West Saint John –
Corrosion Control Investigation
Final Report

182814.00 ● Final Report ● February 2019

Prepared for:

SAINT JOHN

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Solving today's problems with tomorrow in mind

February 5, 2019

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Commissioner – Saint John Water
PO Box 1971
Saint John, NB E2L 4L1

Dear Mr. McGovern:

RE: West Saint John – Corrosion Control Investigation Final Report

Please find enclosed the final report for the West Saint John corrosion control investigation.

We are available, at your request, to discuss the information contained within the report or provide additional discussion or presentation to the City.

Yours very truly,

CBCL Limited

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Project No: 182814.00

CANADA'S BEST MANAGED COMPANIES

Contents

CHAPTER 1 Introduction 1
1.1 Background 1
1.2 Objectives 2
1.3 Summary of Findings 3
CHAPTER 2 Water Quality & Premise Plumbing Corrosion – Industry Review 5
2.1 West Saint John Water Quality 6
2.1.1 Alkalinity, pH and Dissolved Inorganic Carbon Changes 9
2.2 Switching Source Waters 10
2.3 Use of Orthophosphates for Corrosion Control 13
CHAPTER 3 Dalhousie Report – CBCL Review 16
3.1 Dalhousie Report 16
3.2 Bench-scale Testing 16
3.2.1 Scale Analysis 16
3.2.2 Stagnation Study 17
3.2.3 Additional Testing 20
CHAPTER 4 Summary 21
4.1 Discussion of Results 21
CHAPTER 5 References 23

Appendices

A Dalhousie Report - September 2018

B Supplemental Dalhousie Report - January 2019

CHAPTER 1 INTRODUCTION

1.1 Background

Prior to amalgamation in 1967, drinking water for the residents of West Saint John was supplied by the City of Lancaster. After amalgamation, the City of Saint John (City) acquired the existing Lancaster water system and incorporated it into the main City system. Under historical practice, when delivering treated Spruce Lake water to West Saint John customers, the City was committed to supplying water that met water quality guidelines and regulatory obligations of the time. As water quality guidelines and regulations evolved, water in the West Saint John system fell out of compliance with parameters such as turbidity and disinfection by-products (DBPs). As the level of treatment provided by the system did not evolve at the same rate as the regulations, exceedances of the water quality guidelines began to occur and as such the City identified that improving water quality for its customers should be a priority. Efforts to plan and develop improved treatment of water continued over decades, with various options being considered.

As part of the Safe Clean Drinking Water Project, the City committed to supplying all Saint John customers with water that meets or exceeds the Guidelines for Canadian Drinking Water Quality (GCDWQ). As such, the City decided to switch the West Saint John water source from Spruce Lake, to the South Bay Wellfield. The wellfield consists of 3 ground water wells which were commissioned in 2013-2014 and have water quality which meets or exceeds the GCDWQ. In September 2017, the switch from surface water to ground water supply was completed, and customers were provided with potable water which meets or exceeds the GCDWQ. From available practice and technical guidelines, the new ground water source is considered less corrosive than the previous Spruce Lake supply. The new source does have increased hardness, which is comparable to other municipalities using ground water sources.

From a treatment standpoint, the ground water source has a substantial decrease in color and organic matter compared to the Spruce Lake supply, and an increase in mineral content. Based on the improved water quality, the only treatment process required to meet the City's Approval and GCDWQ is chlorine disinfection, with the amount of chlorine required being much less compared to what was historically used for Spruce Lake. The decrease in organic matter and chlorine dose also predicted a decrease in the formation of disinfection by-products, which are classified as "probable carcinogen" by Health Canada and regulated by NBDELG. Based on water quality parameters from the new wellfield, corrosion inhibitors and/or pH adjustment was not included in the new treatment system.

In January 2018, the City of Saint John began to receive complaints of copper pipe leaks from West Saint John customers. Approximately 4% of the 5,400 West Saint John customers reported leaks within a 3-4 week period. The reports were not localized to specific neighbourhoods in West Saint John and there were no abnormal increases within City owned copper services. In February 2018, CBCL and Dalhousie University were tasked with leading an investigation into the source water switch and the reported copper leaks, including bench scale testing of copper piping from West Saint John and reviewing possible corrosion mechanisms.

After the reports of copper leaks, the City examined several available options for temporary corrosion control treatments including pH adjustment and the addition of a corrosion inhibitor. The City elected to install a temporary orthophosphate system in March 2018 to reduce the apparent copper corrosion and to help promote scale stabilization. Corrosion inhibitors, including orthophosphates, are commonly used in Atlantic Canada to prevent corrosion of distribution systems. However, the systems in Atlantic Canada using corrosion inhibitors are surface water supplies with water quality similar to Spruce Lake rather than the South Bay ground water supply. It is not common practice to add orthophosphates to drinking water supplied by ground water, but it was employed in this situation as a tool which could be implemented quickly in attempt to mitigate the copper leaks to the extent possible.

This report was prepared to relay the findings of the research and testing that has been completed to date and to provide recommendations for further testing.

1.2 Objectives

CBCL Limited (CBCL) and Dalhousie University (Center for Water Resources) have a collaborative partnership and have worked together previously on drinking water projects, including the Safe, Clean Drinking Water Project. Dalhousie was engaged for this project to perform laboratory testing and to provide preliminary analysis and reporting (Appendix A). CBCL was engaged to review the preliminary results, comment on industry best practices for corrosion control and provide recommendations to Saint John Water for steps forward.

The objectives for the laboratory testing completed by Dalhousie University were twofold:

1. Analysis of copper pipe corrosion scale on existing West Saint John pipe samples.
2. Perform a stagnation study using new and recovered copper pipe from East and West Saint John to investigate mitigation strategies and the role of source water in copper pipe corrosion.

The CBCL report objectives are as follows:

1. Provide analysis of Dalhousie results, including comments on industry practices for copper corrosion.
2. Provide corrosion control recommendations for Saint John Water.

1.3 Summary of Findings

Because of the reported copper pipe failures in West Saint John after the source water switch, there was a need to conduct further investigation into the mechanisms involved in the leaks. Bench scale testing, which is testing completed in a controlled laboratory setting, is commonly used in the water treatment industry as a tool to optimize process performance and to provide a snap shot of current operating conditions. Testing at bench scale can often be a cost-effective option for quickly implementing a study compared to completing testing at pilot or full scale. The purpose of the bench scale testing was to provide insight into the reported copper pipe failure event by performing preliminary analysis on copper pipe samples from East and West Saint John.

Dalhousie University completed two initial bench scale experiments to analyze the copper corrosion scaling present in West Saint John; one to analyze corrosion present and another to examine copper release from pipes exposed to surface or ground water. The initial analysis found that the scaling present was largely amorphous (does not have a distinct, identifiable crystalline structure) with some cuprite and malachite present (common copper scale materials), but not well defined. As such, the analyzed scale did not match copper scaling composition that is typically cited in literature. Amorphous corrosion scales commonly occur on copper piping; however as the composition of the scaling can vary greatly between systems, there is little research completed on amorphous scaling and copper solubility. Figure 1 of the Dalhousie report (Appendix A) shows examples of copper plumbing corrosion.

The stagnation study was performed in two phases. The first phase investigated the effects of pH, free chlorine concentration and orthophosphate addition on copper release to ground water. It was found that the addition of orthophosphate was statistically significant in decreasing copper release to the ground water. The second phase of the stagnation study looked at the difference in copper release when the pipes were conditioned with surface water or ground water. Using the pipe samples provided by the City and specific water quality representative of West Saint John, the results showed that the pipes conditioned with ground water released more copper than the pipes which were conditioned with surface water. This varied from the copper concentrations predicted from the copper solubility models found in literature, which predicted the surface water to have a higher copper levels. When the testing was performed with new pipe, there was no difference in copper release between surface and ground water. It is noted, however, that the pH of surface water used in the study was higher than historical tap water pH of the Spruce Lake supply. This, in turn, would reduce the rate of copper release to the surface water in the experiments relative to rates expected at historical pH values. This effect was investigated further through supplemental bench-scale testing (Appendix B). The supplemental testing was completed to compare copper release in pipes containing surface water at pH values of 5.5 and 6.8, with the former value being that which was associated with historical water quality. In new pipe, and as predicted, copper release was higher at lower pH. In aged pipe, the supplemental testing at both pH values resulted in substantially higher copper concentrations than the initial testing (Appendix A), with no discernable difference in results between the two pH values. This highlights the variability in copper release from the aged pipe samples under various scenarios. Whether the copper measured was comprised of new corrosion or decomposition of pre-existing scale is not known at this level of investigation. Precise mechanisms for the corrosion were not identified, both due to time constraints of the current investigation and gaps in knowledge with regards to copper corrosion that do not fit the parameters of current cuprosolvency models.

Under the operating life of premise plumbing systems in West Saint John, the historically low pH/alkalinity water undoubtedly resulted in high rates of copper corrosion that occurred for many years. This can be demonstrated through an abundance of literature (Schock et al., 1995; Millette et al., 1987; Schock & Lytle, 2011). Existing pipes had developed stable scaling from the corrosion which helped limit leaks and helped maintain structural pipe integrity. When the water supply transitioned to the higher pH, higher alkalinity water, it is likely that a transient event occurred where the existing scale was disrupted before a new, passivating scale (based on the changed water quality) could be formed. As the existing scale was disrupted, the corroded pipe in the system was exposed and leaks began to occur. This is different than the deterioration of pipe material due to new corrosion. Transient events can vary in length from hours to months and it appears that the one experienced in West Saint John occurred over several months. Such occurrences are not well documented elsewhere and not anticipated from existing corrosion models.

In terms of rationalizing all the information collected to date around the issue, the current evidence suggests that copper pipe systems in West Saint John have undergone changes as a result of a transitioning event, which stands out from anticipated outcomes based on current science and solubility models.

CHAPTER 2

WATER QUALITY & PREMISE PLUMBING CORROSION – INDUSTRY REVIEW

Corrosion of distribution piping and premise plumbing is the deterioration of pipe material including pipes, fittings and linings as it reacts with water within the system and the environment. Corrosion of the distribution and/or premise piping can affect the flow of water throughout the system and the structural integrity of the pipe, which could lead to pipe failure. Leaching of contaminates into the drinking water such as lead, iron and copper can also occur as a result of corrosion and lead to negative health effects. Drinking water guidelines for lead and copper were developed in the early 1990's to minimize concentrations within the distribution system and outline requirements for corrosion control treatments. Technical documents have been developed by regulatory bodies for implementing corrosion control requirements, however the majority of documents are focused on limiting health impacts of water containing corrosion by-products as opposed to maintaining the structural integrity of plumbing piping system. Several key technical documents are:

- Health Canada – *Guidance on Controlling Corrosion in Drinking Water Distribution Systems* (2009).
- US EPA – *Lead and Copper Rule Technical Documents* (1991).
- US EPA – *Optimal Corrosion Control Treatment Evaluation Technical Recommendations for Primary Agencies and Public Water Systems* (2016).
- US EPA – *Corrosion Manual for Internal Corrosion of Water Distribution Systems* (1984).
- AWWA – *M58 Internal Corrosion Control In Water Distribution Systems, Second Edition* (2011).

With the introduction of regulatory guidelines in the US and Canada, there has been an increase in research of corrosion control methods and the effects on the distribution and/or premise plumbing systems, dating principally to the 1990's (Schock et al., 1995; Edwards et al., 1994; Ferguson et al., 1996). As such, there is an emerging knowledge and literature base for corrosion and corrosion control in water piping systems.

Copper corrosion is complex and dependent on many different physical and chemical variables that often conflict. Further, from an industry perspective, copper corrosion takes place principally on private property beyond the limits of public infrastructure ownership and traditional study. Important water quality parameters related to copper corrosion include water age, temperature, pH, alkalinity, velocity profiles, oxidation potential and dissolved inorganic carbon (DIC) concentrations. The addition of disinfectant residuals, polyphosphates and orthophosphates will also contribute to the rate at which corrosion will occur. Physical characteristics of the distribution and/or premise plumbing systems such as the age of the copper pipes, microbial activity and the age of the water within the system will also factor into the rate of corrosion. Copper pipes within residential systems are available with varying pipe thickness, which could also affect the rate at which damage to the pipe integrity from corrosion results in leaks. The most common copper pipe types used in residential systems are Type L and Type M pipe, with Type L pipe having thicker pipe walls. In West Saint John, there is a combination of Type L and Type M pipe used residentially and the reported copper pipe leaks were from a combination of both pipe types.

Cuprosolvency, is a term used to describe the solubility of copper in water. As research into copper corrosion has advanced, some researchers have been able to develop models which can predict cuprosolvency in premise plumbing. Most current cuprosolvency models are based on the formation of relatively soluble cuprous compounds including cuprite (Cu_2O) and copper (I) hydroxide ($CuOH$) and the transformation over time to more stable compounds such as malachite ($Cu_2(OH)_2CO_3$) and tenorite (CuO). Interactions with different parameters such as natural organic matter (NOM), oxidizers such as free chlorine and the addition of corrosion control methods such as orthophosphate will affect the formation of the cupric hydroxide compounds.

