UNDERSTANDING PHOSPHATE FOR CONTROLLING METALS RELEASE AND BIOFILM FORMATION IN DRINKING WATER DISTRIBUTION SYSTEMS

by

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ABSTRACT

Corrosion is a common problem in drinking water distribution systems and leaching of contaminants such as lead is a concern for the health of all consumers. Populations who are more susceptible to lead exposure are infants, young children and pregnant women. Those who are exposed to lead for a period of time are at risk of developing negative impacts to the nervous system such as lower IQ, behavioral problems and intellectual delays.

Two experiments were conducted in order to evaluate the effect of orthophosphate and pH on metals release and biofilm formation in the distribution system: (1) bench scale simulated partial lead service line replacements were used in a controlled laboratory setting using two water sources (surface water and groundwater) in stagnant water conditions and (2) annular reactors were used in a controlled laboratory setting containing copper coupons with 50:50 lead tin solder to simulate pipe material and allow for biofilm accumulation. Additionally, a lead and copper monitoring program was completed in a non-residential building where the groundwater was the water source to determine the potential sources of lead and copper at the consumers tap.

The bench scale simulated partial lead service line replacement experiment resulted in the highest lead levels due to the presence of stagnant water conditions. Additionally, the groundwater had significantly higher lead levels than the surface water due to the presence of a high CSMR (7.7 to 8.3) which was 11 to 12 times higher than the recommended criteria of 0.7. The interaction between pH and orthophosphate was statistically significant in reducing lead levels for both water sources.

Since the groundwater source in the bench scale partial lead service line replacement resulted in significantly higher lead levels, this water source was chosen for the annular reactor experiment and at the tap monitoring. The effluent of the annular reactors had a CSMR between 7 and 8 which was 10 to 11 times the recommended criteria of 0.7. Orthophosphate significantly reduced bulk water total lead levels. Furthermore, chlorine significantly reduced both bulk water and biofilm cATP concentrations. The addition of orthophosphate significantly reduced bulk water cATP concentrations, but significantly increased biofilm cATP concentrations. Lastly, both pH and orthophosphate played a significant role in reducing biofilm total lead concentrations.

The monitoring program determined the at the tap CSMR to be between 7 and 8 which indicated a corrosive environment was present. First draw total lead samples resulted in two locations being above the action level: raw groundwater and bathroom. The sources of lead throughout the distribution system in this case were brass faucets and valves. Additionally, high copper concentrations were found at four out of the five locations throughout the monitoring program due to the presence of copper piping and components along with corrosive water with a high CSMR. A high percentage of samples were not only above Health Canada's aesthetic objective, but also above the EPA action level and the WHO guideline.

LIST OF ABBREVIATIONS AND SYMBOLS USED

AL Action Level

ANOVA Analysis of Variance

cATP Cellular Adenosine Triphosphate

$CaCO_3$ Calcium Carbonate

Cl_2 Chlorine

CSMR Chloride to Sulphate Mass Ratio

DOC Dissolved Organic Carbon

e^- Electron

EDS Energy Dispersive Spectroscopy

EPA Environmental Protection Agency

EPS Exopolymeric Substances

H^+ Hydrogen

HOCl Hypochlorous Acid

ICP-MS Inductively Coupled Plasma Mass Spectrometry

$M_{(s)}$ Solid Metal

MAC Maximum Allowable Concentration

NPC National Plumbing Code of Canada

NTU Nephelometric Turbidity Units

O_2 Oxygen

OCl^- Hypochlorite

$PbCl^+$ Lead Chloride

$PbSO_4$ Lead Sulphate

pKa Acid Dissociation Constant

PO_4 Phosphate

PVC Polyvinyl Chloride

SEM Scanning Electron Microscope

TOC Total Organic Carbon

USEPA United States Environmental Protection Agency

WHO World Health Organization

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CHAPTER 1 INTRODUCTION

Drinking water utilities face a challenge of providing safe drinking water to their consumers despite many factors that can result in the degradation of water quality prior to consumption (Clark, 2011). Raw water is used from either a surface water or groundwater source which undergoes treatment and then transmitted through the distribution system which may be composed of a network of corroded pipes (Clark, 2011). These corroded pipes may release a major contaminant of concern: lead.

Research has proven exposure to small amounts of lead can be harmful to human health (Health Canada, 2007). Populations who are more susceptible to lead exposure are infants, young children and pregnant women. Exposure is most serious to young children as they absorb lead more easily than adults. Exposure to low levels of lead may have negative impacts on an infants intellectual development, behaviour, size and hearing. During pregnancy, lead can cross the placenta and may result in negative impacts such as premature births, smaller babies, decreased mental ability in the infant, learning difficulties and reduced growth in young children. Overall, those who are exposed to lead for a period of time are at risk of developing adverse health effects to the nervous system. Symptoms may include the following: forgetfulness, tiredness, headache, changes in mood and behavior, lower IQ, decreased hand dexterity and weakness of arms, legs, hands, feet (Health Canada, 2007). Exposure to lead may also affect the digestive system, renal system and immune system. In order to address these concerns, Health Canada developed the Guidelines for Canadian Drinking Water Quality to limit the concentration of lead in drinking water to a maximum acceptable concentration (MAC) of 0.010 mg/L or 10 µg/L measured at the consumers tap. This guideline protects the most vulnerable population: children (Health Canada, 2007).

In Canada, for the most part, the concentrations of lead in natural water sources is very low (Health Canada, 2007). Therefore, lead is generally leached into drinking water via lead service lines (water pipes linking the home to the main water supply), premise plumbing, lead solder or brass fittings such as faucets and valves. Lead was a commonly used material for pipes in Canada until 1975 and used in solder until 1986. Although the use of leaded pipes and solder are no longer permitted, the leaded pipes and solder may still be in use in older homes. Thus, exposure to lead via drinking water is still occurring today.

Municipalities, water utilities and regulatory authorities carry out many steps to protect the public from lead exposure. Water utilities work on optimizing the treatment process in order to reduce the potential for corrosion in the distribution system. In order to minimize effects of corrosion, two corrosion control strategies are commonly used: (1) pH adjustment and/or (2) addition of phosphate. Adjustment of pH in drinking water helps to manage the deposition of calcium carbonate (Crittenden et al., 2012) which acts as a protective insoluble film on the pipe surface, thereby decreasing corrosion of lead. Research has proven that the lowest levels of lead at the tap have been found in waters with a pH above 8 (Dodrill & Edwards, 1995; Douglas et al., 2004). Furthermore, the use of phosphate increases passivity of a metal by creating a protective insoluble film on the inside of the pipe surface which can help prevent metals from dissolving in drinking water (United States Environmental Protection Agency, 2011).

Research related to corrosion of lead is of interest to water utilities and regulatory authorities as it is used in the decision making process. The groundwater source used throughout this study was unique due the presence of a high chloride to sulphate mass ratio (CSMR) value between 7 and 8, which indicates a higher potential for corrosion in the distribution system. There is a lack of research on higher CSMR water sources in Atlantic Canada, therefore a monitoring program completed in this study will assess the extent of the problem and bench scale studies will help determine whether corrosion control strategies such as pH adjustment and phosphate addition are effective in mitigating corrosion in a higher CSMR water source.

Addition of phosphate as a corrosion control strategy poses a major concern to water utilities as it can have negative effects on biofilm formation within the distribution system. Bacteria aggregate in biofilms by producing extracellular polymeric substances (EPS), which are charge organic molecules that are able to accumulate on pipe surfaces and adsorb other water contaminants (Videla & Herrera, 2005). Prior research has proven that phosphate acts as a nutrient and therefore increases biofilm growth within the distribution system (Chu et al., 2005; Hozalski et al., 2005; Fang et al., 2009), while other studies have found no impact on biofilm formation (Rompre et al., 2000; Batte et al., 2003). Thus, further research completed in this study will also address the effects of phosphate on biofilm formation within a simulated drinking water distribution system.

1.1 Thesis Objectives

The main objectives of this project were the following:

1. Compare galvanic corrosion potential in two drinking water sources under corrosion control treatment and incubated in simulated partial lead service lines.
2. Examine the effects of varying the doses of orthophosphate on both metal release and biofilm formation in a bench scale simulated drinking water distribution system.
3. Conduct a full scale monitoring program in order to determine if lead and/or copper are of concern in a non-residential setting.

1.2 Thesis Outline

This thesis is organized in six chapters. An outline of each chapter is presented below.

Chapter 1: Provides the purpose for this thesis as well as thesis objectives and the thesis outline.

Chapter 2: Provides a literature review covering corrosion principles, factors affecting corrosion, regulations and current practices for corrosion control.

Chapter 3: Examines the effects of orthophosphate and pH on lead and copper release in high and low CSMR water sources. Bench scale partial lead service line replacements were used in a controlled laboratory setting in order to carry out the study. Two water sources, a surface water and groundwater were used in which the groundwater had a significantly higher CSMR. Water was stagnated in the pipe to represent worst case scenarios such as stagnation over long weekends.

Chapter 4: Evaluates the effect of orthophosphate and pH on both metals release and biofilm formation using a groundwater source with high CSMR. Annular reactors were used in a controlled laboratory setting to simulate the drinking water distribution system. Copper coupons with 50:50 lead tin solder were placed in the annular reactors to simulate pipe material and allow for biofilm accumulation. Each reactor was acclimated without the addition of chlorine to promote biofilm growth. Once biofilm was stable, chlorine was added to each reactor and the effectiveness of orthophosphate addition and pH adjustment on metals and biofilm formation were monitored. Coupons were removed at the end of the experiment and analysed using EDS.

Chapter 5: A lead and copper monitoring program was completed in a non-residential building at a location where the groundwater source was of high CSMR. Samples were collected from one non-residential building using five faucets within the building. The data was then analyzed for both lead and copper released from each faucet.

Chapter 6: The results of the three experimental chapters are summarized and both conclusions and recommendations are made.

CHAPTER 2 LITERATURE REVIEW

2.1 Corrosion Principles

Electrochemical corrosion is the transfer of electrons which causes the destruction of a metal (Snoeyink & Wagner, 1996). In order for electrochemical corrosion to occur, four components must be present to form a corrosion cell shown in Figure 2.1 below: (1) an anode, (2) a cathode, (3) a connection between the anode and cathode for transport of electrons and (4) an electrolyte solution that will conduct ions between the anode and cathode (Health Canada, 2009). In the distribution system, the anode and cathode are sites of differing electrochemical potentials, the connection between the anode and cathode is the metal and the electrolyte is drinking water. Corrosion of drinking water distribution systems leads to two major concerns for water utilities: (1) failure of distribution system pipes and (2) unwanted change in water quality (Snoeyink & Wagner, 1996). Corrosion may occur in the distribution system and/or the plumbing system leading to exposure of contaminants such as lead and copper (Health Canada, 2009).

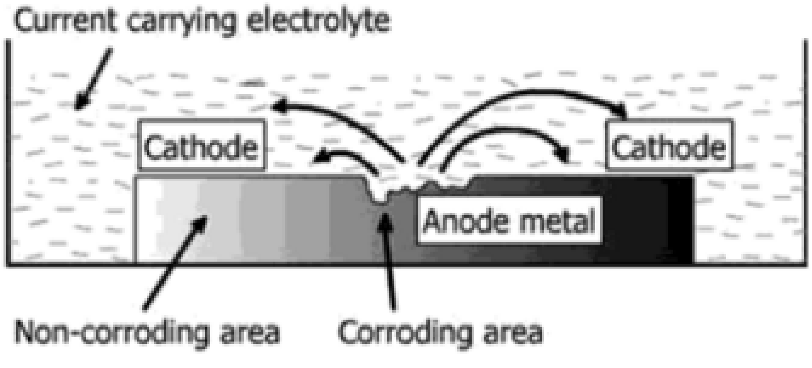

Figure 2.1: Corrosion cell (Ahmad, 2006)

Metal is lost and oxidation reactions occur at the anode. The electrons transfer through the internal circuit from the anode to the cathode where the electrons are discharged to an electron acceptor by a reduction reaction. Positive ions generated at the anode travel to the cathode via the electrolyte; negative ions generated at the cathode travel to the anode. Ions migrate to either the anode or cathode in order to maintain a neutral solution (Snoeyink & Wagner, 1996). When copper is electrically connected to lead, corrosion of lead is accelerated. Drinking water serves as the electrolyte between the two dissimilar metals and forms a galvanic cell where lead is the anode and copper is the cathode. Thus, electrons flow from the lead anode to the copper cathode.

