pH values much higher than the pH of minimum solubility, negatively charged species begin to dominate. The aluminum hydroxide solid phase formed upon precipitation has a surface charge that is dependent on pH (Pernitsky, 2003). The overall distribution of the metal species are also dependent on temperature, as lower temperatures cause a shift of solubility diagrams to a higher pH range. However, the overall affect of temperature is dependent on the chemical coagulant used (Pernitsky and Edzwald, 2006).

The pH of coagulation and coagulant dosage required for the removal of NOM cannot be predicted because of several influencing factors such as particles, temperature, hardness and anions present, which will affect the speciation of NOM in the water. Nevertheless, some generalizations with respect to pH and dose have been made. As pH increases, humic species become more ionized as carboxyl groups lose protons and the charge of metal coagulants is reduced, therefore dictating higher coagulant dosages. In a higher pH range $(\mathrm{pH}>6.5)$, the metal species present is predominantly in contact with precipitated hydroxide to form amorphous species (Pernitsky and Edzwald, 2006). However, in the low pH range $(\mathrm{pH}<5)$, the metal species is predominantly in a dissolved metal form and the higher charge is more effective for complexation and charge neutralization (Pernitsky and Edzwald, 2006).

Direct Filtration. Direct filtration treatment plants do not include a clarification stage between coagulation and filtration processes. Direct filtration processes are typically used for raw water sources with very low turbidity values ( $<10-\mathrm{NTU}$ ) and low coagulant dosage requirements (Pernitsky and Edzwald, 2006). Due to the limited treatment barriers, direct filtration processes require optimal charge neutralization and optimally sized small "pin-point" floc to ensure acceptable solids loadings are applied to the filters to minimize filter headloss and maximize filter run volumes (Pernitsky and Edzwald, 2006). Dosing to meet NOM removal goals in these facilities leads to high solids loading to the filters and results in early breakthrough, increased head loss rates and, therefore, shorter filter run times (Eikebrokk et al., 2007).

In a direct filtration treatment plant, optimizing coagulation processes based solely on the removal of natural organic matter may cause significant problems with filtration performance and overall particle removals. In these plants, coagulation optimization is the primary means of ensuring optimal filtration performance is achieved and the stringent filtration goals of today's regulatory regime are achieved. In addition, the removal of soluble NOM from low-level turbidity source water presents another practical challenge related to the low concentrations of stable particles available to form acceptable floc (Gregor et al., 1997; Eikebrokk et al., 2007). In direct filtration facilities, coagulation processes must be optimized with multiple performance objectives in mind.

Coagulants Studied. There were four coagulants evaluated during the experiments conducted as part of this research project; alum, ferric sulfate, a medium basicity non-
sulfated (MBNS) PACl and a high basicity non-sulfated (HBNS) ACH. These coagulants were chosen based on preliminary jar testing, coagulant supplier recommendations and recent studies supporting their use for treating similar source waters using direct filtration treatment processes.

Recent research has shown that high basicity PACls are well suited for water sources characterized by low turbidity, organic matter and alkalinity due to the highly charged polymeric species present and the low alkalinity consumption of the coagulant (Pernitsky and Edzwald, 2003; Pernitsky and Edzwald, 2006). Polyaluminum coagulants are produced by the partial neutralization of aluminum salts, which results in the creation of highly charged polymeric species as well as the monomeric species present during alum coagulation (Pernitsky and Edzwald, 2003; Pernitsky and Edzwald, 2006). Polyaluminum coagulants are available in a wide range of strengths and basicities, which refers to their degree of neutralization. The basicity of PACl coagulants that are commercially available ranges from 15 to $85 \%$; with a low basicity corresponding to a $15-35 \%$ and a high basicity representing the $60-85 \%$ range (Pernitsky and Edzwald, 2003; Pernitsky and Edzwald, 2006). The basicity of the coagulant affects both the alkalinity consumption of the coagulant and the aluminum species present during coagulation. As the basicity increases, so does the fraction of polymeric species that is present, whereas, the alkalinity consumption decreases. Therefore, high basicity PACls have a higher fraction of polmeric species and are better suited for low alkalinity waters, whereas the opposite is true for low basicity PACl (Pernitsky and Edzwald, 2003; Pernitsky and Edzwald, 2006).

According to Pernitsky (2011), optimal coagulation performance for aluminum-based coagulants is typically seen at pH values close to the pH of minimum solubility where dissolved aluminum residuals are minimized and the presence of aluminum hydroxide precipitates for subsequent NOM adsorption is maximized. In contrast, ferric-based coagulants are more effective at very low pH values, where positively charged species are present and the overall negative charge of NOM is less (Pernitsky, 2010). Volk et al. (2000) reported that several researchers identified optimal precipitation pH ranges of 4-5 with ferric-based coagulants and at 5-6 with alum. For alum, low pH values $(\mathrm{pH}=5.5)$ maximize organic matter removal, whereas these low pH conditions are not required for PACls (Pernitsky, 2010). Furthermore, Pernitsky and Edzwald (2006) noted optimal PACl and ACH performance at coagulation pH values between 6-7, with higher coagulation pHs being associated with higher basicity products.

### 2.3. EFFECTS OF COAGULANT CHANGEOVERS ON LEAD CORROSION

A particular concern associated with coagulation optimization is the potential unintended consequences of a coagulant change on the distribution system, specifically related to lead release from lead pipe and solder materials. Common coagulants are typically chloride and sulfate based (i.e.; alum, ferric chloride, PACl , ferric sulfate, etc). Therefore, coagulant based changes to a water treatment process can significantly alter the ratio of chloride and sulfate concentrations in the finished water. Following the introduction of new DBP regulations, many utilities were faced with coagulant changeovers, which inevitably resulted in unusual lead leaching issues in their distribution system, which were not easily corrected with the usual corrosion control measures (Dodrill and Edwards, 1995; Edwards et al., 1999). Evidence obtained through
lead release data resulting from practical case studies and laboratory-based studies have demonstrated that a high chloride to sulfate mass ratio (CSMR) induces high galvanic currents and governs lead leaching incidences in distribution systems following coagulant changeovers (Dodrill and Edwards, 1995; Edwards et al., 1999; Dudi, 2004; Edwards and Triantafyllidou, 2007; Nguyen et al., 2010a; Nguyen et al., 2010c). When this research project was initiated, high CSMRs were merely hypothesized as the mechanism of attack and the link between the effect of coagulant changes and CSMR disturbances had not yet been undoubtedly linked to lead release concerns.

Galvanic Corrosion. Galvanic corrosion is induced when dissimilar metals come into contact with each other. In this study, galvanic corrosion is induced by the connection of a lead pipe to a copper pipe (Gregory, 1985; Dudi, 2004; Edwards and Triantafyllidou, 2007). For these specific metals, the galvanic series defines lead as the anode and copper as the cathode (Dudi, 2004). Unlike the case of uniform corrosion of an isolated lead pipe, the anodic and cathodic reactions are separated during galvanic corrosion. The copper surface acts as the cathode and is therefore reduced and protected, whereas the lead surface acts as the anode and it is oxidized and sacrificed. Galvanic corrosion increases the rate of lead corrosion above that which occurs in an isolated lead pipe and the rate of cathodic reactions such as oxygen reduction on the copper pipe surface, and therefore pH , is also increased (Dudi, 2004; Edwards and Triantafyllidou, 2007).

When samples are exposed to flowing water conditions, galvanic corrosion is not an issue
because galvanic currents drop to low levels after only a few weeks of conditioning (Dudi, 2004). However, during stagnation, which is more representative of the conditions related to lead exposure in a household, dissolved oxygen (DO) is depleted over time and acidic conditions at the lead anode increase. Lead leaching is higher for galvanic corrosion due to the higher corrosion rates and the local pH drop at the surface of the lead material due to the production of $\mathrm{Pb}^{2+}$, a lewis acid (Dudi, 2004). The local pH drop at the anode under stagnant conditions has been reported to be as low as 3-4 (Dudi, 2004; Edwards and Triantafillydou, 2007; and Nugyen, 2008). This pH range is low enough such that many corrosion inhibitors will not produce a protective scale on the surface of the anode (Dudi, 2004). Additionally, among other parameters, chloride and sulfate levels have been identified in prior research (e.g. Oliphant, 1983) as being highly influential in controlling lead corrosion rates under these circumstances (Triantafillydou, 2006).

Effect of CSMR. The suspicion of the effect of chloride to sulfate levels on lead release instances is not a new theory, as research relating the ratio of such chemicals to lead release dates back almost thirty years (Oliphant, 1983). It has been demonstrated that the quantities of chloride and sulfate in treated water can affect corrosion behavior in the distribution system. Oliphant (1983) and Gregory (1990) showed increases to galvanic corrosion currents and lead leaching when the CSMR ratio was high in bench-scale studies of lead leaching (Dudi, 2004). CSMR influences the conductivity, or oxidation reduction potential (ORP), of the water; where a high CSMR may cause an increase in water conductivity thereby increasing the rate of galvanic lead corrosion (Edwards and

Triantafyllidou, 2007). There have been several bench and case studies that demonstrated that a high CSMR could cause increased lead leaching into potable water (Gregory, 1985; Dodrill and Edwards, 1995; Dudi, 2004; Edwards and Triantafyllidou, 2007). The greatest impact of these anions is observed under low pH and low dissolved inorganic carbon conditions, such as those present under galvanic and stagnant conditions, where there is less hydroxide and carbonate species available to form complexes with $\mathrm{Pb}^{2+}$ (AWWA, 1996).

The presence of either chloride or sulfate alone tends to protect leaded materials when there is no galvanic connection to another metal. However, when a copper connection exists, chloride is drawn to the anode to maintain electroneutrality and stimulates the attack on lead pipe. At this low pH , chloride breaks down passivity by penetrating films through pores or defects easier then other ions such as sulfate (Reive and Uhlig, 2008). In doing so, chloride dissolves any coating or barrier previously on the lead surface and reacts with the lewis acid to form a soluble lead complex, $\mathrm{PbCl}^{+}$, at these low pH conditions. $\mathrm{PbCl}^{+}$increases the exchange, or galvanic current, for anodic dissolution, therefore increasing lead leaching and preventing the formation of solid barriers on the lead surface (Reive and Uhlig, 2008; Clarke et al., 2008; Nguyen et al., 2008). Whereas, sufficient levels of sulfate are drawn to the anode and protects the pipe. $\mathrm{PbSO}_{4(\mathrm{~s})}$ is insoluble at the local pH drop occurring at the anode, therefore acting as a corrosion inhibitor by strengthening the arrangement of the corrosion protective layer on the lead surface (Dudi, 2004; Clarke et al., 2008; Nguyen et al., 2008).

When chloride and sulfate co-exist in a distribution system, the concentration of sulfate must be sufficient to overcome the counteractive effects of $\mathrm{Cl}^{-}$and increase the strength of the corrosion scale (Edwards and Triantafllidou, 2007). Existing solubility models indicate that $\mathrm{PbSO}_{4}(\mathrm{~s})$ can form on the surface of lead anodes despite the depression in pH when sulfate levels become high enough, tending to decrease leaching at the lead surface (Clarke and Edwards, 2008). On the other hand, solubility models predict that higher chloride increases lead solubility by formation of $\mathrm{PbCl}^{+}$under these low pH conditions. The critical CSMR level cited from multiple bench scale and full-scale studies that governs the effects of lead leaching is 0.5 mg of chloride per mg of sulfate (Gregory, 1985, Dodrill and Edwards, 1995). Above this level, galvanic corrosion of lead pipe is increased and below this threshold, lead leaching is mitigated.

According to DeSantis et al. (2009), the mineralogy of corrosion solids that develop at the lead-copper joints are different then the "normal" solids on the adjacent pipe surface (uniform lead corrosion environment). The dissimilar nature of these galvanic deposits indicates that the water quality in this zone differs from that of the bulk water quality in the distribution system. This agrees well with experimental observations of a large pH depression at the lead anode. Evidence of $\mathrm{Cl}^{-}$and $\mathrm{SO}_{4}{ }^{2+}$ corrosion products in this area confirm that there are apparent zones of aggression for these ions. Additionally, the mineralogy of the corrosion scales varied from system to system.

## CHAPTER 3 MATERIALS AND METHODS

The purpose of this chapter is to describe raw source water characteristics, and the equipment and analytical procedures that are common to the experimental designs presented in Chapters 5, 6, 7 and 8. For clarity, materials and methods that are chapter specific will be described within that particular chapter, as well as any statistical analysis performed on the data.

This research involved the testing of Pockwock Lake raw water, which is treated at the JD Kline Water Supply Plant (JDKWSP) and provides drinking water for the greater Halifax area in Halifax, Nova Scotia, Canada.

### 3.1. POCKWOCK LAKE SOURCE WATER

The JDKWSP is a surface water treatment plant that draws water from the nearby Pockwock Lake. Pockwock Lake is in a protected watershed with no industrial or municipal waste influence. Low levels of pH , alkalinity, turbidity and organic carbon, as presented in Ta , characterize the raw water.

Table 3.1 Raw Source Water Characteristics

| Analyte | Warm Water$\text { (10 to } 20-{ }^{\circ} C \text { ) }$ |  | Cold Water$\text { (2 to } 10-{ }^{\circ} \mathrm{C} \text { ) }$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  | Range | Average | Range | Average |
| Temperature - ${ }^{\circ} \mathrm{C}$ | 11.6-20.9 | 16.2 | $1.0-9.6$ | 4.0 |
| pH | $4.9-5.4$ | 5.1 | $4.9-5.3$ | 5.0 |
| Alkalinity - mg/L as $\mathrm{CaCo}_{3}$ | --- | $<1$ | --- | $<1$ |
| Turbidity - NTU | 0.28-0.49 | 0.39 | 0.29-0.46 | 0.37 |
| UV $254-\mathrm{cm}^{-1}$ | 0.051-0.085 | 0.069 | 0.082-0.103 | 0.093 |
| TOC - mg/L | $1.412-2.947$ | 2.545 | $2.771-3.337$ | 2.940 |
| DOC - mg/L | 1.808-3.221 | 2.612 | 2.056-3.184 | 2.858 |
| SUVA - $\boldsymbol{m}^{-1}$ per $m g / L$ of DOC | $2.8-4.2$ | 3.3 | $2.0-2.9$ | 2.5 |

### 3.2. JD KLINE WSP OVERVIEW

The JDKWSP is a direct filtration treatment plant that employs pre-screening, oxidation, pre-chlorination, coagulation, hydraulic flocculation, direct filtration and chlorination. In the first pre-mix tank, lime is added to adjust the $\mathrm{pH}(9.6-10)$ for oxidation of iron and manganese using potassium permanganate $\left(\mathrm{KMnO}_{4}\right)$ and the second pre-mix tank provides additional mixing and detention time for this oxidation process. In the third premix tank, carbon dioxide $\left(\mathrm{CO}_{2}\right)$ is added to adjust the coagulation $\mathrm{pH}(5.5-6.0)$ and alum is added as the primary coagulant at an average dosage of $8 \mathrm{mg} / \mathrm{L}$. During the cold weather months (November through June), a cationic polymer is required to strengthen floc and maintain turbidity performance at an average dosage of $0.05 \mathrm{mg} / \mathrm{L}$. Prechlorination occurs in the third pre-mix tank to control biofilm occurrence in the filters and is maintained at a post-filter total chlorine residual concentration of $0.05 \mathrm{mg} / \mathrm{L}$. Next, water is delivered to four identical flocculation trains that contain three rows of parallel sets of cells ( 6 cells total). Tapered, hydraulic, flocculation occurs in these cells. Next, the flow is distributed between eight dual-media anthracite and sand filters. Finished water
chemicals include the addition of chlorine for disinfection to maintain a total chlorine residual of $1.0 \mathrm{mg} / \mathrm{L}$, sodium hydroxide to a finished water pH of 7.4 , zinc/ortho polyphosphate for corrosion control $\left(0.5 \mathrm{mg} / \mathrm{L}\right.$ as $\left.\mathrm{PO}_{4}\right)$ and hydrofluosilicic acid to provide fluoride addition for dental health.

### 3.3. PILOT PLANT DESCRIPTION

The JDKWSP pilot-scale plant consists of two identical, parallel treatment trains, both capable of simulating direct filtration or conventional treatment processes, manufactured by Intuitech, Inc (Salt Lake City, Utah). The pilot plant operates using Pockwock Lake raw water at a design flow rate of $15-\mathrm{L} / \mathrm{min}$ delivered to each treatment train. Each pilot train contains two treatment skids that contain coagulation, flocculation, sedimentation and filtration processes. A schematic and pictures of the pilot plant are presented in figures 3.1, 3.2 and 3.3.


Figure 3.1 JDKWSP pilot plant treatment process schematic.


Figure 3.2 Photo of pilot plant coagulation, flocculation and sedimentation skid.


Figure 3.3 Photo of pilot plant filtration skid.

Raw water enters the coagulation/ flocculation skid into a series of three 11.3-L rapid mix tanks where chemical addition and mixing occur. The pilot plant has the capacity to feed 6 separate chemicals through peristaltic pumps to the chemical injection ports in the rapid mix tanks. From the rapid mix tanks, water flows into a series of three 189-L mechanical flocculation tanks with paddle mixers and then on to the optional sedimentation tank. The sedimentation tank is a 330-L basin with 30 adjustable plates, each with settling area of $0.1-\mathrm{m}^{2}$. The clarified water is collected in a settled water basin, after passing over the settling plates, and sludge can be pumped to a sampling port or to waste. If direct filtration is desired, the sedimentation tank can be bypassed and the flow is directed straight to the filtration skid.

The pilot plant was operated as a direct filtration plant for the duration of this research project. The filtration skid was built to match the bed depths and weir elevations of the full scale plant and contains a series of three $200-\mathrm{mm}$ ( 8 -inch) diameter dual-media filters containing $61-\mathrm{cm}(2-\mathrm{ft})$ of anthracite and $30.5-\mathrm{cm}(1-\mathrm{ft})$ of sand. There is no capability to add finished water chemicals at the pilot scale. The plant contains inline equipment to monitor pH , temperature, and turbidity at all critical process control points.

This fully automated plant has the flexibility to modify process variables such as chemical dosages, mixing energy, detention times, overflow rates, backwash sequences and filtration rates and the capability to extract water for analysis at any location throughout the treatment process. The pilot plant chemical system is capable of storing
and feeding currently used chemicals and a wide spectrum of potential chemicals over a wide range of dosages.

### 3.4. ANALYTICAL PROCEDURES

Experimental parameters that were monitored throughout this research include pH , turbidity, TOC, DOC, $\mathrm{UV}_{254}$, temperature, alkalinity, THMFP, HAAFP, and HPSEC.

General Water Quality Parameters. Throughout the duration of this research, reverse osmosis (RO) water was used for all cleaning and chemical stock preparations. All glassware was rinsed 3 times using RO water following cleaning. The RO water was obtained from a Milli- $Q^{\circledR}$ purification system. Combination $\mathrm{pH} / \mathrm{mV} /$ Temperature/ DO/ ISE and Conductivity meters (Accumet* XL 25 and XL 60 models) with plastic bodied, gel-filled, combination pH electrodes (Accumet Accu-Cap*) were used for pH readings. Three-point calibration ( $\mathrm{pH} 4,7,10$ ) was conducted each day. Alkalinity analysis was measured according to the potentiometric titration method 2320 (Standard Methods, 1998). A Hach 2100 N laboratory turbidity meter was used for all bench-scale turbidity measurements.

The pilot plant contains inline Hach 1720E low range process turbidimeters to monitor filtered water turbidity and are located on the effluent stream of each individual filter on both pilot trains. When comparing filter run data between the pilot scale and FSP, in-line effluent turbidity data was extracted from HW's online monitoring system that was measured using Hach 1720 series low range process turbidimeters.

Organic Matter. TOC and DOC samples were collected head-space free in $40-\mathrm{mL}$ precleaned glass vials and preserved with concentrated phosphoric acid to a $\mathrm{pH}<2$. Before sample collection, DOC samples were filtered through $0.45-\mu \mathrm{m}$ polysulfone filter membrane (GE Water \& Process Technologies) that had been pre-rinsed with $500-\mathrm{mL}$ of RO water. TOC and DOC measurements were performed using a TOC-V CPH analyzer with a Shimadzu ASI-V autosampler and catalytically aided combustion oxidation nondispersive infrared detector (NDIR) having a method detection limit of $0.08-\mathrm{mg} / \mathrm{L}$ (Shimadzu Corporation, Kyoto, Japan). For TOC and DOC analysis, the TOC analyzer operating conditions were as follows: TOC standard platinum catalyst; injector volume $50-\mu \mathrm{L}$; oven temperature $680^{\circ} \mathrm{C}$; carrier gas flow $150 \mathrm{~mL} / \mathrm{min}$; potassium hydrogen phthalate standards 0 to $10-\mathrm{mg} / \mathrm{L}$; correlation $>0.99$.

UV absorbance at 254-nm $\left(\mathrm{UV}_{254}\right)$ was measured using a HACH DR/4000 UV/VIS spectrophotometer (Hach Company, Loveland, CO) at a wavelength of 254 nm . Before sample collection, $\mathrm{UV}_{254}$ samples were filtered through $0.45-\mu \mathrm{m}$ polsulfone filter membrane (GE Water \& Process Technologies) that had been pre-rinsed with $500-\mathrm{mL}$ of RO water. The nature of NOM in water samples was assessed by calculating the specific $\mathrm{UV}_{254}$ absorbance or SUVA value. SUVA is reported in units of $\mathrm{m}^{-1}$ of absorbance per $\mathrm{mg} / \mathrm{L}$ and was calculated based on the following equation:

$$
\operatorname{SUVA}\left(\mathrm{m}^{-1} / \mathrm{mg} / \mathrm{L}\right)=\frac{\mathrm{UV}_{254}\left(\mathrm{~cm}^{-1}\right)}{\operatorname{DOC}(\mathrm{mg} / \mathrm{L})} * \frac{100 \mathrm{~cm}}{\mathrm{~m}}
$$

Disinfection By-products. THMFP and HAAFP were analyzed using Standard Method 5710 (APHA, 2005) with minor modifications. Samples were buffered to a pH of 8 with borate and incubated for 24 hours following chlorination. Samples were dosed with 1.0$\mathrm{mg} / \mathrm{L}$ of buffered free chlorine to simulate current JDKWSP dosing conditions. THM and HAA samples were then prepared for gas chromatography analysis using liquidliquid extraction (LLE) with pentane and methyl tert-butyl ether (MTBE), correspondingly. Gas chromatography using a Varian CP-3800 GC equipped with a VF-5 column and a Varian CP-8400 auto-sampler, coupled with an electron capture detector (GC-ECD) were used for the detection of THMs and HAAs according to the US EPA Methods 551.1 and 552.2. A a Varian CP-3800 GC equipped with a VF-5 column was used to analayze GC measurements. Samples were analyzed for four THM compounds: chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform. Samples were analyzed for 9 haloacetic acid analytes ( $\mathrm{HAA}_{9}$ ): monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA) and tribromoacetic acid (TBAA).

For THM determination, the gas chromatograph (GC) operating conditions were as follows: injector temperature $220^{\circ} \mathrm{C}$; detector temperature $320^{\circ} \mathrm{C}$; injection volume $1 \mu \mathrm{~L}$; flow rate $1 \mathrm{~mL} / \mathrm{min}$; sample injected at $50^{\circ} \mathrm{C}$ and held for 7 minutes, temperature increased to $115^{\circ} \mathrm{C}$ at a rate of $5 \mathrm{C} / \mathrm{min}$ with no hold, temperature increased to $295^{\circ} \mathrm{C}$ at a
rate of $50 \mathrm{C} / \mathrm{min}$ and held for 0.5 minutes. A coefficient of determination $\mathrm{R}^{2}>0.95$ was consistently achieved for the calibration curves for all four THM compounds.

For HAA determination, the gas chromatograph (GC) operating conditions were as follows: injector temperature $200^{\circ} \mathrm{C}$; detector temperature $300^{\circ} \mathrm{C}$; injection volume $1 \mu \mathrm{~L}$; flow rate $1 \mathrm{~mL} / \mathrm{min}$; sample injected at $35^{\circ} \mathrm{C}$ and held for 10 minutes, temperature increased to $65^{\circ} \mathrm{C}$ at a rate of $2.5 \mathrm{C} / \mathrm{min}$ with no hold, temperature increased to $85^{\circ} \mathrm{C}$ at a rate of $10 \mathrm{C} / \mathrm{min}$ with no hold, temperature is increased to $205^{\circ} \mathrm{C}$ at a rate of $20 \mathrm{C} / \mathrm{min}$ and held for 7 minutes. A coefficient of determination $\mathrm{R}^{2}>0.95$ was consistently achieved for the calibration curves for all nine HAA analytes.

To validate the precision and accuracy of the THM and HAA methods, method blanks (RO water) and quality control (QC) samples (RO spiked with a known amount of standard mixture) were prepared for every 15 samples, for any given analysis. Recovery testing was conducted on QC samples and results were only accepted if QC recoveries were between 70 and $130 \%$.

Size Exclusion Chromatography. Molecular size distribution of organic fractions was determined by HPSEC using high performance liquid chromatography (HPLC, Perkin Elmer Series 200). Prior to analysis, samples were brought to a pH of 3-7 and passed through a $0.45 \mu \mathrm{~m}$ filter membrane. Samples were evaluated using a TSK G3000SW column ( 7.5 mm X 300 mm ) with a TSKgel SW guard column ( 7.5 mm X 70 mm ). The media in the TSK column consists of silica with a pore size of $10 \mu \mathrm{~m}$. These columns
were connected to the Perkin Elmer Series 200 Autosampler and a UV/Vis detector set at UV 254 nm . Samples of $20 \mu \mathrm{l}$ were injected and passed through the columns at a flow rate of $0.7 \mathrm{~mL} / \mathrm{min}$. A sample run time of 30 min was established, whereby all of the compounds in the sample had passed through the column. The molecular size calibration for the column was conducted using sodium polystyrene sulfonate standards (Scientific Polymer Products Inc) with different MWs: 14900, 7540, 5180 and 1530 Daltons (Da). A coefficient of determination $\left(\mathrm{R}^{2}\right)$ greater than 0.90 was consistently achieved.

Coagulant Properties. The coagulants used in this research were alum, ferric sulfate, a MBNS PACl and a HBNS ACH. The alum used in this research was supplied by General Chemical and the ferric sulfate, PACl and ACH were prepared by Kiemera Water Solutions Inc. Table 3.2 summarizes the properties of each coagulant used in this research.

Table 3.2 Coagulant Properties

|  | Alum | Ferric Sulfate | PACl (MBNS) | ACH (HBNS) |
| :---: | :---: | :---: | :---: | :---: |
| Trade Name | Liquid Alum | Ferric Sulfate Solution | PAX-18 | PAX-XL 1900 |
| Chemical <br> Formula | $\mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3} * 14 \mathrm{H}_{2} \mathrm{O}$ | $\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3} * 9 \mathrm{H}_{2} \mathrm{O}$ | $\begin{gathered} \mathrm{Al}_{2}(\mathrm{OH})_{\mathrm{x}} \mathrm{Cl}_{6 \mathrm{c}}-\mathrm{x} \\ 0<\mathrm{x}>6 \end{gathered}$ | $\mathrm{Al}_{2}(\mathrm{OH})_{5} \mathrm{Cl} * 2 \mathrm{H}_{2} \mathrm{O}$ |
| Concentration Supplied (w/w) | $\begin{gathered} 48.5 \% \\ \mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3} * 14 \mathrm{H}_{2} \mathrm{O} \end{gathered}$ | $\begin{gathered} 50-66 \% \\ \mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3} * 9 \mathrm{H}_{2} \mathrm{O} \end{gathered}$ | $\begin{gathered} 8-24 \% \\ \mathrm{Al}_{2}(\mathrm{OH})_{\mathrm{x}} \mathrm{Cl}_{6 \mathrm{c}}-\mathrm{x} \\ 0<\mathrm{x}>6 \end{gathered}$ | $\begin{gathered} 30-60 \% \\ \mathrm{Al}_{2}(\mathrm{OH})_{5} \mathrm{Cl} .2 \mathrm{H}_{2} \mathrm{O} \end{gathered}$ |
| \% Al or Fe <br> Supplied | 4.2-4.4 as Al | $12-13$ as Fe | $8.8-9.2$ as Al | 12.1 - 12.7 as Al |
| Specific Gravity | 1.335 | 1.38-1.59 | 1.15-1.40 | 1.33-1.34 |
| pH (neat) | $2.0-2.4$ | $<2$ | 0.6-1.2 | 4.0-4.4 |
| Basicity (\%) | 0 | 0 | 40-44 | 80 |
| Sulfate (\% wt) | 23.4 | --- | 0 | 0 |

## CHAPTER 4 PAIRING A PILOT-PLANT TO A DIRECT FILTRATION WATER TREATMENT PLANT

### 4.1. ABSTRACT

Pilot-scale drinking water treatment plants are commonly used as investigative tools in the implementation of water quality research programs and to develop effective treatment solutions for full-scale facilities. A successful research program requires that a series of pilot proving experiments be completed to validate that a pilot plant can indeed be used as an effective research tool. This paper outlines experiments that were conducted to establish that statistically equivalent intermittent and finished water quality was demonstrated between pilot treatment trains and the full-scale plant (FSP). First, equivalence was successfully established between the two pilot trains using paired t-tests to confirm that the two trains were producing statistically equivalent water quality (e.g., pH , turbidity) while operating under identical operational and process conditions. Secondly, hypothesized mean differences and paired t-tests were effectively applied to confirm the water quality achieved following each treatment phase in the pilot plant mimicked the corresponding treatment process in the FSP. Successive trials demonstrated equivalence in multiple water quality parameters throughout the two treatment scales, including $\mathrm{pH}, \mathrm{UV}_{254}$, total organic (TOC), dissolved organic carbon (DOC), alkalinity and turbidity. The validation process successfully demonstrated that the pilot plant has the ability to reproduce full-scale behavior and that the results of the pilot research at this facility are in fact real of process changes that, when implemented at full scale, will successfully optimize the performance of the FSP.

### 4.2. INTRODUCTION

Pilot operations and pilot water treatment plants have been used as valuable pre-design tools that are constructed and operated with the intention of generating information to predict the behavior of proposed larger facilities. In recent years, pilot plants have also been erected to facilitate the optimization of current treatment processes, in which case they become more of a calibration tool and allow utilities to test and confirm treatment optimization options before full-scale implementation is attempted. Thus, pilot-plants serve to close the gap between bench and full-scale studies.

Another key advantage of a pilot plant is its ability to study multi-objective issues simultaneously and confirm the effects of variables acting independently and in combination throughout the treatment processes. Identical treatment trains are essential during pilot studies to ensure that the effects of changing raw water characteristics are eliminated by continuously operating one side of the plant such that the same finished water quality as the full-scale plant (FSP) is continuously achieved (Anderson et al., 1993; Bonnet et al., 1996; Piirtola, 1999; Andrews et al., 2005). Following pilot plant installation, both commissioning and proving processes are essential to ensure the plant is installed and operating according to design specifications and also to confirm that equivalent influent, intermittent and finished water quality can be demonstrated between both the parallel pilot trains and the FSP (Anderson et al., 1993; Andrews et al., 2005).

The pilot-plant proving process involves operating the commissioned pilot plant and making the necessary adjustments to ensure the aforementioned criteria are achieved.

This validation procedure is completed to make certain the results of the pilot research are representative of process changes that, when implemented at full scale, will successfully optimize the performance of the plant (Anderson et al., 1993; Bonnet et al., 1996; Piirtola, 1999; Andrews et al., 2005). Therefore, several control experiments must be carried out to establish the pilot and FSP treatment processes produce statistically equivalent results. First, equivalence must be established between the two pilot trains using statistical tests to confirm that the two trains are producing equivalent water quality while operating under identical operational and process conditions. Secondly, the water quality achieved following each treatment phase in the individual pilot plants must mimic the water quality produced in the corresponding treatment process in the FSP. Both of these proving procedures must be successfully completed before detailed optimization experiments can be undertaken and the intended research projects commence.

Objectives. This paper provides details concerning the proving process of a drinking water pilot treatment plant. Specifically, it outlines the experimental and statistical validation procedures used to verify that the pilot treatment process replicates that of a direction filtration plant and that the two pilot treatment trains produced equivalent water quality. A particular challenge of this validation process was the inherent difference in flocculation mixing technologies between the pilot plant mechanical mixers and the fullscale hydraulic flocculators. It is the aim of this paper to provide utilities with a framework for conducting in-house pilot proving trials at their facilities.

### 4.3. MATERIALS AND METHODS

Source Water. This project was conducted at the JD Kline Water Supply Plant (JDKWSP) in Halifax, Nova Scotia, Canada. Low levels of pH, alkalinity, turbidity and organic carbon characterize the raw water. Table 4.1 outlines the source water characteristics during the pilot proving trials.

JD Kline Water Supply Plant. The JDKWSP is a direct filtration treatment plant that employs pre-screening, oxidation, pre-chlorination, coagulation, hydraulic flocculation, direct filtration and chlorination. In the first pre-mix tank, lime is added to adjust the pH (9.6-10) for oxidation of iron and manganese using potassium permanganate $\left(\mathrm{KMnO}_{4}\right)$ and the second pre-mix tank provides additional mixing and detention time for this oxidation process. In the third pre-mix tank, carbon dioxide $\left(\mathrm{CO}_{2}\right)$ is added to adjust the coagulation $\mathrm{pH}(5.5-6.0)$ and aluminum sulfate (alum) is added as the primary coagulant at an average dosage of $8-\mathrm{mg} / \mathrm{L}$. During the cold weather months (November through June), a cationic polymer is required to strengthen floc and maintain turbidity performance, at an average dosage of $0.05-\mathrm{mg} / \mathrm{L}$. Pre-chlorination also occurs in the third pre-mix tank to control biofilm occurrence in the filters and is maintained at a post-filter total chlorine residual of $0.05-\mathrm{mg} / \mathrm{L}$. Next, water is delivered to four identical flocculation trains that contain three rows of parallel sets of cells (6 cells total). Tapered, hydraulic, flocculation occurs in these cells. Next, the flow is distributed between eight dual-media anthracite and sand filters. Finished water chemicals include the addition of chlorine for disinfection to maintain a total chlorine residual of $1.0-\mathrm{mg} / \mathrm{L}$, sodium hydroxide to a finished water pH of 7.4 , zinc/ortho polyphosphate for corrosion control
$\left(0.5-\mathrm{mg} / \mathrm{L}\right.$ as $\left.\mathrm{PO}_{4}\right)$ and hydroflurosilicic acid to provide fluoride addition for dental health.

Pilot Plant Description. The JDKWSP pilot-scale plant consists of two identical, parallel treatment trains, both capable of simulating direct filtration or conventional treatment processes, manufactured by Intuitech, Inc (Salt Lake City, Utah). The pilot plant uses Pockwock Lake as its raw water source and has a design flow rate of $15-\mathrm{L} / \mathrm{min}$ delivered to each treatment train. Figure 4.1 shows a process schematic of the treatment processes at the JDKWSP pilot plant. Each pilot train contains two treatment trains that contain coagulation, flocculation and filtration processes. Raw water enters the coagulation/ flocculation skid into a series of three 11.3-L rapid mix tanks where chemical addition and mixing occur. The pilot plant has the capacity to feed 6 separate chemicals through peristaltic pumps to the chemical injection ports in the rapid mix tanks. From the rapid mix tanks, water flows into a series of three 189-L mechanical flocculation tanks with paddle mixers and then on to the optional sedimentation tank. The sedimentation tank is a 330-L basin with 30 adjustable plates, each with settling area of $0.1-\mathrm{m}^{2}$. The clarified water is collected in a settled water basin, after passing over the settling plates, and sludge can be pumped to a sampling port or to waste. If direct filtration is desired, the sedimentation tank can be bypassed and the flow is directed straight to the filtration skid.

The pilot plant was operated as a direct filtration plant for the duration of this research project. The filtration skid was built to match the bed depths and weir elevations of the
full scale plant and contains a series of three $200-\mathrm{mm}$ (8-in) diameter dual-media filters containing $61-\mathrm{cm}(2-\mathrm{ft})$ of anthracite and $30.5-\mathrm{cm}(1-\mathrm{ft})$ of sand. There is no capability to add finished water chemicals at the pilot scale.

This fully automated plant has the flexibility to modify process variables such as chemical dosages, mixing energy, detention times, overflow rates, backwash sequences and filtration rates and the capability to extract water analysis at any location throughout the treatment process. The pilot plant chemical system is capable of storing and feeding currently used chemicals and a wide spectrum of potential chemicals over a range of dosages. The plant contains inline equipment to monitor pH , temperature, turbidity and particle counts at all critical process control points.

### 4.3.1. Experimental Procedures

The pilot proving methodology was based on both the successes and lessons learned from pilot studies carried out in Ottawa and Windsor, Ontario (Anderson et al., 1993).

Comparison of Pilot Treatment Trains. The first proving step is to ensure equivalence is established between the two pilot trains using a paired t-test to confirm that the two trains are producing statistically equivalent water quality while operating under identical operational and treatment conditions (Anderson et al., 1993). These operating conditions were chosen to simulate the FSP to the extent possible, such that this initial proving stage could provide some insight to the second task of proving, which is adjusting the pilot trains to simulate the full scale performance. The selected operating conditions were synchronized between the parallel pilot trains.

Table 4.2 presents the operating conditions of the parallel pilot trains and FSP during the pilot proving trials (e.g., chemical dosages, mixing speeds, retention times). Since the pilot plant utilizes mechanical mixers, low G-values were chosen to emulate, to the extent possible, the inadequate hydraulic mixing intensities identified through computational fluid dynamics (CFD) modeling in the FSP (Vadasarukkai and Gagnon, 2010). The backwash procedures of filters 1 and 2 on each pilot train were set to simulate the FSP backwash procedure, whereas filter 3 was programmed to simulate an extended terminal sub-fluidization wash (ETSW) on each train. During pilot proving experiments, the filter loading rates were set approximately $40 \%$ higher than the FSP filter loading rates so that experimental time was reduced (Table 4.2).

Each pilot-to-pilot proving trial corresponded with a 48-h filter run time in the pilot plant. A filter run time of $48-\mathrm{h}$ in the pilot plant produced the same number (360) of unit filter run volumes (UFRV) as an 80-hr filter run in the FSP. The trials began with a backwash of each pilot filter and 1-L grab samples were collected at $10-\mathrm{mins}, 4-\mathrm{h}, 24-\mathrm{h}, 28-\mathrm{h}$, and 48-h into the filter run. The $10-\mathrm{min}$ sample time was intended to encompass the water quality during the ripening phase, which was an important filtration step to simulate between the pilot trains. Grab samples were collected from the raw water inlet (RW), post-coagulation (PM3), post-flocculation (Floc 3), and post-filtration (Fil-1, Fil-2 and Fil-3) on each pilot train (Figure 4.1). The grab samples were analyzed for a range of response parameters including $\mathrm{pH}, \mathrm{UV}_{254}$, turbidity, $\mathrm{TOC}, \mathrm{DOC}$ and alkalinity. Additionally, in-line turbidity data for effluent filtered water was collected for each pilot filter.

Paired t-testing was used to determine if the two pilot trains were operating identically. Assessing statistical equivalence using paired t-tests at the 0.05 level of significance is commonly used for validating parallel treatment system performance and also for comparing population differences between the parallel treatment systems during research trials (Anderson et al., 1993; Piirtola et al., 1999; Andrews et al., 2005). Paired t-testing eliminates uncontrolled disturbances, such as changing raw water quality, by ensuring that the uncontrolled factors contribute equally to both of the paired observations (MacBerthouex and Brown, 2002). A response parameter or data point from pilot plant train 1 (PP1) was directly compared with the corresponding data (location and time) collected from pilot plant train 2 (PP2). If the pilot trains were producing equivalent water quality, then ideally the expected difference between the two values forming the data pair would be zero (Anderson et al., 1993; Andrews et al., 2005). Pilot trials continued until the results were deemed not significantly different at the $95 \%$ confidence interval.

Comparison of Pilot Plant and Full Scale Performance. After demonstrating equivalence between the two sides of the pilot plant, the next step was to prove that the pilot plant and full-scale treatment systems were achieving the same intermittent and finished water quality (Anderson et al., 1993; Bonnet et al., 1996; Andrews et al., 2005).