The purpose of this report is not to provide an extensive review of cuprosolvency models, but to take into account the principle factors of these models and apply them to conditions experienced in West Saint John. The following sections describes the water quality changes experienced in West Saint John and industry practices specific to similar systems elsewhere.

2.1 West Saint John Water Quality

Spruce Lake water quality is typical of surface water supplies in Atlantic Canada. It is characterized as having relatively low alkalinity, low pH, low hardness and moderate concentrations of organics matter. This results in soft water which can be corrosive to distribution piping and premise plumbing. From a regulatory stand point under the GCDWQ, parameters such as pH and hardness are considered aesthetic objectives (AO) and do not have health-based maximum allowable concentrations (MAC) such as disinfection by-products, which have to be met by the City. The City's long term treatment objective prioritized compliance with health-based water quality requirements; for the Spruce Lake water supply this would require comprehensive treatment processes such as coagulation, flocculation and filtration, as well as pH correction. As the City was unable to meet health based water quality guidelines with the treatment system at Spruce Lake (chlorination), a new water source with improved water quality was selected for West Saint John. This was completed as part of the Safe, Clean Drinking Water Project. The new ground water source, the South Bay Wellfield, supplies raw water with a pH between 7.5-8, moderate alkalinity, non-aggressive hardness, increased mineral content and meets all health based and aesthetic water quality guidelines with no further treatment (besides disinfection). The raw water quality results for both water supplies are provided in Table 2-1.

Table 2-1: West Saint John Historical Raw Water Quality

Parameter	Units	MAC/ AO	Spruce Lake 2013-2017		Well #1 2013-2014		Well #2 2014	Well #1 2018	Well #2 2018
			Average	Range	Average	Range			
Alkalinity	mg/L as CaCO3		6	2.5-20	98	84-116	106	127	128
pH		6.5-8.5	6.6	6.2-8.1	8.01	7.29-9.41	8.02	8.02	8.02
Turbidity	NTU	1	0.609	0.36-1.1	0.5	0.1-1.5	0.7	0.4	0.9
TOC	mg/L				1	0.5-3.1	1.9	1.5	0.85
Colour True	Pt-Co	15	23	9-35	7.8	<5-15	<5	11	<5
Conductivity	uS/cm		32	28.4-38.1	443	376-528	444	554	519
Chloride	mg/L	<250	4	3.5-4.8	41	29-49	38	72	57
Calcium	mg/L				55	35-66	65.5	68	66
Magnesium	mg/L		0.41	0.3-0.45	8.9	6.3-11.7	7.4	11	10
Hardness	mg/L as CaCO3		5.3	4.8-5.8	174	123-207	194	216	206
Manganese	mg/L	<0.05	0.014	0.01-0.026	0.053	<0.002-0.153	0.022	0.006	0.0025
Iron	mg/L	<0.3	0.07	0.049-0.103	0.084	0.05-0.172	0.10	0.05	0.05
Aluminium	mg/L	<0.1	0.065	0.031-0.101	0.023	0.005-0.073	0.029	0.007	<0.005
Copper	mg/L	1	<0.002	<0.002-0.012	0.066	0.001-0.50	0.003	<0.001	<0.001
Lead	mg/L	0.01	<0.0005	<0.0005	<0.0005	0.0005-0.115	0.0031	<0.0005	<0.005

Quarterly water quality results over a four year period are provided in Table 2.1 for the Spruce Lake water supply. It should be noted that pumping of raw water from Musquash Lake to Spruce Lake took place seasonally as needed during this time. In the South Bay Wellfield, Well #1 and Well #2 are used as primary wells. A third well, Well #3, is located within the Wellfield as a backup supply and is not referenced in this report. The ground water quality reported in Table 2.1 is from the fall of 2014 during the wellfield development and was used for evaluating treatment requirements for the wellfield. As Well #1 was developed first, more data was available compared to Well #2 for the evaluation. The data from 2018 represents water quality while the wells were online and supplying water to West Saint John. During the development of Well #1, there were several manganese results that exceeded the water quality guidelines, which were an aesthetic objective in 2014. The manganese results from both Wells in 2018 met the previous manganese aesthetic objectives along with the proposed updated manganese MAC in the GCDWQ.

In the period shown below in Figure 2-1, Spruce Lake raw water was treated with both chlorine and hydrofluosilic acid (fluoride). Because the water has low alkalinity, addition of hydrofluosilicic acid caused the pH to drop further while in the distribution system. City Council decided to stop the addition of hydrofluosilic acid in 2014 and the pH subsequently begin to trend upwards closer to 6.5, which is within the GCDWQ guidelines. After the switch to the South Bay Wellfield, the pH in the distribution system has been trending closer to 8 as seen in Figure 2-2.

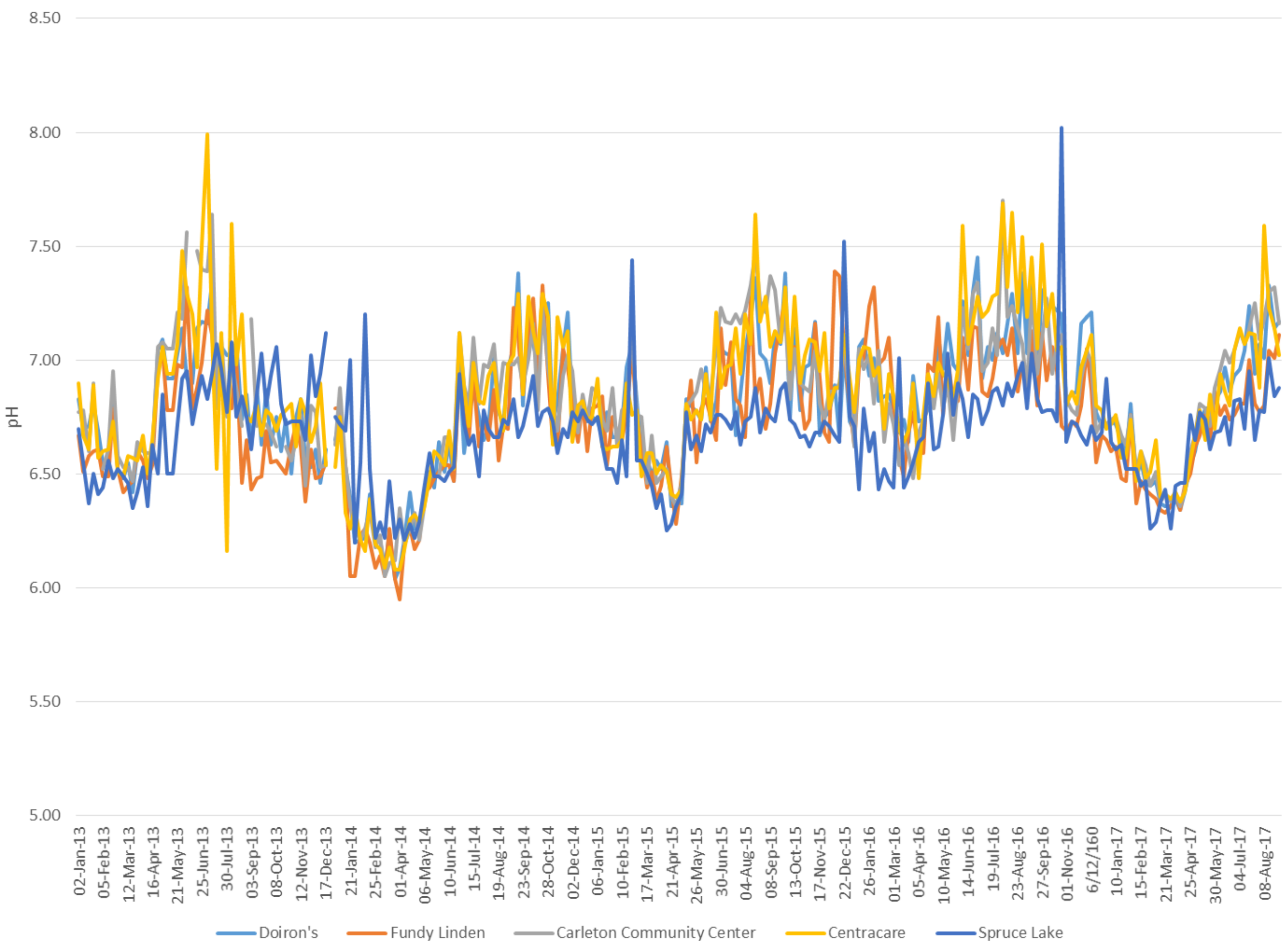


Figure 2-1: **West Saint John Distribution System pH 2013-2017**

It should be noted that the pH values shown in both figures represents pH of flushed samples (water samples collected after letting the water run at a tap for a period of time) rather than stagnation sampling as this was an industry standard practice at the time. Stagnate water in the premise plumbing likely would have a lower pH than the samples collected through flush sampling due to water age and reactions occurring with by-products within the piping system.

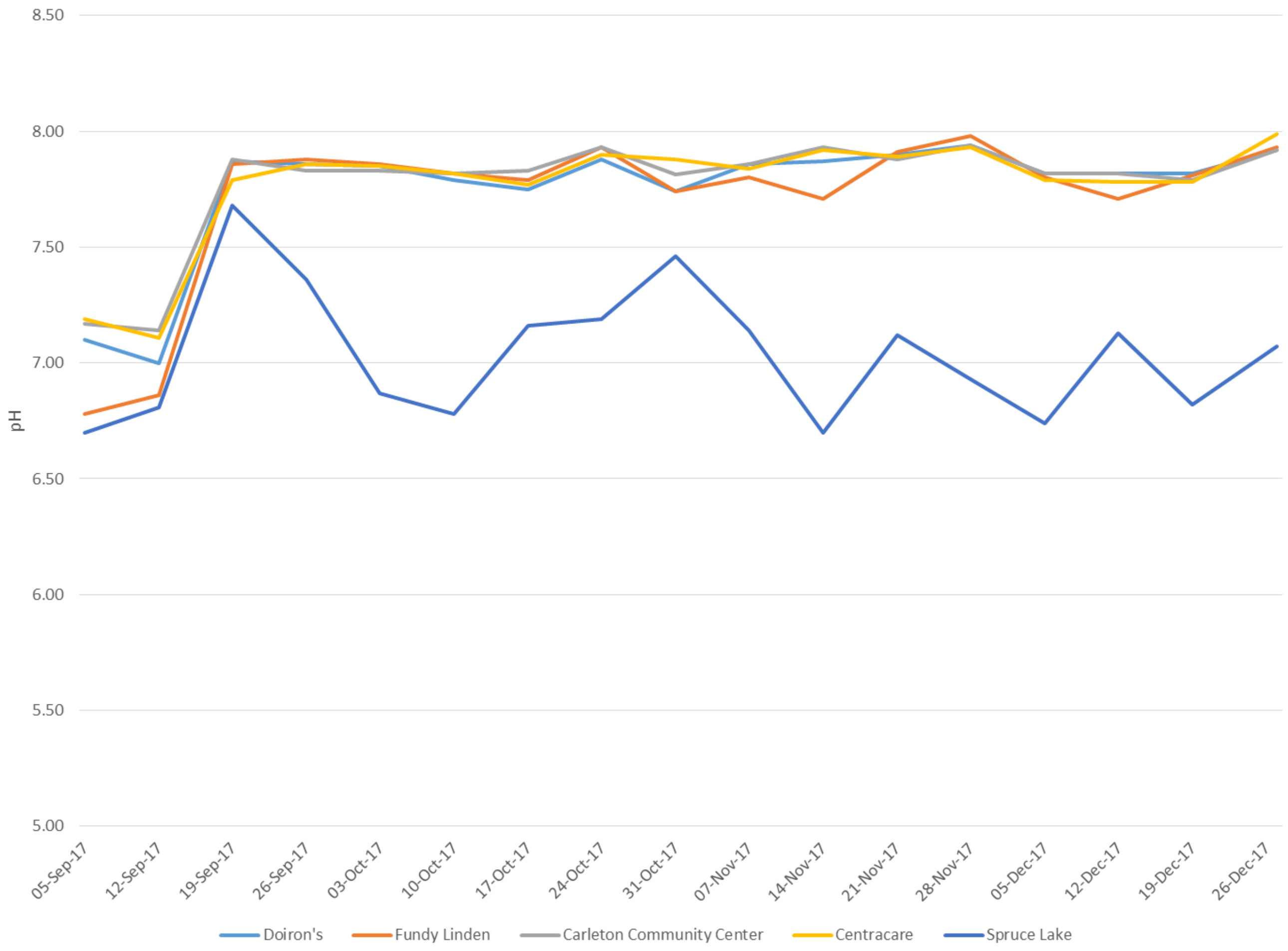


Figure 2-2: **West Saint John Distribution System pH Sept.-Dec. 2017 (after switch to South Bay Wellfield)**

2.1.1 Alkalinity, pH and Dissolved Inorganic Carbon Changes

Changes in alkalinity, pH and dissolved inorganic carbon can play a significant role in either limiting or promoting corrosion. Alkalinity refers to the amount of carbonate, bicarbonate and hydroxide in the water and it provides a measure of its ability to resist changes in pH. In low alkalinity water, chemical additions or reactions in the distribution system can cause rapid changes in pH. This can cause challenges in the treatment process and may be problematic for controlling corrosion in the distribution system and premise plumbing. With the change to the South Bay Wellfield, the source water now has moderate to high alkalinity which provides additional buffering capacity to the system compared to the low alkalinity of Spruce Lake.