Corrosion occurs in the distribution system because pure metals are not in equilibrium with drinking water that flows through the pipes. The magnitude of potential difference between the solution and electrode surface reflects the extent of disequilibrium present (Snoeyink & Wagner, 1996). A series of reactions occur at the anode and cathode. The key reaction in corrosion is the oxidation or anodic dissolution of the metal (Health Canada, 2009):

$$M \rightarrow M^{n+} + ne^-$$

where:

- M is the metal
- e^- is an electron
- n is the valence and the corresponding number of electrons.

Both forward (oxidation) and reverse (reductions) reactions occur at any instant at the phase boundary of a metal in an electrolyte. During oxidation, the metal corrodes which produces electrons. The electrons migrate towards the cathode where they are used in reduction reactions

(Snoeyink & Wagner, 1996). Electron acceptors present in reduction reactions may include dissolved oxygen and the hypochlorite ion. Ions formed may be released as corrosion products or they may react with components present to form a scale on the pipe surface. The scale may range from highly soluble to protective (Health Canada, 2009).

Various types of corrosion can occur in distribution systems. The determinant of the type of corrosion that will occur is the distribution of anodic and cathodic areas over the pipe surface (Snoeyink & Wagner, 1996). If the areas are closer together and potential differences are small, corrosion may be relatively uniform over the pipe surface. However, if the areas are farther apart and potential differences are large, pitting corrosion may occur (Snoeyink & Wagner, 1996).

2.2 Factors Affecting Corrosion

The rate of corrosion is affected by the age of the plumbing system, stagnation time and water chemistry.

2.2.1 Age of Plumbing

Consideration of the age of the pipe within the distribution system is important when measuring lead levels at the tap or in bench and pilot scale studies. Lead concentrations generally deceases with pipe age. Newer pipes do not have the same scale that older pipes have formed during months to years of service. Lead passivation occurs over time through the formation of various corrosion products such as: cerussite [$PbCO_3$], hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], plumbonacrite ($Pb_{10} (CO_3)_6 (OH)_6O$), litharge (PbO), and plattnerite (PbO_2) (Kim & Herrera, 2010). Water quality parameters determine the amount and type of corrosion species formed on the inside of pipe surfaces.

Researchers have found the highest levels of lead within the first year of pipe installation and later decreasing after a number years of use. Edwards et al. (2002) found that both soluble and particulate lead release decreased significantly with aging; soluble lead decreasing to a lesser extent than particulate. Copper concentrations also decreased with pipe age even after 10 to 20 years of service (Edwards et al., 2002).

2.2.2 Stagnation Time

Lead and copper concentrations in drinking water can increase significantly following a period of stagnation of a few hours (Lytle & Schock, 2000). Schock et al. (1996) determined that lead levels increased exponentially after stagnation and approached equilibrium after overnight stagnation. Furthermore, Lytle and Schock (2000) determined that lead levels increased with stagnation time with the critical period of stagnation being the first 20 to 24 hours. Lead concentration increased quickly during the first 10 hours, reaching 50 to 70% of the maximum observed value. However, lead continued to increase even up to 90 hours of stagnation.

Copper levels may also increase after stagnation but researchers found after a particular time copper levels will either continue to increase or decrease. Lytle and Schock (2000) determined that copper levels increased quickly after stagnation but decreased significantly once dissolved oxygen fell below 1 mg/L. Sorg et al. (1999) found that copper concentrations increased to maximum levels after 20 to 25 hours of stagnation then levels decreased after 72 to 92 hours. Overall, peak concentrations were related to the time in which dissolved oxygen decreased to 1 mg/L or less.

2.2.3 Water Chemistry

2.2.3.1 pH and Temperature

Adjustment of pH in drinking water is used to manage the deposition of calcium carbonate and is a key variable in the solubility of materials such as lead and copper (Crittenden et al., 2012). Lead corrosion by-products such as metal oxides, hydroxides and carbonates contribute to lead levels in drinking water and are strongly influenced by pH. Adjustment of pH plays an important role in determining whether an insoluble protective scale will form (passivity) or whether corrosion will be favored. Lower pH favors dissolution of lead while higher pH favors formation of protective scales that prevent corrosion (Crittenden et al., 2012). Reducing the solubility of corrosion by-products by increasing the pH is a common method used by water utilities. Research by Dudi and Edwards (2004) demonstrated that lead released at a pH of 7.5 was significantly higher than lead released at a pH of 8.5. Furthermore, Edwards et al. (2002) proved that lead levels decreased up to a pH of 9.5 regardless of pipe age. Overall, lowest levels of lead at the tap have been found in waters with a pH above 8 (Dodrill & Edwards, 1995; Douglas et al., 2004).

The corrosion rate of lead and copper is expected to increase with increasing temperature (Health Canada, 2009); however, the solubility of corrosion by-products decreases with increasing temperature (McNeill and Edwards, 2002). Changes in temperature during the winter and summer months correlated with changes in lead concentrations; higher lead concentrations occurring during the summer (Douglas et al., 2004).

2.2.3.2 Alkalinity

Alkalinity serves to control the buffer intensity of water systems; a minimum amount of alkalinity is needed in order to stabilize pH throughout the drinking water distribution system (Health Canada, 2009). Since corrosion of lead releases Pb^{2+} ions (a lewis acid), pH at the anode will decrease. If the buffering capacity of the water is low, the pH decrease at the lead surface will be more prominent leading to an overall reduction in pH of the surrounding water, further increasing corrosion. If the buffering capacity is higher, the pH drop at the lead surface is less prominent (Dudi & Edwards, 2004). Lead concentrations are more sensitive to pH changes between a pH of 7 and 8.5 with alkalinities below 50 mg/L as $CaCO_3$. Whereas lead concentrations are insensitive to changes in pH at alkalinities above 100 mg/L as $CaCO_3$ (Hozalski et al., 2005). Optimal alkalinity for lead control is between 30 and 45 mg/L at a pH between 7 and 9.5 (Edwards & McNeill, 2002).

Alkalinity plays an important role in the formation of lead carbonate ($PbCO_3$) which may contribute to the scale on the inside of pipe surfaces. The increase in alkalinity decreases the solubility of corrosion products such as lead carbonate, which increases the formation of solid insoluble metal carbonate scales (Crittenden et al., 2012). This in turn decreases lead levels in drinking water.

2.2.3.3 CSMR

The chloride to sulphate mass ratio (CSMR) is defined as the concentration of chloride divided by the concentration of sulphate (in mg/L), and is used as an indicator of potential for galvanic corrosion (Willison & Boyer, 2012). Bench and field scale studies have shown that higher CSMR values produce higher galvanic currents which leads to higher lead concentrations in drinking water (Edwards & Triantafyllidou, 2007; Nguyen et al., 2011). Accumulation of chloride near the anode surface can form a soluble $PbCl^+$ complex which increases the concentration of lead in water. However, accumulation of sulphate at the anode surface can form an insoluble $PbSO_4$ solid which can precipitate on the inner pipe surface and reduce corrosion (Willison & Boyer, 2012). Literature states that a CSMR greater than 0.7 contributes to increased galvanic corrosion between copper and lead, which leads to higher lead concentrations in drinking water (Nguyen et al., 2011).

A utility survey conducted by Dodrill and Edwards (1995) presented a CSMR boundary of 0.58. Twelve utilities met the EPA lead action level when the CSMR was below 0.58. However, seven utilities exceeded the lead action limit when the CSMR was above 0.58. Triantafyllidou et al. (2010) completed a study with CSMR values of 0.2 and 16.2. Results revealed that lead concentrations were 3 to 11 times greater in the higher CSMR water compared to the lower CSMR water.

2.2.3.4 Free Chlorine Residual

Free chlorine is a commonly used disinfectant in drinking water treatment. When sodium hypochlorite is added to water, two main oxidants are formed: hypochlorous acid and the hypoclorite ion. Hypochlorous acid (HOCl) is a weak acid with a pK_a value of 7.6 at 20°C thus is the predominant form present below pH of 7.6 (Crittenden et al., 2012). However, above pH 7.6, the hypochlorite ion (OCl^-) is the predominant form present (Crittenden et al., 2012). Hypochlorous acid has faster disinfection kinetics than the hypochlorite ion (Crittenden et al., 2012); therefore, free chlorine is more effective below a pH of 7.6.

The impact of free chlorine on lead corrosion and lead levels in drinking water has been previously studied. Both hypochlorous acid and the hypochlorite ion can act as oxidants towards lead which can increase corrosion of lead in the distribution system. Lin et al. (1997) proved that lead leaching was higher with the addition of free chlorine for both pure lead and copper as well as for lead solder coupons. However, Cantor et al. (2003) completed a pipe loop study which revealed that a free chlorine residual of 0.2 mg/L did not increase lead concentrations. Hypochlorous acid can also become a dominant oxidant on copper surfaces in drinking water distribution systems. Free chlorine residual has been shown to increase copper corrosion at a lower pH but decrease copper corrosion at a pH of 9.3 (Edwards et al., 1993).

2.2.4 Biofilm

Biofilms are a gel containing 95% or more water and a matrix of exopolysaccharidic substances (EPS) where microbial cells and inorganic debris are suspended (Videla & Herrera, 2005). Biofilms form on metals over time from the deposition of inorganic ions and organic compounds suspended in water (Videla & Herrera, 2005). The film can then change electrostatic charges on the metal surface which allows for more bacteria to attach at the site. These bacteria can play a major role in accelerating corrosion of pipe materials. They have the ability to (Crittenden et al., 2012):

- Form microzones of high concentrations of corrosive species
- Increase electrolytic concentration
- Favor electron transfers
- Mediate oxidation of reduced species
- Interfere with protective surface films
- Mediate removal of corrosion by-products
- Use local gradients in redox potential as energy for metabolic needs

Microorganisms accelerate the rate of redox reactions thus increasing corrosion kinetics. Chlorination of water supplies has reduced corrosion rates indicating that disinfection can inhibit the role of bacteria in corrosion. In areas of the distribution system where water stagnates, relatively severe corrosion may occur due to a decrease in chlorine residual. Such areas include dead ends where an increase in growth of microorganisms increases corrosion and likelihood of corrosive pipe failures and water main breaks. Hence, it is common practice for water utilities to flush dead ends to minimize bacterial growth by scouring and lowering detention time of chlorinated water (Crittenden et al., 2012).

2.3 Regulations

Lead, the main contaminant of concern is used as the trigger to begin corrosion control programs. When monitoring for lead there are two different situations and exposure patterns to be considered: residential and non-residential settings. Residential monitoring assesses lead concentrations and identifies sources of lead in the distribution system as well as residential plumbing. The overall purpose for residential monitoring is to identify and diagnose systems where corrosion is occurring and to determine the best remedial action. Non-residential monitoring focuses on the source of lead within the plumbing system in the building. The purpose is to locate specific lead issues and identify how to continue with remedial action (Health Canada, 2009). Table 2.3 summarizes the lead action levels for residential and non-residential sampling. If monitoring levels are higher than the action levels shown in Table 2.3, corrective measures need to be implemented and additional sampling will need to be completed.

Table 2.3: Lead action levels for residential and non-residential sampling

Document	Guideline/Action Level
Canadian Drinking Water Guidelines	• Maximum Acceptable Concentration (MAC): 10 µg/L • Based upon health effects in a 2 year old child resulting from chronic exposure
Guidance on Controlling Corrosion in Drinking Water Distribution Systems	**Residential:** • Assesses the overall corrosion behavior of the distribution system • 90th percentile lead action level (AL) of 15 µg/L for 1 L first draw sample following a 6 hour stagnation **Non-Residential:** • Identifies individual sources of lead within a building • Individual fixture AL of 20 µg/L for 250 mL first draw sample following a stagnation period between 8 and 24 hours

Other contaminants that may be leached as a result of corrosion in drinking water distribution systems include copper, iron and aluminum. All three contaminants do not have MAC values set by Health Canada, but they have aesthetic and operational guidelines. The drinking water guidelines for copper and iron are based on aesthetics such as color and taste. The aesthetic objective for copper is ≤ 1.0 mg/L and the aesthetic objective for iron is ≤ 0.3 mg/L. The operational guidance value for aluminum is < 0.1 mg/L for conventional treatment and < 0.2 mg/L for other treatment types (Health Canada, 2014).

2.4 Current Practices for Lead Control

Drinking water utilities have adopted practices from Health Canada's Guidance on Controlling Corrosion in Drinking Water Distribution Systems in order to develop the following three main components to minimize lead (Halifax Water, 2014):

1. Lead Service Line Replacement Program: Replacing older lead pipe in distribution systems with newer copper pipe or PVC pipe.

2. Corrosion Control Program: Use of corrosion inhibitors to help minimize the corrosion of lead and other metals within the distribution system.

3. Monitoring Program: Monitoring programs measure contaminants such as lead and copper at the tap in order to determine population exposure and assess corrosion within the distribution system.