During this proving task the FSP filters were achieving 72-hr filter runs. Due to differences in filter loading rates, a 72-hr filter run time in the FSP was equivalent to a 43-hr filter run time in the pilot or approximately 32 million liters of water per square
meter of filter media ( $\mathrm{ML} / \mathrm{m}^{2}$ ) being processed by each scale of filter. The trials began with a simultaneous backwash of each pilot filter and the FSP filter to eliminate the effects of changing water quality. From the pilot plant, 24-h and 28-h 1-L grab samples were collected, which represented 180 and 210 UFRV, respectively. 28-h and 48-h 1-L grab samples were collected in the FSP, which corresponded to 125 and 214 UFRV, respectively. The 24 -h pilot and 28-h FSP samples and 28-h pilot and 48-h FSP samples were compared during the statistical analysis. For each treatment scale, grab samples were taken from the raw water inlet (RW) and the post-coagulation (PM3), postflocculation (Floc3), and post-filtration (Fil) stages in PP2 and the FSP. The grab samples were analyzed for a range of response parameters including $\mathrm{pH}, \mathrm{UV}_{254}, \mathrm{TOC}$, and DOC. Additionally, in-line turbidity data for effluent filtered water was collected for each filter.

Since equivalence between the two pilot trains was completed first, for the pilot-to-FSP proving stage, equivalence was only determined between one pilot train, PP2, and the FSP. The only difference between operating conditions used in pilot-to-pilot proving and the pilot-to-FSP trials were the backwash procedures used. During pilot-to-FSP proving trials, the full-scale filter backwash procedure was modified from the plants original design conditions to optimize ripening profiles and a 1-h rest period was added to the end of the normal backwash procedure. Thus, a 1-h rest period was inserted at the end of the normal backwash cycle in PP2. Of the eight FSP filters, the same filter was sampled throughout the proving process to remove any unnecessary variability in filter performance.

To determine equivalence, as described by Anderson et al. (1993), a set of performance criteria was established based on acceptable variation limits between the pilot and fullscale systems, since it is generally recognized that performance may not be exactly duplicated between the two scales. Pilot-to-FSP trials were repeated until the pilot plant was producing statistically equivalent water quality to the FSP.

### 4.3.2. Analytical Procedures

Throughout the duration of this research, RO water was used for all cleaning and chemical stock preparations. All glassware was rinsed 3 times using RO water following cleaning. The RO water was obtained from a Milli- $Q^{\circledR}$ purification system. Combination $\mathrm{pH} / \mathrm{mV} /$ Temperature/ DO/ ISE and Conductivity meters (Accumet* XL 25 and XL 60 models) with plastic bodied, gel-filled, combination pH electrodes (Accumet Accu-Cap*) were used for pH readings. Three-point calibration ( $\mathrm{pH} 4,7,10$ ) was conducted each day. Alkalinity was carried out according to the potentiometric titration method 2320 (Standard Methods, 1998). A Hach 2100N laboratory turbidity meter was used for all bench-scale turbidity measurements.

The pilot plant contained inline Hach 1720E low range process turbidimeters to monitor filtered water turbidity and are located on the effluent stream of each individual filter on both pilot trains. When comparing filter run data between the pilot scale and FSP, in-line effluent turbidity data was extracted from HW's online monitoring system that was measured using Hach 1720 series low range process turbidimeters.

TOC and DOC samples were collected head-space free in $40-\mathrm{mL}$ pre-cleaned glass vials and preserved with concentrated phosphoric acid to a $\mathrm{pH}<2$ and measurements were performed using a TOC-V CPH analyzer with a Shimadzu ASI-V autosampler and catalytically aided combustion oxidation non-dispersive infrared detector (NDIR) having a method detection limit of $0.08 \mathrm{mg} / \mathrm{L}$ (Shimadzu Corporation, Kyoto, Japan). UV absorbance at 254-nm $\left(\mathrm{UV}_{254}\right)$ was measured using a Hach DR/4000 UV/VIS spectrophotometer (Hach Company, Loveland, CO) at a wavelength of 254 nm . Before sample collection, $\mathrm{UV}_{254}$ and DOC samples were filtered through a $0.45 \mu \mathrm{~m}$ filter membrane (GE Water \& Process Technologies) that had been pre-rinsed with $500-\mathrm{mL}$ of RO water.

### 4.4. RESULTS AND DISCUSSION

The proving process took several months to complete, due to the variability of parameters beyond the control of the operator, such as seasonal variations in temperature and organics loading, flow rate variations, chemical feed issues and general operational issues not identified during the commissioning process. Before pilot proving began, the operating conditions of the pilot plant were set to mimic, to the extent possible, the operating conditions of the FSP. Setting and maintaining target pH goals in the pilot plant was the most challenging operational task, due to chemical feed issues in the pilot plant which were in a large part due to the challenges of feeding lime at the pilot scale. Such challenges included adequately mixing lime slurries, differences in lime quality and feed lines clogging, which inevitably lead to inconsistent feed concentrations caused by the aforementioned issues. Such pre-proving tasks are normal when you consider the amount of time a FSP takes to be properly commissioned and operate within design
conditions.

Comparison of Pilot Plant Treatment Trains. In total, four pilot-to-pilot proving trials were completed during the months of February through March, 2008. Initially, a statistical analysis was conducted on each baseline parameter measured utilizing a paired t-test analysis. Although the results from the paired t-test were generally favourable at the $95 \%$ confidence interval (Table 4.3), a small number of parameters (6 of 30) did fail this test. Contrastingly, in a pilot plant validation study completed by Andrews et al. (2005), the majority of parameters measured between the parallel trains were not statistically equivalent at the 0.05 level of significance.

The statistical analysis did not incorporate measurement error, therefore a residuals analysis was conducted for each bench-scale parameter measured and these errors were checked for randomness by plotting the residuals (MacBerthouex and Brown, 2002). Profiles of the residuals for representative proving parameters measured ( pH and DOC) are presented in Figure 4.2. Residuals plots suggested that the errors were random and, additionally, the average of residuals for each measured parameter was zero (MacBerthouex and Brown, 2002). The upper and lower boundary lines shown in Figure 4.2 represent two standard deviations of the residual population mean. These boundaries were determined for each analyte measured (Table 4.3) and were used to assess the system tolerance between the pilot-trials by inserting these limits as the hypothesized mean differences in the paired t-tests.

All parameters measured during pilot-to-pilot proving trials markedly passed the revised paired t -test analysis using the measurement errors as the hypothesized mean differences (Table 4.3). Therefore, the pilot-plants were found to be statistically equivalent for pH , $\mathrm{UV}_{254}$, TOC, DOC, and alkalinity. A comparison of the mean differences between the paired pilot samples for pH and DOC over the duration of the pilot-to-pilot proving process is provided in Figure 4.3. Overall, the mean differences between paired samples measured for each parameter were very minor at each stage of the treatment process (Table 4.3) and the differences reported were below $0.1-\mathrm{mg} / \mathrm{L}$ for TOC and DOC, 0.002-$\mathrm{cm}^{-1}$ for UV-absorbance, 0.1 units for pH and $1.0-\mathrm{mg} / \mathrm{L}$ for alkalinity. In addition, the magnitudes of the mean differences reported in this study are comparable or less than those reported by Andrews et al. (2005).

Filter performance was evaluated through the analysis of online filter effluent turbidity data collected for each of the three pilot filters on both pilot treatment trains. Effluent turbidity data was extracted from Halifax Water's online monitoring system at 1-minute intervals over the duration of each filter run. One complete filter run represents the time from which the filter is put into service until it is taken offline for backwashing; therefore, one filter run includes the ripening phase, steady-state filtration operation and turbidity breakthrough.

Figure 4.4 presents turbidity profiles for all three pilot filters for a representative pilot-topilot proving trial. Again, the backwash procedures of filters 1 and 2 on each pilot train were set to simulate the FSP backwash procedure, whereas filter 3 was programmed to
simulate an ETSW procedure on each train. The duration of the filter ripening stage and total filter run lengths (FRLs) are the key stages of a filter profile that would be most affected by water quality differences between the pilot trains. Therefore, a snapshot of the ripening stage of each turbidity profile presented in Figure 4.4(a) is shown in Figure 4.4(b) and was used as another means of assessing the similarity of the pilot filters.

Based on a visual comparison, turbidity profiles are similar and were reproducible for corresponding filters on PP1 and PP2, which is highlighted in the ripening profiles, steady state turbidity readings, and total filter run times. The brief change in steady-state turbidity readings for PP2 filters at approximately 20 hours into the filter run was due to a clog in the lime chemical feed line, but this issue was rectified in time to get the filters back to steady-state conditions before the trial was lost. Temporary lime line clogging occurred during most proving trials and this operational issue was rectified by upgrades to the lime feed system after proving trials were complete.

Since turbidity profiles encompass an extensive data set with several variations of effluent quality trends throughout (filter ripening stage, normal effluent production levels, filter breakthrough, and intermittent turbidity spikes), condensing this data into one number (i.e., an average) for effluent comparison purposes, does not give a complete representation of the data (Hargesheimer et al., 1998). Percentile ranking is a valuable indicator of the performance of individual filters (Hargesheimer et al., 1998) and was used to provide a statistical analysis of the effluent turbidity trends during pilot-to-pilot proving. Percentile ranking of the data summarizes the data into percentile ranking
groups that represent the turbidity profile over the entire filter run and provides an effective means of condensing the data into a format that effectively summarizes the filter performance. The data from each filter run was broken down into the corresponding $10^{\text {th }}, 50^{\text {th }}, 90^{\text {th }}, 95^{\text {th }}$, and $98^{\text {th }}$ percentiles to summarize the performance of each filter (Hargesheimer et al., 1998). Next, the individual percentile turbidity values from each filter run were pooled to obtain an average percentile ranking for each filter over the four proving trials completed.

Figure 4.5 presents the average probability plots for each individual pilot filter throughout the four pilot-to-pilot proving trials. The corresponding probability statistics are presented in Table 4.4. The similar trends observed in these probability plots and statistics provides further evidence there are no significant differences between the effluent turbidities between pilot treatment trains.

Comparison of Pilot Plant and Full Scale Performance. In total, five pilot-to-FSP proving trials were completed during May through August, 2008, comparing the influent, intermittent and effluent water quality between PP2 and the FSP. During pilot-to-FSP proving trials, the pilot plant was operated under identical "same day" operating conditions as the FSP (Table 4.2). Operational changes were made in the pilot plant only to match a simultaneous change in FSP operating conditions. The operating conditions modified throughout these trials were pre-oxidation pH and coagulation $\mathrm{pH} /$ dosage targets.

Although identical operating conditions were maintained, previous pilot proving experiences indicated that this alone would not produce similar finished water quality between the two process scales; and that, in fact, the water quality may be substantially different (Anderson et al., 1993; Andrews et al., 2005). According to Anderson et al. (1993), there are two reasons this occurs, despite the fact that the operating conditions were matched as closely as possible. The first factor involves assumptions that the pilot plant will perform identically when operating under the same conditions as the FSP despite the fact that it has only been operating for a limited amount of time, and the second factor involves scale down problems (i.e., hydraulic versus mechanical flocculation). Therefore, hypothesized mean differences, as shown in Table 4.5, were used as a means of evaluating pilot-to-FSP performance (Anderson et al., 1993; Andrews et al., 2005). These performance benchmarks were determined through steering committee discussions and consultations with pilot operators prior to the commencement of these proving trials.

Paired t-tests were applied to the pilot and FSP data with the pre-determined hypothesized limits inserted as the hypothesized mean differences (Anderson et al., 1993). Although a significant portion of the parameters passed under these conditions, 6 out of 20 parameter pairs did not (Table 4.5). In addition, 3 of the 5 filter effluent parameters failed this test, which is perhaps the most important stage of the process to achieve equivalent water quality. The pre-determined hypothesized mean differences applied in this study were significantly more aggressive than those used by Anderson et al. (1993) and Andrews et al. (2005). Specifically, the acceptable limits of difference
were $10 \%$ for UV-absorbance and 10 to $20 \%$ for organic matter removal in the aforementioned studies and the overall results were favourable under these less stringent limits (Anderson et al., 1993; Andrews et al, 2005). Based on the large measurement errors realized through the pilot-to-pilot proving data analysis, it was decided that performing a residuals analysis on the pilot-to-FSP results would provide a basis for a more realistic set of performance benchmarks to be employed.

As with pilot-to-pilot proving, measurement error limits were determined for each parameter measured (Table 4.5) and were used to assess the system tolerance between the pilot and FSP data by inserting these limits as the hypothesized mean differences in the paired t-tests. All parameters measured during pilot-to-FSP proving trials passed the revised paired t-test analysis and the pilot treatment process and FSP were found to be statistically equivalent for $\mathrm{pH}, \mathrm{UV}_{254}, \mathrm{TOC}$ and DOC . Overall, the filtered water mean differences between pilot and full-scale treatment were less than $10 \%$ for TOC ( $<0.15$ $\mathrm{mg} / \mathrm{L})$ and DOC ( $<0.08-\mathrm{mg} / \mathrm{L}$ ), $15 \%$ for UV-absorbance $\left(<0.004-\mathrm{cm}^{-1}\right)$, and 0.1 units for pH . The magnitudes of the mean differences between the two scales of treatment reported in this study are comparable or less than those reported by Andrews et al (2005).

Filter effluent quality was used to assess the turbidity equivalence between the pilot versus FSP data. Filter performance was evaluated through the analysis of online filter effluent turbidity data. Effluent turbidity data was extracted at 1-min intervals over the duration of each filter run. Figure 4.6 presents the turbidity profiles of a representative pilot-to-FSP proving trial. Steady-state turbidity readings are well within the $0.05-\mathrm{NTU}$
hypothesized mean difference limits. However, the ripening stage turbidities and filter run time criteria are not equivalent between the treatment scales. The main reason for these discrepancies is the inherent differences in flocculation mixing regimes between the pilot and FSP (mechanical versus hydraulic mixing). Although not quantified, such differences can lead to differences in the size and strength of floc particles entering the filters. On average, flocculated water turbidities were $0.32-\mathrm{NTU}$ higher in the pilot plant and this difference was as high as $0.8-\mathrm{NTU}$ during some trials. These differences in postflocculation water quality are further highlighted by the differences reported in TOC and UV-absorbance levels between the treatment scales (Table 4.5). Similar to results reported by Anderson et al (1993), these differences in particle loading to the pilot filters didn't affect the ability of the pilot filter to reduce the turbidity to FSP levels, however the ripening period and filter run times suffered. The ripening turbidity spikes were consistently higher in the pilot filters, however the duration of the ripening sequence was very similar based on equivalent UFRVs (Figure 4.6). Additionally, the FRL was shorter in the pilot plant due to the differences in particle loading; the pilot plant FRL was defined by turbidity breakthrough, whereas the FSP was limited by filter headloss.

Since steady-state turbidity values were within the $0.05-\mathrm{NTU}$ limit applied $\left(90^{\text {th }}\right.$ percentile $<0.02-\mathrm{NTU}$ ), it was deemed unnecessary to implement changes to the pilot plant operating conditions until the ripening stages and FRLs were equivalent. These differences in mixing regimes between the two scales provided a factor of scale between the pilot and full-scale facilities and will be drawn on when recommending process optimization upgrades in the full-scale system. Additionally, CFDs was used to evaluate
the mixing regimes currently achieved by the hydraulic flocculation tanks at the JDKWSP (Vadasarukkai, 2010). It was concluded that a combination of short-circuiting and inadequate mixing regimes are occurring in these tanks; a direct result of a dated design and the plant not achieving design flow rates in the hydraulic flocculators. Experiments are currently being conducted to examine opportunities for an alternate mixing technology and process operations to achieve improved particle and organic matter removal.

Post-proving Pilot Challenges. The only notable post-proving issues experienced with pilot operations corresponded with cold-water temperatures $\left(<10^{\circ} \mathrm{C}\right)$, during which the FSP traditionally supplements their process with a cationic polymer to maintain turbidity performance. Due to the efficiency of the mechanical mixers, adding a polymer to the pilot treatment process presented high particle loading to the filters and filtered water turbidities were unacceptable. This issue was mitigated by increasing the pilot alum dose to approximately $10.5-\mathrm{mg} / \mathrm{L}$ and foregoing the use of a polymer in the pilot treatment process, which brought the filter effluent turbidities to within acceptable levels.

### 4.5. CONCLUSIONS

A series of pilot proving trials were completed and successful in confirming that statistically equivalent water quality was being produced by the parallel pilot treatment trains and the FSP. Both the pilot-to-pilot and pilot-to-FSP proving trials demonstrated equivalence in multiple water quality parameters throughout the two treatment scales.

Correspondence was established between the two pilot trains by applying paired t-testing techniques to the water quality data produced by the parallel treatment trains. Using the measurement error as a basis for train comparison in paired t-tests, the pilot plants were found to be statistically equivalent based on $\mathrm{pH}, \mathrm{UV}_{254}, \mathrm{TOC}, \mathrm{DOC}$ and alkalinity measurements taken at key locations throughout the treatment process. Filtered water turbidity was evaluated by using percentile plotting and visual comparisons of filtered water turbidity profiles. Turbidity profiles were similar and reproducible for corresponding filters on each pilot train, which was highlighted by equivalence throughout the ripening phase, steady-state trends and filter breakthrough profiles.

Paired t-testing using the pre-determined hypothesized mean differences was not a successful means of determining equivalence between the pilot and FSP treatment trains in this study. Although these paired t -test results were generally favorable for the pilot versus FSP data, there were a few parameters that failed this test. In retrospect, the preset acceptable limits were too stringent when you account for the magnitude of measurement errors realized during these proving studies for $\mathrm{pH}, \mathrm{TOC}, \mathrm{DOC}$ and $\mathrm{UV}_{254}$. Inserting the measurement error limits as the revised mean differences in the paired t-tests was deemed a more reasonable approach and each parameter passed using these revised performance benchmarks at each sample location. In future pilot proving studies, it is recommended that the measurement errors for each parameter be considered in order to set achievable and acceptable deviations between pilot and full-scale performance. Contrastingly, the hypothesized mean difference of $0.05-\mathrm{NTU}$ for filter effluent turbidity was not strict
enough and a more appropriate performance benchmark for turbidity differences would have been $0.02-\mathrm{NTU}$.

The pilot proving process demonstrated that the pilot plant has the ability to reproduce water quality outcomes from the full-scale plant and that the results of the pilot facility are representative of process changes that will be used to optimize the performance of the FSP. Differences in mixing regimes between the two scales was the main factor of scale identified between the pilot and full-scale facilities and will be drawn on when recommending process optimization upgrades in the full scale system. Although this proving process was successful, it is important to periodically validate the water quality being produced between parallel pilot treatment trains and to continuously ensure that the control pilot train is producing equivalent water quality as the FSP, especially during particularly challenging treatment events (i.e., heavy organics loading and cold weather operations).

Table 4.1 Raw source water characteristics during the pilot proving trials.

| Analyte | Pilot to Pilot ${ }^{1}$ |  | Pilot to FSP ${ }^{2}$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  | Range | Average | Range | Average |
| Temperature - ${ }^{\circ} \mathrm{C}$ | 4.4-7.9 | 6.2 | 10.1-23.4 | 17.2 |
| pH | $4.0-5.0$ | 4.8 | 4.8-5.2 | 4.9 |
| $\begin{gathered} \text { Alkalinity - } m g / L \text { as } \\ \mathrm{CaCo}_{3} \end{gathered}$ | --- | $<1$ | --- | $<1$ |
| Turbidity - NTU | $0.32-0.54$ | 0.42 | 0.38-0.99 | 0.56 |
| $\mathbf{U V}_{254}-\mathrm{cm}^{-1}$ | 0.100-0.011 | 0.105 | 0.070-0.100 | 0.085 |
| TOC - mg/L | 2.25-3.41 | 2.78 | 2.15-3.08 | 2.62 |
| DOC - mg/L | 2.28-3.16 | 2.28 | 2.02-3.07 | 2.60 |

[^1]Table 4.2 Pilot plant and FSP operating conditions during pilot proving trials.

|  | Unit | Full Scale <br> Plant | Pilot <br> Plant |
| :--- | :---: | :---: | :---: |
| Plowrate | as noted | 98 MLD | $15 \mathrm{~L} / \mathrm{min}$ |
| Target Pre-oxidation pH | pH | 10.1 | 10.1 |
| Potassium Permanganate Dosage | $m g / L$ | 0.015 | 0.015 |
| Target Coagulation pH | pH | 5.7 | 5.7 |
| Alum Dosage | $m g / L$ | 8 | 8 |
| Post-filter Chlorine Residual | $m g / L$ | 0.05 | 0.05 |
| Polymer Dosage | $m g / L$ | 0.055 | 0.055 |
| Rapid mix blade speed | $r p m$ | 45 | 192 |
| Rapid mix velocity gradiant | $s^{-1}$ | 147 | 263 |
| Rapid mix G•t value | dimensionless | 11844 | 11844 |
| Flocculation velocity gradiant | $s^{-1}$ | --- | $30,20,10$ |
| Anthracite effective size | $m m$ | 0.89 | 0.89 |
| Anthracite uniformity coefficient | $m m$ | 1.67 | 1.67 |
| Anthracite depth | $m m$ | 609.6 | 609.6 |
| Sand effective size | $m m$ | 0.52 | 0.52 |
| Sand uniformity coefficient | $m m$ | 1.53 | 1.53 |
| Sand depth | $m m$ | 304.8 | 304.8 |
| Filter hydraulic loading rate | $L / \mathrm{mr}^{2}$ | 4,500 | 7,500 |

Table 4.3 Paired t-test results for pilot-to-pilot proving trials.

$\begin{array}{cccccccc}$\cline { 3 - 7 } \& \& \& Paired T-test Results\end{array}$]$| Past- |
| :---: |
| Parameter |

Table 4.4 Average filtered turbidity percentile statistics for each pilot filter during pilot-to-pilot proving trials.

## Average Turbidity Summary

## Filter 1

Filter 2
Filter 3

| Percentile | PP1 | PP2 | PP1 | PP2 | PP1 | PP2 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1 0}^{\text {th }}$ | 0.199 | 0.207 | 0.221 | 0.183 | 0.205 | 0.197 |
| $\mathbf{5 0}^{\text {th }}$ | 0.223 | 0.254 | 0.248 | 0.227 | 0.229 | 0.247 |
| $\mathbf{9 0}^{\text {th }}$ | 0.319 | 0.352 | 0.357 | 0.319 | 0.328 | 0.338 |
| $\mathbf{9 5}^{\text {th }}$ | 0.383 | 0.427 | 0.412 | 0.399 | 0.380 | 0.412 |
| $\mathbf{9 8}^{\text {th }}$ | 0.508 | 0.520 | 0.531 | 0.461 | 0.479 | 0.491 |

Table 4.5 Paired t -test results for pilot-to-FSP proving trials.

## Paired T-test Results

| Parameter | t-test Limits | Raw Water (RW) | PostCoagulation (PM3) | PostFlocculation (Floc3) | Filtered Water (Fil) |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Hypothesized Mean Differences |  |  |  |  |
| pH | Within 0.1 units | $\begin{gathered} \text { Pass } \\ (0.03)^{1} \end{gathered}$ | $\begin{gathered} \text { Fail } \\ (0.16) \end{gathered}$ | $\begin{aligned} & \hline \text { Pass } \\ & (0.07) \end{aligned}$ | $\begin{gathered} \text { Pass } \\ (0.10) \end{gathered}$ |
| TOC - mg/L | Within 5\% of FSP | $\begin{aligned} & \text { Pass } \\ & (3.8 \%) \end{aligned}$ | $\begin{aligned} & \text { Pass } \\ & (-0.8 \%) \end{aligned}$ | $\begin{aligned} & \text { Pass } \\ & (4.8 \%) \end{aligned}$ | $\begin{aligned} & \text { Fail } \\ & (-8.3) \end{aligned}$ |
| DOC - mg/L | Within 5\% of FSP | $\begin{aligned} & \text { Pass } \\ & \text { (1.7\%) } \end{aligned}$ | $\begin{gathered} \text { Pass } \\ (-4.3 \%) \end{gathered}$ | $\begin{aligned} & \text { Pass } \\ & (-0.2 \%) \end{aligned}$ | $\begin{aligned} & \text { Fail } \\ & (-5.2) \end{aligned}$ |
| $\mathbf{U V} \mathbf{2 5 4}^{-\mathrm{cm}^{-1}}$ | Within 5\% of FSP | $\begin{aligned} & \text { Pass } \\ & (-0.8 \%) \end{aligned}$ | $\begin{aligned} & \text { Fail } \\ & (-9.1 \%) \end{aligned}$ | $\begin{aligned} & \text { Fail } \\ & (-24 \%) \end{aligned}$ | $\begin{aligned} & \text { Fail } \\ & (-14 \%) \end{aligned}$ |
| Turbidity - NTU | $\pm 0.05 \mathrm{NTU}$ | Pass | Pass | Pass | Pass |
| Revised Mean Differences (Measurement Error ${ }^{2}$ ) |  |  |  |  |  |
| pH | Within 0.19 units | $\begin{gathered} \text { Pass } \\ (0.03) \end{gathered}$ | $\begin{aligned} & \text { Pass } \\ & (0.16) \end{aligned}$ | $\begin{gathered} \hline \text { Pass } \\ (0.07) \end{gathered}$ | $\begin{gathered} \hline \text { Pass } \\ (0.10) \end{gathered}$ |
| TOC - mg/L | Within 0.38 | $\begin{aligned} & \text { Pass } \\ & (0.115) \end{aligned}$ | $\begin{aligned} & \text { Pass } \\ & (0.032) \end{aligned}$ | $\begin{aligned} & \text { Pass } \\ & (0.269) \end{aligned}$ | $\begin{aligned} & \text { Pass } \\ & (-0.132) \end{aligned}$ |
| DOC - mg/L | Within 0.31 | $\begin{gathered} \text { Pass } \\ (0.075) \end{gathered}$ | $\begin{gathered} \text { Pass } \\ (-0.076) \end{gathered}$ | $\begin{gathered} \text { Pass } \\ (-0.006) \end{gathered}$ | $\begin{gathered} \text { Pass } \\ (-0.075) \end{gathered}$ |
| $\mathbf{U V}_{254}-\mathrm{cm}^{-1}$ | Within 0.006 | $\begin{gathered} \text { Pass } \\ (-0.001) \end{gathered}$ | $\begin{gathered} \text { Pass } \\ (-0.002) \end{gathered}$ | $\begin{gathered} \text { Pass } \\ (-0.006) \end{gathered}$ | $\begin{gathered} \text { Pass } \\ -0.004) \end{gathered}$ |
| Turbidity - NTU | $\pm 0.05 \mathrm{NTU}$ | Pass | Pass | Pass | Pass |

[^2]

Figure 4.1 JDKWSP pilot plant treatment process schematic.


## Sample Time - trial \# - day \# - sample \#

Figure 4.2 pH and DOC residuals distribution for the pilot-to-pilot proving trials completed (DOC data was not collected during trial 4). Upper and lower boundary lines represent two standard deviations of the residual population mean.


Sample Time - trial \# - day \# - sample \#

Figure 4.3 pH and DOC difference between Pilot Train 1 (PP1) and Pilot Train 2 (PP2) during pilot-to-pilot proving trials (DOC data was not collected during trial 4). Upper and lower boundary lines represent two standard deviations of the residual population mean.
a.)

b.)


Figure 4.4 Turbidity versus filter run time (FRL) for a representative pilot-to-pilot proving trial: a) complete filter run; b) filter ripening period.


Figure 4.5 Average filtered turbidity percentile plots for each pilot filter during the four pilot-topilot proving trials.
a.)

b.)


Figure 4.6 Turbidity versus unit filter run volume (UFRV) for a representative pilot-to-FSP proving trial: a) complete filter run; b) filter ripening period.

## CHAPTER 5 FROM JAR-TESTING TO PILOT STUDIES: OPTIMIZING PARTICLE AND NOM REMOVAL IN A DIRECT FILTRATION WATER TREATMENT PROCESS

### 5.1. ABSTRACT

The goal of this research was to optimize organic matter removal during coagulation, without compromising filtration performance for the direct filtration treatment of a source water characterized by low alkalinity, low turbidity and low organic matter. Bench and pilot-scale experiments were conducted to evaluate the performance of ferric sulfate, polyaluminum chloride $(\mathrm{PACl})$ and aluminum chlorohydrate $(\mathrm{ACH})$ against aluminum sulfate (alum) using variable coagulant dosage and pH conditions. Results from pilottesting demonstrated that favourable conditions identified for increased potential NOM removals during bench-scale testing were not consistent with optimal filtered water particle removal. For example the favourable ACH conditions $(4.0-\mathrm{mg} / \mathrm{L}, \mathrm{pH}=7.0)$ resulted in a $40 \%$ reduction in dissolved organic carbon (DOC) and the lowest trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP) of all coagulants tested; whereas this similar dose resulted in high filtered water turbidity and low unit filter run volumes (UFRVs) when evaluated during pilot experiments. The overall results of this study show that the optimization of coagulant dosages to remove even very low organic matter concentrations can severely compromise the performance of direct filtration processes due to increased solids loading to the filters. Since coagulant overdosing is not an option, low coagulation pH was found to be the most important operating parameter during pilot-scale studies to both reduce coagulant demand and encourage the formation of soluble NOM-aluminum complexes. Finally, a useful framework was developed for interpreting and analyzing the results of various operating conditions and multi-factor response parameters generated during plant optimization studies, using performance indicators (PIs) and graphical heat-mapping techniques.

### 5.2. INTRODUCTION

Over the past decade, the objectives for coagulation based drinking water treatment processes have changed significantly as a result of stringent goals related to natural organic matter (NOM) removal to mitigate subsequent disinfection by-product (DBP) formation potential and the need to achieve adequate filtration performance to ensure adequate particle removal for pathogen control. Balancing NOM and particle removal objectives for the optimization of coagulation processes followed by direct filtration treatment presents significant challenges in source waters characterized by low turbidity, low alkalinity and low organic matter content.

Optimal conditions for turbidity removal are rarely the same as those for NOM removal; in fact, the coagulant demand is usually governed by the concentration of NOM for low turbidity waters (Gregor et al., 1997; Pernitsky and Edzwald, 2006). The charge of NOM in surface waters is generally more negative than that of particulate matter and, in turn, is associated with much higher coagulant demands for effective removal (Pernitsky and Edzwald, 2006). Dosing to meet NOM removal goals in a direct filtration plant leads to high solids loading to the filters and results in early breakthrough, increased head loss rates and, therefore, shorter filter run times (Eikebrokk et al., 2007). In a direct filtration process, coagulation optimization is the primary means of ensuring optimal filtration performance is achieved and the stringent filtration goals of today's regulatory regime are achieved. In addition, the removal of soluble NOM from low-level turbidity source water presents another practical challenge related to the low concentrations of stable particles available to form acceptable floc (Gregor et al., 1997; Eikebrokk et al., 2007). In direct filtration facilities, coagulation processes must be optimized with multiple performance
objectives in mind.

Due to the increased challenges associated with direct filtration facilities, coagulation and flocculation processes in these types of plants are critical for achieving optimal removal of NOM and, subsequently, the mitigation of DBPs. Optimal NOM removal conditions are usually determined through the evaluation of NOM surrogate parameters such as total organic carbon (TOC), dissolved organic carbon (DOC) and UV response at 254 nm $\left(U V_{254}\right)$ and specific UV absorbance (SUVA). The characterization of NOM to determine optimal coagulation conditions is only recently gathering attention. A number of researchers have reported that specific physical and chemical properties of NOM, including the molecular weight (MW) of organic constituents, all impact the removal of NOM during coagulation (Croue et al., 2000; Liang and Singer, 2003; Ates et al., 2007).

Since the organic composition of source waters is site specific, knowledge of the physical and chemical properties of NOM can help to optimize organic matter removal efficiencies for coagulation efforts. Organic matter is often described in terms of hydrophobic and hydrophilic fractions and there is conflicting literature regarding which NOM types are predominant as precursors of the two regulated classes of DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) (Croue et al., 2000; Liang and Singer, 2003; Ates et al., 2007). Identifying the main DBP precursors in a source water assists in the selection of optimal coagulants and coagulation operating conditions to target their removal.

Direct filtration treatment of these specific source water characteristics not only present significant challenges when optimizing current facilities to meet more stringent regulations, but these filtration processes are very difficult to simulate during bench-scale experiments. Therefore, pilot-plant experiments are essential in closing the gap between bench-scale to full-scale coagulation optimization studies in direct filtration facilities. A key advantage of a pilot plant is its ability to study these multi-objective issues simultaneously and confirm the effects of variables acting independently and in combination throughout the treatment processes.

Objectives. The goal of this research was to optimize NOM removal during coagulation, without compromising filtration performance for the direct filtration treatment of a source water characterized by low alkalinity, low turbidity and low organic matter. Bench and pilot-scale experiments were conducted to evaluate the performance of ferric sulfate, polyaluminum chloride $(\mathrm{PACl})$ and aluminum chlorohydrate $(\mathrm{ACH})$ against aluminum sulfate (alum) using variable coagulant dosage and pH conditions. The bench-scale study included a series of parallel jar test studies to identity favorable coagulation dosage and pH conditions for organic matter removal for each of the coagulants being considered. The pilot-scale work aimed to provide a snapshot of feasibility in terms of filter run times, filter ripening times and particle removal for favourable coagulant conditions identified under bench-scale conditions and, also, to determine favourable conditions for filtration performance. In addition, this work aimed to develop a framework for organizing and evaluating the overwhelming quantity of data generated by the various
operating conditions and multi-factor response parameters generated during plant optimization studies.

### 5.3. MATERIALS AND METHODS

Source Water. This project was conducted at the JD Kline Water Treatment Plant (JDKWSP) in Halifax, Nova Scotia, Canada. Low levels of pH, alkalinity, turbidity and organic carbon characterize the raw water. Table 5.1 outlines the source water characteristics during the pilot proving trials.

JD Kline Water Supply Plant. The JDKWSP is a direct filtration treatment plant that employs pre-screening, oxidation, pre-chlorination, coagulation, hydraulic flocculation, direct filtration and chlorination. In the first pre-mix tank, lime is added to adjust the pH (9.6-10) for oxidation of iron and manganese using potassium permanganate $\left(\mathrm{KMnO}_{4}\right)$ and the second pre-mix tank provides additional mixing and detention time for this oxidation process. In the third pre-mix tank, carbon dioxide $\left(\mathrm{CO}_{2}\right)$ is added to adjust the coagulation pH (5.5-6.0) and alum is added as the primary coagulant at an average dosage of $8 \mathrm{mg} / \mathrm{L}$. During the cold weather months (November through June), a cationic polymer is required to strengthen floc and maintain turbidity performance, at an average dosage of $0.05 \mathrm{mg} / \mathrm{L}$. Pre-chlorination occurs in the third pre-mix tank to control biofilm occurrence in the filters and is maintained at a post-filter total chlorine residual concentration of $0.05 \mathrm{mg} / \mathrm{L}$. Next, water is delivered to four identical flocculation trains that contain three rows of parallel sets of cells (6 cells total). Tapered, hydraulic, flocculation occurs in these cells. Next, the flow is distributed between eight dual-media anthracite and sand filters. Finished water chemicals include the addition of chlorine for
disinfection to maintain a total chlorine residual of $1.0 \mathrm{mg} / \mathrm{L}$, sodium hydroxide to a finished water pH of 7.4 , zinc/ortho polyphosphate for corrosion control $(0.5 \mathrm{mg} / \mathrm{L}$ as $\mathrm{PO}_{4}$ ) and hydrofluosilicic acid to provide fluoride addition for dental health.

Pilot Plant Description. The JDKWSP pilot-scale plant consists of two identical, parallel treatment trains, both capable of simulating direct filtration or conventional treatment processes, manufactured by Intuitech, Tnc (Salt Lake City, Utah). The pilot plant operates using Pockwock Lake raw water at a design flow rate of $15-\mathrm{L} / \mathrm{min}$ delivered to each treatment train. Each pilot train contains two treatment trains that contain coagulation, flocculation and filtration processes.

Raw water enters the coagulation/ flocculation skid into a series of three 11.3-L rapid mix tanks where chemical addition and mixing occur. The pilot plant has the capacity to feed 6 separate chemicals through peristaltic pumps to the chemical injection ports in the rapid mix tanks. From the rapid mix tanks, water flows into a series of three 189-L mechanical flocculation tanks with paddle mixers and then on to the optional sedimentation tank. The sedimentation tank is a 330-L basin with 30 adjustable plates, each with settling area of $0.1-\mathrm{m}^{2}$. The clarified water is collected in a settled water basin, after passing over the settling plates, and sludge can be pumped to a sampling port or to waste. If direct filtration is desired, the sedimentation tank can be bypassed and the flow is directed straight to the filtration skid.

The pilot plant was operated as a direct filtration plant for the duration of this research project. The filtration skid was built to match the bed depths and weir elevations of the full scale plant and contains a series of three $200-\mathrm{mm}$ ( 8 -inch) diameter dual-media filters containing $61-\mathrm{cm}(2-\mathrm{ft})$ of anthracite and $30.5-\mathrm{cm}(1-\mathrm{ft})$ of sand. There is no capability to add finished water chemicals at the pilot scale. The plant contains inline equipment to monitor pH , temperature, and turbidity at all critical process control points.

A series of pilot proving experiments were completed to validate that statistically equivalent intermittent and finished water quality was demonstrated between pilot treatment trains and the full-scale plant (FSP). The validation process successfully demonstrated that the pilot plant has the ability to reproduce full-scale behavior and that the results of the pilot research at this facility are representative of process changes that, when implemented at full scale, will successfully optimize the performance of the FSP (Chapter 4).

### 5.3.1. Experimental Procedures

Bench-scale Study. A bench-scale coagulation study was completed to identify the organic matter removal potentials of each alternate coagulant and to identify reasonable coagulant dosage and pH conditions to be used as a starting point for pilot-scale coagulation studies. Since the treatment process being optimized is a direct filtration process, particle removals associated with these favorable conditions could not be evaluated during bench-scale trials. Therefore, the intention of the bench-scale work was not to determine optimum pH and coagulant dose conditions for each coagulant, but instead to establish a benchmark of the potential organic matter removal performance,
which will subsequently be compared against the pH and coagulation conditions required to obtain adequate particle removals as identified through pilot testing.

The determination of reasonable pH ranges for organic matter removal for each coagulant type was determined by conducting jar tests at a constant coagulant dosage with varied pH levels. The optimal pH of coagulation was chosen based on optimal pH ranges reported in literature and overall TOC, DOC and $\mathrm{UV}_{254}$ removals for each coagulant used. To identify favorable coagulant dosages at the selected pH , coagulant concentrations were varied in each jar while the optimum pH value was maintained. The optimal coagulant dosage was identified as the lowest dosage at which there was maximum TOC, DOC and $\mathrm{UV}_{254}$ removal for each coagulant used. The resulting pH and dosage conditions were chosen as favorable operating conditions for NOM removal based on the response parameters used. Table 5.2 outlines the coagulation conditions selected for each coagulant evaluated.

Once favourable conditions were identified for each coagulant type, additional jar tests were conducted to compare these conditions the current treatment plant coagulation pH and dosage conditions, herein referred to as baseline conditions, for NOM and by-product formation potential reductions. Response parameters included TOC, DOC and $\mathrm{UV}_{254}$, as well as more specific and sophisticated NOM indicators such as THM formation potential (THMFP), HAA formation potential (HAAFP), and SEC.

Jar Test Procedure. Bench-scale coagulation studies were conducted using a modified
jar-test method for direct filtration with variable pH and dosage conditions. Response parameters for the bench-scale experiments focused only on NOM removal, since settled water turbidities are not relevant to direct filtration processes and deep bed filtration of direct filtration processes is difficult to adequately reproduce at the bench-scale (Pernitsky et al., 2011).

Pre-oxidized water from the full-scale treatment process was used for jar test experiments. pH was adjusted using nitric acid and sodium hydroxide. Chemicals were injected using graduated syringes and rapid mixed at 142 rpm for 1-min. Rapid mixing was followed by tapered flocculation that employed slow mixing for 12.5 minutes at 37 rpm, 12.5 minutes at 26 rpm and 12.5 minutes at 18 rpm to simulate pilot-plant operating conditions. Mixing velocities were calculated to produce equivalent mixing intensity and retention time products (GT) as the pilot treatment process (Chapter 4).