Low pH in surface waters can be naturally occurring, or due to increased dissolved carbon dioxide in the water and lack of alkalinity. Low pH increases corrosion of most pipes as it increases metal solubility, which results in deterioration of pipes and higher concentrations of metals, such as iron, lead and copper, in the drinking water. As previously mentioned, the source water switch to the South Bay wells resulted in a pH increase to approximately 7.9, which is considered less corrosive than Spruce Lake water.

Dissolved inorganic carbon (DIC) is the sum of all the inorganic carbon species including carbon dioxide, carbonate and bicarbonate in water. DIC is related to alkalinity as carbonate and bicarbonate also contribute to alkalinity. It can be used to determine the availability of carbonate species to react with copper or lead to form passivating scales, which can provide a protective layer on the pipe and limit further corrosion from occurring. Historically, the DIC in Spruce Lake was approximately 10 mg/L, a low value. The South Bay wells have a DIC concentration of 30 mg/L, which is considered a moderate value. The moderate DIC concentrations of the South Bay wells can be a benefit for reducing copper corrosion as it can help buffer pH changes within the system and form passivating scales. Studies have shown that there is a strong relationship between pH, DIC and copper release levels, with copper release increasing with decreasing pH and increasing DIC. At higher pH levels (>9), moderate to high concentrations of DIC can result in calcium carbonate precipitation to occur, which can result in additional operational issues.

Based on the historical water quality of Spruce Lake, it would be expected that corrosion of varying degrees had occurred throughout premise plumbing systems of different ages. The corrosion that occurred may have also resulted in scaling that formed a relatively stable layer on the plumbing systems, also preventing rapid pipe failure from occurring. Deposition of other source water metals such as iron, occurred within the system, which may have provided an additional stability for underlying pitting/corrosion. As the system had operated in this state for many years, it is likely that the corrosion occurring was not perceived by customers as the conditions had become ‘status quo’ and that there was limited visible pipe failure due to the corrosion occurring. Anecdotal details of blue-green scaling typical of copper corrosion have been reported in the area, which would be expected based on the Spruce Lake water quality.

By available industry practice and technical guidance for assessing corrosion risk, the ground water supply from the South Bay Wellfield is less corrosive than Spruce Lake water. However, several months after the switch from Spruce Lake to ground water, reports of domestic copper piping leaks were received by the City, which led the City to undertake additional investigations.

2.2 Switching Source Waters

In Atlantic Canada, many municipal water utilities have undergone water quality changes in recent years as the result of source water changes or treatment upgrades. Where it has occurred, it has typically been a utility switching from a limited treatment surface water supply (disinfection only – similar to historical Spruce Lake treatment) to a treated surface water supply or between two ground water supplies, and was completed to increase production or to improve water quality. Examples of municipalities in Atlantic Canada that switched water supplies similar to West Saint John over the last 20 years include Sydney, NS (chlorinated surface water to ground water), Bridgetown, NS (chlorinated surface water to ground water) and Annapolis Royal, NS (chlorinated surface water to ground water). With the switch to ground water, these utilities did not experience reports of major copper pipe leaks within premise plumbing systems as experienced in West Saint John. There was an experience of buried copper corrosion issues in Sydney, which was tied to the manganese treatment technology being used with the new supply (manganese treatment is not part of the South Bay system). Table 2-2 shows additional examples of communities that have significantly changed water quality within a given distribution system over a similar time period. These examples are primarily switches between treatment of the same surface source water whereby the water distribution systems did not experience the same change in parameters such as pH or alkalinity as occurred in West Saint John. There are many additional examples of the source changes listed in Table 2-2 from across the region where chlorinated surface water was switched to filtered surface water.

Table 2-2: Example Water Supply and Treatment Changes across Atlantic Canada

Location	Previous Water Source	Current Water Source	Corrosion Inhibitor Used
Sydney, NS	CLSW	GW	No
Bridgetown, NS	CLSW	GW	No
Annapolis Royal, NS	CLSW	GW	No
Dartmouth, NS	CLSW	SW	Yes
Yarmouth, NS	CLSW	SW	Yes
Lunenburg, NS	CLSW	SW	Yes
North Sydney, NS	CLSW	SW	Yes
Moncton, NB	CLSW	SW	Yes
Antigonish, NS	CLSW	SW	Yes
Glace Bay, NS	CLSW	SW	Yes
St. John's (3 locations), NL	CLSW	SW	No
New Glasgow, NS	CLSW	SW	Yes

CLSW – Untreated surface water (disinfection only)

SW – Treated surface water supply (coagulation/filtration)

GW – Ground water supply with disinfection (may have additional treatment)

Looking more broadly, there are more examples of utilities changing distribution system water qualities, either by introducing a new supply source or changing the treatment processes, such as disinfection. As in Atlantic Canada, the majority of these cases are between the same types of source waters. While most of the changes in water quality do not negatively affect the distribution system, there are several well-known examples where utilities experienced corrosion related issues after changing water quality. It should be noted that these events were not related to the ground water supply and the corrosion was connected to iron piping within the distribution system and not copper premise plumbing.

Irregular changes in water quality (unlike those which may occur seasonally or are regularly experienced by the system), due to operational issues such as variation in flow, pressure or water quality, are often referred to as a transient condition or event. These events may vary in length from minutes to months (Liu et al., 2017; WHO, 2014), and can cause disruption of pre-existing biofilms and/or scaling, resulting in the release of harboured contaminants or decreased disinfection residuals within the distribution system.

While the drinking water industry is well known for having procedures which have become industry best practices, there are limited documents available outlining procedures for switching a water source or water quality within a distribution system. Some technical documents are available for utilities who practice blending of multiple water sources (Fleet et al., 2001; Taylor et al., 2006; Dewis et al., 2010), but limited information is available for utilities permanently switching a water source. Even less information is available for systems switching from surface water to ground water.

From a water quality standpoint, the source water switch from Spruce Lake to the South Bay Wellfield is considered low risk as the water quality was changing from a corrosive water to one that was less corrosive. Significant sampling was completed both at the wells and in the distribution system prior to the switch, however with regards to corrosion within the distribution system, the study was not as intensive as that for a system deemed a higher risk.

As part of the Safe, Clean, Drinking Water Project, the City of Saint John completed an evaluation of the distribution system with a focus on the public infrastructure, including an assessment of existing pipe corrosion scales prior to the switch in water quality. However, the investigation did not focus on the effect of the water quality switch on premise plumbing. This is reflective of the water industry's research and regulatory focus, where efforts to understand effects on public infrastructure and not private infrastructure have dominated. Utilities have traditionally been responsible for providing safe drinking water to the property line of the customer and was not responsible for what occurred in the premise plumbing. Only recently has the focus for monitoring distribution systems begun to evolve to incorporate the complete network analysis, including private, premise piping. This is reflected in emerging practice guidance from both the EPA and Health Canada on corrosion control. As the research progresses, guidance and regulatory documents will be developed, but there currently is a lag in these documents becoming available compared to those available for public infrastructure.

As the responsibility of the utilities shifts to include premise plumbing, changes to regulatory practices such as sampling have been developed over the past 5 years. Sampling previously included flushing for 2-5 minutes prior to taking a sample, so that the sample represented water from the distribution system, rather than water that was within the premise plumbing, as this was what utilities were interested in. Within the last several years, sampling procedures have been updated to include stagnate sampling which represents water that first comes out of the tap for a user and can often have higher concentrations of contaminants such as lead, copper and microbial activity compared to a flushed sample. However, as this is a big shift in responsibility, the requirements are not fully enacted in Canada by the regulatory bodies and is not fully practiced by utilities. As these sampling protocols have evolved since the initial study for switching the West Saint John water source was completed, the current, updated premise plumbing sampling procedures were not implemented in the surface to ground water study in 2013-2014.

In the period during the transition from surface to ground water, the City performed extensive system flushing to limit water quality impacts. Since the switch occurred, the City has implemented a heightened monitoring program, including an increase in distribution system sampling and stagnation sampling. When reports of copper leaks occurred, the City looked to develop a prevention strategy to mitigate the transition event that was occurring. The City implemented a temporary orthophosphate system as a corrosion control method and continues to monitor the distribution system and premise plumbing for further copper pipe leaks.

2.3 Use of Orthophosphates for Corrosion Control

The addition of a corrosion inhibitor is a common technique used for corrosion control in Atlantic Canadian surface water-supplied municipal water utilities. Orthophosphates or orthophosphate blends are commonly used and work by forming a thin metal-phosphate film over the pipe surface which inhibits the anionic reaction of corrosion from occurring. The majority of municipalities in Atlantic Canada serviced by treated surface water sources add orthophosphate for corrosion control. Systems with untreated surface water similar to the Spruce Lake system do not add orthophosphates. There are no known municipalities with a ground water source using orthophosphates in the region, which is a reflection of the lower corrosion potential of ground water sources. Table 2-3 shows typical raw water quality results for three communities that currently use orthophosphates along with the water quality from the South Bay Wellfield. It is the significant differences in parameters such as pH and alkalinity (i.e. mineral balance) that require the surface water source systems to need orthophosphate for corrosion control.

Table 2-3: Raw Water Quality of Example Communities using Orthophosphate in Atlantic Canada

Parameter	Units	MAC/AO	South Bay Well #1	South Bay Well #2	Halifax (Pockwock)	Moncton	Windsor
			2013-2014 (Average)	2014	2016 (Average)	2012-2015 (Average)	2016 (Average)
Alkalinity	mg/L as CaCO3		98	106	<1.0	11.3	<5
pH		6.5-8.5	8.01	8.02	6.1	7.03	6.5
Turbidity	NTU	1	0.5	0.7	0.32	2.96	1
TOC	mg/L		1	1.9	2.9	4.18	4.3
Colour True	Pt-Co	15	7.8	<5	14.5	32	16
Conductivity	uS/cm		443	444	32	47	22
Chloride	mg/L	<250	41	38	7.2	2.73	3
Calcium	mg/L		55	65	1.1	3.93	0.9
Magnesium	mg/L		8.9	7.4	0.38	0.7	0.3
Hardness	mg/L as CaCO3		174	194	4.4	12.7	10
Manganese	mg/L	<0.05	0.053	0.022	0.028	0.12	0.063
Iron	mg/L	<0.3	0.084	0.10	<0.051	0.26	0.25
Aluminium	mg/L	<0.1	0.023	0.029	0.104	0.096	0.091
Copper	mg/L	1	0.066	0.003	0.033	<0.002	0.005
Lead	mg/L	0.01	<0.0005	0.0031	<0.0005	0.00024	<0.0005

Ground water sources for municipal water utilities are common throughout Canada, with the size varying from small systems servicing less than 10 people to large cities. While the water quality for ground water sources varies, in general they can be characterized as “harder” water sources with stable water quality. On average, ground water sources tend to be less corrosive than surface water sources, having higher alkalinity and pH. Often, ground water sources only require disinfection treatment to meet drinking water guidelines and do not require corrosion control treatment. For sources that do require treatment for corrosion control, pH or alkalinity adjustments are typically used rather than the use of a corrosion inhibitor. Table 2-4 shows water quality results for two Canadian cities that use ground water sources and do not use a corrosion control treatment process, along with water quality from the South Bay Wellfield. The City of Guelph disinfects water with a combination of chlorine and UV disinfection, while the City of Charlottetown uses chlorine for disinfection and also adds fluoride. Based on this comparison, the South Bay source is unique in the application of corrosion control treatment versus other similar sources. However, as experienced in West Saint John, there are multiple factors that can contribute to the need for corrosion control treatment, including pre-existing corrosion and corrosion scaling in mature distribution systems.