2.4.1 Lead Service Line Replacement

Lead service line replacement is a current practice carried to help control lead concentrations in drinking water (Wang et al., 2012). Lead service lines consist of two main sections: the public service pipe and the private service pipe. Figure 2.4.1 below displays the public service pipe carries drinking water from the main distribution system line to the property line and is the responsibility of the utility. The private water service pipe carries drinking water from the property line to the home and is the responsibility of the property owner. Older pipes were commonly made of lead and used prior to 1975 whereas newer pipes are made of copper or polyethylene tubing (Health Canada, 2009). Utilities may replace their portion of the service line with copper piping while homeowners may not replace their portion due to cost. A partial lead service line replacement is when only one section of the service pipe is replaced; the public water service pipe may be replaced with copper while the private water service pipe remains as lead.

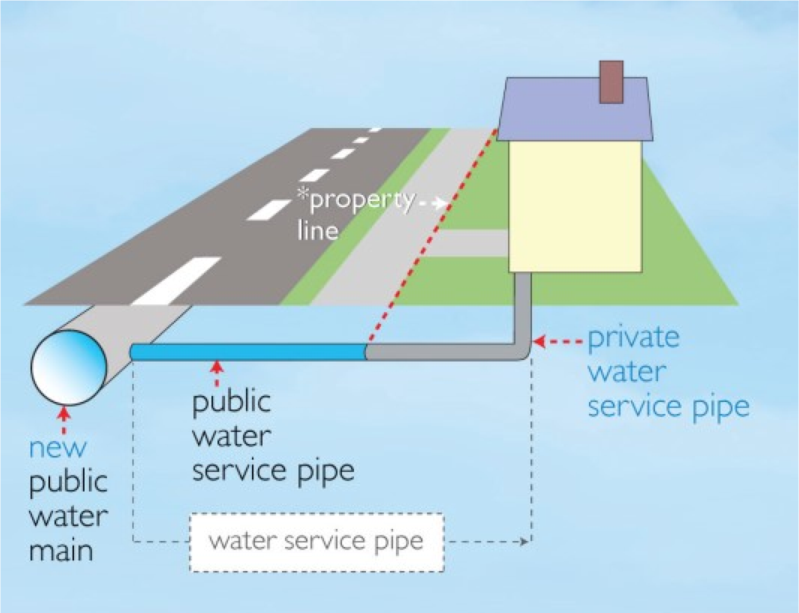

Figure 2.4.1: Public and private water service lines (Halifax Water, 2014)

Lead service line replacements reduce the presence of lead pipe which can also reduce lead concentration in drinking water. Nevertheless, partial lead service line replacements may lead to an increase in galvanic corrosion which in turn increases lead concentrations at consumers' taps (Trueman et al., 2016; Edwards & Triantafyllidou, 2007). There may be also be increased lead release due to the mechanical disturbance of corrosion scales (Boyd et al., 2004).

2.4.2 Corrosion Inhibitor

Phosphates are added to water distribution systems as corrosion inhibitors to prevent leaching of metals into drinking water. Two fundamental types of phosphate compounds used in corrosion control are orthophosphates and polyphosphates (Crittenden et al., 2012). All forms of phosphate used are characterized by $P_nO_{3n+1}^{-(n+2)}$. Those forms that are well-understood in literature are those with n values of 1, 2 and 3. Orthophosphates have a value of n=1 (PO_4^{3-}) and polyphosphates have a value of n > 1 (Crittenden et al., 2012). Addition of phosphate increases passivity of a metal by creating a protective insoluble film (Figure 2.4.2) on the inside of the distribution system which can help prevent metals from dissolving in drinking water (United States Environmental Protection Agency, 2011).

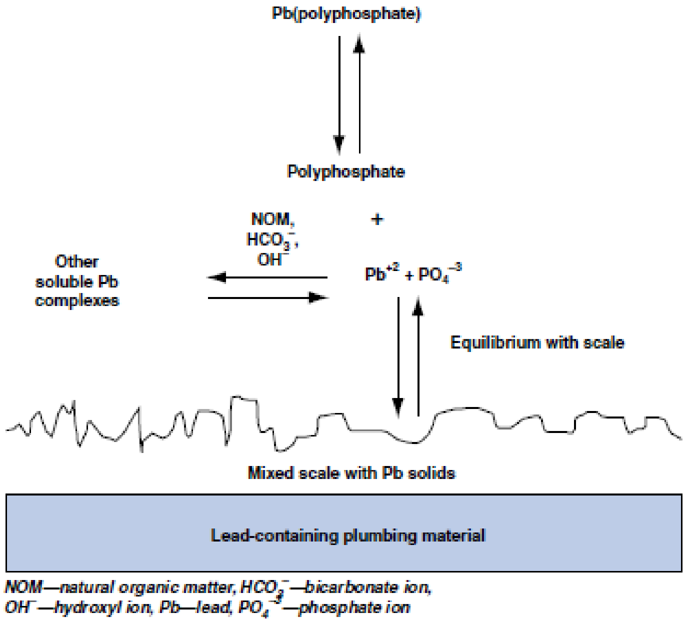

Figure 2.4.2: Formation of an insoluble protective film on the pipe surface (Edwards & McNeill, 2002)

Orthophosphate addition encourages formation of lead phosphate solids such as hydroxypyromorphite [$Pb_5(PO_4)_3OH$] and tertiary lead orthophosphate [$Pb_3(PO_4)_2$] (Schock, 1989). Water chemistry determines the effectiveness of orthophosphate on lead levels in drinking water. Parameters such as pH and alkalinity influence formation of various corrosion species that dominate lead solubility. Solubility models for both lead and copper illustrate that optimal pH for orthophosphate passivity is between 7 and 8 on lead surfaces (Schock, 1989) and between 6.5 and 7.5 on copper surfaces (Schock et al., 1995). Schock et al. (2005) determined a lead solubility diagram for stable Pb (II) compounds as a function of pH ranging from 6 to 10. The diagram included lead carbonate, hydro-cerrusite, lead phosphate, hydroxypyromorphite and chloropyromorphite all of which have the ability to form a passivating layer on the pipe surface. Those solids formed from the addition of phosphate have lower lead solubility as compared to lead carbonate solids; phosphate addition for corrosion control can be effective in reducing lead solubility. Additionally, Arnold et al. (2011) demonstrated that higher alkalinity water (250 mg/L $CaCO_3$) with orthophosphate addition (0 to 2 mg/L) decreased lead release (from 2500 to 1000 μg/L) whereas low alkalinity water (12 mg/L $CaCO_3$) with orthophosphate addition increased lead release (from 6000 to 17000 μg/L). Therefore, higher alkalinity water with orthophosphate decreases corrosion.

2.4.3 Monitoring Program

Many types and sizes of drinking water distribution system are subject to corrosion; therefore, it is important for water utilities to carry out a monitoring program. Monitoring programs involve measuring contaminants such as lead and copper at the tap in order to determine population exposure and assess corrosion within the distribution system (Health Canada, 2009). Health Canada (2009) discusses that corrosion affects leaching of various contaminants, however, the focus should be on lead levels since its presence is most likely to cause adverse health effects. A monitoring program provides information to help determine corrective measures that may need to be taken as well as information on the extent of monitoring to complete in the future. Measuring other parameters such as pH and alkalinity along with metal concentrations are important in order to assess corrosion and provide information towards possible corrective measures. If monitoring determines lead levels to be above action levels, corrective measures will need to be undertaken. Once these measures are in place continuation of a monitoring program will then assess the effectiveness of the corrosion control program.

There are two main settings to consider when monitoring for lead (Health Canada, 2009): residential and non-residential. Residential settings include single family homes and multiple family dwellings. In this case monitoring assesses lead levels throughout the system and identifies sources of lead in both the distribution system as well as residential plumbing. Non-residential settings include child care centers and schools. Unlike residential settings, monitoring focuses solely on the source of lead throughout the plumbing system within the building. The overall purpose for residential monitoring is to identify and detect systems where corrosion is an issue and determine the best corrective measures. On the other hand, the overall purpose for non-residential settings is to detect specific lead issues and determine where and how to continue with corrective measures.

It is important to note that although utilities are not responsible for the residential plumbing system beyond the property line, discussed in Section 2.4.1, drinking water that reaches consumers tap must still meet action level guidelines (Health Canada, 2009). Therefore, corrosion control programs are required to ensure that drinking water is safe to consume even after passing through all components of the distribution system including the plumbing system. If a monitoring program detects the source of lead to be located within the plumbing system and the homeowner is not willing to replace the piping, the utility may need to alter their treatment process in order to improve overall drinking water quality.

CHAPTER 3 EFFECT OF ORTHOPHOSPHATE ON METALS RELEASE IN BENCH SCALE PARTIAL LEAD SERVICE LINE REPLACEMENTS

3.1 Introduction

Lead was a common component used in distribution systems for many years in Canada. All provinces and territories are required to follow the National Plumbing Code of Canada (NPC) which sets all plumbing regulations (Health Canada, 2009). According to the NPC, lead was an acceptable material used in service lines until 1975. The use of lead solders in new plumbing or in repairs to plumbing was officially prohibited in 1990 (Health Canada, 2009). Under the NPC, lead-free solders are permitted to contain up to a maximum of 0.2 % lead (NRCC, 2005). Copper plumbing with lead tin solders were widely used in distribution systems in Canada until 1989. Additionally, brass faucets and fittings were also used in plumbing systems (Churchill et al., 2000). Although lead solders and service lines have been banned since 1990, they are still of concern since many are still in service in older buildings. Lead may leach into drinking water throughout the distribution system via water mains, service lines, soldered joints, lead in brass fittings, valves, etc. (Health Canada, 2009).

Full service replacement of lead service lines can reduce lead levels. However, partial lead service line replacement can increase risks associate with galvanic corrosion and subsequent lead release. The utility owns the service line running from the water main to the property line as shown in Figure 3.1 below (Number 2), whereas the customer owns the line running from the property line to their home (Number 4). It is the customer's responsibility to replace the line on their private property. Water utilities replace their older lead lines with newer lines typically composed of copper; the customer does not always replace their line due to cost (Halifax Water, 2014). As a result, lead and copper lines are joined (Figure 3.1) which may cause an increase in galvanic corrosion. An increase in lead and copper concentrations at consumers' taps poses a public health concern. Lead levels are of concern due to its negative effects on neurological development in children (Barn et al., 2014); copper ingestion can cause temporary gastrointestinal symptoms (Pizarro et al., 2001) but is mainly an aesthetic concern. The increase in galvanic corrosion following partial lead service line replacements may require implementation of corrosion control programs to reduce public health risks.

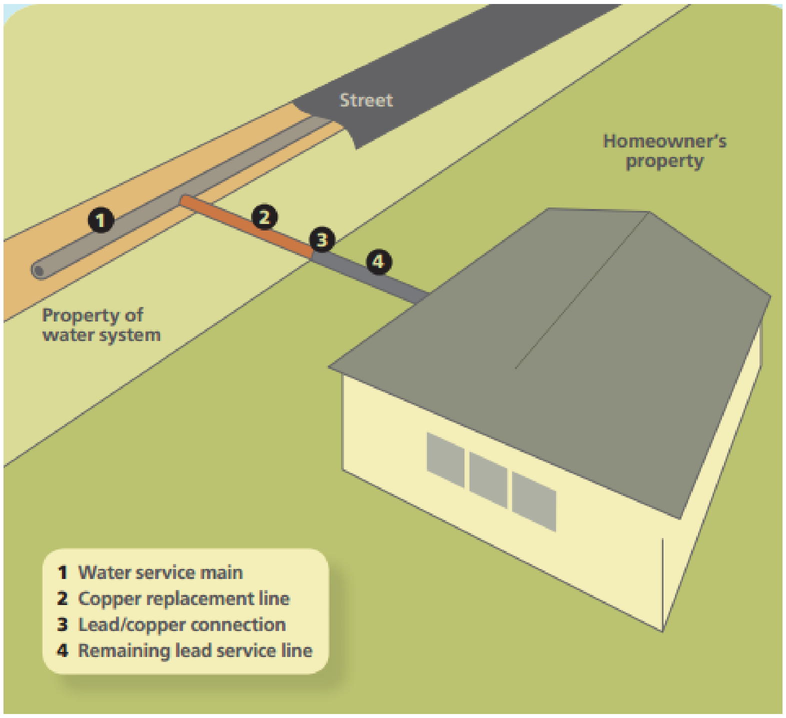

Figure 3.1: Partial lead service line replacement (Renner, 2010)

Orthophosphate corrosion inhibitors and pH are two factors that affect both lead and copper corrosion. Addition of phosphate increases passivity of a metal by creating a protective insoluble film on the inside of the distribution system thus preventing metals from dissolving in drinking water (United States Environmental Protection Agency, 2011). The adjustment of pH alters the solubility of metals within drinking water. Lower pH favors dissolution of lead while higher pH favors formation of protective scales that prevent corrosion (Crittenden et al., 2012). Thus, increasing the pH reduces the solubility of corrosion by-products.