Flocculated water was then immediately filtered through a glass microfiber $1.5-\mu \mathrm{m}$ filter (Whatman 934-AH) to imitate the direct filtration treatment stage. Filter paper was chosen instead of using small-scale filter columns in both the interest of experimental time and because preliminary testing indicated that the effluent quality based on turbidity removal was very similar when FSP coagulated/flocculated water was passed through either the $1.5-\mu \mathrm{m}$ filter papers or small scale filtration columns. Filtered samples were analyzed for TOC, DOC and $\mathrm{UV}_{254}$.

Pilot-plant Trials. Two identical treatment trains were used in the pilot study to ensure that the effects of changing raw water characteristics were eliminated by continuously operating one side of the plant such that the same finished water quality as the full-scale plant (FSP) was continuously achieved. This provided a control measurement and was used to evaluate the success of the operational parameters being evaluated. Therefore, the operating conditions of the control pilot train (e.g., chemical dosages, mixing speeds, retention times) emulated the conditions identified during the pilot proving trials outlined in Chapter 4. As outlined in Chapter 4, since the pilot plant utilizes mechanical mixers, low G-values of 30,20 , and $10-\mathrm{s}^{-1}$ were chosen to emulate, to the extent possible, the inadequate hydraulic mixing intensities of the FSP. The experimental pilot train was operated under identical treatment conditions as the control train, except the coagulation pH and dosage were varied to identify optimal filtration performance coagulation conditions.

Numerous pilot-trials were conducted to evaluate the filter performance for each coagulant under various pH and dosage conditions. The trials began with a backwash of each pilot filter and were terminated based on predetermined limits including a filter effluent turbidity threshold of $0.2-\mathrm{NTU}$, a head loss limit of $2.15-\mathrm{m}$ or a maximum filter run time of $80-\mathrm{h}$. In-line turbidity data for effluent filtered water was monitored continuously.

Coagulants Evaluated. The coagulants evaluated include alum, ferric sulfate, PACl and ACH . The PACl was a medium basicity coagulant containing no sulfate (MBNS) and the

ACH was a high basicity, non-sulfated (HBNS) product. The alum was supplied by General Chemical and the MBNS PACl (basicity $=40 \%$ ) and HBNS ACH (basicity $=$ $80 \%$ ) were supplied by Kiemera Water Solutions Inc. To directly compare coagulant dosages, chemical dosages are report as $\mathrm{mg} / \mathrm{L}$ of Al or $\mathrm{mg} / \mathrm{L}$ of Fe .

### 5.3.2. Analytical Procedures

General Water Quality Parameters. Throughout the duration of this research, reverse osmosis (RO) water was used for all cleaning and chemical stock preparations. All glassware was rinsed 3 times using RO water following cleaning. The RO water was obtained from a Milli- ${ }^{\circledR}$ purification system. Combination $\mathrm{pH} / \mathrm{mV} /$ Temperature/ DO/ ISE and Conductivity meters (Accumet* XL 25 and XL 60 models) with plastic bodied, gel-filled, combination pH electrodes (Accumet Accu-Cap*) were used for pH readings. Three-point calibration ( $\mathrm{pH} 4,7,10$ ) was conducted each day.

Organic Matter. TOC and DOC samples were collected head-space free in $40-\mathrm{mL}$ precleaned glass vials and preserved with concentrated phosphoric acid to a $\mathrm{pH}<2$ and measurements were performed using a TOC-V CPH analyzer with a Shimadzu ASI-V autosampler and catalytically aided combustion oxidation non-dispersive infrared detector (NDIR) having a method detection limit of $0.08 \mathrm{mg} / \mathrm{L}$ (Shimadzu Corporation, Kyoto, Japan). UV absorbance at 254-nm $\left(\mathrm{UV}_{254}\right)$ was measured using a HACH DR/4000 UV/VIS spectrophotometer (Hach Company, Loveland, CO). Before sample collection, $\mathrm{UV}_{254}$ and DOC samples were filtered through $0.45-\mu \mathrm{m}$ polsulfone filter membrane (GE Water \& Process Technologies) that had been pre-rinsed with $500-\mathrm{mL}$ of RO water.

Disinfection by-products. THMFP and HAAFP were analyzed using Standard Method 5710 (APHA, 2005) with minor modifications. Samples were buffered to a pH of 8 with borate and incubated for 24 hours following chlorination. Samples were dosed with 1.0$\mathrm{mg} / \mathrm{L}$ of buffered free chlorine to simulate current JDKWSP dosing conditions. THM and HAA samples were then prepared for gas chromatography analysis using liquidliquid extraction (LLE) with pentane and methyl tert-butyl ether (MTBE), correspondingly. Gas chromatography using a Varian CP-3800 GC equipped with a VF-5 column and a Varian CP-8400 auto-sampler, coupled with an electron capture detector (GC-ECD) were used for the detection of THMs and HAAs according to the US EPA Methods 551.1 and 552.2. Samples were analyzed for four THM compounds: chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform. Samples were analyzed for 9 haloacetic acids ( $\mathrm{HAA}_{9}$ ): monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA) and tribromoacetic acid (TBAA).

To validate the precision and accuracy of the THM and HAA methods, method blanks (milli-q water) and quality control (QC) samples (milli-q spiked with a known amount of standard mixture) were prepared for every 15 samples, for any given analysis. Recovery testing was conducted on QC samples and results were only accepted if QC recoveries were between 70 and $130 \%$. A coefficient of determination $\left(R^{2}\right)$ greater than 0.95 was consistently achieved for all THM and HAA analytes.

HPSEC analysis. Molecular size distribution of organic fractions was determined by high pressure size exclusion chromatography (HPSEC) using high performance liquid chromatography (HPLC, Perkin Elmer Series 200). Prior to analysis, samples were brought to a pH of 3-7 and passed through a $0.45 \mu \mathrm{~m}$ filter membrane. Samples were evaluated using a TSK G3000SW column ( 7.5 mm X 300 mm ) with a TSKgel SW guard column ( 7.5 mm X 70 mm ). The media in the TSK column consists of silica, pore size of $10 \mu \mathrm{~m}$. These columns were connected to the Perkin Elmer Series 200 Autosampler and a UV/Vis detector set at UV 254 nm . Samples of $20 \mu 1$ were injected and passed through the columns at a flow rate of $0.7 \mathrm{~mL} / \mathrm{min}$. A sample run time of 30 min was established, whereby all of the compounds in the sample had passed through the column. The molecular size calibration for the column was conducted using sodium polystyrene sulfonate standards (Scientific Polymer Products Inc) with different MWs: 14900, 7540, 5180 and 1530 Daltons (Da). A coefficient of determination $\left(R^{2}\right)$ greater than 0.90 was consistently achieved.

Turbidity. The pilot plant contains inline Hach 1720E low range process turbidimeters to monitor filtered water turbidity, located on the effluent stream of each individual filter on both pilot trains. When comparing filter run data between pilot trials and the FSP, in-line effluent turbidity data was extracted from HW's online monitoring system which were measured using Hach 1720 series low range process turbidimeters.

### 5.4. RESULTS AND DISCUSSION

### 5.4.1. Bench-scale Results

Organic Matter Removal. DOC concentrations in the raw water are typically low, between 2 to $3-\mathrm{mg} / \mathrm{L}$, and specific UV absorbance (SUVA) values range from 2 to $4-\mathrm{m}^{-1}$ of absorbance per $\mathrm{mg} / \mathrm{L}$ of DOC (Table 5.1). SUVA values are widely used as a predictor of the aromatic organic carbon content of NOM (Croue et al., 2000, Liang and Singer., 2003; Pernitsky and Edzwald, 2006). SUVA guidelines published by Edzwald and Van Benschoten (1990) reference the nature of organic compounds and expected TOC removals associated with specific SUVA ranges (Pernitsky and Edzwald, 2006). According to these guidelines, SUVA values between 2 to $4-\mathrm{m}^{-1}$ of absorbance per $\mathrm{mg} / \mathrm{L}$ of DOC are indicative of an organic matrix that is composed of a combination of aquatic humics and other NOM, a mixture of both hydrophobic and hydrophilic NOM fractions, and a variety of MW organic compounds. NOM characterization studies completed on this source water determined the raw water organic matrix to be primarily comprised of hydrophobic and hydrophilic neutral compounds and the MWs of the organics species ranged from 65 to 1,000-Da (Montreuil, 2011). For SUVA values of 2 to 4, it has be suggested that the NOM present will require a greater coagulant demand than the particles present in the water and reasonable DOC removals (30-40\%) could be expected following coagulation (Pernitsky and Edzwald, 2006).

Again, the bench-scale coagulation study was not intended to identify the optimum pH and coagulation conditions for each coagulant, but instead to establish benchmark coagulation conditions that yield favourable organic matter removal potential to minimize
experimental trials during subsequent pilot studies. TOC, DOC and $U V_{254}$ results for the favourable pH and dosage determination trials are presented Appendix B, Figures B1 through B8. The favourable pH conditions determined through a series of jar tests are presented in Table 5.2 for each coagulant studied. In general, the coagulation pH results agreed well with coagulation pH ranges reported in the literature (Pernitsky and Edzwald, 2003; Edzwald, 2008).

According to Pernitsky (2010), optimal coagulation performance for aluminum-based coagulants is typically seen at pH values close to the pH of minimum solubility where dissolved aluminum residuals are minimized and the presence of aluminum hydroxide precipitates for subsequent NOM adsorption is maximized. In contrast, ferric-based coagulants are more effective at very low pH values, where positively charged species are present and the overall negative charge of NOM is lower (Pernitsky, 2010). Volk et al. (2000) reported that several researchers identified optimal precipitation pH ranges of 4-5 with ferric-based coagulants and at $5-6$ with alum. For alum, low pH values $(\mathrm{pH}=5.5)$ maximize organic matter removal, whereas these low pH conditions are not required for PACls (Pernitsky, 2010). Furthermore, Pernitsky and Edzwald (2006) noted optimal PACl and ACH performance at coagulation pH values between 6-7. Favourable coagulation pH ranges increased as the basicity of the coagulant increased, as expected based on recent coagulant solubility research (Pernitsky and Edzwald, 2003; Pernitsky and Edzwald, 2006).

Since high pre-oxidation pH is required before coagulation occurs, a higher coagulation
pH would significantly reduce the pH adjusting chemicals at this facility. Pernisky and Edzwald (2006) found that the use of a high basicity, non-sulfate (HBNS) PACl blend was the most effective for the removal of particles and organic matter for the direct filtration of a low alkalinity source water with low to moderate total organic matter content. This success was based on the low alkalinity consumption of high basicity PACl and the use of a high pH of coagulation due to a high minimum solubility pH associated with the high basicity PACl . In addition, PACl coagulants are generally more effective than alum in cold-water conditions, a notorious challenging treatment period at this facility, because they are pre-hydrolyzed (Pernitsky and Edzwald, 2003; Pernitsky and Edzwald, 2006). The absence of sulfate in PACl blends reduced headloss during direct filtration processes when compared directly with a sulfated PACl (Pernitsky and Edzwald, 2006).

As expected, dosage requirements increased as the coagulation pH increased for aluminum-based coagulants as shown in Table 5.2 (Pernitsky and Edzwald, 2006). At higher pHs , the coagulant demand required to react with NOM and form floc particles with a charge near neutral is increased. The coagulant dosages for PACl and ACH corresponded well with the dosage demands reported by Pernitsky and Edzwald (2006) at similar pH conditions for a low turbidity, low TOC and low alkalinity source water.

NOM of the coagulated water was predominantly in a dissolved form (Table 5.1). Therefore DOC was the primary metric of organic carbon (rather than TOC) considered when measuring coagulation performance. When compared to raw water DOC levels,
reductions under baseline alum coagulation conditions yielded $20 \%$ removal of DOC and reductions from optimized coagulation conditions yielded $30-40 \%$ removals (Figure 5.1). Low DOC removals (30\%) were also observed by other researchers when treating low SUVA ( $<3-\mathrm{m}^{-1}$ of absorbance per $\mathrm{mg} / \mathrm{L}$ of DOC) source waters using coagulation processes (Croue et al., 2000).

DOC removal was accompanied by a reduction in $\mathrm{UV}_{254}$, which is a known surrogate for aromatic compounds such as humic substances (Figure 5.1). UV ${ }_{254}$ reductions were 60$70 \%$ of raw water levels, which indicates that coagulation was more effective in removing UV-absorbing, aromatic organic fractions (Croue et al., 2000). When average removals are considered, ACH had the greatest DOC and $\mathrm{UV}_{254}$ reductions of $40 \%$ and $70 \%$, respectively. However, the overall DOC and $\mathrm{UV}_{254}$ reductions are not indicative of significant performance differences between the coagulants evaluated (Figure 5.1).

The proportion of aromatic material in treated water samples was assessed by calculating the SUVA value. The raw water SUVA was reduced from 2.6 to approximately 1.5 following coagulation treatment (Figure 5.1). SUVA interpretation guidelines indicate that the remaining NOM is hydrophilic and non-humic in nature, low in MW and only slightly affected by coagulation (Pernitsky and Edzwald, 2006; Ates et al., 2007). Organic matter characterization of FSP treated water by Montreuil (2011) indicated that coagulation efforts primarily removed the hydrophobic acid and the hydrophilic neutral fractions with little to no removal of other fractions. In addition, zeta potential analysis completed on individual organic fractions in this raw source water suggest that the net
colloidal anionic charge in the raw water is driven by the zeta potential contribution of hydrophobic fractions as opposed to the hydrophilic fractions (Montreuil, 2011).

THMFP and HAAFP. DBP formation potential (DBPFP) analysis revealed further indication that the high basicity ACH was the superior performer at the coagulation conditions studied (Figures 5.2 and 5.3). ACH achieved the lowest THMFP with a $37 \%$ reduction compared to baseline coagulation conditions. On an average concentration basis, ACH achieved the greatest HAAFP reductions with a $25 \%$ decrease from baseline coagulation conditions. However, HAAFP contributions were not significantly different for any of the enhanced coagulation conditions examined.

For all treatment conditions, chlorinated by-products dominated over brominated species following treatment (Figures 5.2 and 5.3). This was expected since the bromide concentration in the raw water is $0.3-\mathrm{mg} / \mathrm{L}$ and typically less than $0.05-\mathrm{mg} / \mathrm{L}$ following treatment in the FSP. Although the average concentrations varied, consistent DBP species trends existed following treatment. For all coagulation conditions evaluated, chloroform was the dominant THM species. Small concentrations of DCBM and DBCM were also present, however these fractions were nearing minimum quantification limits. The major HAA species formed following treatment was DCAA, followed by BCAA. Minor concentrations of BDCA, MCAA, and TCAA also contributed to the average HAA concentrations. All other HAA species were below quantification limits.
$\mathrm{UV}_{254}$ has also been demonstrated to be a good predictor of the DBPFP of treated water (Ates et al., 2007; Edzwald 2008). For all coagulation conditions tested, weak linear correlation coefficients $\left(\mathrm{R}^{2}\right)$ were obtained between treated water $\mathrm{UV}_{254}$ values and THMFP and HAAFP; 0.20 and 0.53 , respectively (Appendix B, Figures B11-B12). Although a relatively high correlation coefficient was obtained for the $\mathrm{UV}_{254}$-HAAFP relationship, there was a high variability in HAAFP concentrations at low $\mathrm{UV}_{254}$ values. Since $\mathrm{UV}_{254}$ is only representative of $\mathrm{UV}_{254}$-active, aromatic species, it doesn't capture all NOM fractions that are responsible for DBPFP, particularly for THMFP in this study. These weak correlations suggest that organic structures other than aromatics also contribute to the production of DBPFP in this treated water and the effectiveness of SUVA as a DBP prediction tool is water specific (Ates et al., 2007). That being said, recent research does suggest that HAA precursors have a higher aromatic content than THM precursors and this is likely the reason for the stronger $\mathrm{UV}_{254}$-HAAFP relationship in this study (Liang and Singer, 2003).

Fractionation of NOM using SEC. Treated water was analyzed using SEC to identify and compare the MW distribution of $\mathrm{UV}_{254}$-active DOC following coagulation efforts. Representative elution patterns of $\mathrm{UV}_{254}$ response versus elution time for each treated water condition are presented in Figure 5.4. Elution peaks were numbered for fraction identification and analysis. All chromatograms contained an early peak separated from a group of eluting peaks at later retention times. Elution fractions represent MW ranges from valley to valley on the chromatogram, which were consistent between all coagulation conditions tested (Figure 5.4). Fraction 1 eluted outside of the calibration
range and was therefore not included in the analysis of MW distribution (Allpike et al., 2005). In addition, previous literature suggests that even though fraction 1 appears to be representative of high MW and highly aromatic material, it is typically associated with colloidal material that may be comprised of inorganic materials following coagulation (Allpike et al., 2005). The elution times and molecular weights associated with peaks 1 through 8 for the favourable coagulation conditions as presented in Figure 5.4 are provided in Appendix B, Figure B9.

Relative comparisons of the area of $\mathrm{UV}_{254}$-active DOC for each fraction were made to compare the performance of each coagulant (Figure 5.5). Although SEC analysis using UV absorbance is a useful method to determine the MW distribution of NOM, this technique does not provide a means of assessing the mass of NOM associated with specific MW ranges; rather, it provides a means of assessing relative removals of UVactive NOM fractions within identified MW ranges (Allpike et al., 2005; Ates et al., 2007).

In general, higher removal efficiencies were obtained for large aromatic MW fractions (Figure 5.5). The greatest removals were associated with aromatic fractions greater than $1,100 \mathrm{Da}$, however MW fractions in the $700-1,100 \mathrm{Da}$ size range were also mildly reduced by coagulation efforts. Generally, these highly aromatic and high MW organic compounds are associated with hydrophobic NOM and have been shown to be more amenable to removal by coagulation than hydrophilic NOM (Liang and Singer, 2003; Pernitsky and Edzwald, 2006).

Consistent with other studies, coagulation efforts were not effective at removing smaller MW compounds ( $<700-\mathrm{Da}$ ), which are generally associated with hydrophilic NOM with low aromaticity (Liang and Singer, 2003; Pernitsky and Edzwald, 2006; Ates et al., 2007). Hydrophilic organics typically encompass non-aromatic, low MW colloids with a significantly lower charge density than hydrophobic organic matters and are relatively less amenable to removal by coagulation (Liang and Singer, 2003; Pernitsky and Edzwald, 2006).

DBPFP predictions based on $U V_{254}$ content in water characterized by low SUVA and low MW NOM fractions are generally weak and recent research is highlighting the importance of hydrophilic organic fractions with low aromaticity as being important DBP precursors in low SUVA waters (Liang and Singer, 2003; Ates et al. 2007). Although hydrophobic NOM is seen to be the major DBP precursor, in waters with a low hydrophobic content, hydrophilic organic matter may also an play and important role (Liang and Singer, 2003).

### 5.4.2. Pilot-scale Results

Particle Removal. The filtration performance of ferric sulfate, PACl and ACH were evaluated through a series of pilot tests under variable coagulation pH and dosage conditions (Tables 5.4 through 5.6). Filter performance was evaluated through the analysis of online filter effluent turbidity data collected for each pilot train and the FSP. One complete filter run represents the time from which the filter is put into service, until it is taken offline for backwashing; therefore one filter run includes the ripening phase, steady-state filtration operation and turbidity breakthrough.

The quantity of data generated by the various operating conditions and multi-factor response parameters were initially difficult to interpret using traditional tables or charts. Therefore, a framework was developed for organizing and evaluating this information, which included both rating individual filtration trials using performance indicators (PIs) and graphical heat-mapping techniques.

Since turbidity profiles encompass an extensive data set with several variations of effluent quality trends throughout, condensing this data into one number (i.e.; an average) for effluent comparison purposes, does not give a complete representation of the data (Hargesheimer et al., 1998). Therefore, filtration trials were evaluated based on the combined performance of three response parameters: unit filter run volumes (UFRV), steady-state turbidity values and filter ripening volumes (FRV). Filter ripening was defined as the filtered water volume required to reach a turbidity value of $0.1-\mathrm{NTU}$ following a filter backwash (O'Leary et al., 2003). Each response parameter was assigned a PI score of 0 to 3 based on predefined filtration performance criteria for each response parameter (Table 5.3). PIs were based on experience with FSP filtration response parameters and industry best practice operational requirements. The resulting PI for each coagulation condition was given equivalent significance when calculating the overall treatment score.

Heat-mapping provides a graphical representation of the data using the size of a data point to represent a qualitative value of a given response parameter and the coordinate location to represent the corresponding operating conditions. For consistency, the larger
data points are indicative of superior performance and, for that reason, the inverse of both turbidity and filter ripening volumes were used in the corresponding heat-maps.

Since the performance rating system applies equivalent weight to each response parameter, a means of verifying that this equitable assumption was indeed suitable is required. The conditions identified as the favourable operating region based on a calculated average may not be the appropriate choice if slightly sacrificing the performance of a single response parameter could lead to significant improvements in the other two response parameters without compromising effluent water quality. Therefore, a heat-mapping approach was used to verify that the optimal regions identified through this methodology are an appropriate choice. Heat-mapping is also a useful means of illustrating favourable operating regions for each filter response parameter and offers a means of choosing between two operating conditions that resulted in a similar overall performance rating using the PI methodology.

Pilot plant filtration data and PI ratings for ferric sulfate, PACl and ACH trials are presented, respectively, in Tables 5.4, 5.5 and 5.6. For the ferric sulfate trails completed, poor overall PI ratings ( $<0.6$ ) were achieved for all coagulation conditions evaluated (Table 5.4). Excellent effluent turbidity values were achieved ( $<0.05-\mathrm{NTU}$ ) at lower pH values (4.5-4.7), however filter ripening volumes were unacceptably large and unit filter run volumes were fairly small compared to typical FSP performance (FS-4 and FS-5 in Table 5.4). By viewing the PI ratings alone, it appears that lower ferric sulfate dosages in the $4.5-4.7 \mathrm{pH}$ region may have produced improved filtration performance. However, an
evaluation of the ferric sulfate heat-maps suggests that lower dosages produce inferior turbidity and filter ripening performance (Figure 5.6). This was attributed to the large flocs typically produced during coagulation with ferric sulfate, but was not experimentally verified. In addition, such low coagulant pH conditions would significantly increase operating costs associated with pH adjusting chemicals at a facility that requires a high pre-oxidation pH prior to coagulation.

Pilot-scale trials conducted using favourable PACl treatment conditions identified for organic matter removal during bench-scale trials severely compromised filtration performance (PACl-3 in Table 5.5). The UFRV for these operating conditions was less than $4-\mathrm{m}^{3} / \mathrm{m}^{2}$ and the effluent filtered water turbidities were very high. The reduced filter runs times were attributed to the increased solids loading to the filters when operating under enhanced coagulation conditions. PI ratings for PACl trials were favourable at coagulation dosage of $1.0-\mathrm{mg} / \mathrm{L}$ as Al and a pH of 5.8 ( $\mathrm{PACl}-19$ and $\mathrm{PACl}-20$ in Table 5.5). Although these coagulation conditions provided superior filtered water turbidities and filter ripening volumes, the unit filter run volume are not ideal. This is a great example of the need and value of heat-mapping. Larger unit filter run volumes are produced at the same pH , but at a lower coagulant dosage of $0.9-\mathrm{mg} / \mathrm{L}$ as Al (Figure 5.7). Although turbidities are still acceptable at these operating conditions (0.065-NTU), filter run volumes are double the upper PI limit but could be optimized or managed through other operational means (filter loading rates, backwash optimization, etc).

The favourable ACH coagulation conditions identified during bench scale studies (ACH-
7) produced high filtered water turbidity and low UFRVs when evaluated during pilot experiments (ACH-7 in Table 5.6). Again, this was attributed to the solids loading on the filters being too high for a direct filtration process. Based upon an evaluation of the overall results obtained using ACH , the coagulation conditions for superior filtration performance were similar to those of PACl. Excellent UFRVs, effluent turbidities and FRVs were achieved at a pH value of 5.8 and a dosage range of 1.1 to $1.15-\mathrm{mg} / \mathrm{L}$ as Al (ACH-30 through ACH-37 in Table 5.6). Evaluation of the ACH heat-maps confirms these coagulations conditions as optimal regions (Figure 5.8). For all the coagulants studied, ACH provided the most promising overall results based on large UVRVs, low filtered water turbidity and low FRVs.

Figure 5.9 provides representative filtered water turbidity profiles comparing favourable ACH coagulation conditions (dose $=1.1-\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=5.8$ ) to same day baseline alum pilot conditions (dose $=0.9-\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=5.5)$ and FSP operations $($ dose $=0.7-$ $\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=5.5$, cationic polymer $=0.05-\mathrm{mg} / \mathrm{L}$ ). During cold-water operations $\left(<10^{\circ} \mathrm{C}\right)$, the FSP traditionally supplements their process with a cationic polymer to maintain turbidity performance, without adjusting the coagulation dose or pH . Due to the efficiency of the mechanical mixers in the pilot pant, adding a polymer to the treatment process presented high particle loading to the filters and filtered water turbidities were unacceptable. Increasing the pilot alum dose and foregoing the use of a polymer in the pilot treatment process generally brought the filter effluent turbidities to within acceptable levels (Chapter 4).

Organic Matter Removal. Organic matter removal was assessed for the coagulation conditions that produced favourable ACH filtration performance (dose $=1.1-\mathrm{mg} / \mathrm{L}$ as Al , $\mathrm{pH}=5.8)$ and these results were compared to organic matter removals of same day baseline alum pilot treatment conditions (dose $=0.9-\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=5.5$ ) and practically optimized FSP operations $($ dose $=0.7-\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=5.5$, cationic polymer $=0.05-\mathrm{mg} / \mathrm{L})$.

Treated water was analyzed using SEC to identify and compare the MW distribution of $\mathrm{UV}_{254}$-active DOC following coagulation efforts that yield favourable filtration performance. Elution patterns of $\mathrm{UV}_{254}$ response versus detention time (Figure 5.10) and relative comparisons of the of the area of $\mathrm{UV}_{254}$ active DOC for each fraction remaining after treatment (Figure 5.11) revealed that the removal of aromatic organic matter was not significantly different between these three treatment scenarios. Similar to bench-scale results, high removal efficiencies were obtained for large aromatic MW fractions, whereas low MW fractions were relatively unaffected by coagulation efforts.

In contrast, THMFP and HAAFP for the FSP were significantly higher than pilot-scale treated water. The lack of correlation between Figures 5.11 and 5.12 indicates that the organic structures responsible for the higher THMFP and HAAFP of treated FSP water may not be aromatic structures. This is not conclusive, however, since both scales of treatment are pre-chlorinated at the point of coagulation. The nature and concentration of the organic precursors responsible for the formation of pre-chlorination DBPs are much different than those contributing to DBPs following coagulation. The significant
differences in THMFP and HAAFP between the pilot and full-scale processes does suggest that the superior mixing conditions provided in the pilot plant increased the removal efficiencies of specific organic precursors contributing to increased THMFP and HAAFP in the FSP (Vadasarukkai, 2010).

Direct comparisons cannot be made between bench-scale results and FSP and pilot-scale results because the bench-scale experiments did not include pre-chlorination prior to coagulation since filter paper would not have the same chlorine demand as deep bed filtration. However, this bench-scale data was included in this figure to highlight that although increased THMFP reductions seemed possible following bench-scale coagulation studies, these enhanced coagulation operating conditions were not feasible to obtain acceptable filtration performance in a direct filtration facility. A dosage of 4-mg/L at a pH of 7.0 was associated with superior THMFP removals during bench-scale studies, but significantly lower dosages of 1.1 to $1.15-\mathrm{mg} / \mathrm{L}$ and pH of 5.8 were required to obtain acceptable filtration results at the pilot scale.

These results agree with other studies suggesting that direct filtration coagulation dosage and pH conditions cannot be determined by simply evaluating influent NOM characteristics and treating the water based on organic matter removal objectives (Gregor et al., 1997, Budd et al., 2004; Eikebrokk et al., 2007). Due to the limited treatment barriers present in direct filtration processes coupled with the inadequate mixing conditions identified in the FSP hydraulic flocculators (Vadasarukkai, 2010), other means of organic matter optimization need to be evaluated for this facility such as the removal
of pre-chlorination practices and upgrades to mechanical flocculation.

### 5.5. CONCLUSIONS

Although bench-scale investigations offer a great starting point to evaluate relative performance conditions for organic matter removal, pilot-scale research is vital to effectively evaluating particle removals and filtration performance for direct filtration facilities. Results from pilot-testing demonstrated that favourable conditions identified for NOM control during bench-scale testing were not consistent with optimal filtered water particle removal. The results of this paper demonstrated that, for this source water (low turbidity, low alkalinity), the optimization of coagulant dosages to remove even very low NOM concentrations can severely compromise the filtration performance of direct filtration processes.

The nature of NOM in this source water before and after coagulation was accurately predicted by SUVA interpretation guidelines developed by Edzwald and Van Benschoten (1990) (Pernitsky and Edzwald, 2006). The overall effectiveness of coagulation processes was also correctly described by these guidelines, as the maximum organic matter removals identified during bench-scale coagulation studies were low, as predicted (30-40\%). These low organic matter removal potentials are typical when treating low SUVA ( $<3-\mathrm{m}^{-1}$ of absorbance per $\mathrm{mg} / \mathrm{L}$ of DOC) source waters using coagulation processes. The overall results of this study support the general understanding that high MW, aromatic organic structures are preferentially removed by coagulation processes, whereas low MW, non-aromatic structures are recalcitrant to removal by coagulation.

Although the removals of aromatic organic compounds were shown to be high for this source water, DBPFP results provided evidence that the non-aromatic structures are also important DBP precursors. While other researchers have successfully used $U V_{254}$ as a surrogate for predicting DBPFP, the weak $\mathrm{UV}_{254}$-DBPFP correlations in this study suggest that organic structures other than aromatics also contribute to the production of DBPs. This work supports recent research indicating that DBP predictions based on $\mathrm{UV}_{254}$ content in water characterized by low SUVA and low MW NOM fractions are generally weak and, therefore, highlights the importance of hydrophilic organic fractions with low aromaticity as being important DBP precursors in low SUVA waters.

Although bench-scale studies were indicative of a potential increase in organic matter removals using enhanced coagulation conditions, the pilot-scale studies proved that these operating conditions were not favourable when filtration performance was considered. The greatest limitation faced in removing NOM during direct filtration treatment is the high solids loading resulting from the coagulant demand required for optimal NOM removal. Since coagulant overdosing is not an option, coagulation pH becomes very important for these facilities. For low turbidity source water with low organic content, a low coagulation pH will decrease the negative charge of NOM and, therefore, reduce the amount of coagulant required for charge neutralization, and encourage the formation of soluble NOM-aluminum complexes due to the increased concentrations of highly charged metal species at lower pH values.

The coagulation conditions that were required to obtain favourable filtration performance using an alternate coagulant $(\mathrm{ACH}$ at $1.1-\mathrm{mg} / \mathrm{L}$ and $\mathrm{pH}=5.8)$ did not provide any organic matter removal benefits when compared to the performance of the control pilot train operating using the same day baseline operating conditions (Alum at $0.9-\mathrm{mg} / \mathrm{L}, \mathrm{pH}$ $=5.5)$ as the FSP plant. Although, filtration performance was improved using ACH based on shorter filter ripening time and lower filter effluent turbidities.

Significant differences were identified between the DBPFP between pilot plant treated water and FSP treated water using similar coagulation conditions. The higher DBPFP of FSP treated water demonstrate the poor mixing performance associated with hydraulic flocculators during full-scale treatment and highlighted the increased NOM removal benefits associated with mechanical mixing capabilities of the pilot plant (Vadasarukkai, 2010).

This study also provides a useful framework for analyzing the overwhelming quantity of data generated by the various operating conditions and multi-factor response parameters generated during plant optimization studies. This framework organized and evaluated this information using indicators (PIs) and graphical heat-mapping techniques. Performance indicator scores were used to assess coagulation operating conditions based on the combined performance of unit filter run volumes (UFRV), steady-state turbidity values and filter ripening volumes (FRV). The resulting performance indicator for each coagulation condition was given equivalent significance when calculating the overall treatment score. Heat-mapping techniques were successfully used to verify that this
equitable assumption was indeed suitable and also to visually simplify and identify favourable operating regions for each filter response parameter.

Overall, this research highlights the overall sensitivity and difficulty associated with optimizing direct filtration coagulation processes. It also stresses the importance of investigating coagulation as a multi-objective optimization process in which both turbidity and organic removal are important output parameters. Finally, it emphasizes the need for further research of ways to reduce DBP precursors in direct filtration facilities without compromising filtration performance.

Table 5.1 Raw Water Characteristics

| Analyte | Warm Water (10 to $20-{ }^{\circ} \mathrm{C}$ ) |  | $\begin{aligned} & \text { Cold Water } \\ & \text { (2 to } 10-{ }^{\circ} \mathrm{C} \text { ) } \end{aligned}$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  | Range | Average | Range | Average |
| Temperature - ${ }^{\circ} \mathrm{C}$ | 11.6-20.9 | 16.2 | $1.0-9.6$ | 4.0 |
| pH | $4.9-5.4$ | 5.1 | $4.9-5.3$ | 5.0 |
| Alkalinity - mg/L as $\mathrm{CaCo}_{3}$ | --- | <1 | --- | <1 |
| Turbidity - NTU | 0.28-0.49 | 0.39 | 0.29-0.46 | 0.37 |
| $\mathbf{U V}_{254}-\mathrm{cm}^{-1}$ | 0.051-0.085 | 0.069 | 0.082-0.103 | 0.093 |
| TOC - mg/L | 1.412-2.947 | 2.545 | 2.771-3.337 | 2.940 |
| DOC - mg/L | 1.808-3.221 | 2.612 | 2.056-3.184 | 2.858 |
| $\begin{gathered} \text { SUVA - } m^{-1} \mathrm{per} \\ \mathrm{mg} / \mathrm{L} \text { of DOC } \\ \hline \end{gathered}$ | $2.8-4.2$ | 3.3 | $2.0-2.9$ | 2.5 |

Table 5.2 Coagulation dose and pH conditions determined for enhanced organic matter removal during bench-scale trials.

|  | Dose $\mathbf{( m g} / \mathbf{L})$ | $\mathbf{p H}$ |
| :---: | :---: | :---: |
| Alum | 1.3 as Al | 5.5 |
| Ferric Sulfate | 1.9 a Fe | 4.5 |
| PACl | 1.65 as Al | 6.0 |
| ACH | 4.0 as Al | 7.0 |

Table 5.3 Criteria for pilot plant filtration performance indicators (PI).

| PI | UFRV $-\boldsymbol{m}^{\mathbf{3}} / \boldsymbol{m}^{\mathbf{2}}$ | FRV $\boldsymbol{1}^{\mathbf{1}} \boldsymbol{m}^{\mathbf{3}} / \boldsymbol{m}^{\mathbf{2}}$ | Turbidity $\boldsymbol{N T U}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{0}$ | $<90(<20)^{2}$ | $>4.5(>1)$ | $>0.2$ |
| $\mathbf{1}$ | $90-180(20-40)$ | $2.25-4.5(0.5-1)$ | $0.1-0.2$ |
| $\mathbf{2}$ | $180-270(40-60)$ | $1.125-2.25(0.25-1)$ | $0.05-0.1$ |
| $\mathbf{3}$ | $270-360(60-80)$ | $<1.125(<0.25)$ | $<0.05$ |

${ }^{1}$ Filter ripening volume $=$ volume of water filtered to reach effluent turbidity $<0.1-\mathrm{NTU}$.
${ }^{2}$ Values in parenthesis represent the equivalent filtration time (h) based on a $4,500 \mathrm{~L} / \mathrm{h} / \mathrm{m}^{2}$ filter loading rate.
Table 5.4 Pilot plant filtration data and performance indicator (PI) ratings for ferric sulfate pilot trials.

| Trial No. | Coagulant Dose$m g / L$ as Fe | pH | Temp. ${ }^{\circ} \mathrm{C}$ | Raw Water <br> Turbidity - NTU | UFRV $m^{3} / \boldsymbol{m}^{2}$ | $\begin{gathered} \text { UFRV } \\ \text { PI (X/3) } \end{gathered}$ | $\begin{aligned} & \text { FRV } \\ & m^{3} / m^{2} \end{aligned}$ | $\begin{gathered} \text { FRV } \\ \text { PI (X/3) } \end{gathered}$ | Turbidity NTU | Turbidity PI (X/3) | Overall (X/1) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| FS-1 | 3.6 | 5 | 19.7 | 0.448 | 143* | 1 | 5.6 | 0 | 0.059 | 2 | 0.3 |
| FS-2 | 3.1 | 5.2 | 19.4 | 0.456 | 109 | 1 | NR ${ }^{1}$ | 0 | 0.344 | 0 | 0.1 |
| FS-3 | 2.9 | 5.2 | 19.4 | 0.388 | 5 | 0 | NR | 0 | 0.640 | 0 | 0.0 |
| FS-4 | 3.1 | 4.5 | 15.3 | 0.355 | 167 | 1 | 4.9 | 0 | 0.036 | 3 | 0.4 |
| FS-5 | 3.1 | 4.7 | 14.3 | 0.348 | 181 | 2 | 9.2 | 0 | 0.034 | 3 | 0.6 |
| FS-6 | 3.1 | 5 | 14.3 | 0.391 | 191 | 2 | 8.9 | 0 | 0.060 | 2 | 0.4 |
| FS-7 | 2.6 | 5 | 12.6 | 0.344 | 248** | 2 | 128.3 | 0 | 0.164 | 1 | 0.3 |
| FS-8 | 2.6 | 4.1 | 11.6 | 0.342 | 173 | 1 | 1.3 | 2 | 0.077 | 2 | 0.6 |
| FS-9 | 2.6 | 4 | 10.4 | 0.39 | 265 | 2 | 29.6 | 0 | 0.098 | 2 | 0.4 |
| FS-10 | 2.4 | 5.8 | 10.4 | 0.307 | 5 | 0 | NR | 0 | 1.999 | 0 | 0.0 |
| FS-11 | 2.4 | 6 | 10.4 | 0.337 | 5 | 0 | NR | 0 | 1.999 | 0 | 0.0 |
| FS-12 | 1.2 | 6 | 10.2 | 0.305 | 5** | 0 | NR | 0 | 0.509 | 0 | 0.0 |
| FS-13 | 1.2 | 5 | 9.6 | 0.337 | 5 | 0 | NR | 0 | 1.357 | 0 | 0.0 |
| FS-14 | 2.4 | 5 | 9.6 | 0.326 | 285 | 3 | NR | 0 | 0.246 | 0 | 0.3 |

Table 5.5 Pilot plant filtration data and performance indicator (PI) ratings for PACl (MBNS) pilot trials.