Table 2-4: Sample Municipal Ground Water Quality – Saint John, Guelph, Charlottetown

Parameter	Units	MAC/AO	South Bay Well #1	South Bay Well #2	Guelph	Charlottetown
			2013-2014 (Average)	2014	2016 (Average)	2017
Alkalinity	mg/L as CaCO3		98	106	291	140
pH		6.5-8.5	8.01	8.02	7.92	8.04
Turbidity	NTU	1	0.5	0.7	0.03-0.37	
TOC	mg/L		1	1.9	1.32 (DOC)	
Colour True	Pt-Co	15	7.8	<5		
Conductivity	uS/cm		443	444		
Chloride	mg/L	<250	41	38	150	13.6
Calcium	mg/L		55	65	118	35
Magnesium	mg/L		8.9	7.4	36	18.3
Hardness	mg/L as CaCO3		174	194	441	163
Manganese	mg/L	<0.05	0.053	0.022	0.0143	<0.003
Iron	mg/L	<0.3	0.084	0.10	0.31	<0.009
Aluminium	mg/L	<0.1	0.023	0.029	<0.005	
Copper	mg/L	1	0.066	0.003	0.0025	0.048
Lead	mg/L	0.01	<0.0005	0.0031	0.00099	<0.002

A review of municipal water treatment systems with ground water sources (either sole ground water supplies or blended with surface water) was completed for water systems that use a corrosion inhibitor in Alberta, Ontario, Quebec, New Brunswick, Nova Scotia and PEI. Of the systems reviewed, several smaller systems were found to use a polyphosphate blend, but this was for sequestering iron and/or manganese from the ground water rather than for corrosion control. Of available information, only one system located in Ontario (Asphodel-Norwood) was found to report use of an orthophosphate blend for corrosion control.

A variety of additional ground water treatment processes were identified during the review, and use of these processes was dependent on the raw ground water quality. Treatment for iron and manganese removal was common, and included sodium silicate addition, greensand filtration, and oxidation. Systems with parameters of concern, such as uranium or arsenic, had specific treatment processes for removal. Softening processes were also identified, but the implementation of the processes was site specific and appeared limited to smaller systems. The most common softening processes were lime softening and ion exchange. Examples of systems with high hardness similar to West Saint John were also found that do not use any softening processes. Several of these examples are outlined in Table 2-5.

Table 2-5: Sample Ground Water Systems without Softening Treatment

Location	Hardness	Treatment Processes
Pictou, NS	100 mg/L	Pre-filtration Greensand filtration UV/chlorine disinfection
West Saint John	150-250 mg/L	Chlorination
Rimouski, QC	200 mg/L	Chlorination
Guelph, ON	290 mg/L	Chlorine/UV disinfection
Kitchener, ON	290-550 mg/L	Several ground water systems* Chloramine/UV disinfection *one system has pressure filtration, advanced oxidation and granular activated carbon filtration
Waterloo, ON	290-650 mg/L	Several ground water systems UV/chlorine disinfection

CHAPTER 3 DALHOUSIE REPORT – CBCL REVIEW

3.1 Dalhousie Report

As part of the laboratory testing, Dalhousie prepared reports of the findings (Appendices A & B). The reports outline the methods used for testing, along with the results found during the scale analysis and the stagnation study. CBCL has provided an analysis of the reports in the following sections.

3.2 Bench-scale Testing

3.2.1 Scale Analysis

The first part of the study completed by Dalhousie (Appendix A) involved an analysis of scale on six copper pipes samples collected from West Saint John. Some scale samples were extracted from the pipes, while scales that could not be removed were examined in-situ. The scale samples were analysed using X-ray diffraction (XRD) and compared to known XRD patterns to identify the makeup of the scale.

While the formation of copper corrosion scaling will vary between systems, typical scale structure based on cupric hydroxide models found in literature would consist of relatively soluble copper (II) transitioning over time to thermodynamically favoured and relatively insoluble malachite or tenorite. The formation of a low soluble malachite layer on the pipe can then provide a protective layer for the copper surface. The samples analysed from West Saint John were found to be largely amorphous, meaning the scales lacked well-defined crystalline structures that the available copper solubility models are based on. Cuprite, which can often form underneath malachite layers typical of copper scales was present indicating that a subsurface malachite layer may have been present but was not well defined. It is unclear how the scale structure impacts the pipe integrity as the research found in literature is often focused on the health based effects of corrosion (copper release into the treated water) rather than the integrity of the pipe.

Amorphous scale structures can form when additional constituents are present in the water and react with the soluble copper compounds in the distribution system. Surface water plants in Atlantic Canada typically employ a multi-barrier approach for treatment, including filtration to remove constituents such natural organic matter (NOM) and suspended or dissolved solids. The previous Spruce Lake process did not include filtration, which allowed constituents such as NOM, which is present in the surface water, to pass through the treatment plant and enter the distribution system. The natural organic matter along with low pH may have affected the cuprous hydroxide corrosion scaling that formed so that it did not form a stable crystalline structure. Other elements, including iron, aluminum and potassium were found in the scales sampled and could have also contributed to the complexity of the scaling.

Due to the amorphous nature of the scaling found in West Saint John, the application of copper solubility models and literature has proven to be limited. As several parameters changed with the new water quality (pH, alkalinity, DIC and NOM concentrations) it further increases the difficulty of applying the models to the West Saint John case and determining the mechanism for corrosion and the reported pipe leaks.

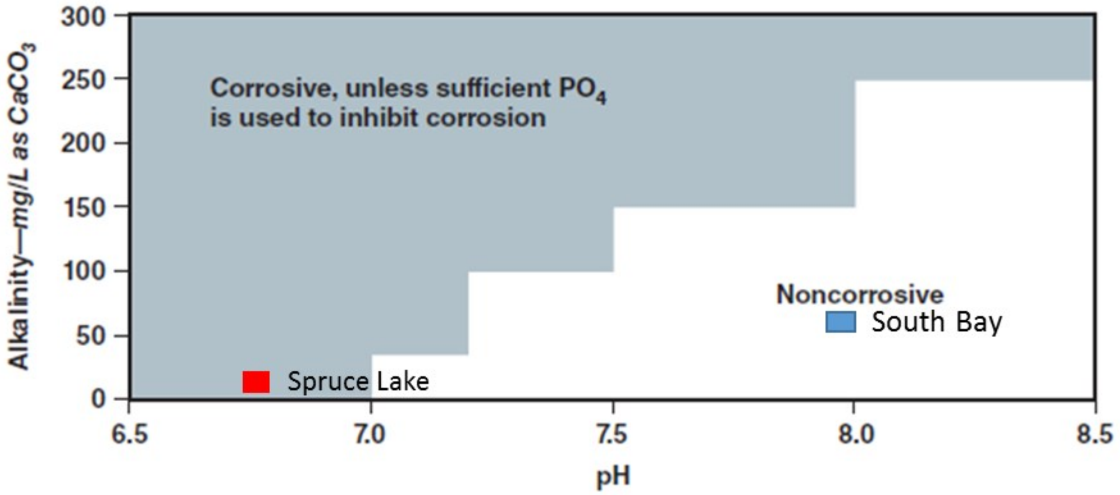
3.2.2 Stagnation Study

A two phase stagnation experiment to investigate the effects of the source water changes was also completed at bench scale (Appendix A). For the first phase, sections of copper pipe recovered from East and West Saint John, along with sections of new copper pipe, were used. As the distribution system in West Saint John had been exposed to the new ground water source prior to testing, copper pipe samples from East Saint John were used to represent West Saint John pipe exposed to surface water only. The first stagnation trial involved comparing ground water conditioned to pH 8 or 9, and with or without chlorine and orthophosphate addition. Water was held in the pipes for 24 hours and then the water was changed. Recovered pipe samples were conditioned 44 times and new pipe samples were conditioned 9 times prior to the copper samples being collected. This was based on the time constraints of the project and the time required to acclimate the pipe samples.

The results of the first phase of the stagnation study showed that the addition of orthophosphate to ground water reduced copper release for all pipe types tested. This was expected, as orthophosphate has been shown to disrupt the typical cupric hydroxide precipitates that typically form and reduce the solubility of copper and is commonly used by utilities as a corrosion inhibitor. Of the three pipe types, the new pipe released substantially less copper compared to the recovered East and West Saint John pipes. This is likely due to the pre-existing corrosion scaling on East and West Saint John pipes, which would be more soluble and release more copper to the water than the virgin pipe.

The other factors (pH and free chlorine dose) were not considered significant in this factorial study, at the levels tested. The pH levels tested were 8 and 9, which would represent typical ground water and ground water that was pH adjusted. A greater difference in the pH (i.e., including a trial with a pH of 6 or a pH greater than 9) may have resulted in a significant difference in copper release, but would not be representative of the ground water quality from the South Bay Wellfield. As mentioned in the Dalhousie report, from an operational standpoint pH adjusting to a pH greater than 9 can help to limit copper release, but would not be practical as it could result in calcium carbonate precipitation due to the moderate levels of dissolved inorganic carbon present in the ground water. While there are cases when a calcium carbonate scale can be beneficial, it often causes operational and maintenance issues along with complaints from customers and is often avoided if possible.

It should be noted, as previously stated in Chapter 2, the use of orthophosphates for corrosion control for a ground water source is not typical for municipal utilities. Ground water sources are typically selected to have water quality not requiring corrosion control, or will use other methods such as pH adjustment for corrosion control. As this is a unique situation where a change in the type of source water and water quality occurred on a mature distribution system, the limited literature available for orthophosphate use in ground water sources and industry norms, at least for a short term, may not be directly applicable to the West Saint John case. Figure 3-1 provides guidance as to when orthophosphate addition is required. Additional testing would be required to determine the long term need for orthophosphate addition.



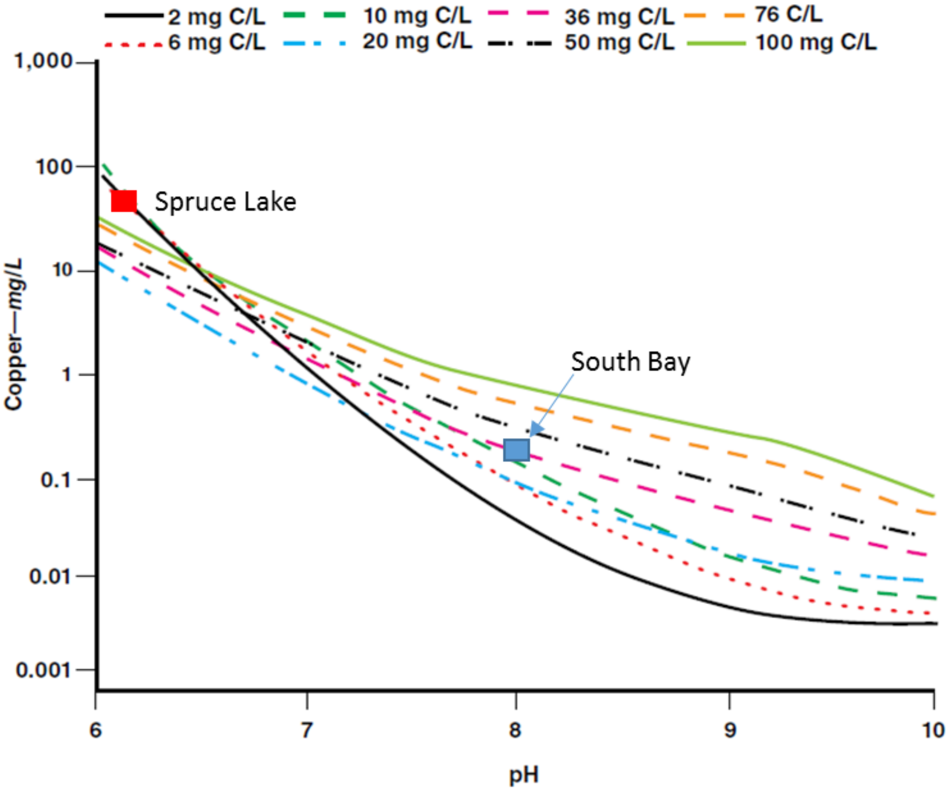
$CaCO_3$—calcium carbonate, LCRWG—Lead and Copper Rule Working Group of the National Drinking Water Advisory Committee, PO_4—orthophosphate

Figure 3-1: Conditions that are Corrosive to Copper as Defined by the Lead and Copper Rule Working Group of the National Drinking Water Advisory Committee (Roth et al, 2016)

The second phase of the stagnation study compared copper release between unaltered surface and ground water. A similar procedure as used in the first stagnation phase was used to condition new copper, East Saint John and West Saint John pipe, with surface water and ground water. The surface water (Spruce Lake) had a pH of 6.8, while the pH of the ground water (South Bay Wellfield) was 8. For this phase, chlorine and orthophosphate was not added.

With the different pipe samples (east, west and new pipe), there are two ways that copper can be released to the water. For all three samples, the copper pipe could be exposed to water which allows the copper pipe to be soluble and release copper from the pipe into the water. In this study, the surface and ground water were used to determine if one water quality allowed for more copper solubility. The second way copper could be introduced to the water is through scale release. This would be applicable to the east and west samples which had pre-existing scaling. In this pathway, the pre-existing scale is released to the water, and not copper from the intact pipe. Further investigation would be required to be able to identify which occurred in Saint John and was outside the scope of the bench scale testing.