The goal of this experiment was to study the effects of orthophosphate and pH on metal release in lead and copper pipe joined via a copper fitting which simulates a partial lead service line replacement. Two doses of orthophosphate were applied using two water sources and two pH levels. The impacts of both orthophosphate and pH on lead and copper release were studied.

3.2 Materials and Methods

3.2.1 Source Water

Two different water sources were used throughout this experiment. A filtered surface water and a raw groundwater source both located in Nova Scotia, Canada. The water quality of each water is displayed in Table 3.2.1 below.

Table 3.2.1: Comparison water quality characteristics for Experimental Water Sources

	Surface Water	Groundwater
Turbidity (NTU)	0.14 ± 0.05	0.36 ± 0.09
TOC (mg/L)	2.18 ± 0.76	0.37 ± 0.10
DOC (mg/L)	1.77 ± 0.56	0.41 ± 0.13
Chloride (mg/L)	4.85 ± 0.44	148.79 ± 6.80
Sulphate (mg/L)	25.79 ± 2.51	18.97 ± 3.57
CSMR	0.19 ± 0.03	8.11 ± 1.49
Alkalinity (mg/L as $CaCO_3$)	12.8 ± 7.75	54.5 ± 8.83

3.2.2 Experimental Design

Harvested pipe sections consisting of lead pipes fixed to copper pipes via a copper fitting were used for a static dump-and-fill bench scale study. The pipes were harvested from the distribution system within the Halifax Regional Municipality. A total of 12 pipe sections were used, 6 for each water source. Pipes were placed horizontally on a laboratory bench during treatment. Chlorine was added to both water sources at a dose of 1.0 mg/L. Additionally, sodium hydroxide was used to adjust pH levels. Two pH levels of 7.5 and 9.5 were used since this is the optimal pH range for lead control (Health Canada, 2007). Prior to the addition of a corrosion inhibitor, pipes were conditioned for two months from September 6th 2014 to November 6th 2014, similar to other studies (Wang et al., 2012) in order to allow for metals stabilization. Both the addition of phosphate and sampling of the effluent began on November 6th 2014. Two orthophosphate doses of 0.5 and 2.0 mg/L were used at each pH level. The experimental set up included four treatment conditions applied to each water source discussed in Section 3.2.3.

3.2.3 Experimental Set Up

Harvested pipe sections displayed in Figure 3.2.3 were used for a dump-and-fill method using two water sources, two pH levels of 7.5 and 9.5 and two orthophosphate doses of 0.5 and 2.0 mg/L. The conditions are outlined in Table 3.2.3 below.

Figure 3.2.3: Harvested pipe sections undergoing treatment

Table 3.2.3: Conditions for the Dump-and-fill method

	Surface Water Orthophosphate Dose (mg/L)	**Groundwater** Orthophosphate Dose (mg/L)
pH 7.5	0.0 (Control)	0.0 (Control)
	0.5	0.5
	2	2
pH 9.5	0.0 (Control)	0.0 (Control)
	0.5	0.5
	2	2

3.2.4 Sampling

Effluent from each pipe section was collected on Monday's and Thursday's. Sampling began November, 2014 and went until the end of October 2015. Parameters measured on a weekly basis were: pH, turbidity, dissolved copper and lead concentrations, total copper and lead concentrations, phosphate and temperature. Since stagnation time was not a factor evaluated in this study, total and dissolved lead and copper concentrations were measured on Monday's while all other parameters including pH, turbidity, phosphate and temperature were measured on Thursday's. Thus, the stagnation period for metal concentrations was 96 hours whereas the stagnation period for the other parameters was 72 hours. Chloride and sulphate were measured seasonally (2 to 3 samples per season). Total organic carbon and dissolved organic carbon were also measured on the source water on a seasonal basis. Glass beakers washed in antibacterial soap and rinsed with milli-Q three times were used to collect samples for pH, turbidity, temperature, phosphate, chloride and sulphate. Suspected particulate lead was observed at the bottom of numerous beakers during sample collection (Figure 3.2.4). Polypropylene 250 mL bottles rinsed in a concentrated nitric acid bath for at least 24 hours then rinsed with milli-Q three times were used to collect samples for metals analysis. Once the sample was poured into the polypropylene bottles, a 10 mL aliquot was immediately syringe filtered for dissolved metals, and the rest of the sample was preserved with concentrated nitric acid for at least 24 hours. A 20 mL sample was then collected for nitric acid heat digestion to analyze for total metals. Samples for chloride and sulphate analysis were transferred directly from the beakers into a 10 mL ion chromatography vial.

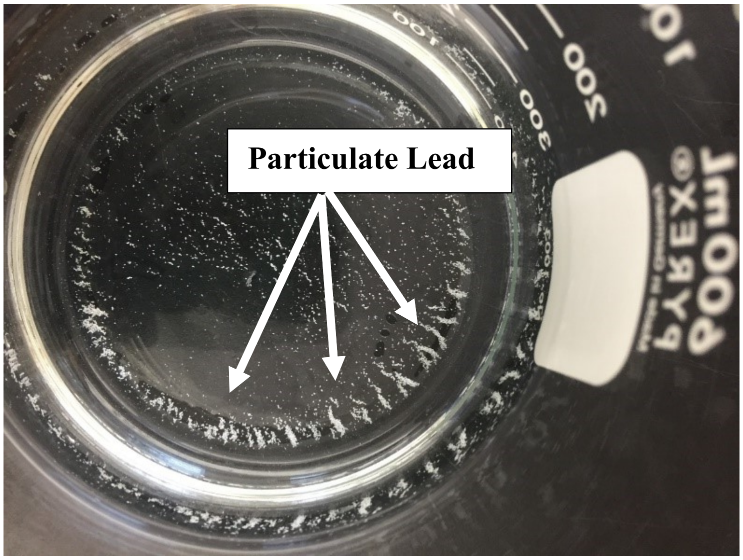

Figure 3.2.4: Suspected particulate lead observed during sample collection

3.2.5 Analytical Methods

The pH was analyzed using an Accumet XL50 dual channel probe (Fisher Scientific, U.S.A.) according to the manufacturer's instructions. Temperature was measured using a thermometer. Turbidity was measured using the HACH 2100N Turbidimeter (HACH, CO, U.S.A.) according to the manufacturer's instructions. Phosphate was measured using a DR 4000 UV-Spectrophotometer (HACH, CO, U.S.A.) according to the manufacturer's instructions. Sulphate, and chloride were measured using a 761 Compact IC (Metrohm, Herisau, Switzerland). The detection limit for chloride and sulphate were 0.6 mg/L and 0.5 mg/L, respectively. Total and dissolved organic carbon were analyzed using a Shimadzu TOC-VCSH TOC Analyzer. Lastly, all total metals samples were prepared by using nitric acid heat digestion. The concentration of metals was analyzed using an X-Series 2 Inductively Coupled Mass Spectrometry (ICP-MS) (Thermo Fisher Scientific, MA, U.S.A.). The limit of detection for copper and lead was 0.7 µg/L and 0.4 µg/L, respectively.

3.2.6 Statistical and Data Analysis

Microsoft Excel (Microsoft, Redmond, WA, U.S.A) was used to organize and analyze data. Additionally, Minitab® software (Minitab® 2010, 17, PA, USA) was used to complete all statistical analysis. The factorial analysis function in Minitab® was used to identify the significance of factors pH and orthophosphate as well as the interaction between pH and orthophosphate on both lead and copper concentrations.

3.3 Results and Discussion

The effluent pH from pipes with an influent treatment pH of 7.5 increased during the stagnation period for both water sources (Figure 3.3.1). However, effluent pH from pipes with an influent treatment pH of 9.5 decreased during the stagnation period. In most cases, pipes with phosphate inhibitor addition had a final pH higher than the control pipes.

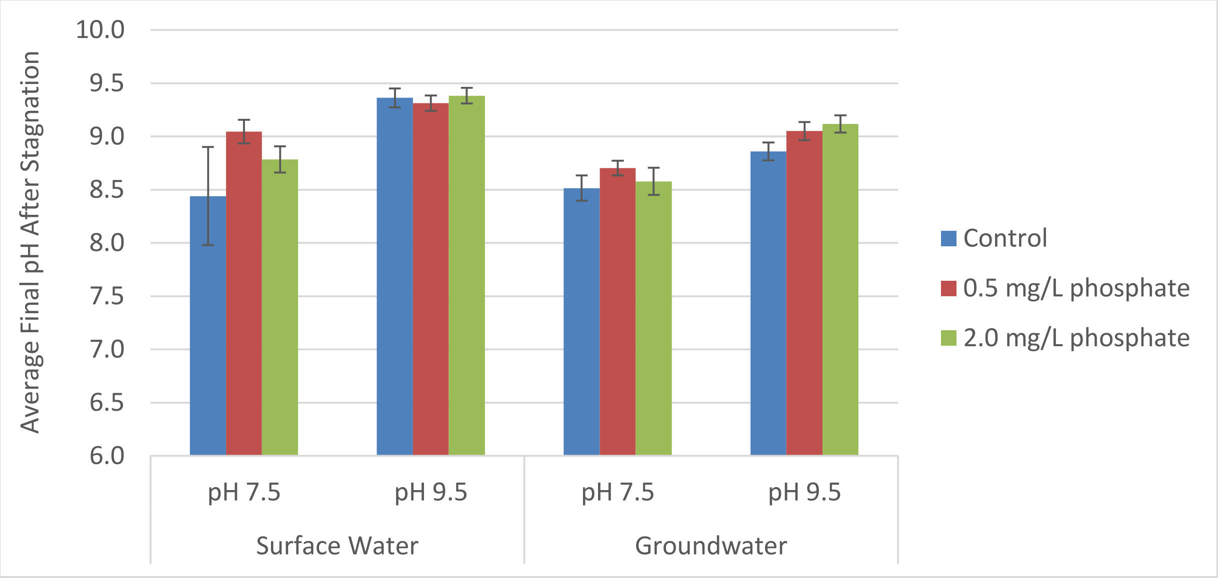

Figure 3.3.1: Final pH after stagnation (Error bars represent the 95% confidence intervals)

During the stagnation period, some soluble phosphate remained in the effluent (Figure 3.3.2). In most cases, treatments with an influent pH of 7.5 contained higher phosphate residuals than treatments with an influent pH of 9.5. Thus, less phosphate was consumed at the lower influent pH of 7.5. Solubility models for lead indicate that the optimal pH for an insoluble phosphate film to form is between 7 and 8 (Schock, 1989). Therefore, there was expected to be a higher consumption of phosphate at treatment of pH 7.5 compared to pH 9.5. Figure 3.3.1 above illustrated that there was an increase in the pH from 7.5 to 8.5 or above after stagnation for both water sources, which is outside of the optimal pH range for the formation of a phosphate based film. Since the initial experimental conditions changed to non-optimal conditions after stagnation, this likely reduced the efficiency of phosphate leading to higher residuals for pH 7.5 than expected.

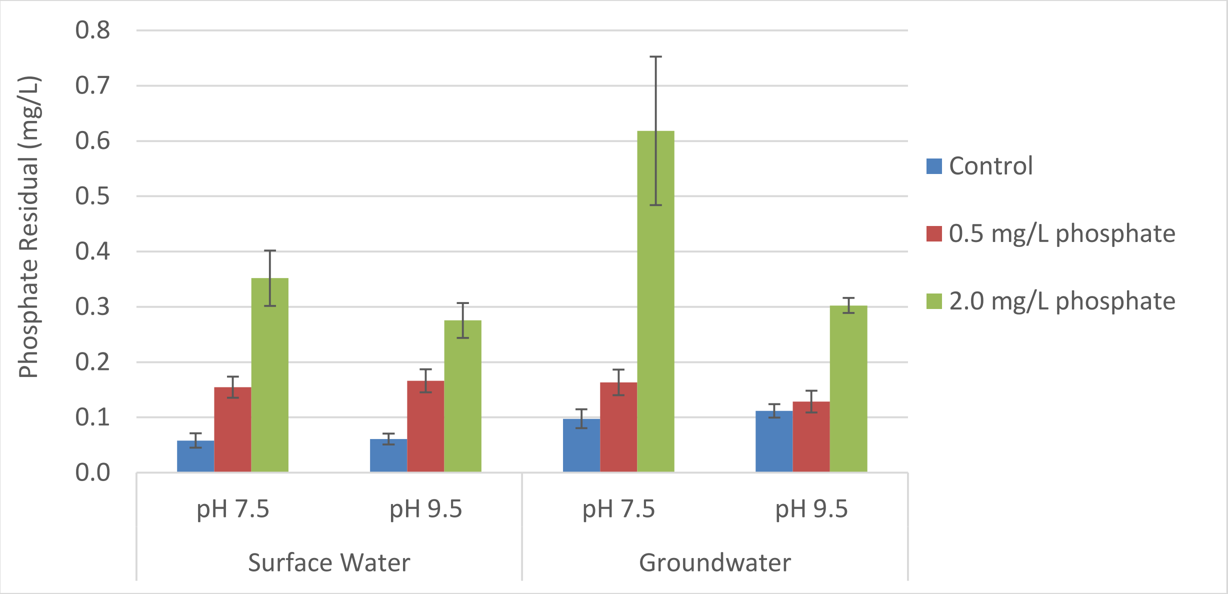

Figure 3.3.2: Phosphate residual after stagnation (Error bars represent the 95% confidence intervals)

Table 3.3.1 displays the turbidity, chloride and sulphate concentrations of the effluent from each treatment after stagnation.