| Trial No. | Coagulant Dose $m g / L$ as $A l$ | pH | Temp. <br> ${ }^{\circ} \mathrm{C}$ | Raw Water Turbidity - NTU | UFRV <br> $m^{3} / \boldsymbol{m}^{2}$ | $\begin{gathered} \text { UFRV } \\ \text { PI (X/3) } \end{gathered}$ | $\begin{aligned} & \text { FRV } \\ & \boldsymbol{m}^{3} / \boldsymbol{m}^{2} \end{aligned}$ | $\begin{gathered} \text { FRV } \\ \text { PI (X/3) } \end{gathered}$ | Turbidity <br> NTU | Turbidity <br> PI (X/3) | Overall (X/1) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| PACl-1 | 1.7 | 6.0 | 5.9 | 0.478 | 81 | 0 | 3.4 | 1 | 0.032 | 3 | 0.4 |
| PACl-2 | 1.7 | 6.2 | 6.4 | 0.468 | 73 | 0 | 2.9 | 1 | 0.034 | 3 | 0.4 |
| PACl-3 | 1.4 | 6.2 | 6.4 | 0.473 | 4 | 0 | NR ${ }^{1}$ | 0 | $>0.2^{2}$ | 0 | 0.0 |
| PACl-4 | 1.5 | 5.9 | 6.4 | 0.462 | 50 | 0 | 2.3 | 2 | 0.035 | 3 | 0.6 |
| PACl-5 | 0.8 | 5.8 | 5.0 | 0.484 | 139 | 1 | 58.4 | 0 | 0.114 | 1 | 0.2 |
| PACl-6 | 0.8 | 5.9 | 6.0 | 0.470 | 0 | 0 | NR | 0 | 0.252 | 0 | 0.0 |
| PACl-7 | 0.8 | 5.7 | 6.0 | 0.441 | 146* | 1 | NR | 0 | 0.133 | 0 | 0.2 |
| ACl-8 | 0.8 | 6.0 | 7.4 | 0.582 | 155 | 1 | 41.7 | 0 | 0.115 | 1 | 0.2 |
| PACl-9 | 0.8 | 6.2 | 7.4 | 0.525 | 0 | 0 | NR | 0 | 0.412 | 0 | 0.0 |
| PACl-10 | 1.1 | 6.0 | 6.9 | 0.603 | 91 | 1 | 15.0 | 0 | 0.078 | 2 | 0.3 |
| PACl-11 | 1.1 | 5.9 | 8.0 | 0.588 | 95 | 1 | 5.3 | 0 | 0.057 | 2 | 0.3 |
| PACl-12 | 1.1 | 5.8 | 8.0 | 0.566 | 86 | 0 | 3.2 | 1 | 0.029 | 3 | 0.4 |
| PACl-13 | 1.1 | 5.7 | 8.0 | 0.604 | 85 | 0 | 11.7 | 0 | 0.029 | 3 | 0.3 |
| PACl-14 | 1.1 | 5.6 | 7.9 | 0.556 | 113 | 1 | 3.1 | 1 | 0.04 | 3 | 0.6 |
| PACl-15 | 0.8 | 5.9 | 20.6 | 0.325 | 248 | 2 | 5.3 | 0 | 0.052 | 2 | 0.4 |
| PACl-16 | 1.0 | 5.8 | 20.4 | 0.323 | 188 | 2 | 4.5 | 1 | 0.035 | 3 | 0.7 |
| PACl-17 | 0.9 | 5.8 | 20.7 | 0.315 | 330 | 3 | 8.0 | 0 | 0.063 | 2 | 0.6 |
| PACl-18 | 0.6 | 5.8 | 21.7 | 0.337 | 0 | 0 | NR | 0 | >0.2 | 0 | 0.0 |
| PACl-19 | 1.0 | 5.8 | 22.1 | 0.305 | 169 | 1 | 1.1 | 3 | 0.032 | 3 | 0.8 |
| PACl-20 | 1.0 | 5.8 | 22.6 | 0.300 | 227 | 2 | 1.7 | 2 | 0.041 | 3 | 0.8 |

Table 5.6 Pilot plant filtration data and performance indicator (PI) ratings for ACH (HBNS) pilot trials.

| Trial No. | Coagulant Dose $m g / L a s A l$ | pH | Temp. ${ }^{\circ} \mathrm{C}$ | $\begin{gathered} \text { Raw Water } \\ \text { Turbidity - } N T U \end{gathered}$ | UFRV <br> $m^{3} / \boldsymbol{m}^{2}$ | $\begin{gathered} \text { UFRV } \\ \text { PI (X/3) } \end{gathered}$ | $\begin{aligned} & \text { FRV } \\ & m^{3} / m^{2} \end{aligned}$ | $\begin{gathered} \text { FRV } \\ \text { PI (X/3) } \end{gathered}$ | Turbidity <br> NTU | Turbidity <br> PI (X/3) | Overall (X/1) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ACH-1 | 0.90 | 6.3 | 22.4 | 0.307 | 300* | 3 | 14.9 | 0 | 0.076 | 2 | 0.6 |
| ACH-2 | 1.50 | 5.6 | 22.5 | 0.373 | 162 | 1 | 2.3 | 2 | 0.037 | 3 | 0.7 |
| ACH-3 | 1.50 | 6.3 | 22.5 | 0.424 | 53 | 0 | 0.8 | 3 | 0.138 | 1 | 0.4 |
| ACH-4 | 3.00 | 5.6 | 21.1 | 0.446 | 146 | 1 | 28.1 | 0 | 0.035 | 3 | 0.4 |
| ACH-5 | 1.25 | 5.6 | 17.4 | 0.434 | 119 | 1 | 3.6 | 1 | 0.068 | 2 | 0.4 |
| ACH-6 | 1.25 | 6.3 | 16.1 | 0.420 | 95 | 1 | 2.6 | 1 | 0.08 | 2 | 0.4 |
| ACH-7 | 4.00 | 7.0 | 11.1 | 0.419 | 30 | 0 | 2.2 | 2 | 0.288 | 0 | 0.2 |
| ACH-8 | 1.20 | 7.0 | 11.3 | 0.411 | 74 | 0 | $\mathrm{NR}^{1}$ | 0 | 0.139 | 1 | 0.1 |
| ACH-9 | 1.00 | 7.0 | 12.0 | 0.411 | 74 | 0 | NR | 0 | 0.179 | 1 | 0.1 |
| ACH-10 | 1.00 | 6.2 | 10.6 | 0.417 | 203 | 2 | 7.0 | 0 | 0.051 | 2 | 0.4 |
| ACH-11 | 1.10 | 6.3 | 10.1 | 0.425 | 153 | 1 | 3.1 | 1 | 0.052 | 2 | 0.4 |
| ACH-12 | 1.20 | 6.3 | 10.1 | 0.446 | 126 | 1 | 2.1 | 2 | 0.031 | 3 | 0.7 |
| ACH-13 | 0.90 | 6.2 | 10.1 | 0.433 | 180 | 1 | NR | 0 | 0.373 | 0 | 0.1 |
| ACH-14 | 1.40 | 6.3 | 8.2 | 0.444 | 108 | 1 | 3.2 | 1 | 0.036 | 3 | 0.6 |
| ACH-15 | 1.50 | 6.3 | 8.2 | 0.493 | 90 | 0 | 1.8 | 2 | 0.039 | 3 | 0.6 |
| ACH-16 | 0.90 | 7.0 | 2.6 | 0.394 | 5 | 0 | NR | 0 | $>0.2^{2}$ | 0 | 0.0 |
| ACH-17 | 0.90 | 7.0 | 2.6 | 0.406 | 203 | 2 | 45.8 | 0 | 0.209 | 0 | 0.2 |
| ACH-18 | 0.90 | 6.5 | 2.8 | 0.421 | 146 | 1 | 68.3 | 0 | 0.129 | 1 | 0.2 |
| ACH-19 | 0.90 | 6.0 | 3.2 | 0.404 | 181 | 2 | 48.4 | 0 | 0.121 | 1 | 0.3 |
| ACH-20 | 1.50 | 6.0 | 3.9 | 0.403 | 118 | 1 | 0.5 | 3 | 0.03 | 3 | 0.8 |
| ACH-21 | 1.50 | 6.0 | 4.5 | 0.483 | 81 | 0 | 3.0 | 1 | 0.029 | 3 | 0.4 |
| ACH-22 | 1.50 | 6.5 | 4.1 | 0.503 | 79 | 0 | 0.5 | 3 | 0.04 | 3 | 0.7 |
| ACH-23 | 0.90 | 6.5 | 4.1 | 0.513 | 5 | 0 | NR | 0 | $>0.2$ | 0 | 0.0 |
| ACH-24 | 2.00 | 6.5 | 6.1 | 0.451 | 59 | 0 | 2.2 | 2 | 0.028 | 3 | 0.6 |
| ACH-25 | 0.50 | 6.5 | 7.6 | 0.485 | 5 | 0 | NR | 0 | $>0.2$ | 0 | 0.0 |
| ACH-26 | 0.70 | 6.0 | 7.3 | 0.492 | 5 | 0 | NR | 0 | $>0.2$ | 0 | 0.0 |


| Trial No. | Coagulant Dose $m g / L$ as $A l$ | pH | Temp. ${ }^{\circ} \mathrm{C}$ | Raw Water Turbidity - NTU | $\begin{aligned} & \text { UFRV } \\ & m^{3} / m^{2} \end{aligned}$ | $\begin{gathered} \text { UFRV } \\ \text { PI (X/3) } \end{gathered}$ | $\begin{gathered} \text { FRV } \\ m^{3} / \boldsymbol{m}^{2} \end{gathered}$ | $\begin{gathered} \text { FRV } \\ \text { PI (X/3) } \end{gathered}$ | Turbidity NTU | Turbidity PI (X/3) | Overall $(\mathrm{X} / \mathbf{1})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ACH-27 | 0.90 | 5.8 | 8.7 | 0.479 | 320 | 3 | 18.0 | 0 | 0.093 | 2 | 0.6 |
| ACH-28 | 1.00 | 5.8 | 10.5 | 0.473 | 360** | 3 | 6.8 | 0 | 0.067 | 2 | 0.6 |
| ACH-29 | 1.00 | 5.8 | 11.0 | 0.442 | 360** | 3 | 4.3 | 1 | 0.053 | 2 | 0.7 |
| ACH-30 | 1.10 | 5.8 | 12.0 | 0.425 | 335 | 3 | 2.9 | 1 | 0.044 | 3 | 0.8 |
| ACH-31 | 1.10 | 5.8 | 14.2 | 0.419 | 253 | 2 | 0.2 | 3 | 0.029 | 3 | 0.9 |
| ACH-32 | 1.10 | 5.8 | 13.7 | 0.425 | 349 | 3 | 0.4 | 3 | 0.026 | 3 | 1.0 |
| ACH-33 | 1.15 | 5.8 | 14.9 | 0.391 | 255 | 2 | 0.6 | 3 | 0.029 | 3 | 0.9 |
| ACH-34 | 1.10 | 5.8 | 16.5 | 0.379 | 267 | 2 | 0.5 | 3 | 0.026 | 3 | 0.9 |
| ACH-35 | 1.10 | 5.8 | 17.2 | 0.341 | 299 | 3 | 0.5 | 3 | 0.03 | 3 | 1.0 |
| ACH-36 | 1.10 | 5.8 | 18.6 | 0.324 | 299 | 3 | 0.4 | 3 | 0.028 | 3 | 1.0 |
| ACH-37 | 1.15 | 5.8 | 21.5 | 0.292 | 344 | 3 | 0.3 | 3 | 0.028 | 3 | 1.0 |

** Indicates trials that were terminated based on total filtration hours $>80-\mathrm{h}$. All other trials were terminated based on turbidity breakthrough $(>0.2-\mathrm{NTU})$ ${ }^{1} \mathrm{NR}=$ Never Ripened (i.e., turbidities were never below 0.1-NTU)


Figure 5.1 $\mathrm{UV}_{254}$, DOC and SUVA results for favourable coagulation conditions identified for organic matter removal during bench-scale coagulation trials ( $\pm$ standard deviation of triplicate conditions).


Figure 5.2 THMFP results for favourable coagulation conditions identified for organic matter removal during bench-scale coagulation trials ( $\pm$ standard deviation of triplicate conditions). Bromoform results were well below minimum quantification limits.


Figure 5.3 HAAFP results for favourable coagulation conditions identified for organic matter removal during bench-scale coagulation trials ( $\pm$ standard deviation of triplicate conditions). All other HAAs tested were well below minimum quantification limits.


Elution Time - min
Figure 5.4 SEC chromatogram for favourable coagulation conditions identified for organic matter removal during bench-scale coagulation trials. Fractions in the chromatograph are numbered for AMW fraction identification.







Figure 5.5 Area of $\mathrm{UV}_{254}$ Active DOC ( $\mathrm{mAU}^{*} \mathrm{sec}$ ) in different MW fractions for favourable coagulation conditions identified for organic matter removal during bench-scale coagulation trials.
a.) UVRV

b.) Turbidity

c.) FRV


Figure 5.6 Heat maps of unit filter run volume (UFRV), inverse turbidity and inverse filter ripening volume (FRV) for ferric sulfate pilot trials.


Figure 5.7 Heat maps of unit filter run volume (UFRV), inverse turbidity and inverse filter ripening volume (FRV) for PACl (MBNS) pilot trials.


Figure 5.8 Heat maps of unit filter run volume (UFRV), inverse turbidity and inverse filter ripening volume (FRV) for ACH (HBNS) pilot trials. Highlighted circles indicate optimal operating conditions.


Figure 5.9 Representative pilot-scale filtered water turbidity profiles comparing favourable ACH (HBNS) filtration conditions to same day baseline Alum pilot conditions and FSP operations.


Figure 5.10 Representative pilot-scale SEC chromatogram comparing favourable ACH (HBNS) filtration conditions to same day baseline Alum pilot conditions and FSP operations. Fractions in the chromatograph are numbered for fraction identification.


Figure 5.11 $\mathrm{UV}_{254}$ Active DOC ( $\mathrm{mAU} * \mathrm{sec}$ ) in different MW fractions remaining following coagulation for favourable pilot-scale ACH (HBNS) filtration conditions and same day raw water, baseline Alum pilot conditions and FSP operations.

*FSP and plot-scale treatment processes included pre-chlorination practices and the bench-scale trials did not include pre-chlorination, therefore direct comparison between these treatment scales cannot be made.

Figure 5.12 THMFP and HAAFP results comparing pilot-scale superior ACH (HBNS) filtration performance to same day baseline pilot Alum and FSP performance and to bench-scale favourable organic matter removal performance for ACH (HBNS) and Alum.

## CHAPTER 6 LEAD RELEASE FOR DRINKING WATER WITH HIGH CHLORIDE TO SULFATE MASS RATIOS

### 6.1. ABSTRACT

Bench-scale experiments investigated the role a coagulant change would have in causing a significant effect with respect to lead leaching in drinking water with a high ( $>0.5$ ) chloride-to-sulfate mass ratio (CSMR). The coagulants evaluated in this bench-scale study included aluminum sulfate (CSMR of 0.9), polyaluminum chloride (CSMR of 2.0) and ferric sulfate (CSMR of 0.9) and the two lead bearing plumbing materials examined were lead:tin solder and passivated lead pipe, both in connection with copper pipe. Although high CSMRs have been shown to be the main mechanism of attack in prior research, CSMR did not govern lead leaching following the coagulant changeover conditions evaluated in this study. Residual concentrations of iron and aluminum remaining following coagulation were principal contributors, as evidenced by positive correlations between lead release and iron and aluminum concentrations following stagnation. The overall influence of these two factors was dependent on the sources of lead in the plumbing scenarios tested. It was hypothesized that an important mechanism involved in the occurrence of lead release was related to the presence of iron and aluminum concentrations and the adsorption of lead on aluminum and iron oxides.

### 6.2. INTRODUCTION

A potential concern associated with coagulation optimization is the potential unintended consequences of a coagulant change on the distribution system, specifically related to lead release from lead pipe and solder materials. Previous studies have reported that coagulant changeovers were a key factor in unexpected high lead concentrations in distribution systems (Dodrill and Edwards, 1995; Edwards et al., 1999). Specifically, it was observed that coagulant switches from a sulfate containing coagulant (e.g., alum or aluminum sulfate) to a chloride containing coagulant (e.g., polyaluminum chloride or ferric chloride) resulted in lead release.

Evidence obtained through lead release data resulting from practical case studies and laboratory-based studies have demonstrated that a high CSMR induces high galvanic currents, which governs lead leaching incidences in distribution systems following coagulant changeovers (Dodrill and Edwards, 1995; Edwards et al., 1999; Dudi, 2004; Edwards and Triantafyllidou, 2007; Nguyen et al., 2010b; Nguyen et al., 2010c). The critical CSMR level cited from multiple bench-scale and full-scale studies that governs the effects of lead leaching is $\sim 0.5 \mathrm{mg}$ of chloride per mg of sulfate (Oliphant, 1983; Gregory, 1990; Dodrill and Edwards, 1995; Edwards et al., 1999; Edwards and Triantafyllidou, 2007). Above this CSMR level, galvanic corrosion of lead pipe is increased and below this threshold, lead leaching is mitigated.

The greatest impact of these anions was observed under stagnant conditions at lead to copper joints where low dissolved inorganic carbon and oxygen conditions exist, the
local pH drops as low as 3 or 4 as $\mathrm{Pb}^{2+}$ (a lewis acid) is released and high corrosion rates prevail (Dudi, 2004; Edwards and Triantafyllidou, 2007; Nguyen et al., 2010a; Nguyen et al., 2010b). Chloride and sulfate concentrations have been identified in prior research as being highly influential in controlling water corrosivity upon lead under these circumstances (Edwards and Triantafyllidou, 2007; Stone et al., 2009; Nguyen et al 2010a; Nguyen et al 2010b).

The presence of either chloride or sulfate alone tends to protect leaded materials when there is no galvanic connection to another metal. However, where a lead to copper connection exists, chloride moves to the anode to maintain electroneutrality and stimulates the attack on lead pipe (Oliphant, 1983; Edwards and Triantafyllidou, 2007; Nguyen et al., 2010a). Further, chloride breaks down passivity by penetrating films through pores or defects easier than other ions such as sulfate (Reive and Uhlig, 2008). Through this process, chloride dissolves any coating or barrier previously on the lead surface and reacts with the lewis acid $\left(\mathrm{Pb}^{2+}\right)$ to form a soluble lead complex, $\mathrm{PbCl}^{+}$. $\mathrm{PbCl}^{+}$increases the galvanic current for anodic dissolution, therefore increasing lead leaching and preventing the formation of solid barriers on the lead surface (Edwards and Triantafyllidou, 2007; Reive and Uhlig, 2008; Nguyen et al., 2010a). In contrast, if sufficient levels of sulfate are present, sulfate is drawn to the anode and protects the pipe during galvanic corrosion (Oliphant, 1983; Edwards and Triantafyllidou, 2007; Stone et al., 2009). $\mathrm{PbSO}_{4}$ is insoluble at the local pH drop occurring at the anode, therefore through precipitation $\mathrm{PbSO}_{4}$ serves as a corrosion inhibitor by strengthening the arrangement of the protective layer on the lead surface (Dudi, 2004; Edwards and

Triantafyllidou, 2007; Stone et al., 2009; Nguyen et al., 2010a).

The objective of this research was to investigate the role of a coagulant change in causing lead leaching in lead and/or copper plumbing. This work contributes to the established data set for coagulant changeover studies with a particular emphasis on very low alkalinity water (less than $10 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ ) and high CSMR values. This work was conducted at the bench-scale using a previously published methodology (Stone et al., 2009, Nguyen et al., 2010a). The coagulants studied in this paper include aluminum sulfate (alum), polyaluminum chloride ( PACl ) and ferric sulfate. In addition, two lead bearing plumbing materials studied were lead:tin solder and passivated lead pipe, both in connection with copper pipe.

### 6.3. MATERIALS AND METHODS

### 6.3.1. Experimental Procedures

The experimental approach was based on lead leaching studies in plumbing materials resulting from coagulant changeovers being conducted by lead researchers in this subject matter. (Stone et al. 2009; Nguyen et al., 2010a).

Apparatus. Bench-scale pipe set-ups were designed to compare the leaching effects of lead:tin solder and harvested lead pipe galvanically connected to copper pipe through two pipe set-ups. Previous studies have shown that lead solder and lead pipe galvanically connected to copper yielded the highest lead leaching instances when high CSMR is a factor (Nguyen et al., 2010a). One pipe set-up consisted of harvested lead pipe with a
pre-existing pipe scale connected to copper using a simulated 40:60 lead:tin solder joint, which will be referred to in charts and tables as "Pb pipe $-\mathrm{Pb}: \mathrm{Sn}$ solder -Cu pipe" and throughout this paper as the combined passivated lead and solder scenario. The lead pipe was harvested from a lead service line replacement in the distribution system in Halifax, Nova Scotia. The other pipe scenario consisted of a copper to copper pipe connection using a simulated 40:60 lead:tin solder joint, which will be referred to in charts and tables as "Cu pipe $-\mathrm{Pb}: \mathrm{Sn}$ solder -Cu pipe".

The combined passivated lead and solder scenario was composed of a $31-\mathrm{cm}(12.2-\mathrm{in})$ length of passivated $1.9-\mathrm{cm}(0.75-\mathrm{in})$ lead pipe connected to a $6.35-\mathrm{cm}(2.5-\mathrm{in})$ length of $1.3-\mathrm{cm}(0.5-\mathrm{in})$ copper pipe using clear tubing and leaving an approximately $2-\mathrm{mm}(0.08-$ in) gap between the two pipes (Figure 6.1). The lead to copper ratio for this scenario was in order of 6.6:1. The system containing only solder material as a source of lead was erected in the same manner, except the simulated solder joint was connecting two copper pipes (Figure 6.1). The lead to copper ratio for this scenario was in order of 1:139. To simulate a soldered joint, $0.08-\mathrm{cm}(0.032-\mathrm{in})$ diameter solder wire was inserted through the $1.3-\mathrm{cm}(0.5-\mathrm{in})$ copper pipe until it reached the interface of the two pipes. The solder and pipes were electrically connected using copper wires and clips to simulate a galvanic connection (Figure 6.2). The pipes were capped using silicone stoppers throughout the experiment. The pipe sizes and experimental set-up were selected to induce the worstcase scenario with respect to high corrosion and lead leaching conditions and to allow for micro-electrode measurements within the pipes (Nguyen et al., 2010a).

Test Water. Test water was collected from the JD Kline Water Treatment Plant (Halifax, Nova Scotia, Canada). This facility is a surface water treatment plant that draws water from the nearby Pockwock Lake. Test water was treated to simulate treatment conditions in the full-scale direct filtration treatment process (i.e.; coagulation, flocculation, filtration). All water conditions were subjected to identical treatment processes, with the only differences being the coagulant type, dosage and coagulation pH used. The coagulants evaluated included alum, ferric sulfate and PACl . The ferric sulfate dosage was calculated as an equivalent metal molar ratio based on the alum dosage currently employed in the full-scale treatment plant and the coagulation pH was determined through jar testing. The optimal coagulation pH and dosage for the PACl condition, a proprietary blend, were determined through jar testing. Pre-oxidized water was drawn from the full-scale plant and was subsequently coagulated, filtered through a $1.5 \mu \mathrm{~m}$ filter paper, and dosed with the following chemicals for final treatment: 1) zincorthopolyphosphate corrosion inhibitor/iron and manganese sequestering agent addition of $1.65 \mathrm{mg} / \mathrm{L}(0.5 \mathrm{mg} / \mathrm{L}$ as phosphate $), 2)$ disinfectant addition of $1.0 \mathrm{mg} / \mathrm{L}$ total chlorine, and 3) final pH adjustment using 0.1 M sodium hydroxide $(\mathrm{NaOH})$ to 7.4. Treated water for each water condition was made in batches as required, but was only treated as far as the filtration stage. Finished water chemicals were added immediately before the water change occurred.

Since this study involved changing the coagulant type, dosage, and coagulation pH , the finished water alkalinity and organic content varied between the three water conditions tested. Table 6.1 presents the raw water and treated water quality characteristics for each
water condition tested. The water condition treated with ferric sulfate was an outlier relative to coagulation performance, as it had twice the alkalinity and more TOC relative to the other coagulant conditions evaluated.

Protocol. During testing, the two pipe set-ups were exposed to the 3 water conditions described above. Each test was performed in duplicate to obtain statistical confidence in trends; therefore, 12 tests were conducted in total. Exposure of the finished water to each pipe condition was via a static "dump-and-fill" protocol three times per week. The water changes occurred on Monday (M), Wednesday (W) and Friday (F), therefore yielding two stagnation periods of 48 hours (M-W, W-F) and one stagnation time of 72 hours (F-M). Stagnation times were chosen based on previous research conducted in this field with the intention of representing the long stagnation times that commonly occur in public buildings over weekends (Nyugen et al 2010c). Over the 27-week duration of the experiment, the samples obtained after each water change were analyzed for bulk water pH , total lead content and chloride and sulfate levels. After week 17, samples were also filtered through $0.45 \mu \mathrm{~m}$ pore size filters and analyzed for dissolved lead concentrations. TOC and DOC concentrations, turbidity, pH , and alkalinity of batched and treated water were monitored throughout the experimental trial. The chloride and sulfate concentrations of finished water conditions were monitored before each water change to monitor CSMR conditions throughout the study.

Measurements of chloride and pH were attempted at the lead and copper material surface using micro-probe technologies to track further mechanisms of corrosive attack.

However, the measurement procedure had a negative effect on the experimental results, and these effects are described in the results section of this paper.

### 6.3.2. Analytical Procedures

Throughout the duration of this research, RO water was used for all cleaning and chemical stock preparations. All glassware was rinsed 3 times using RO water following cleaning. The RO water was obtained from a Milli- $Q^{\circledR}$ purification system. Combination $\mathrm{pH} / \mathrm{mV} /$ Temperature/ DO/ ISE and Conductivity meters (Accumet* XL 25 and XL 60 models) with plastic bodied, gel-filled, combination pH electrodes (Accumet Accu-Cap*) were used for pH readings. Three-point calibration ( $\mathrm{pH} 4,7,10$ ) was conducted each day. Alkalinity measurements were conducted using a Hach Alkalinity Test Kit (Model AL-DT) equipped with a digital titrator.

Lead samples were acidified using concentrated nitric acid and stored at $4^{\circ} \mathrm{C}$ until analysis. Samples were diluted as needed with concentrated nitric acid and analyzed using an atomic absorption graphite furnace (PerkinElmer Analyst 200). Unpreserved chloride and sulfate samples were analyzed with 5 days of sampling and were stored at $4^{\circ} \mathrm{C}$ until analysis. Chloride and sulfate analysis was completed using ion chromatography (Metrohm 761 Compact IC).

To validate the precision and accuracy of the metals and anions analysis, method blanks (deionized water) and quality control (QC) samples (deionized spiked with a known amount of standard mixture) were analyzed every 10 samples for metals analysis and every 15 samples for anion analysis. Recovery testing was carried out on the QC samples
and results were only accepted if QC recoveries were between 70 to $130 \%$. In addition, samples obtained during weeks 4 through 9 were analyzed for metals via Induced Coupled Plasma Mass Spectrometry (ICP-MS), which provided both a QC analysis and an indication of background aluminum and iron concentrations remaining following coagulation for the conditions tested.

TOC and DOC samples were collected head-space free in $40-\mathrm{mL}$ pre-cleaned glass vials and preserved with concentrated phosphoric acid to a $\mathrm{pH}<2$ and measurements were performed using a TOC-V CPH analyzer with a Shimadzu ASI-V autosampler and catalytically aided combustion oxidation non-dispersive infrared detector (NDIR) having a method detection limit of $0.08 \mathrm{mg} / \mathrm{L}$ (Shimadzu Corporation, Kyoto, Japan). Before sample collection, DOC samples were filtered through $0.45 \mu \mathrm{~m}$ polsulfone filter membrane (GE Water \& Process Technologies) that had been pre-rinsed with $500-\mathrm{mL}$ of RO water (APHA, AWWA, and WEF, 1998).

### 6.4. RESULTS AND DISCUSSION

For all water conditions studied, the total lead entering the pipe set-ups was not detectable. Figure 6.3 presents the total lead released from each of the pipe scenarios throughout the 27 weeks of this study. The acclimation period for both pipe scenarios was 6 weeks and dissolved lead monitoring started after 4-months operation, to ensure that stability in the system had occurred.

The total lead spikes observed throughout the first 6 weeks for the combined passivated lead and solder pipes (Figure 6.3) can be attributed to lead particles sloughing off the
passivated pipe during this initial acclimation phase and sitting at the bottom of the pipe set-up during stagnation, therefore causing increased lead concentrations in the sampled water. Additionally, lead spikes were observed in both pipe-setups in Week 11 following micro-electrode measurements (Figure 6.3a). In order to gain more insight into the localized effects at the lead and copper interface, chloride and pH micro-electrodes were placed inside the test pipes before the water was changed at the end of Week 10, which disturbed the lead surfaces within the pipes and increased lead levels in the following weeks. These lead spikes were caused by the electrodes scraping the lead pipe walls and disturbing the lead:tin solder. The increased lead release effects were significantly worse in the passivated lead pipe set-up, due to additional lead particles sloughing off the mature pipe scale inside of the pipe. Thus, microelectrode measurements were not collected for the remainder of the study. Following this disturbance, the lead release data returned to the apparent trends that were surfacing prior to the use of the microelectrodes after one or two weeks.

Generally, lead leaching was very high in this study (Figure 6.3), which was expected since all of the CSMR values exceeded the threshold value of $\sim 0.5$ to 0.6 for all water conditions tested (Nguyen et al., 2010a). Additionally, the geometry and physical experimental set-up were designed to maximize worst-case conditions contributing to lead corrosion. Based on the concept that CSMR is the controlling factor with respect to lead release, it was expected that the ferric sulfate (CSMR of 0.9 ) and alum (CSMR of 0.9 ) water conditions would lead to similar levels of lead leaching, since their CSMR levels were the same, and that the PACl treated water (CSMR of 2) would correlate with
a higher lead release, since the CSMR level was more than double that of the other two water conditions (Table 6.1). The trends reported from this study did not support this hypothesis.

### 6.4.1. Pipe Set-up 1: Pb pipe - $\mathrm{Pb}:$ Sn solder - Cu pipe Scenario

Effect of CSMR. The ferric sulfate water was the most corrosive condition for the combined passivated lead and solder pipe set-up, whereas, the alum and PACl treated waters behaved similarly despite the large CSMR differences between the two water conditions (Figure 6.3a). For all conditions, the lead levels continued to decrease over time; however, more dramatic decreases were observed for the alum and PACl conditions, particularly in the first half of this study. The peak observed in weeks 24 through 25 for the alum water condition was likely a result of the lead solder being exposed to the atmosphere for maintenance of the simulated solder connection (Figure 6.3a). A small portion of the solder was replaced with new material to repair the solder joint.

Average lead release results were synthesized by averaging lead data throughout weeks 17 through 27 of this study (Figure 6.4a and Table 6.2). This time period was chosen to correspond with the measurement of dissolved lead. To assess the difference between average results, statistical significance was determined using a $95 \%$ confidence interval and a p-value limit of 0.15 was chosen to account for variability of corrosion (Nguyen et al., 2010a). The ferric sulfate condition released an average of approximately 2 times more total lead than the PACl and alum conditions (p-values $<0.01$ ), releasing $916 \mu \mathrm{~g} / \mathrm{L}$ of lead (Figure 6.4a and Table 6.2). The difference in average total lead for the alum and

PACl conditions were not significantly different (p-value of 0.70 ) and the $95 \%$ confidence intervals of the water conditions overlapped, however PACl lead release concentrations were higher, on average, throughout the study (Figure 6.3a).

Dissolved lead trends observed throughout the last 10 weeks of the study were significantly less than total lead concentrations (Figure 6.4a) indicating that the majority of the lead released was in a particulate form. On average, the dissolved lead concentrations were approximately $24 \%$ of the total lead measured in the passivated lead scenario. CSMR trends for dissolved lead release were somewhat different than total lead trends (Figure 6.4a). For the passivated lead scenario, the ferric sulfate condition remained the most corrosive condition and leached the highest levels of dissolved lead (p-value $<0.01$ ), however the alum condition contributed $24 \%$ higher dissolved lead concentrations than the PACl condition ( p -value $<0.01$ ).

Effect of Residual Aluminum and Iron. The results obtained through the ICP-MS analysis of weeks 4 through 9 samples revealed positive correlations between total residual concentrations of iron and aluminum remaining following stagnation and total lead release data for the passivated lead scenario (Figure 6.5a). Furthermore, the trend line for a CSMR of 2 is steeper and yields more lead than predicted by the trendline associated with a CSMR of 0.9. This illustrates that the effects of CSMR on lead release were secondary to the effects of iron and aluminum concentrations. The average aluminum, iron and lead concentrations released during weeks 4 through 9 are presented in Table 6.3. It is hypothesized that the mechanism involved in the occurrence of lead
release as a function of iron and aluminum concentrations is the adsorption of lead on aluminum and iron oxides.

Consistent with these findings, past and recent investigations involving both field testing and pipe loop experiments have concluded that particulate lead concentrations are positively correlated with particulate iron concentrations (Hulsmann, 1990; De Rosa and Williams, 1992; Deshommes et al., 2010; Triantafyllidou and Edwards, 2011). It is hypothesized that adsorption of lead on iron particles is a dominant cause of lead release in systems where particulate iron is entering the distribution system (Hulsmann, 1990; Deshommes et al., 2010). Additionally, it has been shown that the effects of particulate iron on lead release are very obvious following periods of stagnation and lead concentrations actually increased with stagnation but were not an issue during flowing conditions (Hulsmann, 1990).

### 6.4.2. Pipe Set-up 2: Cu pipe - Pb:Sn solder - Cu pipe Scenario

Effect of CSMR. Over the duration of the study, the variability in total lead release was such that no considerable difference could be seen among the water conditions for the pipe set-up containing lead:tin solder as the only lead bearing material (Figure 6.3b). Despite the CSMR differences, there was no considerable difference in average total lead concentrations between each water condition tested (Figure 6.4b and Table 6.2). However, the average alum lead release concentration was slightly higher than the ferric sulfate and PACl conditions ( p -value $<0.03$ ), releasing approximately $50-\mu \mathrm{g} / \mathrm{L}$ total lead, whereas the ferric sulfate and PACl lead concentrations were not significantly different (p-value of 0.2).

Dissolved lead trends were significantly less than total lead concentrations for the solder only scenario, again indicating that the majority of the lead released was in a particulate form (Figure 6.4b and Table 6.2). On average, the dissolved lead concentrations were approximately $45 \%$ of the total lead concentrations in the solder only scenario. For the solder only scenario, the alum condition remained the most corrosive environment, yielding $26 \%$ more dissolved lead than the PACl condition ( p -value $<0.08$ ) and $77 \%$ more than the least corrosive ferric sulfate condition (p-value $<0.01$ ).

Effect of Residual Aluminum and Iron. Unlike the passivated lead results, iron and aluminum levels following stagnation did not correlate with total lead release data during weeks 4 through 9 for the solder only scenario (Figure 6.5b). One explanation for the lack of variability between coagulant conditions is that the detrimental effects associated with CSMR and residual iron and aluminum levels are masking each other, therefore yielding no effect on lead leaching. The average aluminum, iron and lead concentrations released during weeks 4 through 9 are presented in Table 6.3.

Effect of other water quality parameters on metals release. As outlined in Table 6.1, TOC, DOC and alkalinity levels following coagulation were higher for the ferric sulfate water condition as compared to the alum and PACl conditions and particulate organic matter is also present in the ferric sulfate condition and not in the others. However, lead release trends did not correlate with TOC or DOC changes that occurred between batched water conditions in either experimental set-up over the duration of the study. It was expected that increased alkalinity would buffer the low pH at the lead solder surface and
help minimize lead levels. However, in this case, a higher alkalinity was associated with increased lead release, therefore the difference in alkalinity was not enough to provide sufficient buffering capacity to overcome the adverse effects of the residual iron and aluminum concentrations for the passivated lead scenario.

### 6.4.3. Comparison of Lead Materials

The combination of passivated lead and lead:tin solder resulted in significantly more lead release (on a mass basis, $\mathrm{mg} / \mathrm{L}$ ) than lead released from the presence of lead:tin solder alone (Figure 6.4). On average, the passivated lead pipe condition resulted in bulk water total lead concentrations 9 times more than the lead/tin solder to copper condition for alum, 13.5 times more for PACl and 33 times more for the ferric sulfate treated water (Figure 6.5). Bulk water lead concentrations were expected to be higher in the passivated lead pipes since there were two sources of lead (lead pipe and solder) and significantly more lead material was exposed to the water in the passivated lead apparatus versus the solder only scenario.

The higher levels of particulate lead in the passivated lead scenario could be attributed to plumbing scales being degraded despite the corrosion inhibitor presence (Table 6.3). It is hypothesized that the instability of the corrosion layer in the passivated pipe under these new treatment conditions led to a high occurrence of particulate lead and subsequently made this condition more vulnerable to the detrimental effects of the residual iron and aluminum concentrations than the solder only scenario. This explains why residual iron and aluminum concentrations were the primary contributor to lead release in the passivated lead scenario, but the effects of these cations were masked by the effects of

CSMR in the solder only scenario. The findings also suggest that iron and aluminum concentrations below regulatory levels may still pose a public health risk in distribution systems, particularly those with iron distribution pipes (Triantafyllidou and Edwards, 2011).

These results are not consistent with recent findings in a case study by Sandvig and Boyd (2010), which evaluated the effects of CSMR on the release of lead from a variety of lead plumbing materials and found that simulated lead solder to copper connections consistently yielded higher particulate lead concentrations than passivated lead pipe connected to copper. These inconsistencies are attributed to differences in the composition and stability of the existing scale on the passivated pipes used in these studies.

To directly compare the average lead released between plumbing scenarios, lead concentrations were normalized as the total mass of lead released per wetted lead material surface area in Figure 6.6. Normalized values were calculated by multiplying the total lead concentrations by the sample volume and dividing by the wetted surface area of leaded material (Nguyen et al., 2010a). The exposed surface area of lead and volume of water exposed to pipe material for each pluming scenario are presented in Table 6.4. The combined passivated lead and solder plumbing scenario contained approximately 100 times more wetted lead surface area than the solder only set-up.

The solder only pipe set-up had the highest lead levels for each water condition when compared to the passivated lead scenario on a lead released per unit surface area basis. Therefore, the galvanic connection of copper pipe soldered together with lead:tin solder exacerbated lead leaching. This is consistent with previous literature in which a lead solder to copper pipe loop consistently produced higher lead levels per wetted surface area than copper pipes coupled with passivated lead pipes under similar CSMR conditions (Nguyen et al., 2010a). The mass of lead released per wetted surface area from the solder only scenario was 4.3 times higher than the passivated lead scenario for the ferric sulfate condition, 10.5 times higher for the PACl condition and 16 times higher than the alum condition (Figure 6.6). The substantially higher lead release associated with the alum condition in the solder only scenario as compared to the combined passivated lead scenario may be attributed to the fact that the passivated lead pipes were exposed to similar water quality in this study as they would have been exposed to in situ.

Although galvanic currents were not measured as part of this study, there is evidence that suggests that significantly higher galvanic currents were sustained by the solder only pipe scenario. The increased mass of lead release per wetted surface area in the solder only pipe scenario is an indication that corrosion rates are significantly higher for the solder only pipe scenario. Also, the bulk water pH values following stagnation were 0.25 to 0.55 pH units lower in the solder only scenario. During stagnant conditions, the pH at the lead surface may decrease significantly and reach levels as low as 3 or 4 (Edwards and Triantafyllidou, 2007; Nguyen et al., 2010a). Since the micro-environment over which the pH drop occurs is very small (Nguyen et al., 2010b), even a slight decrease in the
bulk water pH would indicate a local pH drop at the anode surface. Therefore, this drop in bulk water pH is indicative of a local pH drop at the anode and increased galvanic corrosion rates in the solder only scenario.

### 6.5. CONCLUSIONS

Bench scale experiments were conducted to investigate the role of high CSMRs in lead leaching from lead:tin solder and harvested lead pipe galvanically connected to copper. No definitive trends were observed relating CSMR to lead leaching; the highest CSMR condition ( PACl with a CSMR of 2) did not yield the highest lead concentrations and the replicate CSMR conditions (alum and ferric sulfate with CSMRs of 0.9 ) did not yield similar lead levels. Although high CSMRs have been shown to be the main mechanism of attack in prior research, CSMR was not the primary catalyst for lead leaching following the coagulant changeover conditions evaluated in this study. Residual concentrations of iron and aluminum remaining following coagulation were principal contributors. The overall influence of these two factors was dependent on the sources of lead in the plumbing scenarios tested.

For the passivated lead pipe scenario, positive correlations were found between the total residual iron and aluminum concentrations following coagulation and total lead released during stagnation, for each coagulant tested. It was hypothesized that adsorption of lead on iron and aluminum oxides is the mechanistic explanation for this relationship. The ferric sulfate treated water was the most corrosive treatment condition, which correlated with the highest residual iron and aluminum concentrations following stagnation. CSMR effects were secondary to the corrosive effects of iron and aluminum, as evidenced by

PACl (CSMR of 2.0) yielding higher than predicted lead release trends than alum (CSMR of 0.9 ) despite having similar residual aluminum concentrations in the treated water. The lead release from the scenario where solder was the only lead source was not considerably different for the three water conditions tested. Thus there is potential that the detrimental effects of residual iron and aluminum counteracted the effects of CSMR for this condition.