While the presence of parameters such as NOM or pre-existing copper scaling are not accounted for in current copper solubility models, an attempt was made to apply the models as a comparison to the results achieved through the bench scale testing. Figure 3-2 shows the model of the effect of DIC and pH on soluble copper. Using a pH of 6.2 and DIC concentration of 10 mg/L for surface water to represent historical water quality within the distribution system, the expected soluble copper release would be around 70 mg/L. For the ground water with a pH of 8 and DIC concentration of 30 mg/L, the copper release predicted would be around 0.3 mg/L.



Cu(II)—copper in the +2 oxidation states, DIC—dissolved inorganic carbon

Figure 3-2: Soluble Copper as a Function of pH and Inorganic Carbon (from Brown et al, 2013)

The results of the stagnation study did not match the model predictions for copper release, as it was predicted the pipes conditioned with surface water would release more copper. From the data collected, copper release to the ground water was greater than the copper release to the surface water. As the ground water is considered to be less aggressive towards corrosion, it was expected that the copper release would be similar to the results of the copper solubility models.

It should be noted that the difference in copper release between source waters was found using the recovered East and West Saint John pipe; the difference between copper release for surface and ground water was not found to be statistically significant for the new copper pipes tested. This leads to the assumption that the contact between the water and pre-existing copper scaling is an important factor for copper release. Further investigation would be required to identify the particular mechanisms for the copper release, including if the type of scale present is significant for copper release.

Soluble copper concentrations generally increase with water quality having decreasing pH and increasing DIC concentrations. In the West Saint John case, the two water sources had competing water qualities; the surface water had a lower pH and the ground water had moderate DIC levels. It is expected that the overall water quality of the ground water is less corrosive than the surface water. In this instance, it is possible that the DIC concentration of the ground water had a larger impact on copper release than the benefit of having a higher pH and higher alkalinity. Additional testing would be required to determine if the DIC concentration was statistically significant in the copper release for this scenario as this would vary from what is typically seen in literature and what was expected for West Saint John.

3.2.3 Additional Testing

Due to the fact that the source water has already switched from surface water to ground water, it is difficult or impossible to locate sections of West Saint John copper pipe that have only been conditioned with Spruce Lake sourced water. As the new water treatment plant in East Saint John has also been brought online, it is likely that there are no sources of East Saint John pipe that have not been exposed to water from the new plant that could be used as surrogate pipe for West Saint John. This limits further bench scale corrosion investigations which can be completed using pipe samples reflective of historical norms. As there are not many facilities in Atlantic Canada which have the same treatment train as the Spruce Lake treatment plant (disinfection only), it further limits the availability of surrogate pipes that could be used for testing. Some small communities in Newfoundland have water systems where surface water treated only with disinfection is distributed to the community.

The pH level tested for the surface water was representative of the surface water at the time of the source water switch, but was higher than what was historically experienced by West Saint John. To understand the effect of this difference, supplemental testing was completed by Dalhousie (Appendix B) to compare copper release between pipes conditioned with surface water at pH values of 5.5 and 6.8. As shown in Figure 2 of the Dalhousie report (Appendix B), it was found that for aged pipe the copper release was highly variable at either pH level and that no clear difference in results was observed. For new pipe however, the copper release was consistently higher at the lower pH, illustrating the expected trend and results that would be typical from historical water quality.

Unaltered surface water and ground water were used in the stagnation experiments. This was done to limit the amount of variables. The presence of oxidants, such as chlorine, can accelerate corrosion and dissolution of copper. With the change in the source water to ground water, the chlorine dose required for disinfection decreased compared to what was used to treat the Spruce Lake water. While chlorine addition was considered in the first stagnation phase, it was not considered in the second phase which compared surface water and ground water. The addition of chlorine to the source waters and the difference in chlorine doses required could be considered in future experiments.

While it may be difficult to complete additional testing representative of the distribution conditions at the time of the copper pipe leaks event, it is possible to monitor current and future operating conditions. As a result of the corrosion event that occurred, the City developed a monitoring program for the distribution system and it continues to evolve as the City gains more information. The City is incorporating pipe racks in several locations within the distribution system, which contain sections of copper pipe and can be representative of copper premise plumbing within the system. The pipe racks will allow the city to monitor the effects of orthophosphate addition on premise plumbing.

CHAPTER 4 SUMMARY

4.1 Discussion of Results

A review of available literature and industry best practices was completed to compare the events that occurred in West Saint John to other water treatment systems within Atlantic Canada. The findings of the literature review are as follows:

- Historically, the Spruce Lake water had low alkalinity, low pH and moderate organics and was considered corrosive to distribution system piping. The South Bay Wellfield has a higher pH, moderate alkalinity and is considered a non-aggressive hard water.
- In Atlantic Canada, it is not common to switch from an untreated surface water to a ground water system as was completed in West Saint John. The communities that did switch from untreated surface water to ground water did not report having the same experience as West Saint John.
- Limited literature, research and guidance documents are available for utilities permanently switching from a surface water supply to ground water.
- South Bay Wellfield water quality is similar to other municipal ground water systems that do not use orthophosphates/corrosion control.
- Based on the water quality of the South Bay Wellfield and available information, the corrosion event that occurred was not expected.
- It is likely that the reported copper pipe leaks were the result the existing corrosion undergoing transitional effects as the water quality changed within the system.

Bench scale testing was completed by Dalhousie University to analyze existing corrosion scales on pipe samples collected from Saint John and to investigate mitigation strategies for copper corrosion. The bench scale testing was completed in two stages and the found:

- The corrosion scale analysed from West Saint John was found to be largely amorphous and indicated that copper corrosion had occurred over many years within the system.
- The applicability of available literature and copper solubility models for West Saint John is limited due to the pre-existing corrosion within the system.
- Addition of orthophosphate reduced copper release for all pipe types tested.
- When compared, the copper release from pipe conditioned with unaltered surface water was less than the copper release from pipes conditioned with ground water. This did not match predications based on literature.
- Further testing would be required to identify the specific mechanisms for the reported copper pipe leaks.

With the literature currently available, further testing would be needed to identify and fully understand the mechanisms which caused the reported copper pipe leaks. This study would likely take continuing investigation over several years to complete. As sourcing West Saint John pipe that has not been exposed to the new ground water source may not be possible, additional testing will be within the constraints of materials now available. However, additional testing could be completed to investigate current and future operating conditions at bench and pilot scale.

The study showed that the addition of orthophosphate was beneficial for reducing copper release from both mature and new pipe from West Saint John. However, the testing did not investigate whether permanent orthophosphate addition is required for West Saint John. It is recommended that orthophosphate addition continue until additional testing is completed and sufficient evidence is available which can prove a reduction in orthophosphate would not introduce more corrosion issues or leaks. Testing could include a pipe rack study and additional bench scale testing.

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APPENDIX A

Dalhousie Report – September 2018

Final Report

Understanding copper pipe corrosion in West Saint John

September 14, 2018

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Table of Contents

1 Introduction 1
2 Methods 2
  2.1 Task 1: Scale analysis 2
  2.2 Task 2: Stagnation study 2
3 Results 3
  3.1 Task 1: Scale analysis 3
  3.2 Task 2: Stagnation study 6
4 Conclusion 10
5 Supplementary material 12
6 References 13

1 Introduction

West Saint John has recently experienced an apparent spike in copper pipe failure since switching from a surface water source to a groundwater source. We explored three water quality factors that may influence copper release to the groundwater currently distributed in West Saint John: orthophosphate concentration, pH, and free chlorine concentration.

These factors influence observed copper concentrations in various ways: orthophosphate may reduce copper release by promoting formation of relatively insoluble copper-phosphates, such as $Cu_3(PO_4)_2$, over the more soluble cupric hydroxide ($Cu(OH)_2$) (Edwards *et al*., 2002; Schock & Sandvig, 2009). However, crystalline copper-phosphate minerals have not been identified in drinking water systems to our knowledge, and the mechanism of cuprosolvency reduction by orthophosphate remains poorly understood (Lytle *et al*., 2018). Nevertheless, orthophosphate is often applied to drinking water—including high alkalinity groundwater—as a means of cuprosolvency control (Schock & Fox, 2001). In general, cuprosolvency declines with increasing pH in the range relevant to drinking water distribution (Ferguson *et al.*, 1996). In addition, increasing pH beyond the range 7 – 8 diminishes the positive effect of carbonate and bicarbonate complexation on copper solubility (Edwards *et al*., 2002). That is, additional dissolved inorganic carbon (DIC) does not increase copper solubility as significantly above a pH of approximately 8 (Edwards *et al*., 2002). Free chlorine may also be an important determinant of observed copper levels: it has been correlated with copper release in previous studies and is thought to be the dominant oxidant responsible for copper corrosion under at least some conditions (Boulay & Edwards, 2001).

We also compared copper release to surface and groundwater sources. On the basis of pH alone, greater copper release to surface water (at pH 6.8) than to groundwater (at pH 8) would be expected. However, given that the groundwater had higher levels of dissolved inorganic carbon, we would also expect the pH effect to be counteracted to some degree by the greater propensity of the groundwater for carbonate complexation of soluble copper. Previous research has shown that at constant pH, soluble copper release increases linearly with increasing carbonate alkalinity in the relevant range of concentrations. A priori, it was not clear which effect would dominante, especially given the amorphous nature of the scale (see Section 3.1) and the limited applicability of quantitative solubility modelling to amorphous corrosion scales. Differences in concentration of natural organic matter between the surface and groundwaters may also be important in this comparison: at sufficiently high concentrations, natural organic matter tends to inhibit pitting corrosion of copper (Edwards & Ferguson, 1993; Korshin *et al*., 1996).

We investigated potential mechanisms for copper corrosion—as well as potential mitigation strategies—as follows:

Task 1. Analysis of West Saint John copper pipe corrosion scale

Task 2. A stagnation study using new and recovered copper pipe to investigate mitigation strategies and the role of source water in copper pipe corrosion.

2 Methods

2.1 Task 1: Scale analysis

We analyzed scale from six samples of copper pipe collected in West Saint John (**Figure 1**). We used X-ray diffraction (XRD) to identify crystalline phases present in corrosion scale and hot nitric acid-hydrogen peroxide digestion (EPA method 3050B) with inductively coupled plasma mass spectrometry (ICP-MS, *Standard Method 3125,* American Public Health Association, 2012) to determine elemental composition.

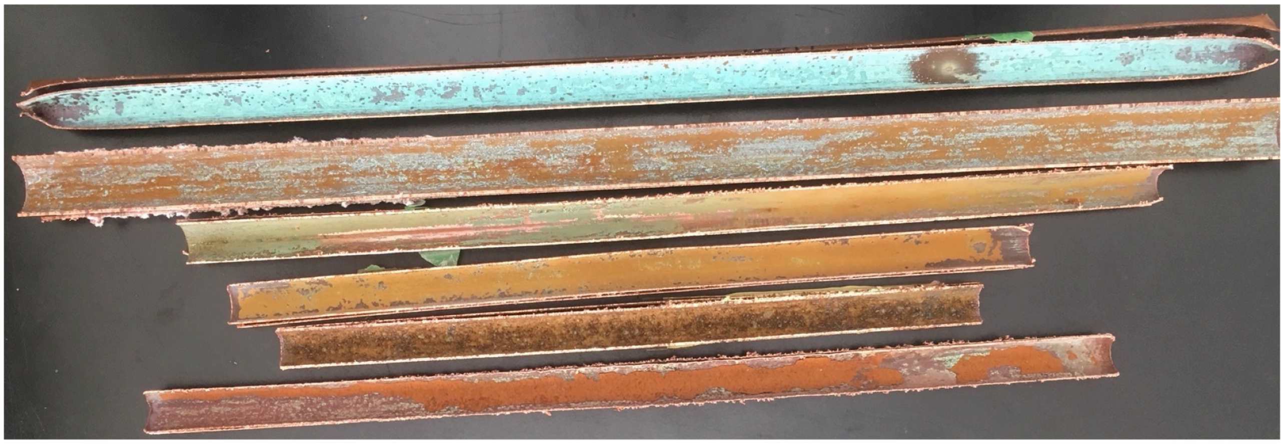

Figure 1. Sections of copper pipe cut longitudinally for scale analysis.

Crystalline phases were identified using an X-ray diffractometer (Siemens D500) with Cu Kα radiation (λ = 1.54 Å) at 35 kV and 30 mA. Scans were performed with a step size of 0.05˚ (2θ) and a count time of 5.0 s per step. Scale was extracted from pipe scale as it appeared in distinct layers that were differentiated by colour and distance from the pipe wall. Tightly adherent scale that was not separable from the copper substrate was analyzed by flattening sections of copper pipe for *in-situ* XRD analysis. Extracted scale samples were finely ground with a mortar and pestle prior to analysis.