Table 3.3.1: Water quality after stagnation

Treatment		**Turbidity (NTU)**		**Chloride (mg/L)**		**Sulphate (mg/L)**	
pH	Phosphate (mg/L)	Surface Water	Groundwater	Surface Water	Groundwater	Surface Water	Groundwater
7.5	0 (Control)	2.2 ± 1.6	8.5 ± 5.0	5.97 ± 0.93	141.63 ± 12.55	22.72 ± 3.88	17.96 ± 1.75
	0.5	3.0 ± 2.1	3.8 ± 2.7	6.21 ± 1.37	140.71 ± 12.14	22.73 ± 2.48	18.47 ± 2.23
	2	2.3 ± 1.6	12.1 ± 8.4	5.98 ± 1.01	144.50 ± 11.83	24.25 ± 3.21	17.43 ± 1.51
9.5	0 (Control)	2.3 ± 1.8	7.9 ± 5.9	5.48 ± 0.65	144.33 ± 11.27	22.99 ± 1.82	17.60 ± 1.61
	0.5	1.9 ± 1.8	6.8 ± 3.9	6.04 ± 0.84	136.82 ± 11.65	24.32 ± 2.48	17.05 ± 1.45
	2	2.7 ± 2.0	3.2 ± 2.3	5.86 ± 0.59	140.32 ± 10.70	23.59 ± 2.55	17.67 ± 1.30

The chloride concentration for the groundwater ranged from 136.82 to 144.50 mg/L while the chloride for the surface water ranged from 5.48 to 6.21 mg/L. The difference in chloride resulted in a high chloride to sulphate mass ratio (CSMR) for the groundwater source. The CSMR of the effluent after stagnation is displayed in Figure 3.3.3 below.

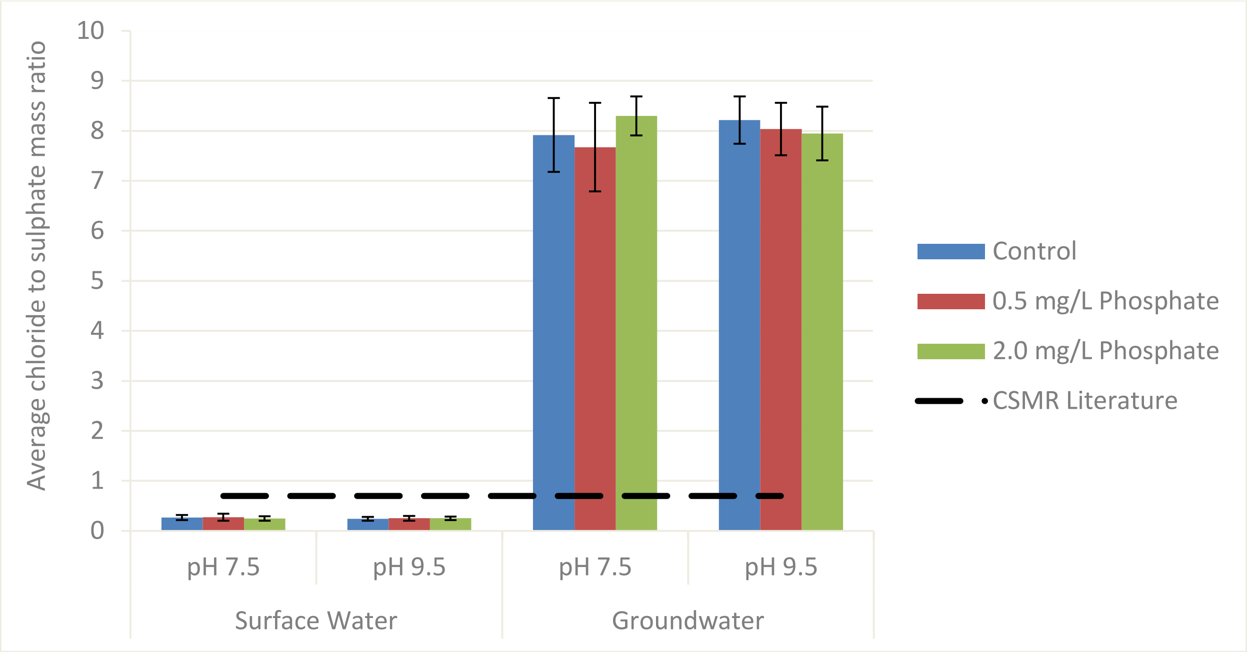

Figure 3.3.3: Average CSMR after stagnation (Error bars represent the 95% confidence interval)

The CSMR of each treatment for the groundwater ranged from 7.7 to 8.3 while the CSMR of each treatment for the surface water ranged from 0.2 to 0.3. The CSMR is used as an indicator of potential for galvanic corrosion (Willison & Boyer, 2012). Bench and field scale studies have shown that higher CSMR values produce higher galvanic currents which leads to higher lead concentrations in drinking water (Edwards & Triantafyllidou, 2007; Nguyen et al., 2011). Accumulation of chloride near the anode surface can form a soluble $PbCl^+$ complex increasing lead concentrations, however accumulation of sulphate at the anode surface can form an insoluble $PbSO_4$ solid thereby reducing lead concentrations (Willison & Boyer, 2012). Literature states that a CSMR greater than 0.7 contributes to increased galvanic corrosion between copper and lead (Nguyen et al., 2011). Overall, the CSMR for the groundwater source was much higher than the literature criteria of 0.7.

The total and dissolved lead concentrations measured after stagnation are displayed in Table 3.3.2. Overall the total lead concentrations were higher for the groundwater treatments which ranged from 5937.6 to 8722.5 µg/L compared to the surface water treatments which ranged from 2203.1 to 4141.5 µg/L. The higher lead levels for the groundwater treatments were expected due to the higher CSMR values calculated in the groundwater compared to the surface water test pipes. Although the surface water was under the recommended CSMR of 0.7, the total lead concentration measured in the effluent was still high. The total lead from both the surface water and groundwater test pipes did exceed the MAC guideline of 10 µg/L. Additionally, higher variability in the lead concentrations was found in the groundwater test pipes. Table 3.3.2 also displays the lead was primarily in particulate form.

Table 3.3.2: Total and dissolved lead concentrations with standard deviation after stagnation

Source Water	pH Treatment	Phosphate Dose (mg/L)	Total Lead (µg/L)	Dissolved Lead (µg/L)
Surface Water	7.5	0 (Control)	2543.5 ± 1696.9	166.8 ± 76.7
		0.5	4141.5 ± 1785.5	186.4 ± 125.5
		2.0	2832.8 ± 1883.6	196.0 ± 138.0
	9.5	0 (Control)	3052.6 ± 1149.1	196.1 ± 170.6
		0.5	2203.1 ± 797.6	149.3 ± 85.0
		2.0	2426.2 ± 804.5	119.1 ± 78.4
Groundwater	7.5	0 (Control)	6077.1 ± 4450.5	248.8 ± 210.0
		0.5	4618.9 ± 1996.6	198.1 ± 122.2
		2.0	8512.1 ± 5070.6	190.4 ± 105.5
	9.5	0 (Control)	7398.1 ± 4961.0	219.2 ± 191.9
		0.5	8722.5 ± 8440.8	165.9 ± 103.1
		2.0	5937.6 ± 3508.7	185.5 ± 96.6

A factorial analysis was completed of all data from the experiment including all three factors (source water, pH and orthophosphate). The analysis revealed that the source water had a significant effect on total lead (P = 0.000) while the effects of pH (P = 0.688) and orthophosphate (P = 0.940) alone did not. The interaction between pH and orthophosphate also had a significant effect on total lead released (P = 0.021) as well as the interaction between the source, pH and orthophosphate (P = 0.000).

A closer look at the average total lead for both water sources is displayed in Figure 3.3.4. Total lead for the surface water source was lowest at a higher pH of 9.5 with a phosphate dose of 0.5 mg/L while the lowest total lead for the groundwater source was at a pH of 7.5 with a phosphate dose of 0.5 mg/L. Since each source water has different optimal treatments for lead control, optimal treatments for lead control varies depending on the source water quality. Therefore, it is important to carry out bench-scale and/or pilot scale studies in order to determine the optimal treatment for corrosion control in the distribution system.

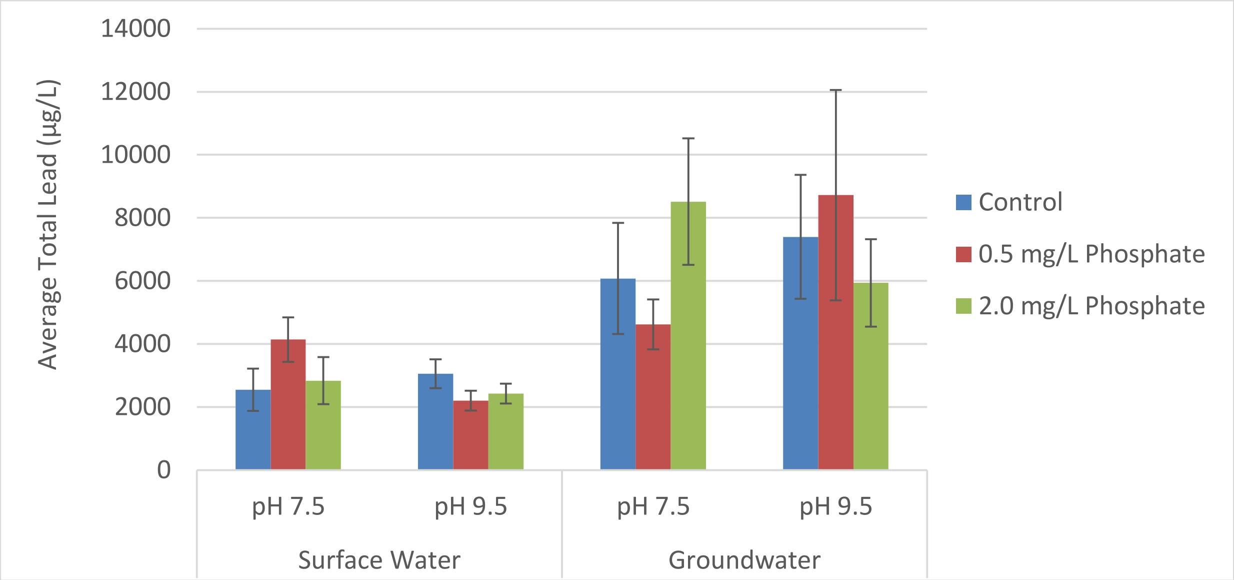

Figure 3.3.4: Average total lead after stagnation (Error bars represent the 95% confidence interval)

A factorial analysis was completed on each water source separately to determine the effects of both pH and orthophosphate. For the surface water source, the analysis revealed that neither pH or orthophosphate alone had a significant effect on total lead released, but the interaction was significant (P = 0.000). Similar results were found for the groundwater source as neither pH or orthophosphate alone were significant but the interaction was (P = 0.004).

Figure 3.3.5 illustrates a closer look at soluble lead release after stagnation. Dissolved lead concentrations for the surface water ranged from 119 to 196 μg/L while dissolved lead concentrations for the groundwater ranged from 166 to 249 μg/L. Dissolved lead concentrations in the pipe effluent were generally lower in the presence of orthophosphate compared to the control without inhibitor except for the surface water source with treatment of pH 7.5. Dissolved lead concentrations were not out of range compared to prior research studies (Schock et al., 1996; Schock, 1989; Edwards et al., 2002). A factorial analysis was completed separately on each water source. The analysis determined that the effects of pH level and/or phosphate addition for both the surface water and groundwater test waters was not significant on the dissolved lead concentrations measured in this set of experiments.