The results of this research highlight the importance of ensuring corrosive factors (i.e.; CSMR and residual iron and aluminum) are not unintentionally introduced as a result of coagulant dosage adjustments or changeovers. Identifying the appropriate solutions to lead release remains a site-specific exercise, but should consider the unintended consequences of coagulation conditions on distribution system water quality.

Table 6.1 Average water quality characteristics for raw and treated water conditions. The error values indicate the $95 \%$ confidence interval.

| Parameter | Raw Water | PACI | Alum | Ferric Sulfate |
| :---: | :---: | :---: | :---: | :---: |
| Coagulant Dosage (mg/L) | --- | 1.5 | 8.0 | 5.4 |
| Coagulant Dosage (mg/L) | --- | 1.5 as Al | 0.7 as Al | 1.4 as Fe |
| Coagulation $\mathrm{pH}^{1}$ | --- | 6.0 | 5.5 | 5.0 |
| Alkalinity (mg/L as $\mathrm{CaCO}_{3}$ ) | 0 | $16.3 \pm 1.6$ | $16.8 \pm 2.8$ | $32.6 \pm 7.4$ |
| TOC (mg/L) | $2.89 \pm 0.13$ | $1.86 \pm 0.57$ | $1.88 \pm 0.10$ | $2.50 \pm 0.20$ |
| DOC (mg/L) | $2.82 \pm 0.13$ | $1.86 \pm 0.55$ | $1.81 \pm 0.24$ | $2.13 \pm 0.41$ |
| CSMR | 1.49 | $2.06 \pm 0.25$ | $0.93 \pm 0.10$ | $0.91 \pm 0.10$ |

${ }^{1}$ Finished water pH is 7.4 .

Table 6.2 Average bulk water total and dissolved lead release concentrations ( $\mu \mathrm{g} / \mathrm{L}$ ) for each water condition during Weeks 17 through 27 of this study ( $\pm$ standard deviation). Data from the duplicate pipes were averaged to obtain the comparisons in this table.

|  | Lead $-\mu g / L$ |  |
| :---: | :---: | :---: |
| Water Condition | Total | Dissolved |
| Pb pipe $-\boldsymbol{P b}:$ Sn Solder $-\mathbf{C u}$ pipe |  |  |
| Ferric Sulfate | $916 \pm 332$ | $203 \pm 81$ |
| PACl | $497 \pm 352$ | $96 \pm 21$ |
| Alum | $422 \pm 302$ | $128 \pm 45$ |
| Ferric Sulfate | Cu pipe $-\boldsymbol{P b}:$ Sn Solder $-\mathbf{C u}$ pipe |  |
| PACl | $27 \pm 28$ | $5.6 \pm 11$ |
| Alum | $37 \pm 27$ | $27 \pm 19$ |

Table 6.3 Average bulk water total lead, aluminum and iron release data ( $\mu \mathrm{mol}$ ) for each water condition during Weeks 4 through 9 of this study ( $\pm$ standard deviation). Data from the duplicate pipes were averaged to obtain the comparisons in this table.

| Water <br> Condition | Total Lead - $\boldsymbol{\mu m o l}$ | Total Aluminum - $\boldsymbol{\mu m o l}$ | Total Iron - $\boldsymbol{\mu m o l}$ |
| :---: | :---: | :---: | :---: |
|  |  | Pb pipe $-\boldsymbol{P b}:$ Sn Solder $-\mathbf{C u}$ pipe |  |
| Ferric Sulfate | $9.3 \pm 1.8$ | $7.0 \pm 0.5$ |  |
| PACl | $4.2 \pm 3.5$ | $5.1 \pm 1.5$ | $12.8 \pm 2.9$ |
| Alum | $7.8 \pm 14.9$ | $9.8 \pm 7.3$ | 0 |
|  |  | Cu pipe - Pb:Sn Solder - Cu pipe |  |
| Ferric Sulfate | $1.2 \pm 0.6$ | $4.8 \pm 0.6$ | $15.4 \pm 3.8$ |
| PACl | $1.1 \pm 0.8$ | $1.2 \pm 0.7$ | 0 |
| Alum | $1.1 \pm 0.6$ | $3.1 \pm 0.5$ | 0 |

Table 6.4 Exposed lead and copper wetted surface area and volume of exposed water for each pipe condition.

|  | Surface Area <br> of Lead <br> Bearing <br> Material <br> Exposed <br> $\left(\mathbf{c m}^{2}\right)$ | Surface Area of <br> Copper Bearing <br> Material <br> Exposed <br> $\left(\mathrm{cm}^{2}\right)$ | Volume of <br> Water <br> Exposed to <br> pipes <br> $(\mathbf{m L})$ |
| :--- | :---: | :---: | :---: |
| Pb pipe $-\mathrm{Pb}: \mathrm{Sn}$ solder -Cu pipe | 158 | 24 | $74.5 \pm 4$ |
| Cu pipe $-\mathrm{Pb}: S n$ solder -Cu pipe | 1.58 | 219 | $106 \pm 2$ |



Figure 6.1 Picture of 4 of 12 pipe setups: a) Pipe set-up 1: Pb pipe $-\mathrm{Pb}: \mathrm{Sn}$ solder -Cu pipe; b) Pipe set-up 2: Cu pipe $-\mathrm{Pb}: \mathrm{Sn}$ solder -Cu pipe


Figure 6.2 Picture of simulated $40: 60 \mathrm{~Pb} / \mathrm{Sn}$ soldered joint.


Figure 6.3 Total lead release as a function of time. Data from the three samples per week and duplicate pipes were averaged to obtain the comparisons in this figure.


Figure 6.4 Average bulk water total and dissolved lead release concentrations ( $\mu \mathrm{g} / \mathrm{L}$ ) for each water condition during Weeks 17 through 27 of this study. Data from the duplicate pipes were averaged to obtain the comparisons in this figure. The error bars indicate the $95 \%$ confidence interval.
$(\mathrm{FS}=$ ferric sulfate, $\mathrm{PACl}=$ polyaluminum chloride, Alum $=$ aluminum sulfate $)$


Figure 6.5 Average lead release as a function of iron and aluminum release for during Weeks 4 through 9 of this study. Data from the duplicate pipes were averaged to obtain the comparisons in this figure.


Figure 6.6 Average total mass of lead released per wetted surface area of lead bearing material $\left(\mu \mathrm{g} / \mathrm{cm}^{2}\right)$ for each water condition during Weeks 17 through 27. Data from the duplicate pipes were averaged to obtain the comparisons in this figure. The error bars indicate the $95 \%$ confidence interval.
$(\mathrm{FS}=$ ferric sulfate, $\mathrm{PACl}=$ polyaluminum chloride, $\mathrm{Alum}=$ aluminum sulfate $)$

## CHAPTER 7 INFLUENCE OF COAGULATION RESIDUALS ON LEAD RELEASE IN DRINKING WATER

### 7.1. ABSTRACT

Bench-scale experiments evaluated the corrosive effects of coagulation residuals following stagnation on lead:tin solder-to-copper connections under variable chloride-tosulfate mass ratio (CSMR) conditions. CSMR conditions, both above and below the 0.5 CSMR threshold cited for lead leaching, were tested using three different coagulants; aluminum sulfate (CSMRs of 0.3 and 1.0), ferric sulfate (CSMRs of 0.3 and 0.9) and polyaluminum chloride (CSMR of 2.8). Both residual particulate iron and aluminum concentrations and CSMR levels were found to be significant factors contributing to lead release in galvanic settings. Overall, results suggest that iron particulates may play a more important role in lead release than aluminum particulates.

### 7.2. INTRODUCTION

Coagulant changeovers can inadvertently induce water chemistry changes that have significant detrimental impacts on distribution system water quality. Specifically, changes in coagulant type or dosage can introduce treated water residuals that have corrosive impacts on leaded materials in the distribution system. Unfavorable residuals that have been shown to have an effect on water corrosivity following a coagulant changeover include iron and aluminum oxides resulting from ineffective treatment conditions or increases in the chloride-to-sulfate mass ratio (CSMR) resulting from changing the coagulant type or dosage (Edwards et al., 2007; Nguyen et al 2010a;, Nguyen et al 2010c).

The correlation between galvanic corrosion and significant changes in pH , sulfate, chloride and lead concentrations following stagnation has been well established in recent literature (Edwards and Triantafllidou, 2007; Nguyen et al., 2010a; Nguyen et al., 2010b; Nguyen et al., 2010c). When lead and copper are coupled in distribution systems, the lead surface behaves anodically, galvanic currents persist and lead corrosion is induced. During stagnation, dissolved oxygen is depleted over time and acidic conditions at the anode are increased as $\mathrm{Pb}^{2+}$, a lewis acid, is released. Consequently, the resulting pH conditions at the anodic surface can reach levels as low as 3-4, which hinders the formation of passive films, increases and sustains galvanic currents and perpetuates the attack of the lead material (Dudi, 2004; Edwards and Triantafyllidou, 2007; Nguyen et al., 2010a; Nguyen et al., 2010b).

Numerous case studies have demonstrated that the magnitudes of chloride and sulfate concentrations present under such galvanic conditions are a primary contributor to lead corrosion rates (Edwards and Triantafyllidou, 2007; Stone et al., 2009; Nguyen et al 2010a; Nguyen et al 2010b). Specifically, when the CSMR is high (CSMR > 0.5) chloride stimulates the attack of lead pipe; whereas, when the CSMR is low (CSMR $<$ $0.5)$, the abundance of sulfate ions outweigh the negative impacts of chloride and act as a corrosion inhibitor (Oliphant, 1983; Gregory, 1990; Dodrill and Edwards, 1995; Edwards et al., 1999; Edwards and Triantafyllidou, 2007). In contrast, the results presented in Chapter 6 concluded that the CSMR was not always the controlling factor with respect to lead release in these corrosive microenvironments and demonstrated the importance of other water quality parameters on leaching incidences.

In Chapter 6, a bench-scale study was conducted to evaluate the effects of high CSMRs on lead leaching from passivated lead pipe and lead:tin solder coupled with copper pipe. While the CSMR did have a secondary impact on lead leaching in this study, lead concentrations following stagnation were significantly affected by the residual concentrations of iron and aluminum remaining following coagulation. The overall impact of these factors on lead release was dependent on the sources of lead in the plumbing scenarios tested. It was suggested that the mechanism involved in the occurrence of lead release was adsorption of lead on aluminum and iron oxides remaining after coagulation.

Anecdotal and field scale data presented in the literature has established a connection
between particulate lead concentrations and particulate iron concentrations in distribution systems (Hulsmann, 1990; De Rosa and Williams, 1992; Deshommes et al., 2010; Triantafyllidou and Edwards, 2011). These studies hypothesized that adsorption of lead on iron particles is a dominant cause of lead release in systems where particulate iron is entering the distribution system (Hulsmann, 1990; Deshommes et al., 2010).

Study Objectives. The objective of this research was to investigate the role of CSMR and residual coagulation particles (i.e., remaining floc particles) in causing lead leaching under stagnant conditions when exposed to lead-to-copper connections in distribution systems. This study was carried out at the bench-scale using a previously published methodology (Nguyen et al., 2010a. Nguyen et al., 2010c). The three coagulants tested were aluminum sulfate (alum), polyaluminum chloride ( PACl ) and ferric sulfate under variable CSMR conditions. This experimental work was conducted to supplement the findings of Chapter 6 which uncovered the influence of iron and aluminum residuals as a prominent contributor to lead leaching under galvanic conditions for high CSMR source waters. Two distinct experimental phases were conducted to 1 . verify the lead release trends reported in Chapter 6 using an augmented experimental setup and 2. explore the overall effect on lead release by lowering the CSMR of the sulfate based coagulants to levels below the 0.5 threshold reported to mitigate lead leaching in past studies (Nguyen et al., 2010a, Nguyen et al., 2010c).

### 7.3. MATERIALS AND METHODS

### 7.3.1. Experimental Procedures

The experimental design and procedure was based on lead leaching studies in plumbing materials resulting from coagulant changeovers being conducted by lead researchers in this subject matter. (Nguyen et al., 2010a, Nguyen et al., 2010c).

Apparatus. Simulated lead-copper joints were prepared using a $2.54-\mathrm{cm}(1-\mathrm{in})$ length of $1.27-\mathrm{cm}(0.5-\mathrm{in})$ diameter copper coupled with a $2.54-\mathrm{cm}$ (1-in) length of $50: 50 \mathrm{~Pb}: \mathrm{Sn}$ solder melted inside (Figure 7.1). The lead to copper mass ratio for the coupons was in order of 1:7.2. The coupons will supplement the findings from the more mechanistic pipe apparatus used in Chapter 6 using this source water. Although the pipe set-up apparatus provided insight into the role a coagulant change would have in causing a significant effect with respect to lead leaching, this set-up might not reflect the magnitude of lead from lead:solder joints.

Test Water. Test water was collected from the JD Kline Water Treatment Plant (Halifax, Nova Scotia, Canada) and was treated to simulate treatment conditions in the full-scale direct filtration treatment process (i.e.; coagulation, flocculation, filtration). All water conditions were subjected to identical treatment processes, with the only differences being the coagulant type, dosage and coagulation pH used. The coagulants evaluated included alum, ferric sulfate and PACl. Pre-oxidized water was drawn from the full-scale plant and was subsequently coagulated, filtered through a $1.5 \mu \mathrm{~m}$ filter paper, and dosed with the following chemicals for final treatment: 1) zinc-orthopolyphosphate corrosion
inhibitor/iron and manganese sequestering agent addition of $1.65 \mathrm{mg} / \mathrm{L}(0.5 \mathrm{mg} / \mathrm{L}$ as phosphate), 2) disinfectant addition of $0.5 \mathrm{mg} / \mathrm{L}$ total chlorine, and 3) final pH adjustment using sodium hydroxide to 7.4. Treated water was made in batches as required, but was only treated as far as the filtration stage. Finished water chemicals were added immediately before the water change occurred.

Two phases of experimentation were carried out in which changing the dose of the coagulant altered the CSMR. In Phase 1, the "high CSMR" phase, the coupons were initially exposed to three different water conditions including alum (CSMR of 1.0), PACl (CSMR of 2.8) and ferric sulfate (CSMR of 0.9). The ferric sulfate dosage was calculated as an equivalent metal molar ratio based on the alum dosage currently employed in the full-scale treatment plant and the coagulation pH was determined through jar testing (Table 7.1). The optimal coagulation pH and dosage for the PACl condition, a proprietary blend, were determined through jar testing. Finally, the alum pH and dose ( pH of 5.5 ; alum dose of $8-\mathrm{mg} / \mathrm{L}$ ) used were equivalent to full-scale operating conditions. In Phase 2, the "low CSMR" phase, the CSMR of the ferric sulfate and alum water conditions were altered to $0.3(<0.5$ threshold) and the PACl treatment condition remained at the CSMR used in the high CSMR phase and behaved as a control condition to compare the two phases of the study (Table 7.1). The test water from the high CSMR phase remained stagnant for approximately one month before the low CSMR water conditions were introduced.

Since this study involved changing the coagulant type, dosage, and coagulation pH , the finished water alkalinity and organic content varied between the three water conditions evaluated. However, these water quality conditions did not impact the amount of lead released during stagnation (Appendix D, Figure D1). Table 7.1 presents the coagulation treatment conditions and treated water quality characteristics for each water condition tested.

Protocol. The solder-copper couplings were exposed to 100 mL of the finished water in a 200 mL glass beaker via a static "dump-and-fill" protocol two times per week, which provided one 72 hour stagnation period and one 96 hour stagnation time. Stagnation times were chosen based on previous research conducted in this field with the intention of representing the long stagnation times that commonly occur in public buildings over weekends (Nyugen et al 2010c). The tests were performed in triplicate for each water condition. The samples obtained after each water change were analyzed for bulk water pH , oxidation reduction potential (ORP), total and dissolved lead and copper concentrations. The TOC, turbidity, pH , ORP and alkalinity of batched and finished water were monitored periodically throughout. The chloride and sulfate concentrations of finished water conditions were monitored before each water change to verify influent CSMR conditions throughout the study. Finally, total and dissolved iron and aluminum concentrations were measured for a short period of time during the low CSMR study.

### 7.3.2. Analytical Procedures

Throughout the duration of this research, RO water was used for all cleaning and
chemical stock preparations. All glassware was rinsed 3 times using RO water following cleaning. The RO water was obtained from a Milli- $Q^{\circledR}$ purification system. Combination $\mathrm{pH} / \mathrm{mV} /$ Temperature/ DO/ ISE and Conductivity meters (Accumet* XL 25 and XL 60 models) with plastic bodied, gel-filled, combination pH electrodes (Accumet Accu-Cap*) and a platinum pin $\mathrm{Ag} / \mathrm{AgCl}$ combination ORP electrode (Accumet* Metallic ORP Combination Electrode) were used for pH and ORP readings, respectively. Three-point calibration ( $\mathrm{pH} 4,7,10$ ) was conducted each day for pH . Alkalinity measurements were conducted using a Hach Alkalinity Test Kit (Model AL-DT) equipped with a digital titrator.

Lead and copper samples were acidified using concentrated nitric acid and stored at $4^{\circ} \mathrm{C}$ until analysis. Samples were diluted with nitric acid and analyzed using an atomic absorption graphite furnace (PerkinElmer Analyst 200). Bulk water samples were filtered through $0.45 \mu \mathrm{~m}$ pore size filters and then analyzed for dissolved lead and copper concentrations. Unpreserved chloride and sulfate samples were analyzed with 5 days of sampling and were stored at $4^{\circ} \mathrm{C}$ until analysis. Chloride and sulfate analysis was completed using ion chromatography (Metrohm 761 Compact IC).

To validate the precision and accuracy of the metals and anions analysis, method blanks (deionized water) and quality control (QC) samples (deionized spiked with a known amount of standard mixture) were analyzed every 10 samples for metals analysis and every 15 samples for anion analysis. Recovery testing was carried out on the QC samples and results were only accepted if QC recoveries were between 70 to $130 \%$. In addition, a
small number of samples from the low CSMR study were analyzed for iron and manganese via Induced Coupled Plasma Mass Spectrometry (ICP-MS).

TOC and DOC samples were collected head-space free in $40-\mathrm{mL}$ pre-cleaned glass vials and preserved with concentrated phosphoric acid to a $\mathrm{pH}<2$ and measurements were performed using a TOC-V CPH analyzer with a Shimadzu ASI-V autosampler and catalytically aided combustion oxidation non-dispersive infrared detector (NDIR) having a method detection limit of $0.08 \mathrm{mg} / \mathrm{L}$ (Shimadzu Corporation, Kyoto, Japan). Before sample collection, DOC samples were filtered through $0.45 \mu \mathrm{~m}$ polsulfone filter membrane (GE Water \& Process Technologies) that had been pre-rinsed with $500-\mathrm{mL}$ of RO water (APHA, AWWA, and WEF, 1998).

### 7.4. RESULTS AND DISCUSSION

For all water conditions tested, the total lead entering the coupon set-ups was not detectable. Figure 7.2a presents the total lead released over the 10 -week duration of the high CSMR study. Figure 7.2b illustrates the total lead released during the 14 -week low CSMR investigation. The acclimation period for both phases was approximately 4 weeks and it was assumed that system stability occurred past this point. Average lead concentrations were synthesized by averaging data throughout Weeks 5 through 10 of the high CSMR study period and weeks 5 through 14 for the low CSMR study period. To assess the difference between average results, statistical significance was determined using a p-value limit of 0.15 to account for variability of corrosion (Nguyen et al., 2010a).

### 7.4.1. High CSMR Results

Comparison of Coagulants. All CSMR values exceeded the threshold value of 0.5 mg of chloride per mg of sulfate for the water conditions tested in the high CSMR phase. For total lead release, the ferric sulfate treated water (CSMR of 0.9) presented the most corrosive conditions, the PACl test water (CSMR of 2.8 ) was the second highest contributor, and the lowest concentrations were observed for the aluminum sulfate water condition (CSMR of 1.0), as illustrated in Figure 7.2a. Following the acclimation stage, the ferric sulfate and PACl lead release concentrations were quite variable for the duration of the study, whereas the alum lead release trends were relatively stable (Table 7.2).

The ferric sulfate treated water resulted in 2.7 times more total lead than the PACl condition (p-value of 0.08) and 15 times more total lead than the alum condition (p-value of $<0.01$ ), releasing $844 \mu \mathrm{~g} / \mathrm{L}$ on average (Figure 7.3). In contrast to total lead release trends, the ferric sulfate and PACl dissolved lead concentrations were not significantly different ( p -value of 0.9 ) and the $95 \%$ confidence intervals overlapped. The alum condition remained the least corrosive condition, leaching an average of 6.8 times less dissolved lead than the other conditions tested. On average, dissolved lead concentrations were $26 \%$ of the total lead concentrations for the ferric sulfate condition, $57 \%$ for the PACl treated water and $39 \%$ for the alum condition. This indicates that a significant amount of particulate lead is being released, particularly for the ferric sulfate condition. The high concentrations of particulate lead are consistent with other studies evaluating the corrosion of lead solder in connection with copper (Nguyen et al., 2010a). There was a considerable amount of variability in lead release data for the ferric sulfate
water condition, due to high variability in lead concentrations throughout the study and amongst the triplicate coupons (Table 7.2).

No positive correlation exists between CSMRs and lead concentrations for the high CSMR conditions studied. However, the lead release trends associated with specific coagulant conditions in this study are consistent with the results of previous bench-scale corrosion studies using this source water under identical treatment conditions, but using a different experimental set-up (Chapter 6). In Chapter 6, it was concluded that the absence of CSMR correlation with lead release was a direct result of the adsorption of lead on residual concentrations of iron and aluminum oxides following coagulation.

Effect of Residual Aluminum and Iron. Iron and aluminum concentrations following stagnation were not measured during the high CSMR phase of this study, but a representative idea of the treated water concentrations of these coagulation residuals can be drawn from the results of Chapter 6 using the same source water. Table 7.3 presents the average treated water total aluminum and iron concentrations ( $\mu \mathrm{mol}$ ) for each water condition tested in Chapter 6 under similar treatment conditions as those tested in the high CSMR phase of this study. Based on the iron and aluminum concentrations reported in Table 7.3, it was hypothesized that the high levels of lead leaching observed following exposure to water treated with ferric sulfate was due to high residual iron concentrations remaining following coagulation. In addition, it was theorized that CSMR effects were secondary to the corrosive effects of iron and aluminum residuals, as evidenced by PACl (CSMR of 2.0) being consistently more corrosive than alum (CSMR 0.9), regardless of
residual aluminum concentrations following coagulation being slightly higher for the water treated with alum.

It is important to note the lead release results reported in Chapter 6 were not considerably different for the three water conditions tested when exposed to lead:tin solder connected to copper and it was concluded that the detrimental effects of residual iron and aluminum counteracted the effects of CSMR. The differences in lead release trends and the overall magnitude of lead release resulting from the connection of lead:tin solder-to-copper observed between this study and the results presented in Chapter 6 can be explained by the difference in lead to copper ratios and fundamental differences in the experimental set-ups used. The lead-to-copper ratio utilized in this study was in the order of 20 times higher than the relative quantities used in Chapter 6 experiments and this study utilized soldered joints as opposed to simulated soldered connections.

### 7.4.2. Low CSMR Results

Comparison of Coagulants. Recent research indicates that lead release problems occurring following coagulant changeovers could typically be mitigated by controlling the type of coagulant and keeping the CSMR below the 0.5 threshold (Nguyen et al., 2010). Therefore, the ferric sulfate and alum CSMRs were lowered to 0.3 to evaluate the effect of a low CSMR on lead release. Although lead release was reduced, it was not mitigated. The ferric sulfate (CSMR of 0.3 ) and $\mathrm{PACl}(\mathrm{CSMR}$ of 2.8$)$ treated waters produced similar lead release concentrations despite the large CSMR differences (Figure 7.3), however, the ferric sulfate treated water was still the most corrosive environment over the duration of the low CSMR study (Figure 7.2b). Consistent with the high CSMR
phase, the alum water condition (CSMR of 0.3 ) was the least corrosive environment (Figure 7.3). The ferric sulfate condition released 1.3 and 5.2 times more lead than the PACl ( p -value of 0.06 ) and alum ( p -value $<0.01$ ) treated waters, respectively. Again, there was a considerable amount of variability in total lead release data for the ferric sulfate treated water, due to daily concentration variability and between the triplicate coupons (Table 7.2).

As was the case for the high CSMR study, dissolved lead concentrations were significantly less than total lead concentrations for all coagulant conditions tested. The ferric sulfate and PACl dissolved lead concentrations were not significantly different (pvalue of 0.8 ) and the alum condition remained the least corrosive condition, leaching approximately 5 times less dissolved lead than the other conditions. On average, dissolved lead concentrations were $42 \%$ of the total lead concentrations for the ferric sulfate condition, $60 \%$ for the PACl treated water and $47 \%$ for the alum condition.

Effect of Residual Aluminum and Iron. Average bulk water total lead, aluminum and iron release data ( $\mu \mathrm{mol}$ ) for each water condition during Weeks 3-5 of the low CSMR phase are presented in Table 7.4. Analysis of these results revealed no linear relationship was observed for the ferric sulfate treated water conditions. Positive correlations (pvalues $<0.05$ ) existed between particulate iron and aluminum remaining following stagnation and particulate lead release data for both the PACl and alum treated water during the low CSMR phase (Figure 7.4 b and c ), suggesting that adsorption of lead to iron and aluminum oxides was indeed occurring for these coagulant conditions.

It was hypothesized that particulate lead release did not correlate with total particulate iron and aluminum concentrations for the ferric sulfate condition because the detrimental effects associated with the high residual iron and aluminum levels were dampened by the beneficial effects of lowering the CMSR below the 0.5 threshold. In spite of this dampening effect, ferric sulfate was still the most corrosive water condition. The PACl treatment condition was the second highest contributor to lead release, despite having both very high particulate aluminum concentrations following stagnation and almost 10 times the CSMR of the ferric sulfate treated water. This suggests that iron particles may be more detrimental to lead release than aluminum particles. As expected, the aluminum sulfate condition was the least corrosive environment and was associated with the lowest particulate residual iron and aluminum particulates and CSMR condition.

The high and low CSMR results could not be directly compared since passivation of the lead surface occurred during stagnant conditions between the two experimental phases (approximately 1 month) and as the coupons were exposed to the various water conditions over time. The effects of passivation are highlighted by the difference in lead leaching observed for the PACl water conditions between phase 1 and phase 2, despite the CSMR conditions and residual aluminum and iron concentrations being identical. In fact, both total and dissolved average lead concentrations were approximately 3.5 times higher during the high CSMR phase for the PACl water condition.

### 7.4.3. Effect of Other Water Quality Parameters on Metals Release

Additional water quality parameters monitored throughout this study were TOC, DOC, alkalinity and ORP. Although TOC, DOC and alkalinity concentrations varied among
the coagulant conditions tested, neither lead or copper release trends correlated with the treated water TOC, DOC or alkalinity concentrations of the treated water conditions (Appendix D, Figure D1). Therefore, organic matter and alkalinity were not considered to be a controlling factor in this study. However, the relatively low alkalinity ( $<20 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ ) of the treated water conditions throughout this study likely contributed to the high lead levels, since a low buffering capacity is expected to amplify the pH drop at the lead anode (Edwards and Triantafyllidou, 2007) and finished water alkalinities less than $50 \mathrm{mg} / \mathrm{L}$ have been shown to lead to serious lead problems (Nguyen et al., 2010a; Nguyen et al., 2010c).

Figure 7.5 presents the ORP of the treated water conditions and the average decrease in ORP that occurred during stagnation for both the high and low CSMR water conditions tested. A decrease in ORP is an indication that the solution is donating electrons to maintain electroneutrality. The overall decrease in ORP in the PACl and alum water conditions were generally higher than that of the FS condition indicating that more electron exchange occurred during these conditions. This electrochemical response could be an indication of the flow of chloride and sulfate ions to the anodic surface.

There most dramatic decrease in ORP occurred in PACl treated water, which also coincided with the highest treated water ORP conditions. For this condition, the decrease is an indication of chloride moving to the anodic surface and perpetuating the attack of the lead surface. The second largest treated water ORP and overall ORP reduction was observed in the alum treated water. In this case, the reduction in ORP is an indication of
sulfate moving to the lead surface and protecting the solder surface. Hence, the dissolution of lead into the water was reduced for the alum treated water. The lowest treated water ORP and smallest change in ORP occurred for the ferric sulfate treated water, which is an indication that movement of sulfate to the anode was impeded and, therefore, hindered passivation of the lead surface.

### 7.5. CONCLUSIONS

Solder-to-copper coupons were exposed to variable coagulation conditions to evaluate the effects of coagulation residuals on lead leaching following stagnation. Consistent with the results of Chapter 6, residual aluminum and iron concentrations following stagnation and the treated water CSMR were both significant contributors to lead release trends. The positive correlations shown between particulate iron and aluminum and particulate lead concentrations following stagnation confirmed that the adsorption of lead to iron and aluminum oxides is a viable hypothesis for lead release.

Despite the variable CSMR conditions tested, ferric sulfate treated water (CSMR of 0.9 and 0.3 ) consistently yielded the highest lead levels following stagnation, due to high residual iron concentrations remaining following coagulation. CSMR effects were secondary to the corrosive effects of particulate iron, as evidenced by PACl (CSMR of 2.8) being consistently more corrosive than alum (CSMR 0.9 and 0.3 ), regardless of residual aluminum concentrations following coagulation. In general, results suggest that iron particulates may be more detrimental to lead release than aluminum particulates.

Problems occurring following coagulant changeovers cannot always be mitigated by controlling the type of coagulant and keeping the CSMR below the 0.5 threshold, as
suggested by past studies (Nguyen et al., 2010). If a utility is planning a coagulant changeover, the effects of coagulation residuals on distribution water quality should be verified before such changes are implemented at full-scale.
Table 7.1 Average water characteristics for treated water conditions. The error values indicate the $95 \%$ confidence interval.

| Test Water | Coagulation Conditions |  |  | Alkalinity (mg/L as $\mathrm{CaCO}_{3}$ ) | $\begin{aligned} & \begin{array}{l} \text { ORP } \\ (m V) \end{array} \end{aligned}$ | $\begin{gathered} \text { TOC } \\ (m g / L) \end{gathered}$ | $\begin{gathered} \hline \text { DOC } \\ (m g / L) \end{gathered}$ | CSMR |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Dosage <br> (mg/L) | Dosage $(m g / L)$ | pH ${ }^{1}$ |  |  |  |  |  |
| High CSMR |  |  |  |  |  |  |  |  |
| Ferric Sulfate | 5.4 | 1.4 as Fe | 5.0 | $15.1 \pm 6.7$ | $494 \pm 26$ | $2.631 \pm 0.28$ | $2.229 \pm 0.12$ | $0.93 \pm 0.07$ |
| PACI | 1.5 | 1.5 as Al | 6.0 | $12.6 \pm 8.4$ | $618 \pm 14$ | $1.800 \pm 0.27$ | $1.838 \pm 0.02$ | $2.79 \pm 0.18$ |
| Alum | 8 | 0.7 as Al | 5.5 | $11.4 \pm 4.5$ | $565 \pm 22$ | $2.091 \pm 0.26$ | $2.040 \pm 0.06$ | $0.99 \pm 0.04$ |
| Low CSMR |  |  |  |  |  |  |  |  |
| Ferric Sulfate | 30 | 7.8 as Fe | 5.0 | $6.2 \pm 1.5$ | $474 \pm 18$ | $1.786 \pm 0.08$ | $1.897 \pm 0.09$ | $0.300 \pm 0.006$ |
| PACI | 1.5 | 1.5 as Al | 6.0 | $14.4 \pm 2.4$ | $567 \pm 15$ | $2.157 \pm 0.10$ | $2.191 \pm 0.09$ | $2.760 \pm 0.100$ |
| Alum | 50 | 4.4 as Al | 5.5 | $5.3 \pm 0.7$ | $569 \pm 18$ | $2.067 \pm 0.08$ | $2.264 \pm 0.01$ | $0.300 \pm 0.003$ |

Table 7.2 Bulk water total and dissolved lead release concentrations ( $\mu \mathrm{g} / \mathrm{L}$ ) for the high CSMR (Weeks 5 through 10) and low CSMR (Weeks 5 through 14) water conditions tested ( $\pm$ standard deviation). Data from the triplicate conditions were averaged to obtain the comparisons in this table.

| Water Condition | Lead $-\mu g / L$ |  |
| :---: | :---: | :---: |
| Ferric Sulfate (CSMR 0.9) | $844 \pm 715$ | Dissolved |
| PACl (CSMR 2.8) | $314 \pm 164$ | $184 \pm 188$ |
| Alum (CSMR 1.0) | $56 \pm 11$ | $171 \pm 94$ |
|  | Low CSMR |  |
| Ferric Sulfate (CSMR 0.3) | $118 \pm 19$ | $27 \pm 4$ |
| PACl (CSMR 2.8) | $88 \pm 6$ | $49 \pm 9$ |
| Alum (CSMR 0.3) | $23 \pm 3$ | $53 \pm 4$ |

Table 7.3 Average treated water total aluminum and iron concentrations ( $\mu \mathrm{mol}$ ) for each water condition during Chapter 6 experiments under identical treatment conditions as those tested in the High CSMR phase of this study ( $\pm$ standard deviation).

| Water <br> Condition | Total Aluminum <br> $\mu$ mol | Total Iron <br> $\boldsymbol{\mu m o l}$ |
| :---: | :---: | :---: |
| Ferric Sulfate | $5.2 \pm 0.5$ | $14.8 \pm 4.1$ |
| PACl | $1.1 \pm 0.4$ | 0 |
| Alum | $4.1 \pm 0.6$ | 0 |

Table 7.4 Average bulk water total lead, aluminum and iron release data ( $\mu \mathrm{mol}$ ) for each water condition during Weeks $3-5$ of the Low CSMR phase ( $\pm$ standard deviation). Data from the triplicate conditions were averaged to obtain the comparisons in this table.

| Water <br> Condition | Particulate Lead <br> $\boldsymbol{\mu} \boldsymbol{m o l}$ | Particulate <br> Aluminum <br> $\boldsymbol{\mu m o l}$ | Particulate Iron <br> $\boldsymbol{\mu m o l}$ |
| :---: | :---: | :---: | :---: |
| Ferric Sulfate | $0.45 \pm 0.29^{1}$ | $0.20 \pm 0.22$ | $0.65 \pm 0.30$ |
| PACl | $0.27 \pm 0.18$ | $0.47 \pm 0.55$ | $0.04 \pm 0.03$ |
| Alum | $0.08 \pm 0.03$ | $0.17 \pm 0.17$ | $0.03 \pm 0.03$ |



Figure 7.1 Picture of 50:50 lead/tin solder melted to a copper coupon and submerged in 100 ml of test water in a glass beaker.
a.) High CSMR


Figure 7.2 Total lead concentrations for the high and low CSMR trials throughout the duration of each study. Data from the two samples per week and triplicate set-ups were averaged to obtain the comparisons in this figure.
$(\mathrm{FS}=$ ferric sulfate, $\mathrm{PACl}=$ polyaluminum chloride, Alum $=$ aluminum sulfate $)$


Figure 7.3 Average bulk water total and dissolved lead released ( $\mu \mathrm{g} / \mathrm{L}$ ) for the high CSMR (Weeks 5 through 10) and low CSMR (Weeks 5 through 13) water conditions tested. Data from the triplicate conditions were averaged to obtain the comparisons. The error bars indicate the $95 \%$ confidence interval.
$(\mathrm{FS}=$ ferric sulfate, $\mathrm{PACl}=$ polyaluminum chloride, Alum $=$ aluminum sulfate $)$
a.) Ferric Sulfate, $\mathrm{CSMR}=0.3$

b.) $\mathrm{PACl}, \mathrm{CSMR}=2.8$

c.) Alum, $\mathrm{CSMR}=0.3$


Figure 7.4 Average lead release as a function of iron and aluminum release for during Weeks 3 through 5 for the Low CSMR phase of this study. Data from the triplicate conditions were averaged to obtain the comparisons in this figure.


Figure 7.5 Average treated water ORP $(\mathrm{mV})$ and decrease in ORP $(\mathrm{mV})$ during stagnation period for the High CSMR (Weeks 5 through 10) and Low CSMR (Weeks 5 through 13) water conditions tested. Data from triplicate conditions were averaged to obtain the comparisons. The error bars indicate the $95 \%$ confidence interval.
$(\mathrm{FS}=$ ferric sulfate, $\mathrm{PACl}=$ polyaluminum chloride, Alum $=$ aluminum sulfate $)$

## CHAPTER 8 RECOMMENDATIONS

Based on the findings of this research, several opportunities for future research projects were identified that were beyond the scope of this thesis, but merit additional investigation. Future research recommendations are presented for each major research topic presented in this thesis.

### 8.1. PILOT-PLANT PAIRING

Pilot proving methodology. Although the validation methodology, outlined in Chapter 4, used to pair the pilot plant to the full-scale treatment process was an overall success, there were some post-proving operational and experimental scaling issues related to the differences in mixing regimes between the two scales of treatment. Due to the efficiency of the mechanical mixers in the pilot plant, adding a polymer to the pilot treatment process during cold winter months was not required and, when attempted, produced high particle loading to the filters and filtered water turbidities were unacceptable. This issue was deemed a factor of scale between the two treatment processes and was mitigated by increasing the pilot alum dose to approximately $0.9-\mathrm{mg} / \mathrm{L}$ as Al (from $0.7-\mathrm{mg} / \mathrm{L}$ as Al ) and foregoing the use of a polymer in the pilot treatment process, which brought the filter effluent turbidities to within acceptable levels. In addition, the results of Chapter 5 identified substantial differences between the DBPFP between pilot-plant treated water and FSP treated water using during cold-water operations. The higher DBBfp of the FSP treated water was attributed to the poor mixing performance associated with hydraulic flocculators during full-scale treatment and evidenced increased NOM removal benefits associated with the mechanical mixing capabilities of the pilot plant (Vadasarukkai, 2010).

In light of these post-proving issues, it is recommended that DBPFP and organic matter fractionation techniques be added to the list of response parameters used for pilot-proving trials to provide a more robust means of identifying differences in organic removal performance. It is also recommended that proving trials be repeated during exceptionally challenging treatment events (i.e.; cold-water treatment) to verify that results obtained through pilot-studies will be representative of process changes that will successfully optimize the performance of the FSP.

Pilot proving statistical approach. In future pilot proving studies, it is recommended that the measurement errors for each parameter be considered in order to set achievable and acceptable deviations between pilot and full-scale performance. Contrastingly, the hypothesized mean difference of $0.05-\mathrm{NTU}$ for filter effluent turbidity was not strict enough and a more appropriate performance benchmark for turbidity differences would have been $0.02-\mathrm{NTU}$ in future studies.

### 8.2. DIRECT-FILTRATION COAGULATION OPTIMIZATION

 NOM characterization of FSP versus pilot treated water. The findings of this research exposed significant differences in DBPFP between the FSP and pilot treated water. These differences were primarily attributed the differences in mixing energy applied between the two scales of treatment. In light of these findings, it is recommended that NOM characterization studies be completed on both treated waters, to identify the physical and chemical characteristics of the organic precursors that are increasingly removed by mechanical mixing in the pilot plant and not by the hydraulic flocculators in the FSP.Mixing optimization studies. Based on the results of Chapter 5, enhanced coagulation is not a viable option for achieving DBP reductions without comprising filtration performance at a this direct filtration facility. Since the differences in DBPFP between the FSP and pilot plant are indicative that upgrading to mechanical mixing in the FSP could yield substantial DBP reductions in FSP treated water, it is recommended that mixing studies are conducted in the pilot plant to identify the optimal mixing intensities required to enhance organic matter removal and, subsequently, reduce DBPs at this facility.

Zeta potential investigation. Since higher coagulant dosages required to meet DBP regulations often lead to unacceptable solids loading in direct filtration facilities, as highlighted by Chapter 5 results, other means of optimizing organic matter removal need to be addressed for such facilities. Recent research has shown that the use of zeta potential, which provides a direct measurement of the surface charge of floc particles, can be used as an effective means of optimizing filtration performance through the addition of a cationic polymer to provide adequate floc formation and increased organic matter removals using reduced coagulant dosages at these facilities (Pernitsky et al., 2011). It is recommended that zeta potential measurements be used as a performance indicator when conducting future optimization studies at this facility.