2.2 Task 2: Stagnation study

We used sections of copper pipe recovered from East and West Saint John and sections of new copper pipe to assess the impact of water quality and source water changes. Sections were filled with water modified according to the experimental design (**Table 1**, supplementary material), sealed with rubber stoppers at either end, and held for 24 hours to achieve an approximate equilibrium. Prior to collecting samples for determination of copper release, we conditioned new and recovered pipes with 9 and 44 changes of water, respectively. Total copper was measured in pipe section effluent by ICP-MS (*Standard Method 3125*) after hot nitric acid digestion according to *Standard Method 3030* (American Public Health Association, 2012).

3 Results

3.1 Task 1: Scale analysis

Copper solubility is largely controlled by the mineralogical composition of corrosion scale (Lytle *et al.*, 2018). Here we sought to understand scale composition to inform our analysis of copper release to surface and groundwaters. A simplified representation of the proposed scale structure typical of the six copper pipe samples is provided in **Figure 2.**

Figure 2. A simplified representation of the proposed scale structure as characterized by X-ray diffraction.

Corrosion scale extracted from West Saint John copper pipes was largely X-ray amorphous at the water-scale interface (**Figure 3**, layers L0 and L1), as indicated by the low signal-to-noise ratio in the XRD patterns. This means that the scale lacked a long-range molecular order; since thermodynamic data are not typically available for amorphous copper phases, this limits the applicability of copper solubility models to the conditions prevalent in West Saint John. More generally, the tendency for copper to exist in amorphous phases represents a limitation of predictive cuprosolvency models (Lytle *et al.*, 2018). In West Saint John, the lack of crystallinity in the surface scale layer may have been due to the presence of natural organic matter in the surface water distributed historically. This would accord with previous work on the effect of natural organic matter on copper corrosion scale (Korshin *et al.*, 1996). Natural organic matter is also known to inhibit pitting corrosion of copper, except at very low concentrations (0.1 – 0.2 mg/L) where it may promote pit formation (Korshin *et al.*, 1996).

The predominant identifiable crystalline phase present in copper pipe scale was cuprite (Cu_2O, **Figures 3**, *ex situ* and **4**, *in situ*). Cuprite often forms a thin film below a surface layer of malachite ($Cu_2CO_3(OH)_2$) or possibly even cupric orthophosphate ($Cu_3(PO_4)_2$) (Schock and Sandvig, 2009). Several experimental patterns representing sub-surface scale layers were also consistent with the presence of malachite. Given its low solubility, the occurrence of malachite at the water-scale interface is desirable (Schock and Sandvig, 2009), but it is unclear whether sub-surface malachite influenced observed copper levels in Saint John West. Iron, potassium, calcium, aluminum, and sodium were also present in scale as major elements (**Figure 5**). They did not occur as distinct crystalline phases with well-defined chemical formulas and structures, illustrating the complexity of the West Saint John corrosion scale samples.

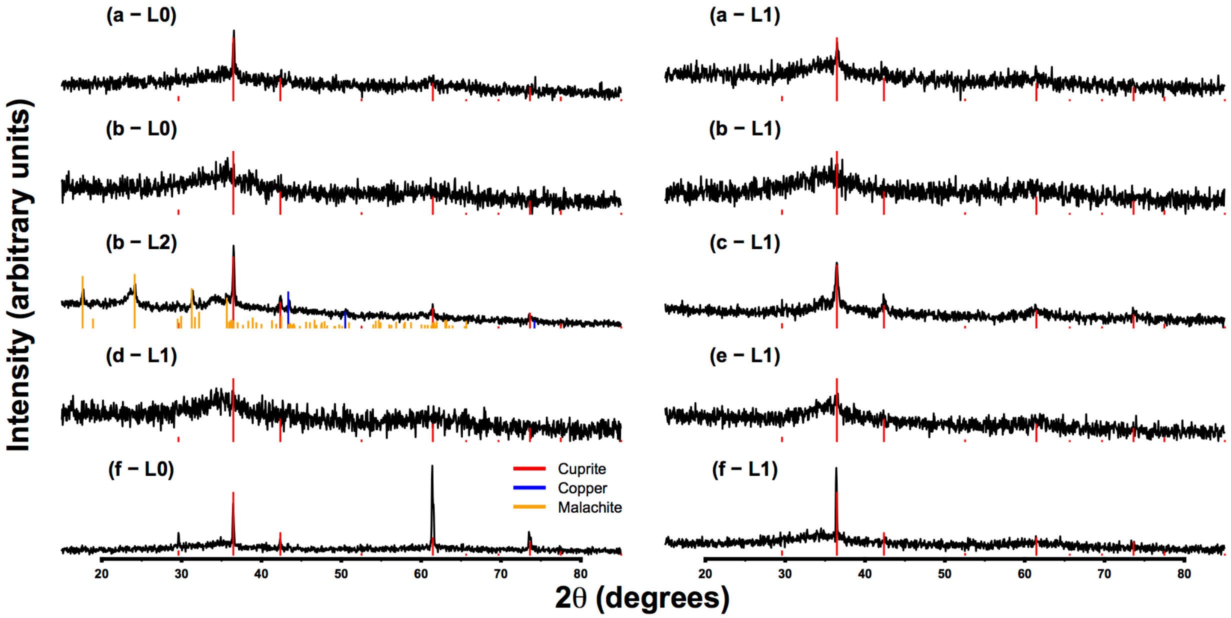

Figure 3. X-ray diffraction patterns for samples extracted from loosely-adherent corrosion scale present in six West Saint John copper pipe samples. Scale samples were largely amorphous (i.e., lacked a distinct structure at the molecular scale), or poorly-ordered cuprite (Cu_2O). (L0 = loosely adherent scale dislodged by inverting the pipe, L1 = top layer of scale, L2 = underlying scale layer, letters a – f denote individual sites/pipe samples.)

Prior to the initiation of orthophosphate corrosion control in West Saint John, phosphorus concentrations in scale ranged from 1,723 – 5,500 µg/g dry weight (0.17 – 0.55 %) with a median of 2,231 µg/g (0.23 %). Approximately two months after orthophosphate corrosion control was initiated, the phosphorus concentration in scale sampled at the water interface was 15,683 µg/g

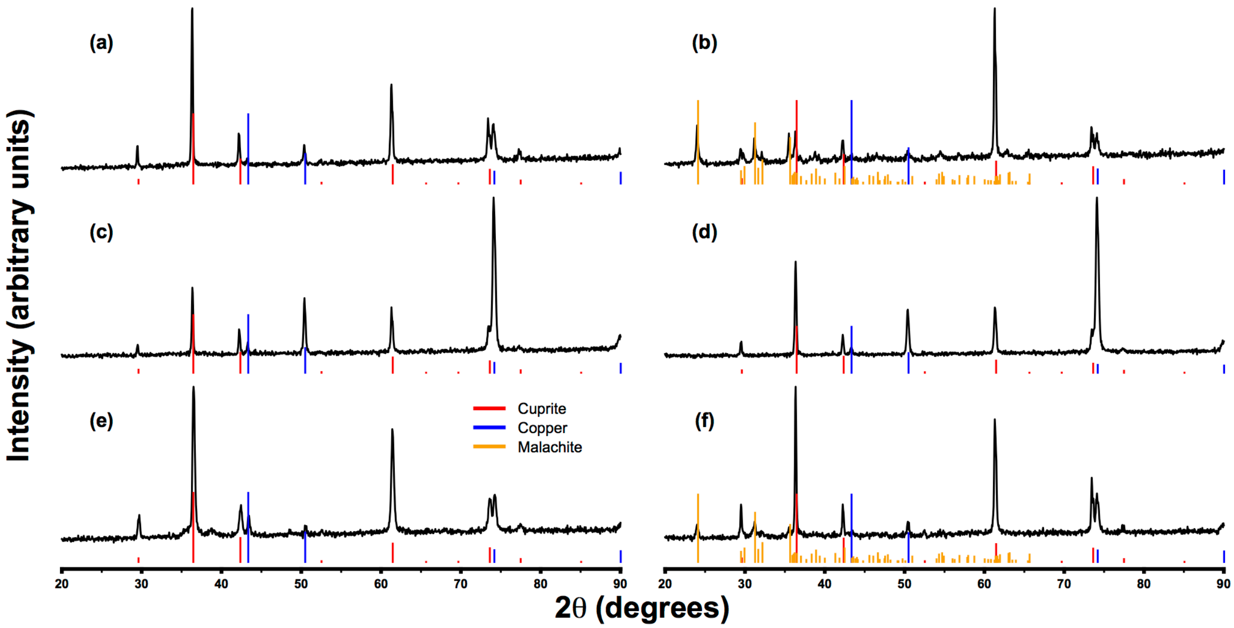

Figure 4. X-ray diffraction patterns for samples characterized in-situ as the tightly-adherent sub-surface corrosion scale present in six West Saint John copper pipe samples. Scale samples were largely composed of cuprite, Cu_2O, or malachite, $Cu_2CO_3(OH)_2$. (Letters a – f denote individual sites/pipe samples.)

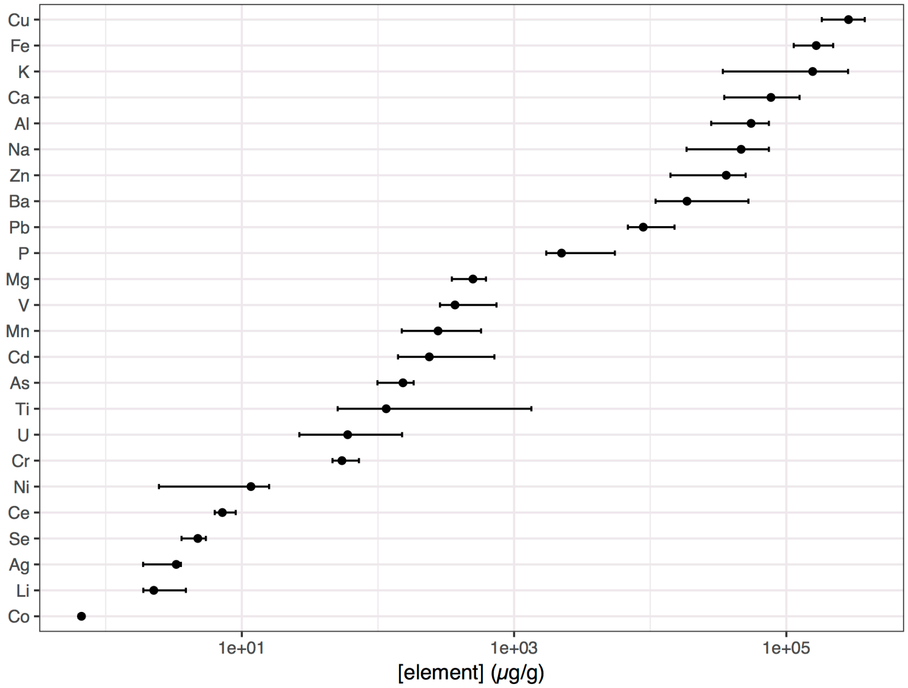

Figure 5. Elemental composition of corrosion scale collected from six West Saint John pipe sections. Points represent medians, and error bars span the interquartile range (25th to 75th percentile). Major elements included iron, potassium, calcium, aluminum, and sodium; these were not present as distinct crystalline phases with well-defined chemical formulas and structures.

(1.57 %) (a pure $Cu_3(PO_4)_2$ phase is approximately 16% phosphorus by mass). This represents an increase by factors ranging from 2.2 – 9.6 over phosphorus concentrations at the water interface sampled prior to the initiation of orthophosphate corrosion control. Although the observed increase in phosphorus is broadly consistent with formation of copper-phosphate corrosion products, no crystalline copper-phosphate phases were identified by XRD (**Figure 6**). This is not surprising: while orthophosphate can effectively reduce cuprosolvency, no crystalline copper-phosphate compounds have been identified in actual distribution system pipe samples (Lytle *et al*., 2018). Nevertheless, incorporation of phosphorus with corrosion scale in West Saint John suggests that orthophosphate treatment is acting as predicted.

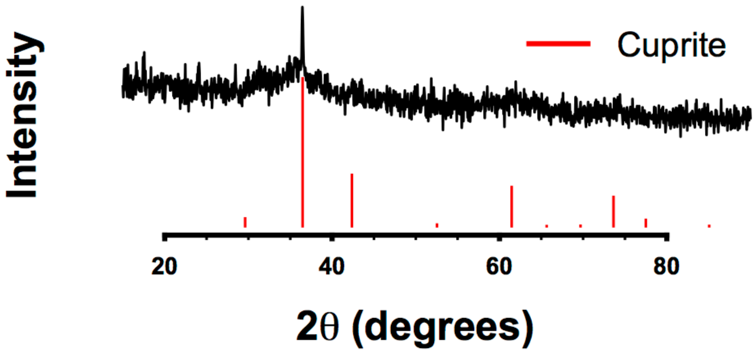

Figure 6. X-ray diffraction pattern representing a surface layer scale sample, approximately 2 months after orthophosphate dosing was initiated; no crystalline copper-phosphate phase was identified.