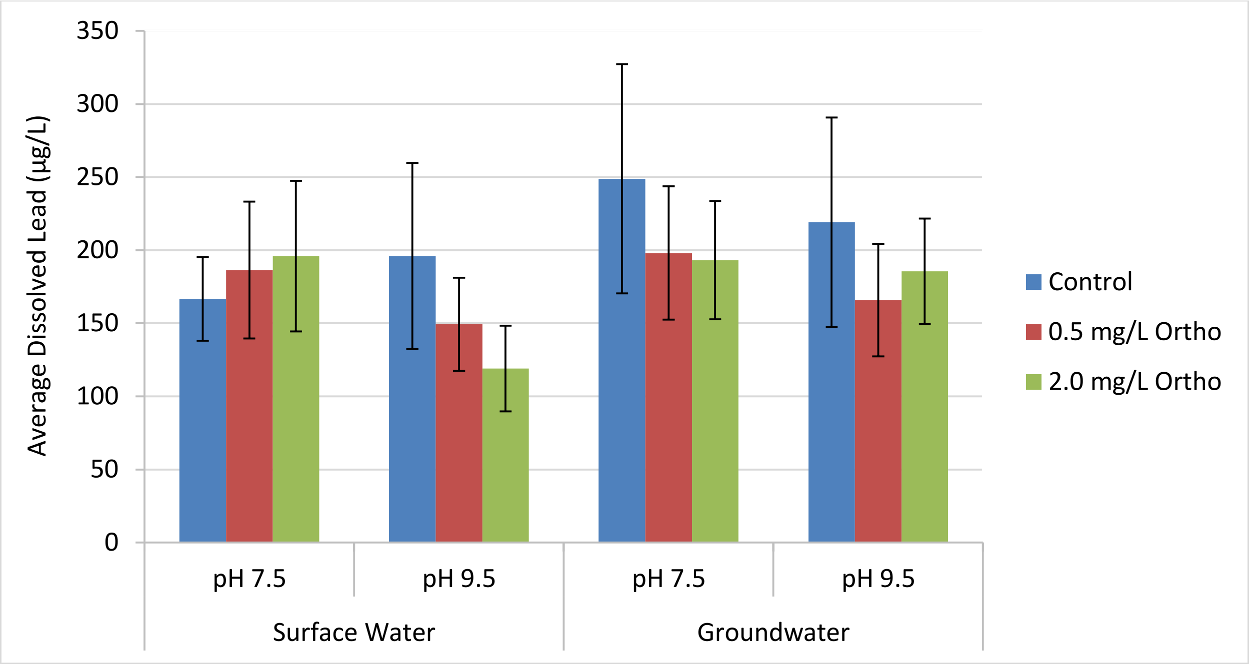

Figure 3.3.5: Average dissolved lead after stagnation (Error bars represent the 95% confidence interval)

The percent change in total lead is displayed in Figure 3.3.6. Percent changes were calculated based on the following equation (Edwards et al., 2002):

$$Percent\ change = \frac{(\text{lead release with inhibitor} - \text{lead release without inhibitor})}{lead\ release\ without\ inhibitor} \times 100\%$$

In this study, percent changes were calculated by pairing each sample with the control at each pH level. Positive percent changes represent an increase in total lead concentrations indicating a detrimental effect. However, negative percent changes in total lead concentrations represent a beneficial effect. Treatment at a pH of 9.5 with 0.5 mg/L resulted in a 16.7% decrease in total lead for the surface water source. Other research by Edwards and McNeill (2002) determined that orthophosphate dosing led to at least a 70 % decrease in total lead release for both 8 and 72 hour stagnation times when the pipe was aged six months. Furthermore, in this study, the addition of phosphate had a detrimental effect on the total lead released for the groundwater source. Figure 3.3.7 displays the percent change in dissolved lead released. The addition of phosphate led to a 19% decrease in the dissolved lead released for the surface water at a pH of 9.5 and a phosphate dose of 2.0 mg/L. However, the addition of phosphate led to an increase in dissolved lead released for the groundwater source.

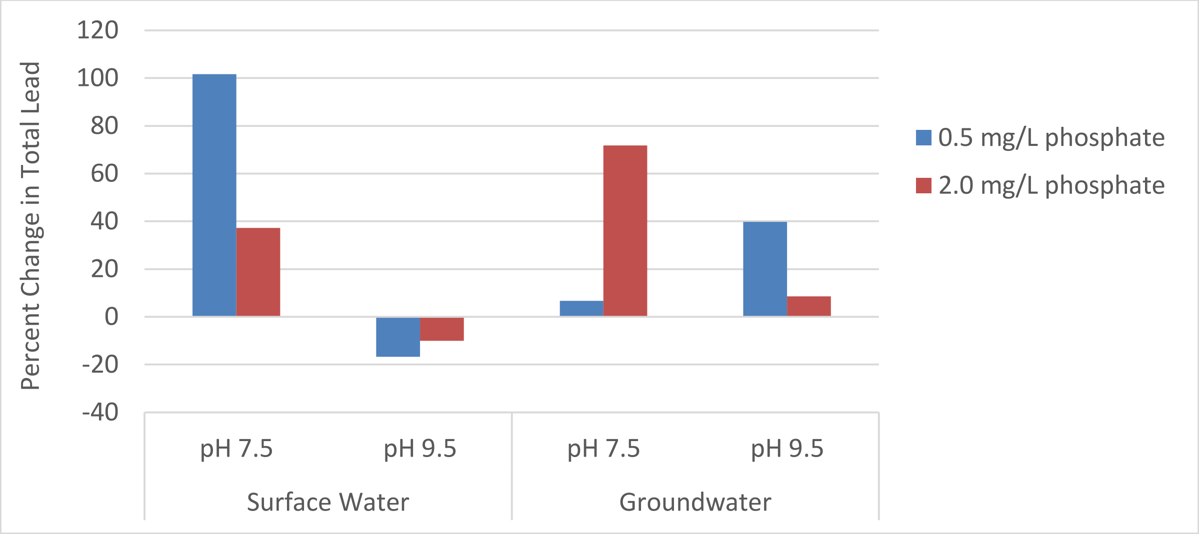

Figure 3.3.6: Percent change in total lead

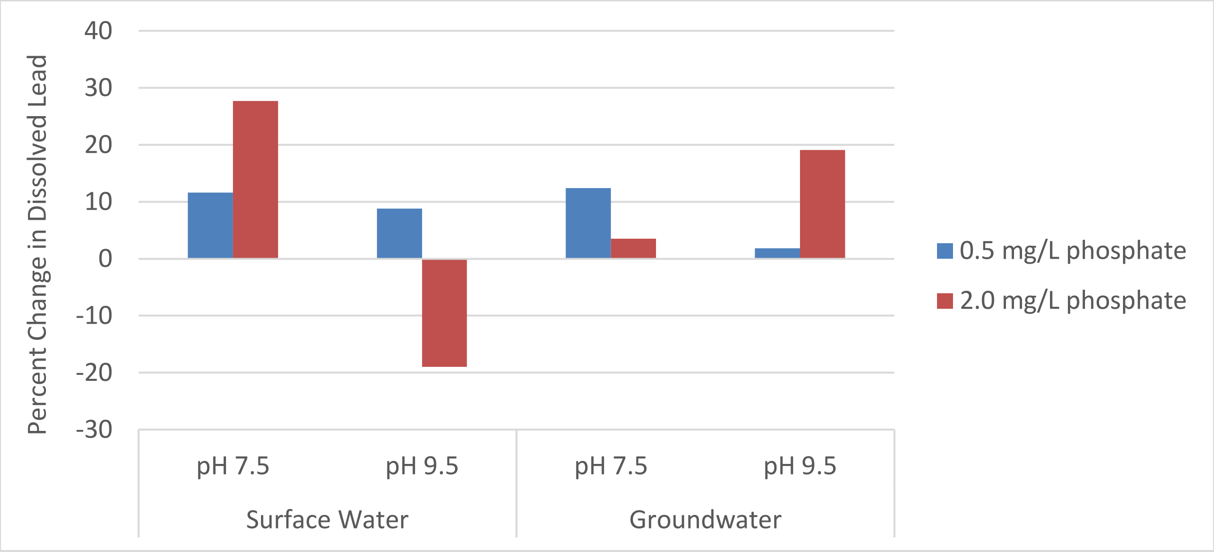

Figure 3.3.7: Percent change in dissolved lead

The average total copper concentrations after stagnation shown in Figure 3.3.8 were all below Health Canada's aesthetic objective of 1000 µg/L (Health Canada, 2014). Total copper concentrations for the surface water ranged from 17.2 to 23.6 µg/L while total copper concentrations for the groundwater ranged from 7.8 to 24.9 µg/L. The addition of phosphate at pH 7.5 increased the total copper concentrations compared to the control without phosphate. However, in general, the addition of phosphate at pH 9.5 decreased total copper concentrations compared to the control. The control without phosphate at pH 7.5 for both water sources resulted in the lowest total copper concentrations, thus was the best treatment for copper corrosion. A factorial analysis was completed on each water source which determined no significant effects on total copper for the surface water but the interaction between pH and orthophosphate was significant (P = 0.027) for the groundwater.

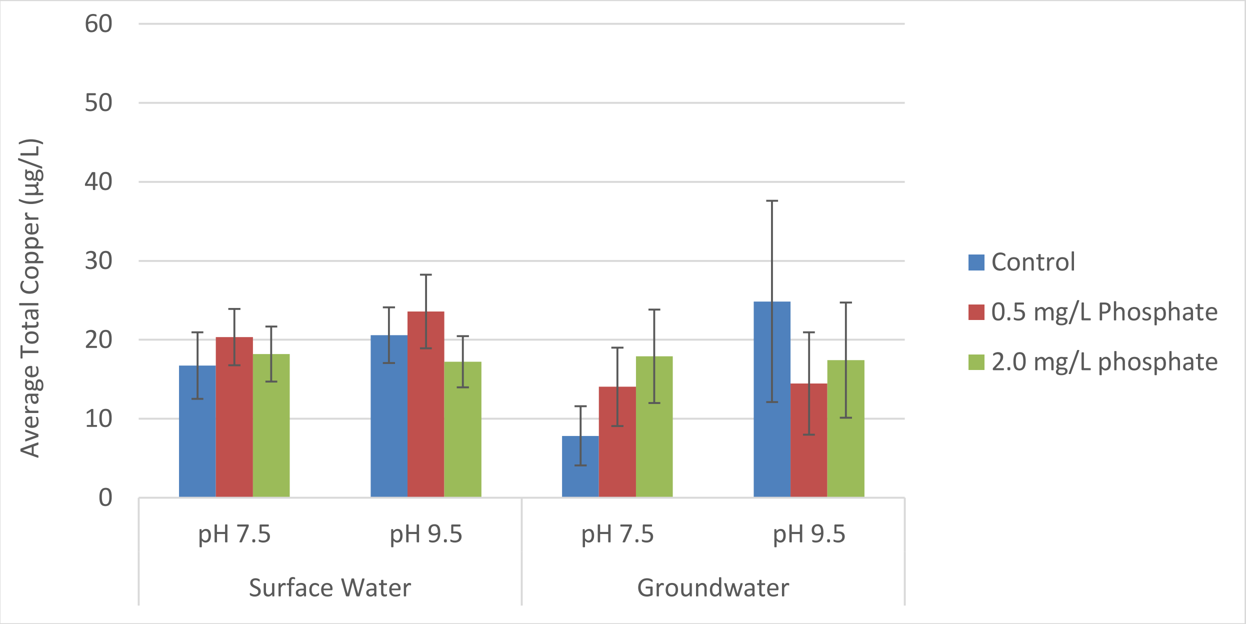

Figure 3.3.8: Average total copper concentrations (Error bars represent the 95% confidence interval)

Figure 3.3.9 displays the dissolved copper levels for both water sources. The dissolved copper levels were low for both sources with all treatments averaging under 10 µg/L. The concentration of dissolved copper for the surface water ranged from 6.5 to 9.5 µg/L while the concentration of dissolved copper for the ground water ranged from 3.05 to 4.66 µg/L. The addition of phosphate at pH 7.5 increased the dissolved concentrations while the addition of phosphate at pH 9.5 decreased the dissolved concentrations which is similar to the trend observed for the total copper concentrations. A factorial analysis completed on each water source separately revealed no significant effects of pH and/or phosphate on dissolved copper for the surface water, however, pH was found to have a significant ($P = 0.019$) effect on dissolved copper concentrations for the groundwater source.