Pre-chlorination investigation. Chapter 5 presented results that showed substantial differences between DBPFPs achieved during bench-scale and pilot plant experiments simulating the baseline coagulation pH and dosage conditions of the FSP. The key difference between these experiments was the absence of pre-chlorination during bench-
scale experiments. If the utility did not depend on pre-chlorination for microbial control in their filters, there is the potential that significant decreases in DBPs could be realized, as eliminating pre-chlorination is an effective way to control DBP levels in finished water (Xie, 2003). It is recommended that a study be conducted to evaluate potential DBP reductions that can be achieved through eliminating pre-chlorination practices in the FSP. As part of this investigation, the option of operating biologically active filters could also be examined for this facility, which may lead to further removal of biodegradable NOM, which are typically recalcitrant to coagulation treatment. If biologically active filters are identified as posing too high of a threat to microbial contamination at this facility, chlorination could be added to filter backwash water to act as a filter aid for microbial control in the filters.

Rapid fractionation techniques for low NOM waters. Although the use of organic size distribution was a useful tool in assessing the relative removals of aromatic organic materials during the coagulation optimization experiments conducted during this thesis project, it would be useful to develop a rapid organic matter characterization procedure to identify the removals of both aromatic and non-aromatic materials during coagulation processes. The organic matter characterization techniques used by Montreuil (2011) for this specific source water required long experimental times, which are not ideal considering the large number of trials required during optimization studies. There have been rapid fractionation techniques used by other researchers (Chow et al., 2004), however, these rapid fractionation techniques would not be successful for characterizing
the low organic matter concentrations present in the source water being studied, due to the small volumes of water used.

## Identification of surrogate parameters for predicting DBPs for low SUVA waters.

 This work supports the hypothesis of recent research indicating that DBP predictions based on $U V_{254}$ content in water characterized by low SUVA and low MW NOM fractions are generally weak and, therefore, highlights the importance of hydrophilic organic fractions with low aromaticity as being important DBP precursors in low SUVA waters. It is recommended that a surrogate tool be identified for predicting DBPFP for low SUVA waters to aid in organic matter removal studies and be used in optimizing daily plant operations of such source waters.
### 8.3. COAGULANT CHANGEOVER CORROSION IMPLICATIONS

Impact of Al and Fe. Results from Chapters 6 and 7 indicate that an important mechanism involved the occurrence of lead release following a coagulant changeover was related to the presence of iron and aluminum concentrations and the adsorption of lead on aluminum and iron oxides. It was also speculated that iron particulates are more detrimental to lead release than aluminum particulates. It is recommended that experiments be designed to specifically study mechanisms associated with Al and Fe particulates contributing to lead release. It is also recommended that the secondary regulatory standards for Al and Fe concentrations following treatment be evaluated based on this hypothesis. In particular, the effects of Fe particulates being released from iron pipes must be further studied in light of practical issues that are being identified by other
researchers studying the contribution to lead in drinking water from iron corrosion scales (Deshommes et al., 2010 and McFadden et al., 2011).

Overall contribution of CSMR and Residual AI and Fe. Though the results of Chapters 6 and 7 indicated that CSMRs and residual Al and Fe concentrations following coagulation are significant factors contributing to lead in galvanic settings, the overall contribution of these two factors on lead release was not determined and warrants further research. In particular, it would be interesting to learn if a specific CSMR threshold exists that would mitigate the adsorption of lead on to iron and aluminum oxides under galvanic conditions.

Most importantly, due to the exceptional corrosivity of the ferric-based coagulant in comparison to aluminum-based coagulants, it is recommended that utilities contemplating changing to ferric-based coagulants investigate the potential consequences of adverse effects related to lead release. In general, it is also recommended that utilities that are considering treatment changes examine the potential CSMR and residual Fe and Al concentrations resulting from the change of coagulant and what potential consequences for lead release might be expected from these changes.

Further investigation of corrosion impacts for low alkalinity water. It is believed that the relatively low alkalinity $\left(<20 \mathrm{mg} / \mathrm{L}\right.$ as $\left.\mathrm{CaCO}_{3}\right)$ of the treated water conditions investigated in Chapters 6 and 7 likely contributed to the high lead levels presented from each treatment condition studied, since a low buffering capacity is expected to amplify
the pH drop at the lead anode under galvanic circumstances (Edwards and Triantafyllidou, 2007) and finished water alkalinities less than $50-\mathrm{mg} / \mathrm{L}$ have been shown to trigger serious lead problems in other case studies (Nguyen et al., 2010a; Nguyen et al., 2010c). Although the JDKWSP is currently meeting the lead $90^{\text {th }}$ percentile rule suggested by Health Canada, if a coagulant change is made at this facility down the road or if corrosion ever becomes an issue, is recommended that increased alkalinities be investigated as a means of improved corrosion control for this utility.

Impact of corrosion inhibitors. Though, recently, there has been a reasonable amount of research dedicated to the mechanisms behind CSMR causing lead leaching in water distribution systems, there have been very little recommendations regarding means of mitigating these issues aside from ensuring that the CSMR is maintained below a threshold value of 0.5 through coagulant dose and type control. However, this is not always an option when controlling CSMRs through coagulant dosing is not possible, as would be the case for many direct filtration facilities. For the JDKWSP, the current CSMR of the treated water is approximately $1.0(0.7-\mathrm{mg} / \mathrm{L}$ as Al$)$ and to reduce the CSMR to 0.3 , a dosage of $4.4-\mathrm{mg} / \mathrm{L}$ as Al is required using alum. Significant increases in coagulant dosages at this facility would lead to significant problems with filtration performance and overall particle removals. Therefore, currently, there is significant potential for lead leaching occurrence resulting from partial lead service line replacements, especially considering the low alkalinity of the treated water. It is recommended that future research consider the type and dosage of corrosion inhibitors that could counter adverse consequences of higher CSMR.

## CHAPTER 9 CONCLUSION

### 9.1. SUMMARY

The overall goal of this thesis was to optimize the removal of organic matter DBP precursors in a direct filtration facility treating surface water with low levels of turbidity, alkalinity and organic matter while ensuring filtration performance is not compromised and significant or harmful effects with respect to lead leaching in the distribution system are not triggered. Four alternate coagulants were evaluated, including ferric sulfate, PACl (MBNS) and ACH (HBNS), against the baseline performance of alum coagulation efforts that are currently practiced at the JDKWSP. Bench-scale and pilot-scale experiments were designed to satisfy the following research objectives:

1. Determine favourable NOM removal coagulation conditions for a low turbidity, low alkalinity, and low organic matter source water.
2. Evaluate particle removal and filtration performance associated with the favourable coagulation conditions determined for NOM removal using a direct filtration pilot plant. If these conditions are significantly different, determine if balanced conditions to meet performance goals can be achieved.
3. Evaluate potential "unintended consequences" of chemical changeovers on finished water quality and distribution systems related to lead release.
4. Develop a framework to assess and optimize coagulation optimization studies to be used by other utilities.

Pilot Proving Experiments. Since direct filtration processes are well known for both sensitivity to solids loading and an inability to be adequately reproduced on a bench-scale
(Eikebrokk et al., 2007 and Pernitsky et al., 2011), pilot-scale testing of optimization options for processes upstream of the direct filtration process is key. Pilot testing essentially closes the uncertainty gap between bench-scale studies and full-scale implementation of research results. Before this research program could begin, it was necessary to carry out a pilot proving process to ensure the results of any research conducted at the pilot-scale would adequately represent process changes that, when implemented at full scale, successfully optimize the performance of the plant. Therefore, several control experiments were carried out to establish that the parallel trains produced statistically equivalent water quality and that the pilot and FSP treatment processes produced comparable effluent quality. The pilot plant proving process included operating the commissioned pilot plant and making necessary adjustments to ensure the aforementioned criteria was achieved. The proving approach applied was based on both the successes and lessons learned from pilot studies carried out in both Ottawa and Windsor, Ontario (Anderson et al., 1993).

Bench-scale NOM Removal Trials. To address concerns associated with DBP regulations, many utilities have adopted or considered the use of alternative chemical coagulants to enhance the removal of NOM prior to disinfection. Previous studies have shown that optimal coagulation conditions for turbidity removal are rarely the same as those for NOM removal; and that, in fact, coagulant demand is usually governed by the concentration of NOM for low turbidity waters (Gregor et al., 1997 and Pernitsky and Edzwald, 2006).

Bench-scale coagulation jar tests were conducted to identify favourable coagulation pH and dosage conditions for NOM removal using alum, ferric sulfate, PACl (MBNS) and ACH (HBNS). These favourable operating conditions were then directly compared to the current coagulation conditions being used in the full-scale treatment plant. NOM removal performance was evaluated using several organic matter response parameters including TOC, DOC, UV $_{254}$, DBPFP and HPSEC. Particle removal was not evaluated during bench-scale trials since adequate simulation of deep-bed filtration processes was not possible.

Pilot-scale Coagulation Evaluation Trials. Pilot-scale coagulation trials were conducted to provide a snapshot of the feasibility of favourable organic matter removal conditions in terms of filtration performance and to, subsequently, identify favourable pH and dosage conditions that provided acceptable direct filtration performance. Filtration performance indicators included unit filter run volumes, steady-state effluent turbidity and filter ripening volumes. Organic matter removals were also assessed for the coagulation conditions identified as providing favourable filtration performance results.

In addition, a framework was developed for organizing and analyzing the overwhelming amounts of data generated by the various operating conditions and multi-factor response parameters evaluated during pilot testing. This framework used performance indicators to practically score the filtration performance of each coagulant and the corresponding coagulation conditions studied and used graphical heat-mapping techniques to visually assess the results of the performance indicator evaluation and identify optimal operating
regions for filtration performance.

Lead Release Consequences. A particular concern associated with coagulation optimization is the potential unintended consequences of a coagulant change on the distribution system, specifically related to lead release from lead pipe and solder materials. Several case studies have concluded that the seemingly innocuous changes induced by changing coagulant types and dosages can result in unexpected high lead concentrations in distribution systems (Dodrill and Edwards, 1995; Nguyen et al., 2010a; Nguyen et al., 2010c). Coagulant changeover case studies have shown that under galvanic conditions, a high CSMR governs lead leaching incidences in distribution systems (Dodrill and Edwards 1995; Edwards and Triantafyllidou 2007; Nguyen et al., 2010a and Nguyen et al., 2010c).

Several bench-scale experiments were conducted to evaluate the potential "unintended consequences" associated with a potential coagulant changeover at the JDKWSP on finished water quality and distribution system corrosion. In Phase 1, bench-scale experiments investigated the role a coagulant change would have in causing a significant effect with respect to lead leaching in drinking water with a high CSMR (> 0.5). The coagulants evaluated in this bench-scale study included alum (CSMR of 0.9), PACl (CSMR of 2.0) and ferric sulfate (CSMR of 0.9 ) and the two lead bearing plumbing materials examined were lead:tin solder and passivated lead pipe, both in connection with copper pipe. A simple dump and fill protocol was successfully used to screen for significant changes in lead leaching resulting from the coagulation conditions tested.

These experiments lasted for 27 weeks total. The overall results indicated that CSMR was not the controlling factor with respect to lead leaching following the coagulant changeover conditions evaluated in this study. Ferric sulfate was the most corrosive coagulant during this study and residual concentrations of iron and aluminum were identified as the principal lead corrosion contributors.

Next, experiments were designed to determine why ferric sulfate was contributing so much to lead leaching and evaluate if lowering the CSMR of the sulfate based coagulants below the hypothesized lead leaching threshold $(<0.5)$ would mitigate lead leaching and the negative implications of residual Al and Fe . The experimental set-up for Phase utilized lead solder-to-copper coupons. Two distinct experimental trials were conducted to 1 . verify the lead release trends reported in Phase 1 using an augmented experimental setup and 2. explore the overall effect on lead release by lowering the CSMR of the sulfate based coagulants to levels below the 0.5 threshold reported to mitigate lead leaching in past studies (Nguyen et al., 2010a, Nguyen et al., 2010c). Trial 1 and 2 experiments lasted 10 and 14 weeks, respectively.

Combining the results from these coagulant changeover experiments provided significant insights into the detrimental effects a coagulant change cause with respect to lead leaching in the distribution system.

### 9.2. CONCLUSION

Although the overall outlook for reducing DBP precursors through organic matter optimization is not a positive one for the JDKWSP, the overall results of this research
project were successful in evaluating coagulation optimization options for this facility and, in the end, did identify several avenues that this facility can pursue to successfully reduce DBP precursors (see Chapter 9). Additionally, this research program provides a successful framework to be used by other utilities as a guide for conducting and analyzing coagulation optimization studies from preliminary bench-scale experiments through to pilot-scale optimization trials.

Pilot Proving Experiments. Modified paired t-tests were successfully applied to establish that equivalent water quality was being produced between the two parallel pilot trains and to verify that the water quality achieved following each treatment phase in the pilot plant mimicked the corresponding treatment process in the FSP. Successive proving trials demonstrated equivalence in multiple water quality parameters throughout the two treatment scales, including $\mathrm{pH}, \mathrm{UV}_{254}, \mathrm{TOC}, \mathrm{DOC}$, alkalinity and turbidity.

The incorporation of an experimental residuals analysis to identify measurement errors for each response parameter used in pilot proving trials was deemed a necessary statistical approach for establishing equivalence between each scale of treatment. Without the incorporation of these experimental errors, using paired t -tests and predetermined hypothesized mean differences to compare the pilot treatment trains and pilot to FSP processes, respectively, was an approach destined for failure. Although results were generally favourable, these statistical approaches were determined to be too stringent for performance comparison without the experimental errors being taken into account.

Using the measurement error as a basis for train comparison in paired t-tests, correspondence was established between the two pilot trains. For pilot-to-pilot proving trials, the absolute differences between the parallel treatment trains were very minor at each stage of the treatment process and the differences reported were below $0.1-\mathrm{mg} / \mathrm{L}$ for TOC and DOC, $0.002-\mathrm{cm}^{-1}$ for UV-absorbance, 0.1 units for pH and $0.1-\mathrm{mg} / \mathrm{L}$ for alkalinity. Overall, the magnitudes of the average absolute mean differences reported in this study are comparable or less than those reported by other researchers (Andrews et al., 2005). In addition, percentile ranking was found to be a valuable indicator of filter performance and a useful means of assessing filtration performance between the two pilot treatment trains. Turbidity profiles were found to be similar and reproducible for corresponding filters on each pilot train, which was highlighted by equivalence throughout the ripening phase, steady-state trends and filter breakthrough profiles

Inserting the measurement error limits as the revised mean differences in the paired ttests was deemed a more reasonable approach for establishing correspondence between the pilot and FSP data and each parameter passed using these revised performance benchmarks at each sample location. Overall, the finished water absolute differences between pilot and full-scale treatment were less than $10 \%$ for TOC ( $<0.15-\mathrm{mg} / \mathrm{L}$ ) and DOC ( $<0.08-\mathrm{mg} / \mathrm{L}$ ), $15 \%$ for UV-absorbance $\left(<0.004-\mathrm{cm}^{-1}\right), 0.1$ units for pH and 0.02 NTU for steady-state turbidities. The magnitudes of the average absolute mean differences reported in this study are comparable or less than those reported by Andrews et al. (2005).

The pilot proving process demonstrated that the pilot plant has the ability to reproduce water quality outcomes from the FSP and that experimental results from the pilot facility are representative of process changes that will be used to optimize the performance of the FSP. Differences in mixing regimes between the two scales was the main factor of scale identified between the pilot and full-scale facilities and was later highlighted during pilot optimization trials as an opportunity for significant organic DBP precursor reductions in the full scale system. Incorporating the recommendations of Chapter 9, this pilot-proving methodology can be used by utilities to assess the performance of a pilot plant or benchscale prototype to be used for full-scale optimization studies and provides a systematic process of calibrating prototypes for full-scale optimization.

Bench-scale NOM Removal Trials. Bench-scale NOM removal studies indicated that 30-40\% DOC removals were achievable for this source water using favorable coagulation and pH conditions identified through a series of jar test experiments using alum, ferric sulfate, $\mathrm{PACl}(\mathrm{MBNS})$ and $\mathrm{ACH}(\mathrm{HBNS})$. These removal potentials were $10-20 \%$ higher than the organic matter removals currently being achieved during full-scale treatment ( $\sim 20 \%$ ). Significantly higher $\mathrm{UV}_{254}$ reduction potentials were identified (60-70\%), confirming that aromatic organics were more readily removed by coagulation efforts. Although ACH appeared to yield the highest DOC and $\mathrm{UV}_{254}$ reduction potentials, on average, these results alone were not convincing. DBPFPs revealed further indication that the high basicity $\mathrm{ACH}(4-\mathrm{mg} / \mathrm{L}$ as Al and $\mathrm{pH}=7.0)$ was the superior performer, achieving the lowest overall THMFP ( $37 \%$ reduction compared to baseline coagulation conditions) and the greatest HAAFP reductions ( $25 \%$ decrease from baseline coagulation
conditions). However, HAAFP contributions were not significantly different for any of the enhanced coagulation conditions examined. Compared to the other coagulants tested, the high basicity ACH also yielded the highest potential coagulation pH which provided hope for significant cost savings related to pH adjusting chemicals if these conditions were feasible at the pilot scale.

Organic size distribution results indicated that high MW, aromatic organic constituents were readily removed by coagulants, whereas low MW, aromatic structures were not at all affected by the coagulation conditions tested. The overall nature of NOM in this source water before ( $\mathrm{SUVA}=2.6$ ) and after (SUVA=1.5) coagulation was accurately predicted by SUVA interpretation guidelines developed by Edzwald and Van Benschoten (1990) (Pernitsky and Edzwald, 2006). The overall effectiveness of coagulation processes was also correctly described by these guidelines, as the maximum organic matter removals identified during bench-scale coagulation studies were low (30-40\%), as predicted when treating low SUVA $(<3)$ source waters. The overall results of this study were consistent with the findings of other researchers who observed high MW, aromatic organic structures are preferentially removed by coagulation processes, whereas low MW, non-aromatic structures are generally recalcitrant to removal by coagulation (Liang and Singer, 2003; Pernitsky and Edzwald, 2006; Ates et al., 2007).

The weak $\mathrm{UV}_{254}$-DBPFP correlations identified during bench-scale studies support the hypotheses of recent researchers finding that organic structures other than aromatics also contribute to the production of DBPs and that DBP predictions based on $\mathrm{UV}_{254}$ content in
water characterized by low SUVA and low MW NOM fractions are generally weak. These results highlight the importance of low MW hydrophilic organic fractions with low aromaticity as being important DBP precursors in low SUVA waters.

Pilot-scale Coagulation Evaluation Trials. Results from pilot testing demonstrated that favourable conditions identified for increased potential NOM removals during benchscale testing were not consistent with optimal filtered water particle removal. Consistent with the findings of other researchers, the pilot-scale results show that for low turbidity waters, the optimization of coagulant dosages to remove even very low NOM concentrations can severely compromise the filtration performance of direct filtration processes.

When tested at the pilot scale, the favourable organic matter removal coagulation conditions resulted in low UFRV, high effluent filter turbidities and unacceptably long filter ripening times. This poor filtration performance was attributed to the higher than acceptable solids loadings to the filters resulting from the high coagulant dosages required to achieve desirable organic matter removals and the limited treatment barriers present in a direct filtration process (i.e.; lack of a clarification stage prior to filtration). Since coagulant overdosing was evidently not an option, coagulation pH was identified as the most important operating parameter for direct filtration processes. Low coagulation pHs are desirable to increase the charge density of NOM and, therefore, reduce the amount of coagulant required for charge neutralization, and encourage the formation of
soluble NOM-aluminum complexes due to the increased concentrations of highly charged metal species at lower pH values.

Favourable filtration conditions were identified using both PACl and ACH (1.0-1.15$\mathrm{mg} / \mathrm{L}$ as Al and pH of 5.8), producing short filter run volumes, low effluent turbidities and short filter ripening times. However, the coagulation conditions that were required to obtain favourable filtration performance using ACH ( $1.1-\mathrm{mg} / \mathrm{L}$ and $\mathrm{pH}=5.8$ ) did not provide any organic matter removal benefits when compared to the performance of the control pilot train operating using the same day alum baseline operating conditions as the FSP plant $(0.9-\mathrm{mg} / \mathrm{L}, \mathrm{pH}=5.5)$.

Perhaps the most important conclusion of this thesis, significant differences were identified between the DBPFP of pilot plant treated water and FSP treated water operating using coagulation conditions deemed "equivalent" during pilot proving studies. The higher DBBfp of FSP treated water demonstrated the poor mixing performance associated with hydraulic flocculators during full-scale treatment and highlighted significant potentials for increased NOM removal benefits associated with mechanical mixing capabilities of the pilot plant.

Finally, a generic framework was developed to organize and evaluate the large quantities of filtration data generated during pilot studies using PIs and graphical heat-mapping techniques. PI scores were used to assess coagulation operating conditions based the combined performance of UFRV, steady-state turbidity values and FRV. Heat-mapping
techniques were successfully used to verify that PI scores were accurate representations of the data and also to visually simplify and identify favourable operating regions for each filter response parameter. As was true with the pilot proving methodology, these techniques are directly applicable to other facilities and can be used by other utilities to interpret and assess optimization results.

Overall, results from pilot-testing demonstrated that the optimal conditions for NOM control from bench-scale testing are not consistent with optimal filtration performance at a direct filtration facility. Although bench-scale investigations offer a great starting point to evaluate relative performance conditions for organic matter removal, pilot-scale research is vital to effectively evaluating particle removals and filtration performance for direct filtration facilities. Considering the overall results from all of the coagulant conditions study during pilot testing, it appears that the coagulation pH and dosage window for optimal filtration performance is very tight for this source water and treatment process. The results are also indicative that enhanced coagulation treatment to reduce DBP precursors is not feasible at this facility without comprising filtration performance. These findings also stress the importance of investigating coagulation as a multi-objective optimization process in which both turbidity and organic removal are important output parameters. Finally, this work emphasizes the need for further research of ways to reduce DBP precursors in direct filtration facilities without compromising filtration performance (see Chapter 9 recommendations).

Lead Release Consequences. Both practical case studies and laboratory-based studies have demonstrated that a high CSMR induces high galvanic currents and governs leachleaching incidences in lead-to-copper connections in distribution systems following coagulant changeovers (Dodrill and Edwards, 1995; Edwards et al., 1999; Edwards and Triantafyllidou, 2007, Nguyen et al., 2010). However, CSMR was not the primary catalyst for lead leaching following coagulant changeovers for the conditions evaluated in this study. Residual concentrations of iron and aluminum remaining following coagulation were found to be the principal contributors.

Analysis of the results revealed positive correlations between residual total iron and aluminum concentrations following coagulation and total lead concentrations following stagnation for each coagulant tested. The positive correlations shown between particulate iron and aluminum and particulate lead concentrations following stagnation confirmed that the adsorption of lead to iron and aluminum oxides is a viable hypothesis for lead release. Despite the variable CSMR levels tested, both above and below the 0.5 CSMR threshold cited for lead leaching, ferric sulfate consistently yielded the highest lead levels following stagnation, due to high residual iron concentrations remaining following coagulation. In addition, overall results suggest that iron particulates may play a more important role in lead release than aluminum particulates. CSMR effects were secondary to the corrosive effects of particulate iron, as evidenced by PACl (CSMR of 2.0 and 2.8) being consistently more corrosive that alum (CSMR 0.9 and 0.3 ), regardless of residual aluminum concentrations following coagulation.

Consistent with the findings in this study, past and recent investigations involving both field testing and pipe loop experiments have concluded that particulate lead concentrations are positively correlated with particulate iron concentrations (Hulsmann, 1990; Deshommes et al., 2010 and Triantafyllidou and Edwards, 2011). It is hypothesized that adsorption of lead on iron particles is a dominant cause of lead release in systems where particulate iron is entering the distribution system (Hulsmann, 1990; Deshommes et al., 2010).

In general, the results of this research underline the importance of ensuring corrosive factors are not unintentionally introduced by seemingly innocuous changes such as coagulant dosage adjustments or changeovers. Although suggested by other researchers, problems occurring following coagulant changeovers are not always controlled by reducing CSMRs below the 0.5 threshold (Nguyen et al., 2010a and Nguyen et al., 2010c). If a utility is planning a coagulant changeover, the effects of coagulation residuals on distribution water quality should be experimentally verified before such changes are implemented at full-scale.

Since the coagulation optimization studies conducted as part of this research project found that a coagulant changeover would not lead to additional DBP precursor reductions at the JDKWSP, distribution system lead leaching issues are not a pressing concern for this facility. Of the three coagulants tested, alum was the least corrosive chemical at CSMR levels both above and below the lead-leaching threshold. If an increase in alum dose is identified as a feasible optimization change at this facility in future studies, the
lower CSMR induced would not be a potential corrosion concern, however, residual Al concentrations should be minimized to ensure corrosion issues are not unintentionally triggered. That being said, the current CSMR of the treated water at the JDKWSP is approximately $1.0(0.7-\mathrm{mg} / \mathrm{L}$ as Al$)$ and to reduce the CSMR to less than 0.5 requires significantly higher dosages of alum. As shown in Chapter 5, significant increases in coagulant dosages at this facility would lead to significant problems with filtration performance and overall particle removals. Therefore, currently, there is significant potential for lead leaching occurrence resulting from partial lead service line replacements, especially considering the low alkalinity of the treated water.

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## APPENDIX A - Chapter 4 Raw and Supplemental Data



Figure A1. UV 254 error analysis distribution for the four the pilot-to-pilot proving trials completed. Upper and lower boundary lines represent two standard deviations of the residual population mean.


Sample Time - trial \#- day \#-sample \#

Figure A2. Alkalinity error analysis distribution for the pilot-to-pilot proving trials completed (no alkalinity data was collected during trial 4). Upper and lower boundary lines represent two standard deviations of the residual population mea


Sample Time - trial \# - day \# - sample \#

Figure A3. TOC error analysis distribution for the pilot-to-pilot proving trials completed (no TOC data was collected during trial 4). Upper and lower boundary lines represent two standard deviations of the residual population mean.


Sample Time - trial \#- day \#-sample \#

Figure A4. UV 254 absolute difference between Pilot Train 1 (PP1) and Pilot Train 2 PP2 for the pilot-to-pilot proving trials completed. Upper and lower boundary lines represent two standard deviations of the residual population mean.


Sample Time - trial \# - day \# - sample \#

Figure A5. Alkalinity absolute difference between Pilot Train 1 (PP1) and Pilot Train 2 PP2 for the pilot-to-pilot proving trials completed (no alkalinity data was collected during trial 4). Upper and lower boundary lines represent two standard deviations of the residual population mean.


Figure A6. TOC absolute difference between Pilot Train 1 (PP1) and Pilot Train 2 PP2 for the pilot-to-pilot proving trials completed (no TOC data was collected during trial 4). Upper and lower boundary lines represent two standard deviations of the residual population mean.




## APPENDIX B - Chapter 5 Raw and Supplemental Data



Figure B1. TOC and $\mathrm{UV}_{254}$ profiles for Alum dosed at 0.7 and $1.1-\mathrm{mg} / \mathrm{L}$ as Al over a range of pH values.


Figure B2. TOC, DOC and $\mathrm{UV}_{254}$ results for Alum at $\mathbf{p H}=\mathbf{5 . 5}$.


Figure B3. TOC, DOC and $\mathrm{UV}_{254}$ profiles for $\mathrm{PACl}(\mathrm{MBNS})$ dosed at $1.65-\mathrm{mg} / \mathrm{L}$ as Al over a range of pH values.


Figure B4. TOC, DOC and $\mathrm{UV}_{254}$ results for PACl (MBNS) at $\mathbf{p H}=\mathbf{6 . 0}$.


Figure B5. TOC, DOC and UV ${ }_{254}$ profiles for ACH (HBNS) dosed at $4.8-\mathrm{mg} / \mathrm{L}$ as Al over a range of pH values.


Figure B6. TOC, DOC and $\mathrm{UV}_{254}$ results for ACH (HBNS) at $\mathbf{p H}=\mathbf{6 . 5}$ and 7.0.


Figure B7. TOC, DOC and UV ${ }_{254}$ profiles for Ferric Sulfate dosed at $1.1-\mathrm{mg} / \mathrm{L}$ and $2.0-\mathrm{mg} / \mathrm{L}$ as Fe .


Figure B8. TOC, DOC and $\mathbf{U V}_{254}$ profiles for Ferric Sulfate at $\mathbf{p H}=4.5$.


Figure B9. UV ${ }_{254}$-THM relationship for optimal coagulation trials.


Figure B10. UV $_{254}$-HAA relationship for optimal coagulation trials.

Table B1. Bench-scale SEC Data

| Alum Dose $0.7-\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=5.5$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| -1 1 | 7.591 | 24398.2 | 56.136 | 73539.5 | 162578.7 | 13355.9 |
| 2,3 | 16.35 | 2346.6 | 5.402 | 827.8 | 1201.1 | 668.5 |
| 4 | 17.023 | 7426.2 | 17.086 | 477.4 | 668.5 | 332.7 |
| 5 | 17.953 | 3347.5 | 7.702 | 279.4 | 332.7 | 228.8 |
| 6 | 18.629 | 2136.3 | 4.915 | 198 | 228.8 | 163.1 |
| 7 | 19.263 | 662.9 | 1.525 | 143.5 | 163.1 | 120.8 |
| 8 | 20.06 | 3143.9 | 7.234 | 66.2 | 120.8 | 26.3 |


| Alum Dose $0.7-\mathrm{mg} / \mathrm{L}$ as Al, $\mathrm{pH}=5.5$ |  |  |  |  |  |  |  |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| Peak | RT | Area |  | \%Area | Mw | StartMw | EndMw |
|  | 1 | 7.698 | 31649.8 | 71.461 | 122580.3 | 244212.4 | 49468.5 |
|  | 2,3 | 16.469 | 1539.1 | 3.475 | 1448.8 | 1849.6 | 1219.2 |
|  | 4 | 17.2 | 4035.2 | 9.111 | 918.5 | 1219.2 | 690.3 |
|  | 5 | 17.993 | 2483.9 | 5.608 | 569.8 | 690.3 | 461.4 |
|  | 6 | 18.432 | 1917.8 | 4.33 | 388.2 | 461.4 | 308.4 |
|  | 79.256 | 517.8 | 1.167 | 274.1 | 308.4 | 236.3 |  |
|  | 7 | 2146.8 | 4.847 | 148.8 | 224.1 | 82.9 |  |


| Alum Dose $0.7-\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=5.5$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 8.43 | 1111.1 | 1.973 | 80270.1 | 105699.1 | 61213 |
| 2,3 | 16.352 | 10833.2 | 19.24 | 1694.8 | 4156.1 | 1131.7 |
| 4 | 16.989 | 14258.4 | 25.323 | 899.2 | 1131.7 | 690.3 |
| 5 | 17.675 | 8863.8 | 15.742 | 571.6 | 690.3 | 461.4 |
| 6 | 18.665 | 6145.9 | 10.915 | 389.9 | 461.4 | 308.4 |
| 7 | 19.421 | 2036.8 | 3.617 | 266.7 | 308.4 | 227.2 |
| 8 | 19.932 | 13057.1 | 23.189 | 88.7 | 227.2 | 6 |


| Alum Dose 1.3-mg/L as Al, $\mathrm{pH}=5.8$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 7.699 | 10534.3 | 19.739 | 119082.4 | 204363.7 | 61677.3 |
| 2,3 | 16.344 | 10623.6 | 19.907 | 1512.4 | 2929 | 1117.9 |
| 4 | 17.012 | 12910.6 | 24.192 | 895.3 | 1117.9 | 690.3 |
| 5 | 17.747 | 7526.6 | 14.104 | 573.4 | 690.3 | 461.4 |
| 6 | 18.396 | 4904.4 | 9.19 | 389.7 | 461.4 | 308.4 |
| 7 | 19.2 | 1346.9 | 2.524 | 267.7 | 308.4 | 224.4 |
| 8 | 20.567 | 5520.1 | 10.344 | 131.6 | 224.4 | 47.5 |


| Alum Dose $1.3-\mathrm{mg} / \mathrm{L}$ as Al, $\mathrm{pH}=5.8$ |  |  |  |  |  |  |  |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
|  | RT | Area | \%Area | Mw | StartMw | EndMw |  |
| Peak | 1 | 8.373 | 2433.1 | 4.462 | 91697.4 | 155642.4 | 51013.3 |
| 2,3 | 16.354 | 12776.7 | 23.429 | 1526.1 | 3843.8 | 1125.4 |  |
|  | 4 | 16.976 | 16390.5 | 30.055 | 900.2 | 1125.4 | 690.3 |
|  | 5 | 17.622 | 9220.3 | 19.907 | 573.4 | 690.3 | 461.4 |
|  | 6 | 18.388 | 5762.5 | 10.567 | 391.5 | 461.4 | 308.4 |
|  | 7 | 19.248 | 1675.6 | 3.073 | 265 | 308.4 | 224.4 |
|  | 20.208 | 6275.6 | 11.508 | 129.8 | 224.4 | 44.7 |  |


| Alum Dose $1.3-\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=5.8$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 8.26 | 2197.8 | 3.994 | 80656.2 | 123145.1 | 48847 |
| 2,3 | 16.369 | 15318.8 | 27.836 | 1613.4 | 4407.8 | 1130.5 |
| 4 | 17.014 | 16390.4 | 30.764 | 903.9 | 1130.5 | 690.3 |
| 5 | 17.81 | 9012.9 | 16.377 | 574 | 690.3 | 461.4 |
| 6 | 18.688 | 5486.7 | 9.97 | 392 | 461.4 | 308.4 |
| 7 | 19.288 | 1372.1 | 2.493 | 265.8 | 308.4 | 224.4 |
| 8 | 20.162 | 4714.3 | 8.566 | 132.9 | 224.4 | 45.4 |


| Ferric Sulfate Dose 1.9-mg/L as Al, $\mathrm{pH}=4.5$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 2,3 | 16.427 | 7724.2 | 18.3945875 | 1447.6 | 2795.4 | 1128.8 |
| 4 | 16.987 | 12685.3 | 30.2090651 | 880.3 | 1128.8 | 690.3 |
| 5 | 17.793 | 8288.2 | 19.7377101 | 563.8 | 690.3 | 461.4 |
| 6 | 18.433 | 5544.4 | 13.2035617 | 386.7 | 461.4 | 308.4 |
| 7 | 19.223 | 1561.8 | 3.71930643 | 263.4 | 308.4 | 224.2 |
| 8 | 20.138 | $6187.8$ | 14.7357692 | 101.1 | 224.2 | 41.1 |
|  |  |  |  |  |  |  |
| Ferric Sulfate Dose 1.9-mg/L as Al, $\mathrm{pH}=4.5$ |  |  |  |  |  |  |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 2,3 | 16.391 | 8209.9 | 18.515119 | 1620.5 | 3551.5 | 1102.5 |
| , | 17.033 | 11973.5 | 27.0028596 | 885.1 | 1102.5 | 690.3 |
| 5 | 17.928 | 8528.6 | 19.2338571 | 570.3 | 690.3 | 461.4 |
| 6 | 18.43 | 5847 | 13.186263 | 389.8 | 461.4 | 308.4 |
| 7 | 19.227 | 1806 | 4.07292475 | 265.5 | 308.4 | 224.4 |
| 8 | 20.165 | 7976.6 44341.6 | 17.9889765 | 112.9 | 224.4 | 28.3 |
|  |  | 44341.6 |  |  |  |  |
| Ferric Sulfate Dose 1.9-mg/L as Al, $\mathrm{pH}=4.5$ |  |  |  |  |  |  |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 2,3 | 16.419 | 7303 | 18.0677435 | 1555.4 | 3098.7 | 1195.7 |
| 4 | 17.007 | 14560.3 | 36.0224245 | 920.1 | 1195.7 | 690.3 |
| , | 17.94 | 8151.2 | 20.1662044 | 571.7 | 690.3 | 461.4 |
| 6 | 18.605 | 5297.3 | 13.1056083 | 391.9 | 461.4 | 308.4 |
| 7 | 19.273 | 1266.9 | 3.13433168 | 267.6 | 308.4 | 224.4 |
| 8 | 20.178 | 3841.4 | 9.50368752 | 145 | 224.4 | 67.3 |
|  |  | 40420.1 | 100 |  |  |  |
| PACl Dose $1.65-\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=6.0$ |  |  |  |  |  |  |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 2,3 | 16.425 | 6755.9 | 15.281 | 1740 | 3939.9 | 1181.2 |
| 4 | 17.038 | 12733.4 | 28.802 | 915.7 | 1181.2 | 702.8 |
| 5 | 17.988 | 8800.3 | 19.906 | 572.6 | 702.8 | 453.8 |
| 6 | 18.722 | 5288.6 | 11.962 | 386.9 | 453.8 | 308.9 |
| 7 | 19.21 | 1792.5 | 4.054 | 259.3 | 308.9 | 213.6 |
| 8 | 20.023 | 8839.6 | 19.994 | 94.8 | 213.6 | 14.5 |
|  |  |  |  |  |  |  |
| PACl Dose $1.65-\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=6.0$ |  |  |  |  |  |  |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 2,3 | 16.41 | 7591.4 | 19.071 | 1673.6 | 4215.1 | 1182.7 |
| 4 | 17.002 | 13292.6 | 33.393 | 918.6 | 1182.7 | 697.5 |
| 5 | 17.815 | 8625.3 | 21.668 | 564.1 | 697.5 | 439.9 |
| 6 | 18.538 | 4417.6 | 11.098 | 377.9 | 439.9 | 291.8 |
| 7 | 19.435 | 1075.1 | 2.701 | 251.1 | 291.8 | 213.4 |
| 8 | 20.088 | 4804.3 | 12.069 | 109.9 | 213.4 | 18.5 |
|  |  |  |  |  |  |  |
| ACH Dose 4.0-mg/L as Al, $\mathrm{pH}=7.0$ |  |  |  |  |  |  |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 5.405 | 3522.8 | 7.686 | 226854.7 | 466460.2 | 93968.7 |
| 2 | 8.6 | 1703.4 | 3.716 | 60358.1 | 93968.7 | 35446 |
| 1 |  | 5226.2 |  |  |  |  |
| 2,3 | 16.369 | 5033.4 | 10.982 | 1921.3 | 4649.1 | 1161.7 |
| 4 | 17.074 | 10848.9 | 23.67 | 901.3 | 1161.7 | 700.5 |
| 5 | 17.958 | 9016 | 19.671 | 562.9 | 700.5 | 439.9 |
| 6 | 18.697 | 5119.4 | 11.17 | 375 | 439.9 | 291.8 |
| 7 | 19.833 | 1741 | 3.798 | 250.7 | 291.8 | 213.4 |
| 8 | 20.13 | 8848.3 | 19.305 | 105.7 | 213.4 | 17.6 |


| ACH Dose $4.0-\mathrm{mg} / \mathrm{L}$ as $\mathrm{Al}, \mathrm{pH}=7.0$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 7.79 | 7874.5 | 18.35 | 113740.8 | 270520.7 | 33557 |
| 2,3 | 16.334 | 6379.4 | 14.866 | 1926.5 | 4507.1 | 1185.3 |
| 4 | 17.025 | 10611.2 | 24.728 | 912 | 1185.3 | 700.5 |
| 5 | 17.83 | 7749.4 | 18.059 | 564.3 | 700.5 | 439.9 |
| 6 | 18.578 | 4371.6 | 10.187 | 374.1 | 439.9 | 291.8 |
| 7 | 19.405 | 1073.6 | 2.502 | 258.9 | 291.8 | 222.7 |
| 8 | 20.044 | 4852.8 | 11.309 | 138.2 | 222.7 | 58.9 |


| ACH Dose 4.0-mg/L as Al, $\mathrm{pH}=7.0$ |  |  |  |  |  |  |  |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| Peak | RT |  | Area | \%Area | Mw | StartMw | EndMw |
| 2,3 | 16.4 | 5535.8 | 16.995 | 946.7 | 2161.2 | 606.1 |  |
|  | 4 | 17.036 | 9533 | 29.267 | 482.3 | 606.1 | 378.5 |
|  | 5 | 17.982 | 8690.6 | 26.681 | 297.3 | 378.5 | 224.9 |
|  | 6 | 18.502 | 3899.1 | 11.971 | 194.8 | 224.9 | 156.3 |
|  | 7 | 19.418 | 1407.8 | 4.322 | 128.2 | 156.3 | 103.3 |
|  | 8 | 20.004 | 3506.3 | 10.764 | 68.7 | 103.3 | 33.7 |
|  |  |  |  |  |  |  |  |



| Raw Water |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 7.685 | 11980.1 | 12.053 | 116454.1 | 268970.3 | 40632.5 |
| 2,3 | 16.315 | 39611.4 | 39.852 |  | 7304.1 | 1117.5 |
| 4 | 16.935 | 19848.8 | 1.969 | 911.9 | 1117.5 | 702.8 |
| 5 | 17.952 | 11007 | 11.074 | 577.6 | 702.8 | 453.8 |
| 6 | 18.401 | 5979.1 | 6.015 | 385.6 | 453.8 | 308.9 |
| 7 | 19.274 | 2375.2 | 2.39 | 262.5 | 308.9 | 213.6 |
| 8 | 20.043 | 8594.5 | 8.647 | 109.2 | 213.6 | 22 |


| JM_Raw_Sep24-09001 |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 7.678 | 26093.2 | 34.587 | 123993.9 | 268970.3 | 52387.1 |
| 2 | 15.999 | 11879.1 | 15.746 | 2243.6 | 7304.1 | 1584.1 |
| 3 | 16.263 | 11347.2 | 15.041 | 1338.4 | 1584.1 | 1117.5 |
| 2,3 |  | 23226.3 |  |  |  |  |
| 4 | 16.908 | 11913.5 | 15.791 | 913.2 | 1117.5 | 702.8 |
| 5 | 17.757 | 6752.1 | 8.95 | 568.4 | 702.8 | 435.8 |
| 6 | 18.605 | 2927.6 | 3.881 | 377.2 | 435.8 | 308.9 |
| 7 | 19.161 | 1305.7 | 1.731 | 263 | 308.9 | 213.6 |
| 8 | 20.041 | 3224.1 | 4.274 | 147.8 | 213.6 | 79.8 |

Table B2. Pilot-scale SEC Data

| 27-May-10 ACH |  | 24hr |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 17.017 | 4146.9 | 7.955759767 | 1166.3 | 2002.3 | 971.8 |
| 2 | 17.447 | 10876.5 | 20.86638721 | 827.4 | 971.8 | 709.5 |
| 3 | 18.045 | 17445.1 | 33.46813878 | 570.4 | 709.5 | 433.4 |
| 4 | 19.014 | 12222.5 | 23.44866617 | 341.3 | 433.4 | 258 |
| 5 | 19.888 | 4009.9 | 7.69292751 | 235.6 | 258 | 199.8 |
| 6 | 20.54 | 2034.8 | 3.903730491 | 155.4 | 195.7 | 138 |
| 7 | 21.169 | 1388.8 | 2.664390066 | 122.1 | 138 | 102 |
|  |  | 52124.5 |  |  |  |  |


| 27-May-10 Alum |  | 24h |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 17.021 | 3894.3 | 7.83685938 | 1175.4 | 1835 | 969.2 |
| 2 | 17.412 | 10372.1 | 20.8727343 | 815.2 | 969.2 | 681.8 |
| 3 | 18.075 | 15368.9 | 30.9282562 | 559.5 | 681.8 | 427.3 |
| 4 | 19.056 | 11344.3 | 22.8291821 | 338.2 | 427.3 | 257.5 |
| 5 | 19.876 | 3923.5 | 7.895621236 | 235.1 | 257.5 | 203.1 |
| 6 | 20.55 | 2780.5 | 5.595456823 | 166.3 | 199.1 | 138.9 |
| 7 | 21.142 | 2008.5 | 4.041889958 | 119.5 | 138.9 | 93.7 |
|  |  | 49692.1 |  |  |  |  |


| 27-May-10 FSP |  | 24h |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 17.023 | 2399.5 | 5.157863512 | 1126.1 | 1474.5 | 979.4 |
| 2 | 17.414 | 8723.1 | 18.75080608 | 816.3 | 979.4 | 682.9 |
| 3 | 18.071 | 14656.9 | 31.5058511 | 559 | 682.9 | 427 |
| 4 | 19.057 | 11324.9 | 24.3435251 | 337.2 | 427 | 258.4 |
| 5 | 19.854 | 4170.5 | 8.964730059 | 235.5 | 258.4 | 201.6 |
| 6 | 20.579 | 2675.4 | 5.750926459 | 164.6 | 196.5 | 138 |
| 7 | 21.213 | 2570.9 | 5.526297688 | 116.4 | 138 | 86.5 |
|  |  | 46521.2 |  |  |  |  |


| 27-May-10 Raw |  | 24h |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Peak | RT | Area | \%Area | Mw | StartMw | EndMw |
| 1 | 16.961 | 27372.6 | 28.94002045 | 1236.3 | 2368.8 | 932.5 |
| 2 | 17.407 | 21594.2 | 22.83073546 | 807.8 | 932.5 | 681 |
| 3 | 18.068 | 23594.2 | 24.94526024 | 554.8 | 681 | 411.1 |
| 4 | 19.009 | 13403.9 | 14.17143933 | 334.2 | 411.1 | 258 |
| 5 | 19.856 | 4228.5 | 4.470634009 | 233.6 | 253.8 | 205 |
| 6 | 20.512 | 2326.1 | 2.459298041 | 165.4 | 196.5 | 138.4 |
| 7 | 21.137 | 2064.4 | 2.182612474 | 118.3 | 138.4 | 90.5 |
|  |  | 94583.9 |  |  |  |  |

## APPENDIX C - Chapter 6 Raw and Supplemental Data

a.) Pb pipe - $\mathrm{Pb}:$ Sn solder - Cu pipe

b.) Cu pipe - Pb:Sn solder - Cu pipe


Figure C1. CSMR plotted against average total mass of lead release per wetted lead surface area $\left(\mu \mathrm{g} / \mathrm{cm}^{2}\right)$ for both pipe scenarios and each water condition evaluated during Weeks 17 through 27 of this study.