3.2 Task 2: Stagnation study

Addition of orthophosphate accompanied a statistically significant ($\alpha = 0.05$) reduction in copper release to ground water for all pipe types as a group. **Figure 7** summarizes the results of a linear model of log-transformed copper levels on orthophosphate concentration (0 or 1 mg P/L), free chlorine concentration (0 or 2 mg/L), pH (8 or 9), and pipe type (new, recovered East, recovered West). The effects associated with "New pipe" and "West pipe" (**Figure 7**) represent comparisons against copper release from recovered East Saint John pipe ("East pipe"). For example, "New pipe" released significantly less copper to groundwater than "East pipe". Effects with 95% confidence intervals that include zero ("Free chlorine", "pH", and "West pipe", **Figure 7**) were not statistically significant.

Of the water quality variables we tested, orthophosphate was the only statistically significant predictor of copper release. This is consistent with the tendency of orthophosphate to reduce copper solubility and release under a variety of conditions (Lytle *et al*., 2018). Given the known effects of pH (Dodrill & Edwards, 1995; Edwards *et al*., 1996; Boulay & Edwards, 2001) on copper release, we assume that a higher-powered experiment would have found this factor to be statistically significant as well. Indeed, increasing pH from 8 to 9 did accompany a statistically significant decrease in copper release to groundwater from new pipe sections. However, from a practical perspective a pH of 9 may cause undesired calcium carbonate precipitation.

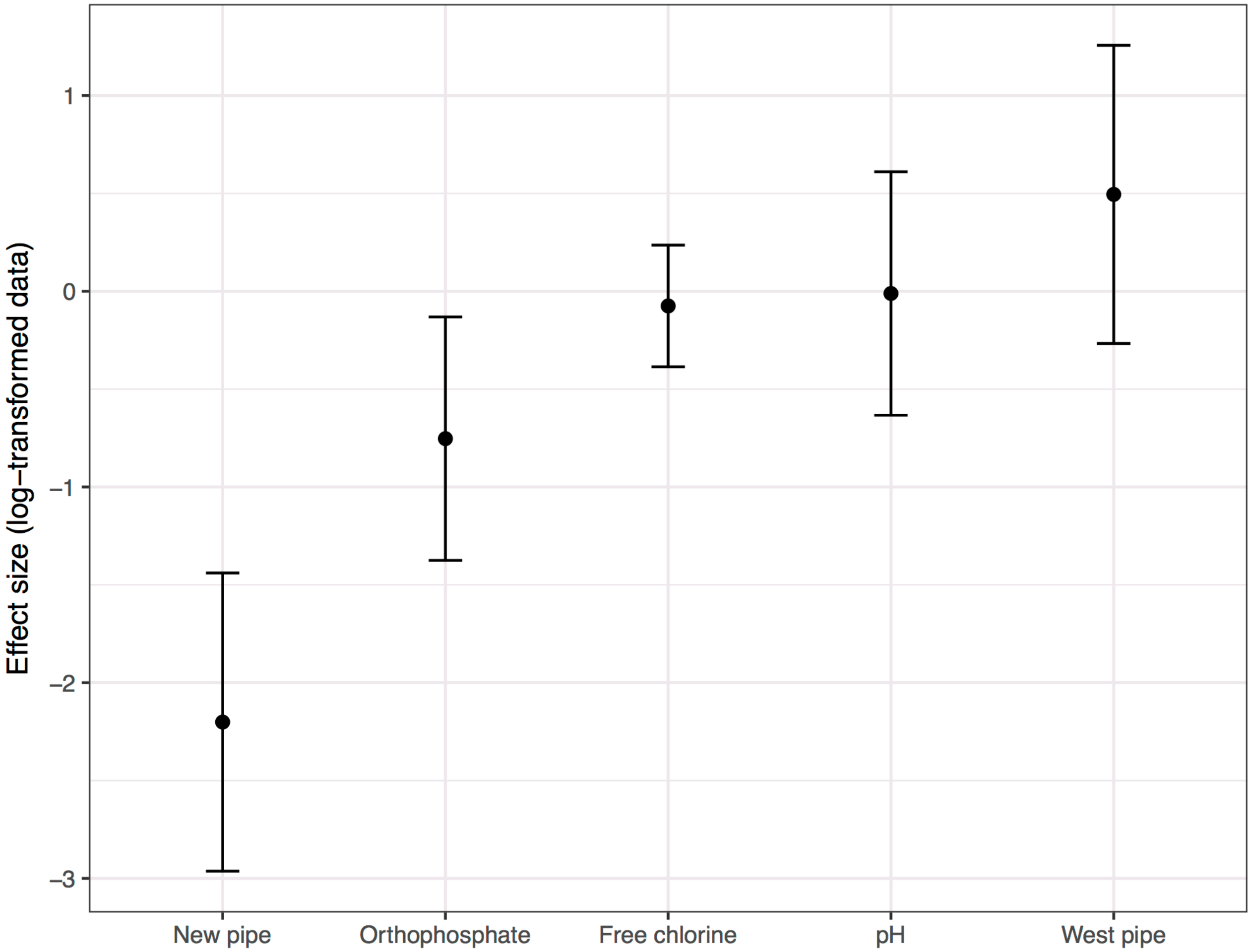

Figure 7. Orthophosphate was associated with a decrease in observed copper release, based on a linear model describing the effects of pH (8 or 9), orthophosphate (0 or 1 mg P/L), and free chlorine (0 or 2 mg/L) on copper release from new, recovered East Saint John and recovered West Saint John pipe sections exposed to groundwater. That is, adding 1 mg P/L to groundwater decreased copper release significantly to all pipe types as a group. Points denote effect sizes calculated for the log-transformed data, and error bars give the corresponding 95% confidence intervals. Confidence intervals that do not include zero represent statistically significant effects. Note that a negative effect indicates a decrease in copper release associated with a given factor. The factors 'West pipe' and 'New pipe' represent comparisons against recovered East Saint John pipes. East Saint John pipes were used in this experiment to represent copper pipe prior to groundwater introduction in West Saint John; the only available West Saint John pipe had been exposed to groundwater for some time before the experiment was initiated.

The effect of orthophosphate is summarized in **Figure 8** as a set of box-and-whisker plots. In the presence of orthophosphate, the distribution of observed copper concentrations exhibited a translation to lower values for all three pipe types compared with the 0 mg/L orthophosphate condition. Median copper release was lower by 3.3, 0.7, and 5.8 mg/L from recovered East Saint John, new, and recovered West Saint John pipe sections, respectively, at 1 mg P/L orthophosphate (this can be seen graphically as the difference between the bold black lines in each box/panel). Note that copper release from new pipe was substantially lower than from recovered pipe. Copper release from recovered pipe was considerably higher than would be expected in field samples, due probably to the relatively short conditioning period. Note also that while orthophosphate clearly reduced copper release, this study was not designed to determine whether orthophosphate would have inhibited pitting corrosion of copper exposed to groundwater.

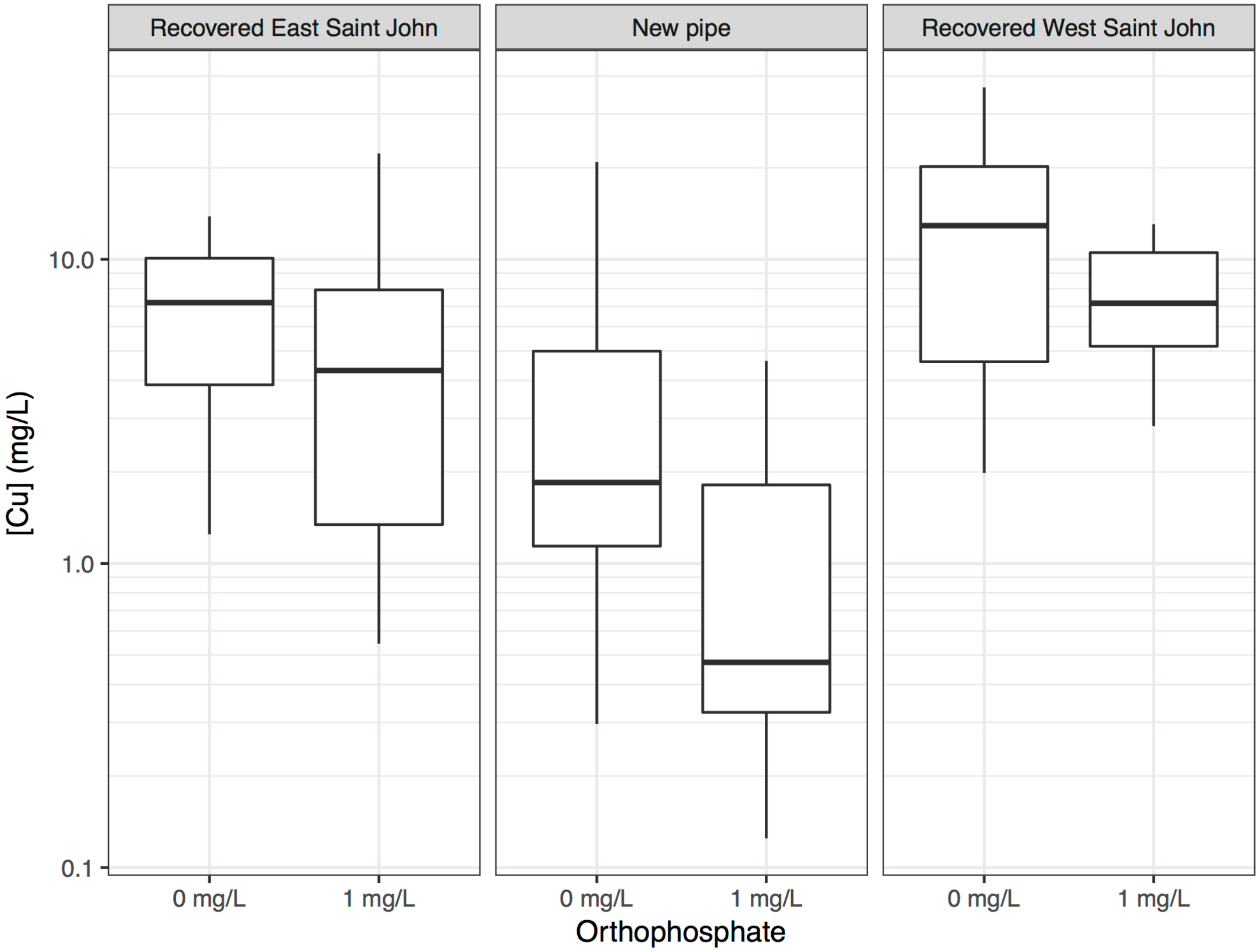

Figure 8. Median copper (log scale) was lower in effluent from pipe sections with orthophosphate; panels represent the different types of copper pipe. *Boxplots are represented as follows: boxes enclose the interquartile range (25th to 75th percentile), bold black lines denote medians, vertical lines outside the boxes extend to the most extreme value about the median that is less than or equal to 1.5 times the interquartile range, and more extreme values are plotted as points.*

We used a similar stagnation protocol to compare copper release to unaltered surface and groundwater. Differences in copper release between surface and groundwater may be influenced by pH, dissolved inorganic carbon, and natural organic matter, among other factors. All else being equal, cuprosolvency decreases with increasing pH (Ferguson et al., 1996) and increases with increasing inorganic carbon due to the formation of soluble carbonate and bicarbonate complexes (Edwards *et al*., 1996). **Figure 9** illustrates the effect of pH and inorganic carbon on cuprosolvency at constant ionic strength, but these data do not take into account the effect of particle mobilization on observed copper release. They also assume equilibrium with $Cu(OH)_2$ and this compound was not identified in our study. Despite its limited applicability to West Saint John, this model predicts greater copper solubility in surface water (pH 6.8) compared with groundwater (pH 8). Furthermore, given that historical data indicate a surface water pH of approximately 6.2, the model predicts an even greater difference between surface water and groundwater comparing historical conditions against the present scenario (i.e., distribution of groundwater).