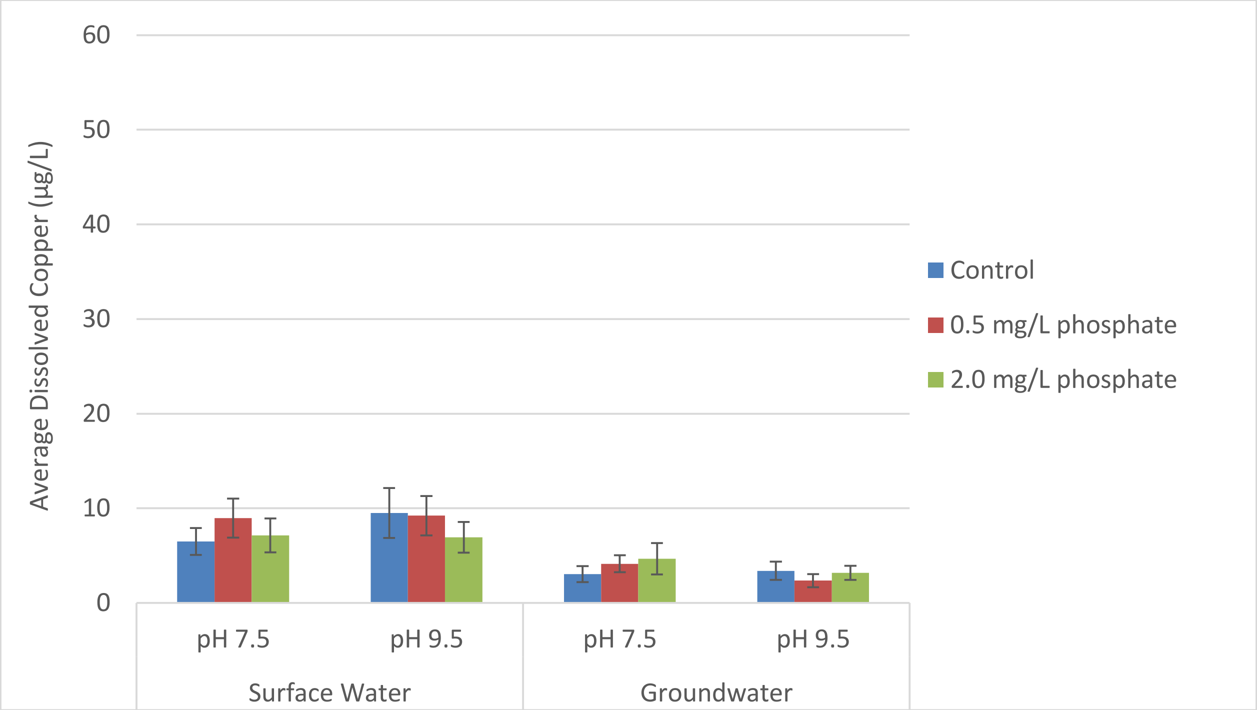

Figure 3.3.9: Average dissolved copper concentrations (Error bars represent the 95% confidence intervals)

3.4 Conclusions

The stagnant dump and fill bench scale experiment was completed using two different water sources (surface water and groundwater), two pH levels (7.5 and 9.5) and two orthophosphate doses (0.5 and 2.0 mg/L) resulted in the following conclusions:

- Higher chloride concentrations resulted in a higher CSMR for the groundwater source. The CSMR for the groundwater ranged from 7.7 to 8.3 while the CSMR for the surface water ranged from 0.2 to 0.3.
- Overall higher total lead concentrations were found for the groundwater treatments which ranged from 5930 to 8720 µg/L compared to the surface water treatments which ranged from 2200 to 4140 µg/L. The higher lead levels for the groundwater treatments were expected due to the presence of a higher CSMR.
- Neither pH or orthophosphate alone had a significant effect on total lead released, but the interaction was statistically significant for both water sources.
- Although the effects of pH and/or phosphate on the dissolved lead for both the surface water and groundwater source were not significant, the dissolved lead concentrations in the pipe effluent were generally lower in the presence of orthophosphate.
- Addition of phosphate resulted in at most a 16.7 % decrease in total lead for the surface water source while the addition of phosphate led to an increase in dissolved lead released for the groundwater source.
- The average total copper concentrations after stagnation for both water sources were all below 25 µg/L which was well below Health Canada’s aesthetic objective of 1000 µg/L (Health Canada, 2014). Neither pH or orthophosphate had a significant effect on total

copper concentrations for the surface water, but the interaction between pH and orthophosphate played a significant role in reducing total copper for the groundwater.

- Dissolved copper concentrations were all under 10 μg/L. No significant effects of pH and/or phosphate were found on dissolved copper concentrations for the surface water, however, pH had a significant effect on reducing dissolved copper concentrations for the groundwater source.

CHAPTER 4 EFFECT OF ORTHOPHOSPHATE ON METALS RELEASE AND BIOFILM FORMATION IN SIMULATED DRINKING WATER SYSTEMS

4.1 Introduction

Corrosion of lead and copper is a major challenge many water utilities face worldwide. The principle concerns for a water utility are: (1) corrosion of the distribution system pipes may lead to water leakage and loss of hydraulic capacity due to the accumulation of corrosion products and (2) premature pipe failure (Tam & Elefsiniotis, 2009). Lead has been recognized as a toxin in the human body that can cause irreversible damage to the nervous system and lead to neurological complications especially in infants and children. To minimize possible exposure to lead and copper, corrosion control programs have been implemented. A corrosion control program may involve addition of orthophosphate or adjustment of pH.

Addition of phosphate increases passivity of a metal by creating a protective insoluble film on the inside of pipe surfaces thereby reducing corrosion (United States Environmental Protection Agency, 2011). A water utility survey reported that 56% of utilities in the U.S were adding phosphate based inhibitors in 2001 (McNeill et al., 2002). Reported phosphate doses ranged from less than 0.2 mg/L to greater than 3 mg/L. The survey reported that 84% of utilities were dosing phosphate inhibitors to control lead or copper corrosion.

Phosphate based corrosion inhibitors may reduce corrosion in drinking water distribution systems but the effects on biofilm formation also need to be considered. Biofilms are composed of a collection of cells entrapped within a gelatinous matrix (Fang et al., 2009). The cells excrete insoluble exopolysaccharides (EPS) which forms the majority of the matrix. Production of EPS is critical for biofilm formation since it protects cells, traps nutrients and binds water (Sutherland, 2001). External environmental conditions which affect biofilm formation in the drinking water distribution system include nutrient levels, pipe material, water temperature and flow velocity, etc. (Fang et al., 2009). Phosphate has been proven to increase biofilm growth within the distribution system (Chu et al., 2005; Hozalski et al., 2005; Fang et al., 2009) since phosphorous acts as a nutrient; addition as low as 3 μg/L increased biofilm growth. However, many other studies have proven the addition of phosphate to show contradictory results; addition of 1 to 2 mg/L had no impact on biofilm formation in a full-scale distribution system and led to a decrease in biofilm in an annular reactor study (Rompre et al., 2000). Furthermore, Batte et al. (2003) found the addition of 500 μg/L phosphorous in an annular reactor system had no impact on biofilm growth. Fang et al. (2009) also determined that phosphorous addition might decrease both stability and homogeneity of the biofilm in the simulated drinking water distribution system which can lead the biofilm to become less resistant to disinfectants. So, although the addition of phosphate may lead to an increase in biofilm growth, the biofilm structure may become less stable thus more susceptible to disinfectants.

Adjustment of pH levels in the drinking water distribution system is another method commonly used by water utilities for corrosion control of lead and copper. The deposition of calcium carbonate can be managed by adjustment of pH and is a key variable in the solubility of lead and copper (Crittenden et al., 2012). Lower pH favors dissolution of lead while higher pH favors formation of protective scales that prevent corrosion (Crittenden et al., 2012). Thus, adjustment of pH can determine whether an insoluble protective scale will form (passivity) or whether corrosion will be favored. Increasing the pH reduces the solubility of corrosion by-products which in turn reduces the concentration of lead and copper levels in drinking water. Dudi and Edwards (2004) confirmed that lead released at a pH of 7.5 was significantly higher than lead released at a pH of 8.5. The lowest levels of lead measured at the tap have been found in waters with a pH above 8 (Dodrill & Edwards, 1995; Douglas et al., 2004).

The objective of this study was to use bench scale annular reactors (operated under conditions relevant to drinking water) to evaluate the effectiveness of orthophosphate and pH on both metals released and biofilm formed. Two doses of orthophosphate and two levels of pH were applied to the reactors to study the effects on lead and copper released as well as biofilm formed.

4.2 Materials and Methods

4.2.1 Source Water

A groundwater source located in Nova Scotia was used throughout the study with water quality displayed in Table 4.2.1.

Table 4.2.1: Groundwater source water quality

Parameters	Groundwater
pH	6.91 ± 0.43
Turbidity (NTU)	0.36 ± 0.09
TOC (mg/L)	0.37 ± 0.10
DOC (mg/L)	0.41 ± 0.13
Chloride (mg/L)	148.79 ± 6.80
Sulphate (mg/L)	18.97 ± 3.57
CSMR	8.11 ± 1.49

4.2.2 Experimental Design

Raw groundwater was fed into three annular reactors (BioSurface Technologies Corporation, USA) consisting of a stationary outer cylinder made of glass and a rotating inner cylinder made of polycarbonate (Fang et al., 2009). Each annular reactor housed twenty copper coupons with 50:50 lead tin solder (Figure 4.2.2) on the external surface of the inner rotating cylinder. Each reactor contained a total volume of 1000 mL and the hydraulic retention time was set at six hours as Health Canada recommends a six-hour stagnation time prior to sampling for lead (Health Canada, 2009). The hydraulic retention time was achieved by adjusting the total influent flow rate to 2.78 mL/min. All reactors were operated at a rotational speed of 50 rpm in order to achieve a simulating shear stress of 0.25 N/m^2 corresponding to a flow of 0.3 m/s, similar to other bench scale distribution system studies (Gagnon & Slawson, 1999; Jang et al., 2011; Zhu et al., 2014). Moreover, each reactor was covered with aluminum foil in order to reduce phototropic growth in the simulated drinking water distribution system (Zhu et al., 2014); the reactors were also placed in a dark lab with no windows.

Figure 4.2.2: Coupons with 50:50 lead tin solder prior to corrosion

Prior to experimental use, the annular reactors were cleaned with Liquinox soap and rinsed with milli-Q. Coupons were also cleaned with antibacterial soap, rinsed with milli-Q three times and then placed in the slots of the inner rotating cylinder within each annular reactor. The reactors containing the coupons were then flushed with 70% ethanol for 24 hours prior to use. All tubing was set up and also flushed with ethanol for 24 hours. Once the reactors were flushed with ethanol, they were flushed with aquifer water for two days. Each reactor was acclimated with raw groundwater as the only influent for three months from September, 2014 to November, 2014 in order to ensure biofilm growth. Sodium hydroxide was added in AR2 and AR3 on November 24, 2014 in order to begin pH adjustment. AR1 was the control with no pH adjustment, AR2 was adjusted to a pH of 7.5 while AR3 was adjusted to a pH of 9.5. Orthophosphate was added in AR2 and AR3 at a dose of 0.5 mg/L on November 27, 2014. Chlorine was then added to the three annular reactors on January 28, 2016 to achieve a goal residual of 0.8 mg/L throughout the experiment. Orthophosphate was later increased in AR2 and AR3 to a dose of 2.0 mg/L on August 14, 2015 for the remainder of the experiment.

Coupons were removed for biofilm and metals analysis; one coupon was removed from each AR on a weekly basis. All 20 coupons in each AR were not retrievable due to corrosion; a total of 14 coupons were removed from each AR. Since AR2 and AR3 were treated with two phosphate doses, 7 coupons were removed at each dose.

4.2.3 Experimental Setup

Three annular reactors were set up as shown in Figure 4.2.3 below. The raw groundwater and solutions were fed into the reactors via a peristaltic pump. Table 4.2.3 summarizes the experimental conditions of each AR.