Figure C2. CSMR plotted against average total mass of lead release per wetted lead surface area $\left(\mu \mathrm{g} / \mathrm{cm}^{2}\right)$ for both pipe scenarios and each water condition evaluated during Weeks 17 through 27 of this study. The dashed line represents the critical CSMR threshold of 0.5 mg of chloride per mg of sulfate.
a.) Pb pipe - $\mathrm{Pb}: \mathrm{Sn}$ solder - Cu pipe


Figure C3. Average bulk water total iron and aluminum release ( $\mu \mathrm{mol}$ ) for each water condition during Weeks 5 through 9 of this study. Data from the duplicate pipes were averaged to obtain the comparisons in this figure. The error bars indicate the standard deviation of the data.
$(\mathbf{F S}=$ ferric sulfate, $\mathrm{PACl}=$ polyaluminum chloride, Alum = aluminum sulfate $)$
Table C1. Total and Dissolved Lead

| (1) |  |  |  |  |  |  |  |  |  |
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## APPENDIX D - Chapter 7 Raw and Supplemental Data

○High CSMR ■Low CSMR


Figure D1. Total organic carbon (TOC), dissolved organic carbon (DOC) and alkalinity plotted against average total lead and copper release for the High CSMR (Weeks 5 through 10) and Low CSMR (Weeks 5 through 14) water conditions tested.




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Table D2. Low CSMR Total and Dissolved Lead

|  |  | Pb (Total) |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Week ID | Sample id | 1 | 2 | 3 | Mean | sD | \%RSD | $\begin{gathered} \text { Average Pb (per } \\ \text { pipe) } \end{gathered}$ | $\begin{array}{\|c\|} \hline \text { Daily Average } \\ \text { (Triplicate Pipe } \\ \text { Type) } \end{array}$ | Std. dev. | Week | Weekly Average (Pipe Type) | Std. Dev. |
| W1-F | Alum-1 | 87.020 | 94.230 | 99.750 | 93.670 | 6.382 | 6.810 | 93.670 | 95.463 | 3.729 | w1 | 95.463 | 3.729 |
| W2-T | Alum-1 | 64.87 | 59.56 | 68.4 | 64.28 | 4.447 | 6.92 | 64.28 | 64.19 | 1.10 | W2 | 57.49 | 7.76 |
| W2-F | Alum-1 | 52.850 | 53.720 | 52.430 | 53.000 | 0.657 | 1.240 | 53.000 | 50.783 | 3.796 | w3 | 37.935 | 5.241 |
| w3-T | Alum-1 | 40.64 | 41.98 | 46.09 | 42.9 | 2.843 | 6.63 | 42.9 | 41.32 | 1.70 | w4 | 37.28 | 6.62 |
| w3-F | Alum-1 | 41.970 | 33.060 | 38.580 | 37.870 | 4.497 | 11.870 | 37.870 | 34.550 | 5.604 | w5 | 34.313 | 11.608 |
| W4-T | Alum-1 | 35.13 | 33.1 | 37.9 | 35.38 | 2.412 | 6.82 | 35.38 | 32.08 | 4.74 | w6 | 16.50 | 8.42 |
| W4-F | Alum-1 | 46.340 | 42.450 | 46.970 | 45.260 | 2.452 | 5.420 | 45.260 | 42.480 | 2.481 | w7 | 14.152 | 7.131 |
| ws-T | Alum-1 | 42.6 | 43.92 | 43.62 | 43.38 | 0.69 | 1.59 | 43.38 | 42.90 | 9.26 | w8 | 27.23 | 5.37 |
| W5-F | Alum-1 | 31.950 | 32.130 | 31.880 | 31.990 | 0.125 | 0.390 | 31.990 | 25.727 | 5.474 | w9 | 26.813 | 6.701 |
| w6-T | Alum-1 |  |  |  |  |  |  |  |  | \#DIV/0! | w10 | 35.67 | 6.96 |
| W6-F | Alum-1 | 26.360 | 25.480 | 26.260 | 26.030 | 0.478 | 1.840 | 26.030 | 16.500 | 8.421 | wi1 | 11.285 | 2.658 |
| W7-T | Alum-1 | 17.81 | 16.74 | 15.9 | 16.82 | 0.959 | 5.7 | 16.82 | 10.53 | 5.45 | W12 | 17.54 | 2.66 |
| W7-F | Alum-1 | 30.540 | 23.430 | 26.150 | 26.550 | 3.328 | 12.540 | 26.550 | 17.770 | 7.626 | W13 | 17.940 | 1.130 |
| w--T | Alum-1 | 26.65 | 19.66 | 28.64 | 24.65 | 4.572 | 18.55 | 24.65 | 23.78 | 3.65 | W14 | 11.08 | 1.75 |
| w8-F | Alum-1 | 36.140 | 36.480 | 36.100 | 36.240 | 0.208 | 0.580 | 36.240 | 30.670 | 4.824 |  |  |  |
| w9-T | Alum-1 | 37.93 | 37.17 | 35.92 | 37.01 | 1.012 | 2.73 | 37.01 | 30.44 | 5.73 | W14 | 14.00 | 4.83 |
| w9-F | Alum-1 | 29.920 | 31.440 | 29.480 | 30.280 | 1.029 | 3.400 | 30.280 | 23.190 | 6.329 | w15 | 24.170 | 3.047 |
| W10-T | Alum-1 | 38.95 | 34.77 | 37.52 | 37.08 | 2.125 | 5.73 | 37.08 | 29.20 | 6.96 | W16 | 27.57 | 3.35 |
| W10-F | $\mathrm{Alum}^{\text {a }}$ | 25.690 | 25.610 | ${ }^{27.880}$ | 26.400 | ${ }^{1.286}$ | 4.872 | 26.400 | 42.130 | ${ }^{33.035}$ | W17 | 17.173 | 6.670 |
| W11-T | Alum-1 | 13.84 | 14.36 | 9.515 | 12.57 | 2.661 | 21.1616 | 12.57 | 7.42 | 5.65 | W18 | 20.78 | 2.28 |
| WII-F | Alum-1 | 18.610 | 18.330 | 17.520 | 18.150 | 0.565 | 3.114 | 18.150 | 15.150 | 2.658 | W19 | 14.277 | 1.649 |
| W12-T | Alum-1 | 21.7 | 23.72 | 19.29 | 21.57 | 2.22 | 10.2896 | 21.57 | 16.21 | 4.73 |  |  |  |
| W12-F | Alum-1 | 22.470 | 22.130 | 22.850 | 22.490 | 0.360 | 1.603 | 22.490 | 18.870 | 3.343 |  |  |  |
| W13-T | Alum-1 | 23.2 | 13.76 | 14.27 | 17.08 | 5.312 | 31.1036 | 17.08 | 17.56 | 0.68 |  |  |  |
| W13-F | Alum-1 | 19.620 | 19.490 | 19.560 | 19.550 | 0.067 | 0.340 | 19.550 | 18.323 | 1.515 |  |  |  |
| W1-F | Alum-2 | 96.750 | 86.980 | 95.120 | 92.970 | 5.249 | 5.650 | 92.970 |  |  |  |  |  |
| W2-T | Alum-2 | 61.68 | 63.61 | 63.86 | 63.05 | 1.191 | 1.89 | 63.05 |  |  |  |  |  |
| W2-F | Alum-2 | 44.870 | 55.990 | 57.980 | 52.950 | 7.065 | 13.340 | 52.950 |  |  |  |  |  |
| W3-T | Alum-2 | 39.31 | 40.99 | 38.24 | 39.52 | 1.386 | 3.51 | 39.52 |  |  |  |  |  |
| W3-F | Alum-2 | 38.890 | 39.970 | 34.250 | 37.700 | 3.040 | 8.060 | 37.700 |  |  |  |  |  |
| W4-T | Alum-2 | 33.29 | 33.17 | 36.2 | 34.22 | 1.716 | 5.02 | 34.22 |  |  |  |  |  |
| w4-F | Alum-2 | 41.110 | 39.530 | 40.820 | 40.490 | 0.842 | 2.080 | 40.490 |  |  |  |  |  |
| ws-T | Alum-2 | 51.73 | 51.71 | 52.8 | 51.91 | 0.335 | 0.64 | 51.91 |  |  |  |  |  |
| ws-F | Alum-2 | 21.600 | 21.980 | 21.990 | 21.860 | 0.226 | 1.040 | 21.860 |  |  |  |  |  |
| w6-T | Alum-2 |  |  |  |  |  |  |  |  |  |  |  |  |
| W6-F | Alum-2 | 13.580 | 13.290 | 13.380 | 13.410 | 0.149 | 1.110 | 13.410 |  |  |  |  |  |
| W7-T | Alum-2 | 8.359 | 7.24 | 7.348 | ${ }^{7} .649$ | 0.6173 | ${ }^{8.07}$ | $\begin{array}{r}7.649 \\ \hline 1280\end{array}$ |  |  |  |  |  |
| ${ }_{\text {W7-F }}^{\text {W7-T }}$ | Alum-2 | 12.4440 18.94 | ${ }_{25.56}^{14.460}$ | ${ }_{14.81 .500}^{11}$ | ${ }_{19.77}^{12.800}$ | $\begin{gathered} 1.514 \\ 5.422^{2} \end{gathered}$ | 11.830 27.43 | 12.800 19.77 |  |  |  |  |  |
| W8-F | Alum-2 | ${ }_{28.54} 7.540$ | ${ }^{25.56} 27.890$ | 28.180 | 27.870 | ${ }^{5} .422$ | 1.140 <br> 1.45 | 27.870 |  |  |  |  |  |
| w9-T | Alum-2 | 25.32 | 27.78 | 26.47 | 26.52 | 1.23 | 4.64 | 26.52 |  |  |  |  |  |
| w9.F | Alum-2 | 18.390 | 17.090 | 18.850 | 18.110 | 0.910 | 5.220 | 18.110 |  |  |  |  |  |
| W10-T | Alum-2 | 24.18 | 23.53 | 23.9 | ${ }^{23.87}$ | 0.324 | 1.36 | 23.87 |  |  |  |  |  |
| W10-F | Alum-2 | 21.760 | 15.500 | 22.440 | 19.900 | 3.828 | 19.235 | 19.900 |  |  |  |  |  |
| W11-T | Alum-2 | 12.03 | 10.98 | 11.11 | 1.38 | 0.573 | 5.0351 | 1.38 |  |  |  |  |  |
| ${ }_{\text {W11-F }}^{\text {W1-F }}$ W12-T | Alum-2 | 13.530 13.34 | 13.220 | ${ }_{13.67}^{12.510}$ | ${ }_{12.63}{ }^{13.090}$ | $1.445{ }^{0.527}$ | 4.026 11.3969 | 13.090 12.63 |  |  |  |  |  |
| ${ }_{\text {W12-F }}$ | Alum-2 | ${ }_{13.34 .250}^{13.4}$ | ${ }_{11.02}^{16.580}$ | ${ }_{13.67}^{15.870}$ | 12.63 <br> 15.900 | ${ }^{1.445} 0.665$ | 11.3969 4.180 | 12.63 <br> 15.900 |  |  |  |  |  |
| W13-T | Alum-2 | 20.9 | 20.26 | 10.63 | 17.26 | 5.753 | 33.3232 | 17.26 |  |  |  |  |  |
| W13-F | Alum-2 | 16.760 | 16.980 | 16.140 | 16.630 | 0.435 | 2.615 | 16.630 |  |  |  |  |  |
| W1-F | Alum-3 | 95.810 | 103.100 | 100.300 | 99.750 | 3.696 | 3.700 | 99.750 |  |  |  |  |  |
| W2-T | ${ }^{\text {Alum-3 }}$ | ${ }^{6} 2.31$ | 66.27 | ${ }^{67.17}{ }^{4} 780$ | ${ }^{65.25}$ | 2.587 | 3.96 | ${ }^{65.25}$ |  |  |  |  |  |
| W2-F | Alum-3 | 47.130 | 46.280 | 45.780 | 46.400 | 0.686 | 1.480 | 46.400 |  |  |  |  |  |
| W3-T | Alum-3 | 40.76 | 41.2 | 42.66 | 41.54 | 0.997 | 2.4 | 41.54 |  |  |  |  |  |
| w3-F | Alum-3 | 28.320 | 26.220 | 29.690 | 28.080 | 1.745 | 6.220 | 28.080 |  |  |  |  |  |
| W4-T | Alum-3 | 30.62 | 24.2 | 25.14 | 26.65 | 3.47 | 13.02 | 26.65 |  |  |  |  |  |
| W4-F | Alum-3 | 41.720 | 40.660 | 42.680 | 41.690 | 1.014 | 2.430 | 41.690 |  |  |  |  |  |
| ws-T | Alum-3 | 33.24 | 34.36 | 32.64 | 33.41 | 0.872 | 2.61 | 33.41 |  |  |  |  |  |
| ws-F | Alum-3 | 22.830 | 24.080 | 23.090 | 23.330 | 0.660 | 2.830 | 23.330 |  |  |  |  |  |
| W6-T | Alum-3 |  |  |  |  |  |  |  |  |  |  |  |  |
| W6-F | Alum-3 | 11.230 | 7.420 | 11.520 | 10.060 | 2.290 | 22.760 | 10.060 |  |  |  |  |  |
| W7-T | Alum-3 | 7.242 | 7.326 | 6.836 | 7.135 | 0.262 | 3.67 | 7.135 |  |  |  |  |  |
| W7-F | Alum-3 | 13.580 | ${ }_{27}^{12.520}$ | ${ }_{2687}^{15.770}$ | ${ }_{2692}^{13.960}$ | ${ }_{0339}{ }^{1.661}$ | ${ }^{11.900}$ | ${ }^{13.960}$ |  |  |  |  |  |
| W8-F | Alum-3 | ${ }_{26.61}^{28.620}$ | $\begin{aligned} & 27.28 \\ & 28.050 \end{aligned}$ | ${ }_{26.87}^{27.020}$ | ${ }_{26.92}^{26.900}$ | ${ }^{0.339}{ }_{0.809}$ | 1.26 2.900 | 26.92 27.900 |  |  |  |  |  |
| W9-T | Alum-3 Alum-3 | $27.78{ }^{2.620}$ | 27.29 .050 | ${ }_{28.26}{ }^{27.020}$ | ${ }_{27.78}^{27.900}$ | 0.486 | 2.900 <br> 1.75 | 27.900 27.78 |  |  |  |  |  |
| w9-F | Alum-3 | 20.610 | 20.750 | 22.190 | 21.180 | 0.876 | 4.130 | 21.180 |  |  |  |  |  |
| w10-T | Alum-3 | 27.36 | 25.8 | 36.83 | 26.66 | 0.79 | 2.96 | 26.66 |  |  |  |  |  |
| W10-F | Alum-3 | 81.050 | 76.720 | 82.510 | 80.090 | 3.008 | 3.756 | 80.090 |  |  |  |  |  |
| ${ }_{\text {W11-T }}^{\text {W1-T }}$ | Alum-3 Alum-3 | ${ }_{11.75}^{14.270}$ | ${ }_{1}^{7.425} 13.820$ | ${ }^{5.748} 14.530$ | 8.308 14.210 | ${ }^{3.0973}{ }_{0.360}$ | $\begin{array}{r}37.2889 \\ \hline 534\end{array}$ | 8.308 14210 |  |  |  |  |  |
| W12-T | Alum-3 Alum-3 | ${ }_{14.4}^{14.270}$ | ${ }_{14.25}^{13.820}$ | ${ }_{14.63}{ }^{14.530}$ | ${ }_{14.43}{ }^{14.210}$ | $0_{0.194}{ }^{0.360}$ | 2.534 <br> 1.341 | 14.210 <br> 14.43 |  |  |  |  |  |
| W12-F | Alum-3 | 18.590 | 17.810 | 18.250 | 18.220 | 0.394 | 2.160 | 18.220 |  |  |  |  |  |
| W13-T | Alum-3 | ${ }^{18.61}$ | 18.18 | 18.19 | ${ }^{18.33}{ }_{18.790}$ | ${ }^{0.246}$ | 1.3443 | 18.33 <br> 18.790 |  |  |  |  |  |



|  |  | Pb (Total) |  |  |  |  |  |  |  |  |  |  |  |
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| Week ID | Sample ID | 1 | 2 | 3 | Mean | SD | \%RSD | $\begin{gathered} \text { Average Pb (per } \\ \text { pipe) } \end{gathered}$ | $\begin{array}{\|c\|} \hline \begin{array}{c} \text { Daily Average } \\ \text { (Triplicate Pipe } \\ \text { Type) } \end{array} \\ \hline \end{array}$ | Std. dev. | Week | Weekly Average (Pipe Type) | Std. Dev. |
| W1-F | PaCl-1 | 215.800 | 225.100 | 222.500 | 221.100 | 4.780 | 2.160 | 221.100 | 298.100 | 68.285 | w1 | 298.100 | 68.285 |
| W2-T | PACl-1 | 194.7 | 195.4 | 184.4 | 191.5 | 6.17 | 3.22 | 191.5 | 175.50 | 16.41 | w2 | 198.77 | 61.43 |
| W2-F | PACl-1 | 175.400 | 169.300 | 168.800 | 171.200 | 3.635 | 2.130 | 171.200 | 222.033 | 86.836 | w3 | 14.333 | 46.058 |
| w3-T | PACl-1 | 180.5 | 181.5 | 189.5 | 183.9 | 4.94 | 2.69 | 183.9 | 159.30 | 44.35 | w4 | 123.17 | 45.35 |
| w3-F | PACl-1 | 100.800 | 102.600 | 105.400 | 102.900 | 2.300 | 2.240 | 102.900 | 135.367 | 53.913 | w5 | 111.105 | 31.316 |
| W4-T | PACl-1 | 98.69 | 98.34 | 97.43 | 98.15 | 0.648 | 0.66 | 98.15 | 120.63 | 55.93 | w6 | 81.59 | 12.77 |
| W4-F | PACl-1 | 104.200 | 104.200 | 102.900 | 103.800 | 0.760 | 0.730 | 103.800 | 125.710 | 44.666 | w7 | 77.687 | 13.088 |
| wS-T | PACl-1 | 108.7 | 107 | 106.5 | 107.4 | 1.16 | 1.08 | 107.4 | 127.60 | 39.67 | w8 | 99.09 | 27.68 |
| WS-F | PACl-1 | 90.670 | 92.030 | 92.810 | 91.830 | 1.084 | 1.180 | 91.830 | 94.610 | 7.877 | w9 | 118.893 | 26.093 |
| w6-T | PACl-1 |  |  |  |  |  |  |  |  | \#DIV/0! | w10 | 90.30 | 15.78 |
| W6-F | PACl-1 | 74.390 | 76.140 | 72.500 | 74.350 | 1.817 | 2.440 | 74.350 | 81.590 | 12.766 | W11 | 64.337 | 7.380 |
| W7-T | PACl-1 | 66.75 | 66.84 | 65.6 | 66.4 | 0.689 | 1.04 | 66.4 | 70.38 | 11.64 | W12 | 73.07 | 7.38 |
| W7-F | PACl-1 | 89.390 | 70.450 | 86.870 | 82.240 | 10.284 | 12.510 | 82.240 | 84.990 | 11.524 | W13 | 68.937 | 7.346 |
| w8-T | PACl-1 | 83.7 | 73.06 | 86.61 | 81.12 | 7.138 | 8.8 | 81.12 | 79.87 | 4.83 | w14 | 20.80 | 0.55 |
| w8-F | PACl-1 | 106.600 | 104.300 | 106.000 | 105.700 | 1.220 | 1.150 | 105.700 | 118.320 | 27.992 |  |  |  |
| w9-T | PACl-I | 104.2 | 105.9 | 106.8 | 105.6 | 1.3 | 1.23 | 105.6 | 119.93 | 29.72 | W14 | 24.67 | 1.94 |
| w9-F | PACl-1 | 106.800 | 105.100 | 106.600 | 106.200 | 0.930 | 0.880 | 106.200 | 117.853 | 28.562 | W15 | 73.198 | 59.488 |
| wio-T | PACl-1 | 120.4 | 120.9 | 117.5 | 119.6 | 1.88 | 1.57 | 119.6 | 114.90 | 15.78 | W16 | 71.84 | 22.63 |
| W10-F | PACl-1 | 63.560 | 71.380 | 69.890 | 68.270 | 4.153 | 6.083 | 68.270 | 65.707 | 6.647 | W17 | 57.674 | 18.046 |
| W11-T | PACl-1 | 63.24 | 61.7 | 62.97 | 62.63 | 0.822 | 1.3125 | 62.63 | 65.53 | 8.52 | W18 | 50.11 | 23.88 |
| W11-F | PACl-1 | 63.730 | 63.840 | 60.560 | 62.710 | 1.861 | 2.968 | 62.710 | 63.143 | 7.380 | W19 | 29.380 | 23.671 |
| W12-T | PACl-1 | 67.63 | 66.12 | 69.29 | 67.68 | 1.589 | 2.3473 | 67.68 | 65.63 | 9.90 |  |  |  |
| W12-F | PACl-1 | 80.720 | 79.680 | 78.650 | 79.680 | 1.037 | 1.302 | 79.680 | 80.520 | 5.181 |  |  |  |
| W13-T | PACl-1 | 70.91 | 58.51 | 71.1 | 66.84 | 7.217 | 10.7974 | 66.84 | 66.04 | 7.51 |  |  |  |
| W13-F | PACl-1 | 74.620 | 72.750 | 74.490 | 73.950 | 1.040 | 1.407 | 73.950 | 71.837 | 7.303 |  |  |  |
| Wl-F | PACl-2 | 373.100 | 329.200 | 351.700 | 351.300 | 21.960 | ${ }^{6.250}$ | 351.300 |  |  |  |  |  |
| W2-T | PACl-2 | 184.4 | 181.5 | 163.1 | 176.3 | 11.54 | 6.54 | 176.3 |  |  |  |  |  |
| W2-F | PACl-2 | 297.700 | 301.300 | 367.900 | 322.300 | 39.540 | 12.270 | 322.300 |  |  |  |  |  |
| w3-T | PACl-2 | 188.1 | 192.9 | 176.8 | 185.9 | 8.24 | 4.43 | 185.9 |  |  |  |  |  |
| W3-F | PACl-2 | 104.400 | 108.300 | 104.300 | 105.600 | 2.300 | 2.180 | 105.600 |  |  |  |  |  |
| W4-T | PaCl-2 | 194.1 | 175.4 | 183.1 | 184.3 | 9.24 | 5.01 | 184.3 |  |  |  |  |  |
| W4-F | PaCl-2 | 178.400 | 175.600 | 177.400 | 177.100 | 1.430 | 0.810 | 177.100 |  |  |  |  |  |
| wS-T | PACl-2 | 179 | 170.1 | 170.9 | 173.3 | 4.9 | 2.83 | 173.3 |  |  |  |  |  |
| WS-F | PACl-2 | 101.700 | 102.300 | 106.500 | 103.500 | 2.610 | 2.520 | 103.500 |  |  |  |  |  |
| W6-T | PACl-2 |  |  |  |  |  |  |  |  |  |  |  |  |
| W6-F | PACl-2 | 95.600 | 96.190 | 97.190 | 96.330 | 0.805 | 0.840 | 96.330 |  |  |  |  |  |
| W7-T | PaCl-2 | 83.9 | 82.97 | 83.6 | 83.49 | 0.472 | 0.56 | 83.49 |  |  |  |  |  |
| W7-F | PACl-2 | 102.600 | 89.900 | 100.400 | 97.640 | 6.789 | 6.950 | 97.640 |  |  |  |  |  |
| w8-T | PaCl-2 | 77.28 | 97.56 | ${ }^{77.03}$ | ${ }^{83.95}$ | 11.781 | 14.03 | 83.95 150.400 |  |  |  |  |  |
| W8-F | ${ }_{\text {PaCl-2 }}$ | ${ }_{155.2}^{149.400}$ | ${ }_{150.3}^{152.700}$ | ${ }_{156.7}^{149.200}$ | ${ }_{154.1}^{150400}$ | 1.960 | 1.300 <br> 2.15 | 150.400 154.1 |  |  |  |  |  |
| w9-F | PACl-2 | 150.300 | 151.400 | 149.600 | 150.400 | 0.880 | 0.580 | 150.400 |  |  |  |  |  |
| wio-T | PACl-2 | 133.8 | 125 | 124.4 | 127.8 | 5.24 | 4.1 | 127.8 |  |  |  |  |  |
| W10-F | PACl-2 | 67.950 | 72.990 | 71.130 | 70.690 | 2.548 | 3.604 | 70.690 |  |  |  |  |  |
| W11-T | PACl-2 | 74.16 | 77.71 | 73.49 | 75.12 | 2.264 | 3.0138 | 75.12 |  |  |  |  |  |
| W11-F | PACl-2 | 69.350 | 71.650 | 71.200 | 70.730 | 1.218 | ${ }^{1.722}$ | 70.730 |  |  |  |  |  |
| W12-T | PACl-2 | ${ }^{76.88} 86$ | 74.68 | ${ }^{71.46}$ | 74.34 | 2.725 | 3.6657 1 1 | 74.34 |  |  |  |  |  |
| ${ }_{\text {W12-F }}^{\text {W12-T }}$ | ${ }^{\text {PaCl-2 }}$ | 86.980 69.56 | 87.130 75.29 | ${ }^{84.48} 8$ | ${ }^{\text {73.11.070 }}$ | 1.711 | 1.988 4.2447 | 86.070 73.11 |  |  |  |  |  |
| W13-F | ${ }_{\text {PACl-2 }}$ | ${ }^{6.8 .680}$ | 75.29 79.310 | 74.48 76.600 | 73.17 <br> 77.850 | 3.103 <br> 1.369 | 4.2447 <br> 1.758 <br> 1 | 77.11 77.850 |  |  |  |  |  |
| W1-F | PACL-3 | 317.500 | 324.000 | 324.100 | 321.900 | 3.780 | 1.170 | 321.900 |  |  |  |  |  |
| w2-T | $\mathrm{PACl}-3$ | 160.3 | 160.8 | 155 | 158.7 | 3.22 | 2.03 | 158.7 |  |  |  |  |  |
| W2-F | PACl-3 | 169.600 | 1277.900 | 170.200 | 172.600 | 4.620 | 2.638 | 172.600 |  |  |  |  |  |
| W3-T | PACl-3 | 106.7 | 109.4 | 108.3 | 108.1 | 1.38 | 1.27 | 108.1 |  |  |  |  |  |
| W3-F | PACl-3 |  | 189.300 | 205.200 | 197.600 | 7.970 | 4.040 | 197.600 |  |  |  |  |  |
| W4-T | PACl-3 | 79.86 | 82.41 | 76.04 | 79.44 | 3.206 | 4.04 | 79.44 |  |  |  |  |  |
| W4-F | PACl-3 | 96.000 | 97.040 | 95.650 | 96.230 | 0.720 | 0.750 | 96.230 |  |  |  |  |  |
| wS-T | $\mathrm{PACl}-3$ | 102.1 | 100.4 | 103.9 | 102.1 | 1.77 | 1.73 | 102.1 |  |  |  |  |  |
| wS-F | PACl-3 | 86.900 | 87.890 | 90.700 | 88.500 | 1.973 | 2.230 | 88.500 |  |  |  |  |  |
| w6-T | PACl-3 |  |  |  |  |  |  |  |  |  |  |  |  |
| W6-F | PACl-3 | 73.880 | 72.990 | 75.410 | 74.090 | 1.226 | 1.650 | 74.090 |  |  |  |  |  |
| W7-T | PaCl-3 | 62.68 | 60.34 | 60.76 | 61.26 | 1.25 | 2.04 | ${ }^{61.26}$ |  |  |  |  |  |
| W7-F | ${ }^{\text {PACLI-3 }}$ | 77.780 | 77.980 | ${ }^{60} 99.520$ | 75.090 | $4.829$ | $6_{6.430}$ | 75.090 7453 |  |  |  |  |  |
| ${ }_{\text {W8-T }}^{\text {w8-F }}$ | ${ }_{\text {PaCl-3 }}$ | $\begin{aligned} & 76.5 \\ & 102.600 \end{aligned}$ | $\begin{aligned} & 76.17 \\ & 97.440 \end{aligned}$ | $\begin{gathered} 70.91 \\ 96.440 \end{gathered}$ | $\begin{aligned} & 74.53 \\ & 98.860 \end{aligned}$ | $\begin{aligned} & 3.139 \\ & 3.307 \end{aligned}$ | 4.21 3.340 | 74.53 98.860 |  |  |  |  |  |
| w9-T | PACl-3 | 98.39 | 100.6 | 101.2 | 100.1 | 1.48 | 1.48 | ${ }_{100.1}$ |  |  |  |  |  |
| w9-F | PACL-3 | 96.180 | 97.220 | 97.480 | 96.960 | 0.690 | 0.710 | 96.960 |  |  |  |  |  |
| wio-T | PACL-3 | 98.14 | 96.7 | 97.06 | 97.3 | 0.748 | 0.77 | 97.3 |  |  |  |  |  |
| W10-F | PACl-3 | 58.090 | ${ }^{61.750}$ | 54.630 | 58.160 | 3.563 | ${ }^{6.126}$ | 58.160 |  |  |  |  |  |
| W11-T | ${ }_{\text {PaCl-3 }}$ | ${ }_{59.53}^{58.140}$ | 58.22 .40 | ${ }_{58.76}^{58380}$ | ${ }_{58}^{58.84} 5$ | 0.661 | 1.1235 <br> 7038 <br> .038 | 58.84 55.990 |  |  |  |  |  |
| W12-T | ${ }^{\mathrm{PaCl}-3}$ | ${ }_{58.23}^{58.140}$ | ${ }_{53.13}{ }^{\text {1.440 }}$ | ${ }_{53.21}{ }^{58.380}$ | ${ }_{54.86}^{55.990}$ | 2.921 | 7.038 <br> 5.3252 | 55.990 54.86 |  |  |  |  |  |
| W12-F | PACL-3 | 76.570 | 74.610 | 76.250 | 75.810 | 1.052 | 1.388 | 75.810 |  |  |  |  |  |
| W13-T | PACl-3 | 64.64 | 54.09 | 55.76 | 58.16 | 5.672 | 9.7526 | 58.16 |  |  |  |  |  |
| W13-F | PACl-3 | 65.140 | 64.720 | 61.270 | 63.710 | 2.122 | 3.331 | 63.710 |  |  |  |  |  |