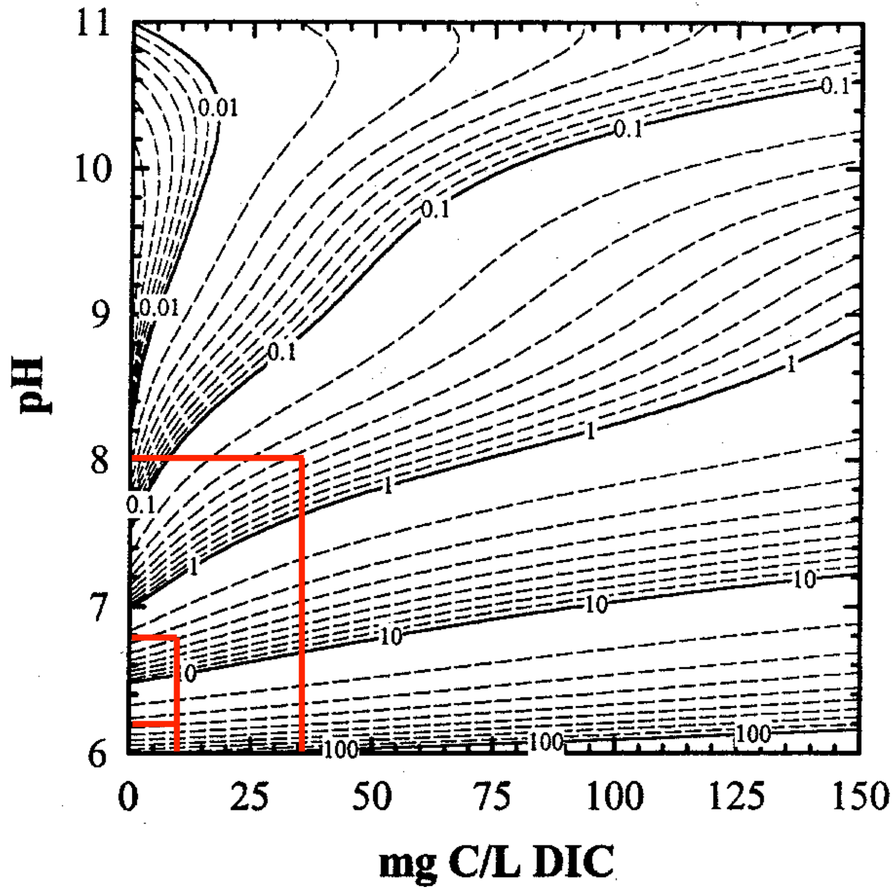

Figure 9. Soluble copper(II) as a function of pH and dissolved inorganic carbon (DIC), assuming equilibrium with $Cu(OH)_2$ and a constant ionic strength. Predicted copper solubility in surface (pH 6.8 presently or pH 6.2 historically) and groundwater (pH 8) are indicated; copper solubility contours are labelled and units are mg Cu/L (figure adapted from Schock *et al*., 1995).

In contrast to the model predictions, copper release to groundwater was greater than copper release to surface water at 0 mg/L free chlorine and 0 mg/L orthophosphate (**Figure 10**). This difference was statistically significant (α = 0.05) based on a linear regression of copper concentration on pipe type (recovered East or West Saint John pipe) and water source (surface or groundwater). The lack of agreement between model and experiment here may be attributed to particle mobilization (not accounted for in the solubility model) or differences between surface water and groundwater in the concentration of natural organic matter or inorganic ions. Notably, water source was not a statistically significant predictor of copper release when data from new copper pipe were included in the regression: median copper release from new copper pipe was slightly higher to surface water (1.9 mg/L) than to groundwater (1.5 mg/L). This suggests that interaction between the bulk water and the surface scale are an important aspect of observed differences in copper release, but the precise mechanism is unclear.

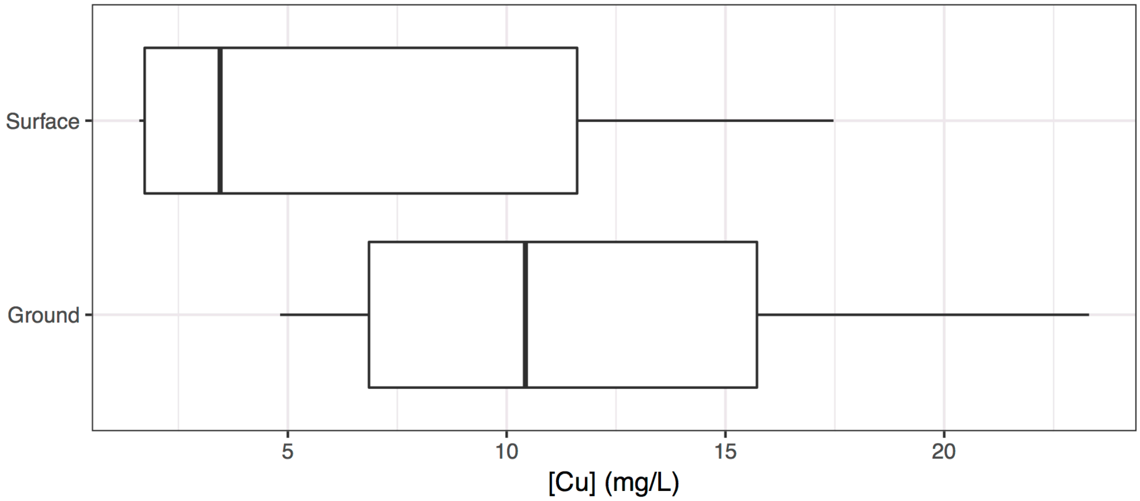

Figure 10. Median copper was lower in effluent from recovered East and West Saint John pipe sections supplied with surface water. *Boxplots are represented as follows: boxes enclose the interquartile range (25th to 75th percentile), bold black lines denote medians, horizontal lines outside the boxes extend to the most extreme value about the median that is less than or equal to 1.5 times the interquartile range, and more extreme values are plotted as points.*

4 Conclusion

We investigated the effects of free chlorine, pH, and orthophosphate on copper release to West Saint John groundwater. Of these factors, orthophosphate was the only statistically significant predictor of copper release. That is, copper release was significantly lower to groundwater amended with orthophosphate at 1 mg P/L compared with unaltered groundwater. We also compared copper release to West Saint John surface water (distributed historically) and groundwater (distributed currently). On the basis of pH and dissolved inorganic carbon alone, an established solubility model predicts greater cuprosolvency in surface water, but our experiment showed greater copper release from recovered pipes to groundwater. This discrepancy may stem from violations of the model assumptions:

1) We did not identify $Cu(OH)_2$ in West Saint John copper pipe scale, but this compound is assumed to control solubility in the model. Moreover, West Saint John scale was largely amorphous (i.e., lacked a long-range molecular order), limiting the applicability of solubility models in general and perhaps indicating that natural organic matter was a significant unexamined factor in our observations (cuprosolvency models do not generally account for the influence of natural organic matter, and at a sufficient concentration it may be protective against pitting corrosion).

2) The cuprosolvency model does not account for particle mobilization, but particulate copper release was an important phenomenon in our study.

5 Supplementary material

Table 1. Experimental design for stagnation study A.

Run	Pipe type	Water source	Free chlorine (mg/L)	P (mg/L)	pH
1	west	ground	0	0	8
2	west	ground	2	0	8
3	west	ground	0	1	8
4	west	ground	2	1	8
5	west	ground	0	0	9
6	west	ground	2	0	9
7	west	ground	0	1	9
8	west	ground	2	1	9
9	east	ground	0	0	8
10	east	ground	2	0	8
11	east	ground	0	1	8
12	east	ground	2	1	8
13	east	ground	0	0	9
14	east	ground	2	0	9
15	east	ground	0	1	9
16	east	ground	2	1	9
17	new	ground	0	0	8
18	new	ground	2	0	8
19	new	ground	0	1	8
20	new	ground	2	1	8
21	new	ground	0	0	9
22	new	ground	2	0	9
23	new	ground	0	1	9
24	new	ground	2	1	9
25	west	surface	0	0	6.8
26	east	surface	0	0	6.8
27	new	surface	2	0	6.8
28	new	surface	0	0	6.8

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APPENDIX B

Supplemental Dalhousie Report – January 2019

Final Report

Evaluating the effect of pH on copper release in West Saint John

January 21, 2019

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Table of Contents

1 Introduction 1
2 Methods 1
  2.1 Evaluating the effect of pH on copper release 1
3 Results 2
4 References 3

1 Introduction

In West Saint John there is a need to understand historical trends in copper release with variations in the distributed drinking water pH. Measured pH has varied from approximately 5.5 to almost 7 over time. In general, cuprosolvency declines with increasing pH in non-linear fashion (Ferguson *et al.*, 1996). However, between pH 5.5 and 7 this relationship is approximately linear (Ferguson *et al*., 1996), and we assumed that measuring copper release at the endpoints (pH 5.5 and ~7) would be sufficient to estimate the relationship between copper release and pH on this interval. The objective of this study was to gain a qualitative understanding of the pH-cuprosolvency relationship using a stagnation study with new and recovered West Saint John copper pipe.

2 Methods

Raw surface water from the historical West Saint John source was used in all tests. Sections of ½ inch diameter copper pipe recovered from West Saint John were used in addition to new copper pipe of the same dimensions.

2.1 Evaluating the effect of pH on copper release

We evaluated the effect of pH using two new and two recovered copper pipe sections at each of the two target pH values (8 pipe sections total, pH 5.5 and unaltered pH 6.8, Table 1). Sections of copper pipe were sealed with stoppers (as in Figure 1) and conditioned by filling with test water 12 times with at least 24 hours between changes. Following the conditioning period, total copper release was monitored in 24-hr stagnant pipe effluent by ICP-MS.

Table 1: Experimental design evaluating the effect of pH on copper release.

Reactor	pH adjustment
New Cu pipe	No
New Cu pipe	No
New Cu pipe	Yes, pH 5.5
New Cu pipe	Yes, pH 5.5
Old West SJ pipe	No
Old West SJ pipe	No
Old West SJ pipe	Yes, pH 5.5
Old West SJ pipe	Yes, pH 5.5

Figure 1: A section of new copper pipe sealed at either end with a rubber stopper.

3 Results

Figure 2 shows the copper released to 24-hr stagnant samples as a function of influent pH. New copper pipe behaved more or less as predicted based on theoretical solubility curves, with substantially higher copper release at pH 5.5 compared to pH 6.8. The effect of pH on copper release from recovered West Saint John copper pipe was not clearly identifiable. We assume this is because it was eclipsed by the greater inherent variability in release from recovered pipe due to particle detachment from the corrosion scale.

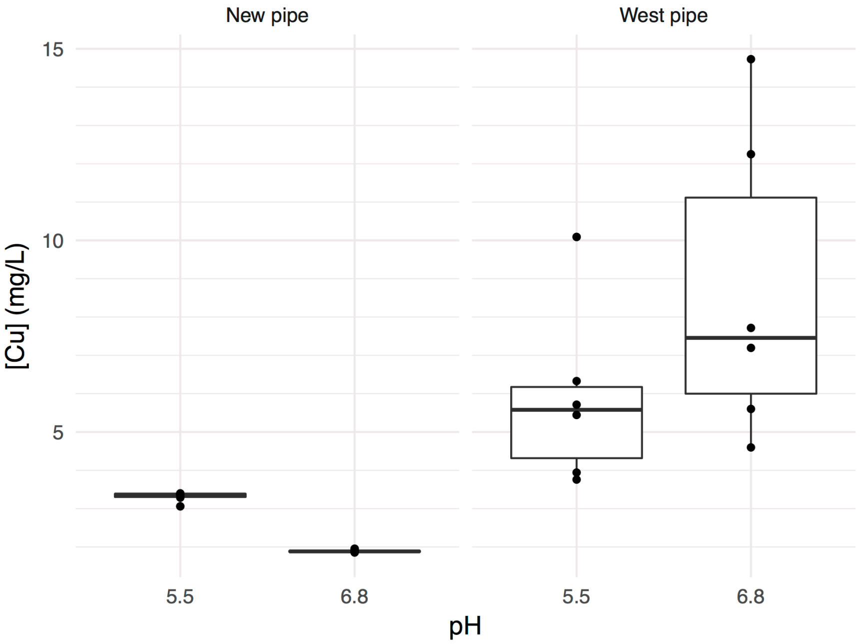

Figure 2. Copper release after 24-hour stagnation in new ("New pipe") and recovered West Saint John ("West pipe") copper pipe. Points represent copper concentrations corresponding to six measurements collected from two copper pipes per experimental condition; boxplots are superimposed on the raw data. *Boxplots are represented as follows: boxes enclose the interquartile range (25th to 75th percentile), bold black lines denote medians, vertical lines outside the boxes extend to the most extreme value about the median that is less than or equal to 1.5 times the interquartile range, and more extreme values are plotted as points.*

Based on the data from new copper pipe, we estimate that decreasing pH from 6.8 to 5.5 increased copper release by a median of 1.5 mg/L (95% confidence interval 1.2 – 1.5 mg/L, $p = 0.002$, rank-sum test, $n = 6$ per group). Based on the data from recovered copper pipe, we estimate that the same pH change decreased copper release by 1.9 mg/L (95% confidence interval -8.4 – 1.1 mg/L, $p = 0.180$, rank-sum test, $n = 6$ per group). That is, the change in copper release from recovered pipe was not statistically significant (*n.b.*, we assumed the replicate measurements from each pipe section to be independent).

4 References

Ferguson, J. F., von Franque, O., Schock, M. R. (1996). Corrosion of copper in potable water systems. In Internal Corrosion of Water Distribution Systems, AWWA Research Foundation: Denver, CO, pp. 231−268.