Table D2. Low CSMR

|  |  | Pb (Dissolved) |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Week ID | Sample ID | 1 | 2 | 3 | Mean | SD | \%RSD | $\begin{gathered} \text { Average Pb (per } \\ \text { pipe) } \end{gathered}$ | $\begin{gathered} \text { Daily Average } \\ \text { (Triplicate Pipe } \\ \text { Type) } \end{gathered}$ | Std. dev. | Week | Weekly Average (Pipe Type) | Std. Dev. |
| W1-F | Alum-1 | 70.990 | 69.220 | 64.000 | 68.070 | 3.635 |  | 68.070 | 59.137 | 7.766 |  | 59.137 | 7.766 |
| W2-T | Alum-1 | 36.98 | 43.27 | 43.31 | 41.19 | 3.643 | 8.84 | 41.19 | 36.10 | 4.60 | W2 | 32.02 | 6.90 |
| W2-F | Alum-1 | 33.600 | 37.800 | 36.170 | 35.850 | 2.119 | 5.910 | 35.850 | 27.930 | 6.922 | w3 | 17.918 | 7.922 |
| W3-T | Alum-1 | 28.37 | 32.44 | 28.14 | 29.65 | 2.421 | 8.16 | 29.65 | 21.94 | 6.96 | w4 | 19.26 | 6.69 |
| w3-F | Alum-1 | 21.240 | 18.210 | 28.990 | 22.810 | 5.556 | 24.350 | 22.810 | 13.898 | 7.742 | w5 | 18.668 | 7.411 |
| W4-T | Alum-1 | 17.65 | 14.21 | 15.85 | 15.9 | 1.722 | 10.83 | 15.9 | 13.73 | 2.06 | w6 | 6.30 | 4.04 |
| W4-F | Alum-1 | 29.470 | 29.100 | 29.640 | 29.400 | 0.273 | 0.930 | 29.400 | 24.787 | 3.995 | w7 | 5.453 | 3.115 |
| ws-T | Alum-1 | 30.38 | 30.41 | 29.3 | 30.03 | 0.634 | 2.11 | 30.03 | 24.23 | 5.33 | ws | 15.23 | 6.13 |
| ws-F | Alum-1 | 17.940 | 17.810 | 17.320 | 17.690 | 0.327 | 1.850 | 17.690 | 13.103 | 4.000 | w9 | 17.325 | 5.554 |
| w6-T | Alum-1 |  |  |  |  |  |  |  | \#DIV/0! | \#DIV/0! | wio | 10.80 | 2.51 |
| W6-F | Alum-1 | 11.880 | 9.896 | 10.370 | 10.720 | 1.035 | 9.660 | 10.720 | 6.304 | 4.036 | W11 | 6.562 | 1.204 |
| W7-T | Alum-1 | 8.458 | 6.692 | 6.153 | 7.101 | 1.2061 | 16.98 | 7.101 | 3.75 | 2.91 | W12 | 11.08 | 1.20 |
| W7-F | Alum-1 |  |  |  |  |  |  |  | 8.010 | 0.340 | W13 | 1.761 | 4.637 |
| w8-T | Alum-1 | 14.36 | 15.94 | 9.482 | 13.26 | 3.368 | 25.39 | 13.26 | 10.28 | 3.00 | W14 | 2.42 | 2.67 |
| w8-F | Alum-1 | 23.180 | 24.930 | 23.590 | 23.900 | 0.917 | 3.840 | 23.900 | 20.183 | 3.355 |  |  |  |
| w9-T | Alum-1 | 26.09 | 25.39 | 26.06 | 25.85 | 0.398 | 1.54 | 25.85 | 21.45 | 3.84 | W14 | 0.62 | 1.96 |
| w9.F | Alum-1 | 17.380 | 17.280 | 16.550 | 17.070 | 0.451 | 2.640 | 17.070 | 13.197 | 3.357 | W15 | 9.473 | 3.991 |
| w10-T | Alum-1 | 14.59 | 14.58 | 13.95 | 14.37 | 0.369 | 2.57 | 14.37 | 11.57 | 2.51 | W16 | 14.16 | 4.89 |
| W10-F | Alum-1 | 2.576 | ${ }^{1.495}$ | ${ }_{5} .956 .313$ | ${ }^{2.128}$ | ${ }^{0.564}$ | 26.483 | ${ }_{2}^{2.128}$ | 10.025 | 13.584 | W17 | 7.562 | 3.867 |
| W11-T | Alum-1 | 6.344 | 4.871 | 5.956 | 5.724 | 0.7636 | 13.3417 | 5.724 | 4.03 | 1.62 | W18 | 8.27 | 3.49 |
| W11-F | Alum-1 | 10.340 | 10.420 | 10.690 | 10.480 | 0.182 | 1.740 | 10.480 | 9.994 | 1.204 | W19 | 6.709 | 2.517 |
| W12-T | Alum-1 | 12.8 | 15.08 | 12.54 | 13.47 | 1.396 | 10.3659 | 13.47 | 11.19 | 2.02 |  |  |  |
| W12-F | Alum-1 | 11.580 | 10.730 | 10.280 | 10.860 | 0.658 | ${ }^{6.059}$ | ${ }^{10.860}$ | 10.966 | 4.152 |  |  |  |
| W13-T | Alum-1 | 6.009 | 7.138 | 3.023 | 5.39 | 2.1263 | 39.4426 | 5.39 | 3.86 | 1.34 |  |  |  |
| W13-F | Alum-1 | -5.972 | -6.774 | -7.228 | -6.658 | 0.636 | 9.550 | -6.658 | -0.340 | 6.224 |  |  |  |
| W1-F | Alum-2 | 53.370 | 53.990 | 54.610 | 53.990 | 0.619 | ${ }^{1.150}$ | 53.990 |  |  |  |  |  |
| W2-T | Alum-2 | 31.74 | 32.31 | 32.67 | 32.24 | 0.466 | 1.44 | 32.24 |  |  |  |  |  |
| W2-F | Alum-2 | 22.310 | 26.570 | 25.820 | 24.900 | 2.273 | 9.130 | 24.990 |  |  |  |  |  |
| W3-T | Alum-2 | 19.71 | 20.3 | 20.13 | 20.05 | 0.305 | 1.52 | 20.05 |  |  |  |  |  |
| W3-F | Alum-2 | 8.435 | 9.390 | 12.320 | 10.050 | 2.026 | 20.160 | 10.050 |  |  |  |  |  |
| W4-T | Alum-2 | 13.66 | 15.34 | 11.45 | 13.49 | 1.951 | 14.46 | 13.49 |  |  |  |  |  |
| W4-F | Alum-2 | 24.120 | 23.880 | 21.840 | 22.480 | 0.728 | 3.240 | 22.480 |  |  |  |  |  |
| ws-T | Alum-2 | 22.78 | 23.09 | 23.51 | 23.12 | 0.365 | 1.58 | 23.12 |  |  |  |  |  |
| wS-F | Alum-2 | 11.570 | 11.090 | 11.180 | 11.280 | 0.254 | 2.250 | 11.280 |  |  |  |  |  |
| W6-T | Alum-2 |  |  |  |  |  |  |  |  |  |  |  |  |
| W6-F | Alum-2 | 6.317 | 5.696 | 4.105 | 5.386 | 1.119 | 20.770 | 5.386 |  |  |  |  |  |
| ${ }_{\text {W7-T }}^{\text {W7-F }}$ | Alum-2 | ${ }^{2.424}{ }_{8} .496$ | ${ }^{2.411}{ }_{7} 323$ | ${ }^{1.84}{ }_{8}{ }_{8} 958$ | ${ }^{2.225}{ }_{8} 825$ | ${ }^{0.3335}$ | 14.99 10.170 | 2.225 <br> 8 |  |  |  |  |  |
| W7-F | Alum-2 | ${ }^{11.55} 8.496$ | $11.75{ }^{7.323}$ | ${ }_{7617} 8.958$ | ${ }^{8.250}$ | ${ }^{0332.839}$ | 10.170 | 8.250 |  |  |  |  |  |
| W8-F | Alum-2 | ${ }_{11.55}^{19.250}$ | ${ }^{11.75} 18.990$ | ${ }^{7.617}{ }_{10} 570$ | 10.31 | ${ }^{2.332}$ | 22.62 1.500 | 10.31 19270 |  |  |  |  |  |
| W8-F | Alum-2 | ${ }_{19.93}{ }^{19.250}$ | ${ }_{19.25}^{18.990}$ | ${ }_{20} 0^{19.570}$ | ${ }_{19} 19.73$ | ${ }_{0.414}{ }^{0.289}$ | 1.500 2.1 | 19.270 19.73 |  |  |  |  |  |
| w9-F | Alum-2 | 11.640 | 11.600 | 10.190 | 11.140 | 0.825 | 7.400 | 11.140 |  |  |  |  |  |
| wio-T | Alum-2 | 11.02 | 11.22 | 10.19 | 10.81 | 0.546 | 5.05 | 10.81 |  |  |  |  |  |
| W10-F | Alum-2 | 1.168 | 2.138 | 3.403 | 2.237 | 1.121 | 50.113 | 2.237 |  |  |  |  |  |
| W11-T | Alum-2 | 3.863 | 2.065 | 4.557 | 2.495 | 1.2861 | 36.7949 | 2.495 |  |  |  |  |  |
| W $\begin{gathered}\text { W11-F } \\ \text { W12-T }\end{gathered}$ | Alum-2 | ${ }_{10.67}^{8.639}$ | $10.85{ }^{7.607}$ | ${ }_{7313}{ }^{8.707}$ | ${ }_{9.611}{ }^{8.317}$ | ${ }_{1.9927}{ }^{0.617}$ | 7.412 20.733 | 8.317 9.611 |  |  |  |  |  |
| W12-F | Alum-2 | ${ }^{10.67 .430}$ | ${ }_{5.802}$ | 7.35 | ${ }^{9} 6.618 .869$ | ${ }^{1} 9.927$ | 13.454 | 6.869 |  |  |  |  |  |
| W13-T | Alum-2 | 3.65 | 3.217 | 3.03 | 3.299 | 0.3182 | 9.6459 | 3.299 |  |  |  |  |  |
| W13-F | Alum-2 | -0.152 | -0.101 | -0.184 | -0.146 | 0.042 | 28.860 | -0.146 |  |  |  |  |  |
| W1-F | Alum-3 | 54.670 | 54.610 | 56.870 | 55.350 | 1.317 | 2.380 | 55.350 |  |  |  |  |  |
| W2-T | Alum-3 | 34.43 | 35.32 | 34.88 | 34.88 | 0.445 | 1.28 | 34.88 |  |  |  |  |  |
| W2-F | Alum-3 | 21.980 | 22.380 | 24.750 | 23.040 | 1.496 | 6.490 | 23.040 |  |  |  |  |  |
| W3-T | Alum-3 | 16.11 | 15.19 | 17.03 | 16.11 | 0.919 | 5.7 | 16.11 |  |  |  |  |  |
| W3-F | Alum-3 | 8.756 | 9.344 | 8.404 | 8.835 | 0.475 | 5.380 | 8.835 |  |  |  |  |  |
| W4-T | Alum-3 | 9.361 | 10.9 | 15.18 | 11.81 | 3.017 | 25.54 | 11.81 |  |  |  |  |  |
| W4-F | Alum-3 | 23.270 | 22.340 | 21.840 | 22.480 | 0.728 | 3.240 | 22.480 |  |  |  |  |  |
| w5-T | Alum-3 | 20.2 | 19.42 | 19.04 | 19.55 | 0.592 | 3.03 | 19.55 |  |  |  |  |  |
| ws-F | Alum-3 | 10.950 | 10.320 | 9.754 | 10.340 | 0.599 | 5.790 | 10.340 |  |  |  |  |  |
| w6-T | Alum-3 |  |  |  |  |  |  |  |  |  |  |  |  |
| W6-F | Alum-3 | 2.261 | 2.296 | 3.862 | 2.807 | 0.915 | 32.590 | 2.807 |  |  |  |  |  |
| W7-T | Alum-3 | 2.658 | 2.024 | 1.073 | 1.918 | 0.7975 | 41.57 | 1.918 |  |  |  |  |  |
| W7-F | Alum-3 | ${ }^{7.54893}$ | 6.726 | 8.990 | 7.769 | 1.143 | ${ }^{14.710}$ | 7.769 |  |  |  |  |  |
| W88-T | Alum-3 | ${ }^{8.548} 17.000$ | ${ }_{1.556}^{17.640}$ | ${ }^{7.694} 17.500$ | ${ }_{7.266}^{17.380}$ | ${ }^{1.5416}{ }_{0.338}$ | $\begin{array}{r}21.22 \\ 1.940 \\ \hline\end{array}$ | 7.266 17.380 |  |  |  |  |  |
| w9-T | Alum-3 | 18.75 | 19.27 | 18.32 | 18.78 | 0.475 | 2.53 | 18.78 |  |  |  |  |  |
| W9.F | Alum-3 | 11.610 | 12.130 | 10.380 | 11.380 | 0.901 | 7.920 | 11.380 |  |  |  |  |  |
| W10-F | Alum-3 | 9.424.720 | ${ }^{26.620}$ | ${ }^{9} 9.425 .800$ | ${ }^{9.522} 2.710$ | 0.1774 <br> 0.954 <br> 0.2 | 1.86 | $\begin{array}{r}12.527 \\ \hline 2.710\end{array}$ |  |  |  |  |  |
| w11-T | Alum-3 | 4.195 | 3.436 | 3.99 | 3.874 | 0.3925 | 10.1342 | 3.874 |  |  |  |  |  |
| W11-F | Alum-3 | 8.172 | 8.941 | 8.340 | 8.484 | 0.404 | 4.764 | 8.484 |  |  |  |  |  |
| W12-T | Alum-3 | 9.616 | 9.991 | 12.75 | 10.48 | 1.977 | 18.8548 | 10.48 |  |  |  |  |  |
| W12-F | Alum-3 | 15.420 | 14.800 | 15.280 | 15.170 | 0.328 | 2.163 | 15.170 |  |  |  |  |  |
| W13-F | Alum-3 | ${ }^{3.785} 7.616$ | ${ }^{1.329} 3.102$ | ${ }^{3.567}{ }_{6.637}$ | ${ }^{2.894}{ }_{5.785}$ | ${ }^{1.3596}{ }_{2.375}$ | 46.9842 41.044 | 2.894 <br> 5.785 |  |  |  |  |  |


|  |  | Pb (Dissolved) |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Week ID | Sample ID | 1 | 2 | 3 | Mean | SD | \%RSD | $\begin{gathered} \text { Average Pb (per } \\ \text { pipe) } \end{gathered}$ | $\begin{gathered} \text { Daily Average } \\ \text { (Triplicate Pipe } \\ \text { Type) } \end{gathered}$ | Std. dev. | Week | Weekly Average (Pipe Type) | Std. Dev. |
| W1-F | Fs-1 | 282.400 | 27.800 | 291.200 | 283.400 | 7.250 | 2.560 | 283.400 | 166.667 | 101.145 | wi | 166.667 | 101.145 |
| W2-T | FS-1 | 105.6 | 106.5 | 106.2 | 106.1 | 0.46 | 0.43 | 106.1 | 202.23 | 113.74 | W2 | 162.17 | 90.83 |
| W2-F | FS-1 | 81.370 | 78.550 | 80.760 | 80.230 | 1.483 | 1.850 | 80.230 | 122.110 | 53.589 |  | 127.997 | 58.912 |
| w3-T | FS-1 | 94.73 | 95.24 | 93.88 | 94.62 | 0.686 | 0.73 | 94.62 | 141.37 | 68.18 | W4 | 105.23 | 59.40 |
| W3-F | FS-1 | 80.810 | 74.370 | 74.680 | 76.620 | 3.633 | 4.740 | 76.620 | 114.620 | 59.092 | ws | 87.420 | 38.801 |
| w4-T | FS-1 | 55.72 | 57.24 | 55.74 | 53.23 | 0.873 | 1.55 | 53.23 | 106.28 | 70.82 | w6 | 58.95 | 31.75 |
| W4-F | FS-1 | 63.330 | 62.410 | 64.060 | 63.260 | 0.826 | 1.310 | 63.260 | 104.170 | ${ }_{61} 1.668$ | w7 | 34.310 | 28.733 |
| ws-T | FS-1 | 68.82 | 69.42 | 67.84 | 68.69 | 0.801 | 1.17 | 68.69 | 104.71 | 50.55 | w8 | 49.29 | 29.08 |
| ws-F | FS-1 | 56.190 | 54.670 | 53.910 | 54.920 | 1.160 | 2.110 | 54.920 | 70.127 | 17.643 | w9 | 63.812 | 59.417 |
| w6-T | FS-1 |  |  |  |  |  |  |  | *DIV0! | \#DIV/0! | wio | 38.89 | 38.83 |
| W6-F | FS-1 | 34.820 | 36.120 | 35.960 | 35.630 | 0.708 | 1.990 | 35.630 | 58.947 | 31.753 | wil | 36.497 | 33.891 |
| w7-T | FS-1 | 27.89 | 26.26 | 26.34 | 26.83 | 0.918 | 3.42 | 26.83 | 49.13 | 36.92 | W12 | 43.80 | 33.89 |
| W7-F | FS-1 | 23.530 | 23.330 | 22.070 | 22.980 | 0.792 | 3.450 | 22.980 | 19.493 | 6.512 | w13 | 37.026 | 38.723 |
| w8-T | FS-1 | 28.15 | 28.7 | 26.9 | $27.92$ | 0.921 | 3.3 | 27.92 | 50.03 | 37.78 | W14 | 32.11 | 43.95 |
| W8-F | ${ }_{\text {FSS-1 }}$ | 35.680 38.18 | ${ }_{35}^{33} 323$ | ${ }_{36.4}^{34.410}$ | ${ }^{36.4770}$ | ${ }_{1335}^{1.181}$ | 3.430 3.63 | 34.470 3677 | ${ }^{48.553}$ | 26.162 |  |  |  |
| w9-T | FS-1 | 38.18 | 35.53 | 36.6 | 36.77 | 1.335 | 3.63 | 36.77 | 83.40 | 76.26 | W14 | 30.88 | 47.73 |
| w9.F | FS-1 | 19.000 | 17.630 | 18.220 | 18.280 | 0.688 | 3.760 | 18.280 | 44.227 | 43.127 | W15 | 40.698 | 47.230 |
| W10-T | FS-1 | 15.72 | 13.69 | 14.98 | 14.8 | 1.027 | 6.94 | 14.8 | 38.41 | 38.83 | W16 | 31.89 | 38.33 |
| W10-F | FS-1 | 20.770 | 20.710 | 19.780 | 20.420 | 0.558 | 2.734 | 20.420 | 39.360 | 33.553 | W17 | 39.221 | 72.084 |
| W11-T | FS-1 | 12.82 | 12.53 | 10.85 | 12.07 | 1.064 | 8.8194 | 12.07 | 35.10 | 38.99 | W18 | 43.49 | 65.78 |
| W11-F | FS-1 | 20.030 | 19.020 | 20.220 | 19.760 | 0.641 | 3.245 | 19.760 | 37.890 | 33.891 | W19 | 26.900 | 47.069 |
| W12-T | FS-1 | 19.49 | 17.45 | 19.09 | 18.68 | 1.082 | 5.7945 | 18.68 | 45.69 | 50.37 |  |  |  |
| W12-F | FS-1 | 19.860 | 20.810 | 19.500 | 20.060 | 0.678 | 3.382 | 20.060 | 41.913 | 40.946 |  |  |  |
| W13-T | FS-1 | 8.673 | 8.873 | 8.304 | 8.616 | 0.2887 | 3.3505 | 8.616 | 36.03 | 38.99 |  |  |  |
| W13-F | FS-1 | 12.300 | 11.860 | 10.840 | 11.670 | 0.746 | 6.395 | 11.670 | 38.026 | 47.175 |  |  |  |
| W1-F | FS-2 | 105.900 | 113.000 | 115.600 | 111.500 | 5.050 | ${ }^{4.530}$ | 111.500 |  |  |  |  |  |
| w2-T | FS-2 | 185.3 | 163.6 | 169.5 | 172.8 | 11.23 | 6.5 | 172.8 |  |  |  |  |  |
| W2-F | $\mathrm{FS}^{\text {P-2 }}$ | 101.000 | 110.600 | 99.350 | 103.600 | ${ }^{6.050}$ | 5.840 | 103.600 |  |  |  |  |  |
| W3-T | FS-2 | 106.2 | 107.8 | 115.6 | 109.9 | 4.98 | 4.53 | 109.9 |  |  |  |  |  |
| w3-F | FS-2 | 85.320 | 84.370 | 83.430 | 84.540 | 0.969 | 1.170 | 84.540 |  |  |  |  |  |
| W4-T | FS-2 | 76.09 | 81.36 | 79.28 | 78.91 | 2.656 | 3.37 | 78.91 |  |  |  |  |  |
| W4-F | FS-2 | 74.530 | 74.440 | 73.490 | 74.150 | 0.577 | 0.780 | 74.150 |  |  |  |  |  |
| w5-T | FS-2 | 82.97 | 83.21 | 82.66 | 82.95 | 0.272 | 0.33 | 82.95 |  |  |  |  |  |
| ws-F | FS-2 | 67.420 | 64.560 | 65.990 | 65.990 | 1.427 | 2.160 | 65.990 |  |  |  |  |  |
| w6-T | FS-2 |  |  |  |  |  |  |  |  |  |  |  |  |
| ${ }^{\text {W6-F }}$ | ${ }^{\text {FSS-2 }}$ | 45.980 | 47.620 | 44.700 | 46.100 | 1.465 | 3.180 | 46.100 |  |  |  |  |  |
| ${ }_{\text {c }}^{\text {W7-T }}$ | ${ }_{\text {FS-2 }}$ | 27.92 | 28.79 | 29.71 | ${ }^{28.81}$ | 0.894 | 3.1 | 28.81 |  |  |  |  |  |
| ( $\begin{aligned} & \text { W7-F } \\ & \text { w8-T }\end{aligned}$ | ${ }_{\text {FS-2 }}$ | 23.360 | 23.310 | 23.890 | 23.520 | 0.320 | 1.360 | 23.520 |  |  |  |  |  |
| (\%8-T | ${ }_{\text {Fse }}^{\text {FS-2 }}$ | ${ }^{24.46}$ | ${ }^{36.65}$ | 24.43 | ${ }_{38.52}^{28.450}$ | 7.048 | 24.72 | 28.52 |  |  |  |  |  |
| w9-T | FS-2 | 42.49 | 41.4 | 42.8 | 42.02 | 0.562 | 1.34 | +22.02 |  |  |  |  |  |
| w9-F | FS-2 | 21.400 | 20.410 | 19.360 | 20.390 | 1.024 | 5.020 | 20.390 |  |  |  |  |  |
| W10-T | FS-2 | 17.76 | 16 | 17.87 | 17.21 | 1.048 | 6.09 | 17.21 |  |  |  |  |  |
| W10-F | FS-2 | 18.560 | 18.330 | 21.800 | 19.560 | 1.943 | 9.930 | 19.560 |  |  |  |  |  |
| W11-T | ${ }_{\text {FSS-2 }}$ | ${ }^{13.14}$ | ${ }^{13.09}$ | 13.12 | 13.12 | 0.024 | 0.1853 | 13.12 |  |  |  |  |  |
| ${ }_{\text {W11-F }}^{\substack{\text { W1-F } \\ \text { W12-T }}}$ | $\mathrm{FS}^{\mathrm{F}}$-2 | 17.540 | 16.790 | 16.440 | 16.920 | 0.563 | 3.325 | 16.920 |  |  |  |  |  |
| ${ }_{\text {W }}^{\text {W12-T }}$ | ${ }_{\text {FSS-2 }}$ | 13.47 | 15.23 | ${ }^{15.04}$ | 14.58 | ${ }^{0.962}$ | ${ }^{6.5963}$ | 14.58 |  |  |  |  |  |
| $\mathrm{W}_{\text {W12-F }}^{\text {W12-T }}$ | $\stackrel{\text { FSS-2 }}{\text { FS-2 }}$ | ${ }_{18.72}^{15.610}$ | ${ }^{16.780}$ | ${ }_{17.65}^{17.200}$ | ${ }_{18.8}^{16.530}$ | $1_{1.191}{ }^{0.823}$ | 4.976 6.3228 | 16.530 18.8 |  |  |  |  |  |
| W13-F | FS-2 | 9.794 | ${ }^{10.140}$ | ${ }^{1} 9.822$ | 9.918 | 0.192 | 1.934 | 9.918 |  |  |  |  |  |
| Wl-F | ${ }_{\text {FPS-3 }}$ | ${ }^{106.000}$ | 103.600 | 105.800 | 105.100 | ${ }^{1.290}$ | 1.230 | ${ }^{105.100}$ |  |  |  |  |  |
| W2-T | $\mathrm{FS}^{\mathrm{FS}} 3$ | 317.1 | 377.1 | 289.2 | 327.8 | 45.01 | 13.73 | 327.8 |  |  |  |  |  |
| W2-F | $\mathrm{FS}^{\mathrm{FS}} 3$ | 186.300 | 178.100 | 183.100 | 182.500 | 4.150 | 2.270 | 182.500 |  |  |  |  |  |
| w3-T | FS-3 | 199.3 | 227.9 | 231.6 | 219.6 | 17.66 | 8.04 | 219.6 |  |  |  |  |  |
| w3-F | FS-3 | 176.800 | 189.500 | 181.600 | 182.700 | 6.420 | 3.510 | 182.700 |  |  |  |  |  |
| W4-T | FS-3 | 202.8 | 158.8 | 198.6 | 186.7 | 24.27 | 13 | 186.7 |  |  |  |  |  |
| W4-F | FS-3 | 177.800 | 17.500 | 175.900 | 175.100 | 3.220 | 1.840 | 175.100 |  |  |  |  |  |
| ws-t | FS-3 | 160.2 | 162.6 | 164.7 | 162.5 | 2.25 | 1.38 | 162.5 |  |  |  |  |  |
| w5-F | FS-3 | 90.460 | 89.170 | 88.780 | 89.470 | 0.880 | 0.980 | 89.470 |  |  |  |  |  |
| w6-T | FS-3 |  |  |  |  |  |  |  |  |  |  |  |  |
| W6-F | ${ }_{\text {FSS }}$ | 98.040 | 93.920 | 93.360 | 95.110 | 2.557 | 2.690 | 95.110 |  |  |  |  |  |
| W7-T | ${ }_{\text {FS-3 }}$ | ${ }^{90.81}$ | ${ }^{92.79}$ | 91.62 | 91.74 | 0.999 | 1.09 | 91.74 |  |  |  |  |  |
|  | $\stackrel{\mathrm{FSS}}{\mathrm{FS}-3}$ | $\begin{array}{r} 12.490 \\ 84.75 \end{array}$ | 11.890 | ${ }_{95.32}^{11.570}$ | 11.980 93.66 | $8.2{ }^{0.470}$ | 3.920 8.75 | 11.980 9366 |  |  |  |  |  |
| ( $\begin{gathered}\text { W8-T } \\ \text { w8-F }\end{gathered}$ | $\stackrel{\mathrm{FS}-3}{ } \mathrm{FS} 3$ | ${ }^{84.75} 77.110$ | 100.9 <br> 77.660 | ${ }_{95.32} 81.440$ | ${ }^{93.66} 78.740$ | ${ }^{8.2}{ }_{2.354}$ | 8.75 2.990 | 193.66 78.740 |  |  |  |  |  |
| w9-T | FS-3 | 171.9 | 170.7 | 171.5 | 171.4 | 0.63 | 0.37 | 171.4 |  |  |  |  |  |
| w9-F | FS-3 | 97.730 | 89.920 | 94.400 | 94.010 | 3.919 | 4.170 | 94.010 |  |  |  |  |  |
| wio-T | FS-3 | 84.06 | 82.65 | 83.23 | 83.23 | 0.711 | 0.85 | 83.23 |  |  |  |  |  |
| ${ }_{\text {W10-F }}^{\text {W10-T }}$ | $\mathrm{FS}^{\text {S }} 3$ | 87.830 | 68.460 | 78.020 | 78.100 | 9.684 | 12.399 | 78.100 |  |  |  |  |  |
| W11-T | $\underset{\text { FSS-3 }}{ }$ |  | ${ }^{78.09} 78.110$ | ${ }^{80.35}$ | ${ }^{80.12}$ | ${ }^{1.933}$ | $\begin{array}{r}2.4121 \\ 1305 \\ \hline 0.751\end{array}$ | ${ }^{80.12}$ |  |  |  |  |  |
| W12-T | $\stackrel{\text { FSS-3 }}{ }$ | 104 | 104.5 | $103{ }^{76.170}$ | ${ }^{103.8} 7$ | ${ }_{0.8}^{1.005}$ | 1.305 <br> 0.7704 | 76.990 103.8 |  |  |  |  |  |
| W12-F | FS-3 | 89.460 | 88.390 | 89.600 | 89.150 | 0.664 | 0.745 | 89.150 |  |  |  |  |  |
| W13-T | $\mathrm{FSS}^{\text {P3}}$ | 95.15 | 73.45 | 73.37 | 80.66 | 12.548 | 15.5579 | 80.66 |  |  |  |  |  |
| W13-F | FS-3 | 92.920 | 91.080 | 93.440 | 92.490 | 1.240 | 1.340 | 92.490 |  |  |  |  |  |


|  |  | Pb (Dissolved) |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Week id | Sample ID | 1 | 2 | 3 | Mean | SD | \%RSD | $\begin{gathered} \text { Average } \mathrm{Pb} \text { (per } \\ \text { pipe) } \end{gathered}$ | $\begin{aligned} & \hline \text { Daily Average } \\ & \text { (Triplicate Pipe } \\ & \text { Type) } \end{aligned}$ | Std. dev. | Week | Weekly Average (Pipe Type) | Std. Dev. |
| W1-F | PACl-1- | 55.590 | 56.000 | 57.130 | 56.250 | 0.795 | 1.410 | 56.250 | 60.680 | ${ }^{8.402}$ | W1 | 60.680 | 8.402 |
| W2-T | PACl-1 | 57.5 | 64.43 | 63.15 | 61.69 | 3.688 | 5.98 | 61.69 | 67.28 | 5.24 | W2 | 67.57 | 4.98 |
| W2-F | PACl-1 | 66.710 | 63.910 | 65.930 | ${ }^{65.520}$ | 1.450 | 2.210 | 65.520 | 67.853 | 5.859 | W3 | 61.570 | 8.282 |
| w3-T | PACl-1 | 62.22 | 60.58 | 64.4 | 62.4 | 1.916 | 3.07 | 62.4 | 65.46 | 9.07 | W4 | 60.43 | 18.09 |
| W3-F | PACl-1 | 51.650 | 49.040 | 52.630 | 51.510 | 1.854 | 3.630 | 51.510 | 57.680 | 6.624 | ws | 73.495 | 15.738 |
| W4-T | PACl-1 | 36.31 | 31.95 | 34.28 | 34.18 | 2.181 | 6.38 | 34.18 | 45.76 | 10.89 | W6 | 52.04 | 9.77 |
| W4-F | PACl-1 | 68.570 | 68.510 | 70.310 | 69.130 | 1.022 | 1.480 | 69.130 | 75.093 | 7.347 | w7 | 46.833 | 9.334 |
| ws-T | PACl-1 | 77.3 | 78.31 | 77.7 | 77.77 | 0.507 | 0.65 | 77.77 | 85.23 | 10.89 | w8 | 65.39 | 17.46 |
| W5-F | PACl-1 | 60.120 | 59.970 | 58.857 | 59.650 | 0.685 | 1.150 | 59.650 | 61.757 | 9.340 | w9 | 65.453 | 11.877 |
| w6-T | PACl-1 |  |  |  |  |  |  |  | \#Div/0! | \#DIV/0! | wio | 47.69 | 14.53 |
| W6-F | PACl-1 | 45.360 | 46.010 | 46.610 | 45.990 | 0.626 | 1.360 | 45.990 | 52.043 | 9.775 | W11 | 47.602 | 5.808 |
| W7-T | $\mathrm{PACl}-1$ | 39.57 | 39.96 | 41 | 40.18 | 0.736 | 1.83 | 40.18 | 44.58 | 8.37 | W12 | 44.58 | 5.81 |
| W7-F | PACl-I | 39.020 | 38.250 | 48.690 | 41.980 | 5.819 | 13.860 | 41.980 | 49.087 | 11.513 | W13 | 26.103 | 8.426 |
| ws-T | PACl-1 | 47.29 | 48.94 | 48.18 | 48.114 | 0.827 | 1.72 | 48.114 | 51.18 | 3.56 | W14 | 5.13 | 0.24 |
| ws-F | PACl-1 | 74.960 | $77.510$ | 76.090 | 76.180 | 1.278 | 1.680 | 76.180 | 79.597 | 12.005 |  |  |  |
| w9-T | PACl-I | 65.43 | 61.49 | 63.48 | 63.47 | 1.97 | 3.1 | 63.47 | 70.33 | 13.95 | W14 | -1.33 | 0.39 |
| w9-F | PACl-1 | 61.830 | 56.710 | 57.850 | 58.800 | 2.689 | 4.570 | 58.800 | 60.577 | 9.313 | W15 | 23.020 | 22.847 |
| W10-T | PACl-I | 47.07 | 50.49 | 47.28 | 48.28 | 1.915 | 3.97 | 48.28 | 55.48 | 14.53 | W16 | 30.85 | 7.57 |
| W10-F | PACl-1 | 39.120 | 39.850 | 39.300 | 39.420 | 0.379 | 0.961 | 39.420 | 39.897 | 7.896 | W17 | 31.422 | 10.776 |
| W11-T | PACl-1 | 48.7 | 47.46 | 46.53 | 47.57 | 1.089 | 2.2901 | 47.57 | 50.63 | 4.50 | W18 | 8.89 | 53.59 |
| W11-F | PACl-1 | 42.050 | 41.520 | 42.380 | 41.980 | 0.431 | 1.028 | 41.980 | 44.577 | 5.808 | W19 | 28.850 | 7.493 |
| W12-T | PACl-I | 54.78 | 51.33 | 54.31 | 53.48 | 1.871 | 3.4984 | 53.48 | 50.27 | 10.71 |  |  |  |
| W12-F | PACl-1 | 50.870 | 45.180 | 46.730 | 47.590 | 2.939 | 6.176 | 47.590 | 51.417 | 6.302 |  |  |  |
| W13-T | PACl-1 | 22.33 | 27.44 | 30.66 | 26.81 | 4.2 | 15.6635 | 26.81 | 31.26 | 8.63 |  |  |  |
| W13-F | PACl-1 | 22.410 | 22.400 | 22.230 | 22.340 | 0.097 | 0.436 | 22.340 | 20.943 | 4.810 |  |  |  |
| W1-F | PACl-2 | 67.530 | 70.700 | 72.870 | 70.370 | 2.683 | ${ }^{3.810}$ | 70.370 |  |  |  |  |  |
| W2-T | PACl-2 | 70.83 | 74.82 | 70.57 | 72.08 | 2.38 | 3.3 | 72.08 |  |  |  |  |  |
| W2-F | PACl-2 | 68.800 | 78.450 | 76.310 | 74.520 | 5.070 | 6.800 | 74.520 |  |  |  |  |  |
| w3-T | PACl-2 | 69.94 | 78.87 | 78.15 | 75.66 | 4.961 | 6.56 | 75.66 |  |  |  |  |  |
| w3-F | PACl-2 | 64.620 | 64.840 | 64.580 | 64.680 | 0.140 | 0.220 | 64.680 |  |  |  |  |  |
| W4-T | PaCl-2 | 57.13 | 54.45 | 55.82 | 55.8 | 1.34 | 2.4 | 55.8 |  |  |  |  |  |
| W4-F | PaCl-2 | 85.970 | 79.340 | 84.610 | 83.300 | 3.500 | 4.200 | 83.300 |  |  |  |  |  |
| ws-T | PACl-2 | 97.34 | 97.83 | 98.01 | 97.73 | 0.349 | 0.36 | 97.73 |  |  |  |  |  |
| wS-F | PACl-2 | 71.130 | 71.810 | 72.980 | 71.970 | 0.938 | 1.300 | 71.970 |  |  |  |  |  |
| W6-T | PACl-2 |  |  |  |  |  |  |  |  |  |  |  |  |
| W6-F | PACl-2 | 63.090 | 64.420 | 62.440 | 63.320 | 1.009 | 1.590 | 63.320 |  |  |  |  |  |
| ${ }_{\text {W7-T }}^{\text {W7- }}$ | PACl-2 | 53.39 | 55.11 | 54.18 | 54.23 | ${ }^{0.859}$ | 1.58 | 54.23 |  |  |  |  |  |
| ${ }_{\text {W }}^{\text {W7-F }}$ | PACl-2 | 61.950 | 62.750 | 62.400 | 62.370 | 0.398 | ${ }^{0.640}$ | 62.370 |  |  |  |  |  |
| W8-F | ${ }^{\text {PaCl-2 }}$ | ${ }_{96.3680}^{56.380}$ | ${ }^{54.48} 9$ | ${ }_{9}^{53.94}{ }_{94}$ | ${ }^{55.09}{ }_{92,940}$ | ${ }_{1.556}^{1.699}$ | 2.82 1.830 | 55.09 92.940 |  |  |  |  |  |
| W9-T | ${ }^{\text {PaCl-2 }}$ | ${ }_{84.93} 9.380$ | ${ }_{84.79}{ }^{92.700}$ | $8{ }^{\text {86.42 }}$ 9450 | ${ }_{86.38}{ }^{92.940}$ | 0.904 | 1.830 <br> 1.06 | 92,940 86.38 |  |  |  |  |  |
| w9-F | PACl-2 | 70.470 | 71.840 | 69.630 | 70.650 | 1.119 | 1.580 | 70.650 |  |  |  |  |  |
| wio-T | PACl-2 | 67.34 | 72.96 | 76.3 | 72.2 | 4.524 | 6.27 | 72.2 |  |  |  |  |  |
| W10-F | PACl-2 | 48.190 | 48.100 | 47.780 | 48.020 | 0.212 | 0.442 | 48.020 |  |  |  |  |  |
| W11-T | ${ }^{\text {PaCl-2 }}$ | ${ }_{54.88}^{51.950}$ | ${ }_{56.67}^{51130}$ | ${ }_{56.05}^{56590}$ | 55.8 | $1.02{ }^{0.683}$ | ${ }_{1.8882}$ | [55.8 |  |  |  |  |  |
| ${ }_{\text {W }}^{\text {W11-F }}$ | ${ }_{\text {PaCl-2 }}$ | ${ }_{6}^{51.17}{ }^{51950}$ | ${ }_{\text {51.130 }}$ | 50.590 <br> 65.11 | 51.230 59.01 | ${ }_{8.951}{ }^{0.683}$ | 1.333 15.169 | 51.230 59.01 |  |  |  |  |  |
| W12-F | PACl-2 | 57.830 | 57.970 | 60.280 | 58.6 | ${ }^{1.378}$ | 2.348 | 58.690 |  |  |  |  |  |
| W13-T | PACl-2 | 48.76 | 37.45 | 37.43 | 41.21 | 6.536 | 15.8609 | 41.21 |  |  |  |  |  |
| W13-F | PACl-2 | 25.940 | 24.770 | 24.000 | 24.900 | 0.978 | 3.926 | 24.900 |  |  |  |  |  |
| W1-F | PACl-3 | 47.430 | 57.070 | ${ }^{61.760}$ | 55.420 | ${ }^{7.306}$ | 13.180 | 55.420 |  |  |  |  |  |
| w2-T | PACl-3 | 73.69 | 65.81 | 64.69 | 68.06 | 4.908 | 7.21 | 68.06 |  |  |  |  |  |
| W2-F | PACl-3 | 61.370 | 67.650 | 61.550 | 63.520 | 3.578 | 5.630 | 63.520 |  |  |  |  |  |
| W3-T | PACl-3 | 56.69 | 59.28 | 58.97 | 58.32 | 1.414 | 2.43 | 58.32 |  |  |  |  |  |
| w3-F | PACl-3 | 53.980 | 54.890 | 61.670 | 56.850 | 4.201 | 7.390 | 56.850 |  |  |  |  |  |
| W4-T | PACl-3 | 46.82 | 47.23 | 47.87 | 47.31 | 0.532 | 1.12 | 47.31 |  |  |  |  |  |
| W4-F | PACl-3 | 73.050 | 73.040 | 72.470 | 72.850 | 0.331 | 0.450 | 72.850 |  |  |  |  |  |
| ws-t | $\mathrm{PACl}-3$ | 81.28 | 80.55 | 78.76 | 80.2 | 1.297 | 1.62 | 80.2 |  |  |  |  |  |
| wS-F | PACl-3 | 53.050 | 54.920 | 52.970 | 53.650 | 1.106 | 2.060 | 53.650 |  |  |  |  |  |
| w6-T | PACl-3 |  |  |  |  |  |  |  |  |  |  |  |  |
| W6-F | PACL-3 | 45.740 | 48.730 | 45.990 | 46.820 | 1.660 | 3.550 | 46.820 |  |  |  |  |  |
| W7-T | PaCl-3 | 39.05 | 40.1 | 38.84 | 39.33 | 0.673 | 1.71 | 39.33 |  |  |  |  |  |
| ${ }_{\text {W\%-T }}^{\text {W7-F }}$ | ${ }_{\text {PACLI-3 }}$ | ${ }_{51.98}{ }^{43.520}$ | ${ }_{50.4}^{44.040}$ | ${ }_{48.6}^{41.190}$ | ${ }_{50}{ }^{42.910}$ | ${ }_{1.693}{ }^{1.519}$ | 3.540 3 3 | 42.910 5033 |  |  |  |  |  |
| W8-F | ${ }_{\text {PACl-3 }}$ | ${ }^{51.98} 70.120$ | ${ }_{50.48 .970}$ | ${ }_{6}^{48.69 .910}$ | ${ }_{60.33} 69.670$ | ${ }^{1.693} 0$ | 3.36 0.880 | 50.33 <br> 69.670 |  |  |  |  |  |
| w9-T | PACl-3 | 62.21 | 58.86 | 62.34 | 61.14 | 1.972 | 3.23 | 61.14 |  |  |  |  |  |
| w9-F | PACL-3 | 52.720 | 52.760 | 51.340 | 52.280 | 0.808 | 1.550 | 52.280 |  |  |  |  |  |
| W10-T | PACl-3 | 47.07 | 46.24 | 44.58 | 45.96 | 1.268 | 2.76 | 45.96 |  |  |  |  |  |
| W10-F | PACL-3 | ${ }^{31.840}$ | 31.510 | 33.380 | ${ }^{32.250}$ | 1.000 | 3.102 | 32.250 |  |  |  |  |  |
| W11-T | ${ }_{\text {PaCl-3 }}$ | ${ }^{47.21} 38.750$ | ${ }^{47.65}$ | ${ }^{50.68}{ }_{41760}$ | ${ }^{48.51}{ }_{40}$ | $1.89{ }_{1575}$ | 3.8952 <br> 3.887 | 48.51 40.520 |  |  |  |  |  |
| W12-T | ${ }_{\text {PACl-3 }}$ | ${ }_{37.47}{ }^{38} 70$ | ${ }_{41.4}{ }^{4.040}$ | ${ }_{36.14}^{4.760}$ | ${ }_{38.33}{ }^{40.520}$ | 2.733 | 3.129 7.129 | ${ }^{48.33}$ |  |  |  |  |  |
| W12-F | PACL-3 | 48.310 | 48.470 | 46.130 | 47.970 | 1.650 | 3.440 | 47.970 |  |  |  |  |  |
| W13-T | $\mathrm{PACL}-3$ | 31.33 | 23.7 | 22.29 | 25.77 | 4.867 | 18.883 | 25.77 1590 |  |  |  |  |  |
| W13-F | PACl-3 | 15.740 | 15.220 | 15.810 | 15.590 | 0.321 | 2.062 | 15.590 |  |  |  |  |  |


[^0]:    Signature of Author

[^1]:    ${ }^{1}$ Pilot-to-pilot proving trials were conducted from February through March, 2008.
    ${ }^{2}$ Pilot-to-FSP proving trials were conducted from May through August, 2008.

[^2]:    ${ }^{1}$ Values in parentheses represent the mean difference between the pilot and FSP measurements for each response parameter.
    ${ }^{2}$ The measurement error represents two standard deviations of the residual population mean for each response parameter.