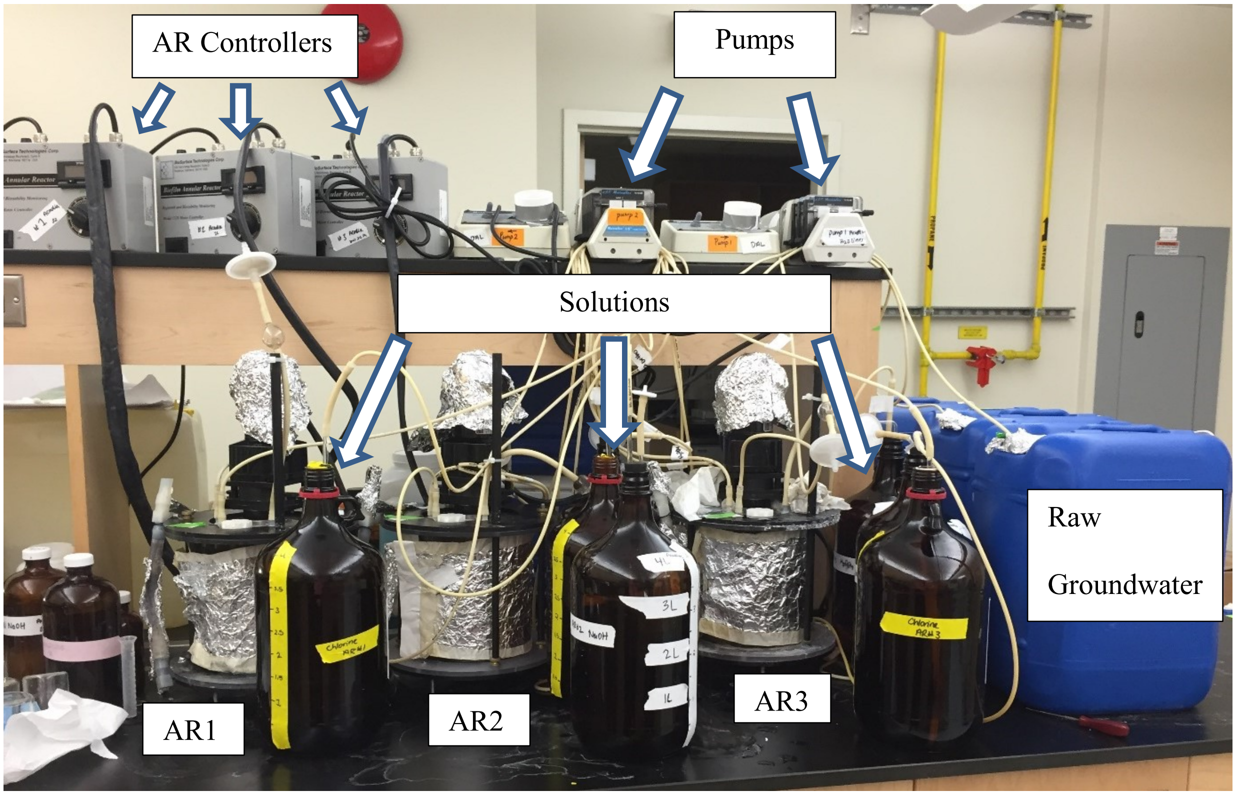

Figure 4.2.3: Annular reactor experimental set up

Table 4.2.3: Summary of AR experimental conditions

	AR1	***AR2***	***AR3***
pH	No adjustment	7.5	9.5
Phosphate dose (mg/L)	0	0.5; later increased to 2.0	0.5; later increased to 2.0
Chlorine residual goal (mg/L)	0.8	0.8	0.8

4.2.4 Sampling

During the acclimation period (no chlorine addition), pH, temperature, turbidity, phosphate and bulk water ATP were measured on a weekly basis. After the acclimation period (addition of chlorine), effluent residual chlorine was measured twice a week to maintain the goal residual of 0.8 mg/L. Additionally, parameters measured on a weekly basis were: pH, turbidity, dissolved copper and lead concentrations, total copper and lead concentrations, phosphate and temperature. Chloride and sulphate were measured seasonally (2 to 3 times per season) from September 2014 to May 2015. Bulk water ATP was completed on a bi-weekly basis; coupons were removed on a weekly basis for ATP and metals analysis. Additionally, alkalinity, total organic carbon and dissolved organic carbon were measured on a seasonal basis (2 to 3 times per season). Glass beakers washed in antibacterial soap and rinsed with milli-Q three times were used to collect samples for pH, turbidity, phosphate and temperature. Plastic 250 mL bottles rinsed in a concentrated nitric acid bath, then rinsed with milli-Q three times and dried in a dust free area were used to collect samples for metals analysis. Once the 250 mL sample was collected, a 10 mL sample was immediately filtered using a syringe and filter apparatus for dissolved metals analysis. Then, the rest of the sample was preserved with concentrated nitric acid for at least 24 hours before a 10 mL sample was collected for total metals analysis. Ion chromatography vials were rinsed with milli-Q three times and used to collect samples for chloride and sulphate for ion chromatography analysis.

Coupons were removed for biofilm and metals analysis at each dose of orthophosphate. The outside of each AR and bench were sprayed with ethanol and allowed to dry prior to opening the AR. A flame sterilized screw driver was used as a wedge inside the AR in order to prevent the inside cylinder from displacing off the bearing. A flame sterilized metal hook and clamp were used to remove coupons. The metal hook was placed through the hole of the coupon (Figure 4.2.4a) while the coupon was set up in the AR. A set of flame sterilized plyers were then attached to the metal hook and a hammer was used on the plyers in order to successfully remove the coupons. The screw driver wedge, plyers and hammer were tools required for successful removal of coupons due to the corrosion that occurred. All 20 coupons in each AR were not retrievable due to corrosion; total of 14 coupons were removed from each AR. Since AR2 and AR3 were treated with two phosphate doses, 7 coupons were removed at each dose totaling 14 coupons. One coupon was removed from each AR on a weekly basis.

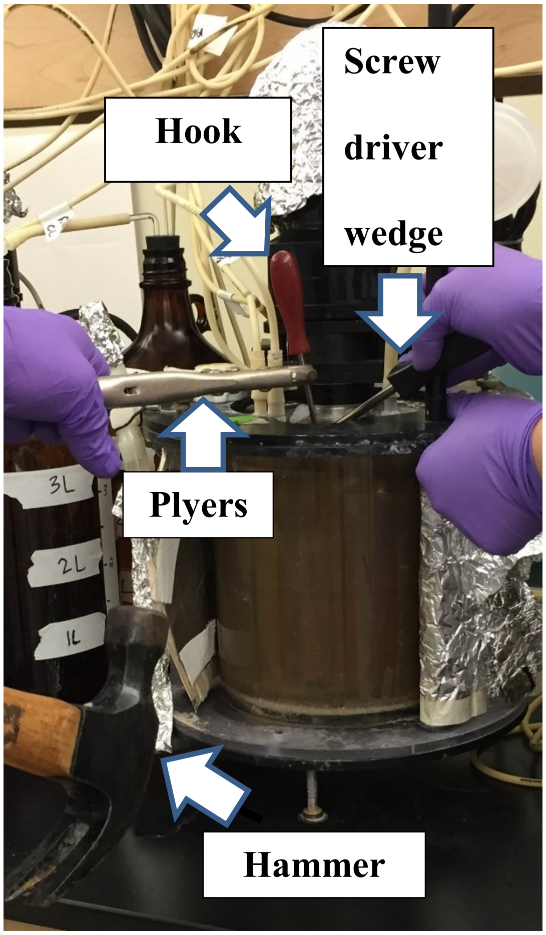

Figure 4.2.4a: Coupon removal method

Figure 4.2.4b: Coupon after being exposed to corrosion

Once a corroded coupon was removed (Figure 4.2.4b) from each reactor, sterile swabs were used to swab the coupon 10 times into 100 mL of sterile milli-Q in a sterile beaker. The solution was then poured into a sterile stomaching bag and stomached at 230 RPM for 2 minutes in a MIX 2 Stomacher (AES Laboratories, Bruz, France). Sterile 50 mL falcon tubes were used to collect the suspended biofilm solution; solution was sampled for ATP and dissolved and total metals. Once coupons were swabbed, they were sprayed with ethanol and cleaned with paper towel. The coupons were then sprayed with ethanol again and allowed to air dry before placing back inside the reactor.

One coupon was removed from each annular reactor using the same method as above at the end of the experiment. Each coupon was dried in a vacuum sealed environment for 24 hours. The coupons were cut and placed in a desiccator until further analysis. Coupons were then mounted on SEM plates using a glue gun and then both SEM and EDS analysis were completed.

4.2.5 Analytical Methods

Effluent pH was analyzed using an Accumet XL50 dual channel probe (Fisher Scientific, U.S.A.) according to the manufacturer's instructions. Temperature was measured using a thermometer. Turbidity was measured using the HACH 2100N Turbidimeter (HACH, CO, U.S.A.) according to the manufacturer's instructions. Free Chlorine and phosphate were measured using a DR 4000 UV-Spectrophotometer (HACH, CO, U.S.A.) according to the manufacturer's instructions. ATP was measured using a Quench-Gone Aqueous test kit from LuminUltra and analyzed using a Lumitester C-100. Sulphate and chloride were measured using a 761 Compact IC (Metrohm, Herisau, Switzerland). Total and dissolved organic carbon were analyzed using a Shimadzu TOC-VCSH TOC Analyzer. Samples for total metals were nitic acid heat digested and then the concentration of metals was analyzed using an X-Series 2 Inductively Coupled Mass Spectrometry (ICP-MS) (Thermo Fisher Scientific, MA, U.S.A.). The limit of detection for copper and lead was 0.7 µg/L and 0.4 µg/L, respectively. SEM and EDS were completed with a Hitachi-S4700 FEG Scanning Electron Microscope with an accelerating voltage of 20 kV and an emission current of 10 µA.

4.2.6 Statistical and Data Analysis

Microsoft Excel (Microsoft, Redmond, WA, U.S.A) was used to organize and analyze data. Additionally, Minitab® software (Minitab® 2010, 17, PA, USA) was used to complete all statistical analysis. The factorial analysis function in Minitab® was used to identify the significance of factors pH and orthophosphate as well as the interaction between pH and orthophosphate on both lead and copper concentrations.

4.3 Results and Discussion

The bulk water chemistry of each annular reactor is displayed in Tables 4.3.1 and 4.3.2 below. The dissolved organic carbon (DOC) in Table 4.3.2 was always slightly higher than the total organic carbon (TOC). Because this was the case, three samples were taken for each sampling date in order to ensure the values were consistent. Since the DOC was higher than TOC, this indicated the organic material present was all in dissolved form and the higher values for DOC are likely due to experimental error.

Table 4.3.1: Bulk water quality average values with standard deviation for each annular reactor

			pH	**Temperature (°C)**	**Turbidity (NTU)**	**Chlorine Residual (mg/L)**	**Phosphate Residual (mg/L)**
Treatment	Chlorine	Phosphate Dose (mg/L)					
Control	No Chlorine	-	7.36 ± 0.43	19.5 ± 2.01	0.280 ± 0.122	-	0.07 ± 0.1
	Chlorine	0	7.66 ± 0.23	21.2 ± 1.64	0.298 ± 0.561	1.17 ± 0.84	0.1 ± 0.06
pH 7.5	No Chlorine	-	7.44 ± 0.35	19.7 ± 2.01	0.261 ± 0.026	-	0.07 ± 0.08
	Chlorine	0.5	7.57 ± 0.29	21.9 ± 1.69	0.216 ± 0.106	0.72 ± 0.57	0.32 ± 0.35
		2.0	7.59 ± 0.13	20.2 ± 0.83	0.252 ± 0.221	1.04 ± 0.45	1.45 ± 0.33
pH 9.5	No Chlorine	-	7.99 ± 0.70	19.7 ± 2.01	0.312 ± 0.230	-	0.08 ± 0.09
	Chlorine	0.5	9.48 ± 0.53	21.9 ± 1.70	0.244 ± 0.160	0.85 ± 0.63	0.49 ± 0.40
		2.0	9.72 ± 0.32	20.2 ± 0.83	0.554 ± 0.415	1.04 ± 0.47	0.86 ± 0.34

Table 4.3.2: Bulk water quality average values with standard deviation measured seasonally for each annular reactor

Treatment	TOC (mg/L)	DOC (mg/L)	CSMR
Control	0.75 ± 0.28	0.84 ± 0.11	7.9 ± 0.6
pH 7.5	0.81 ± 0.39	0.90 ± 0.28	7.8 ± 0.5
pH 9.5	0.62 ± 0.10	0.65 ± 0.10	7.6 ± 0.5

The CSMR for each annular reactor was between 7 and 8 (Table 4.3.2). This value is between 10 to 11 times the recommended criteria of 0.7 (Nguyen et al., 2011). Since the coupons contained 50:50 lead tin solder and were placed in the reactors filled with groundwater of CSMR between 7 and 8 which posed serious concern for lead corrosion (Figure 4.3.1). Thus, an initial assessment indicated that a corrosive environment was present.

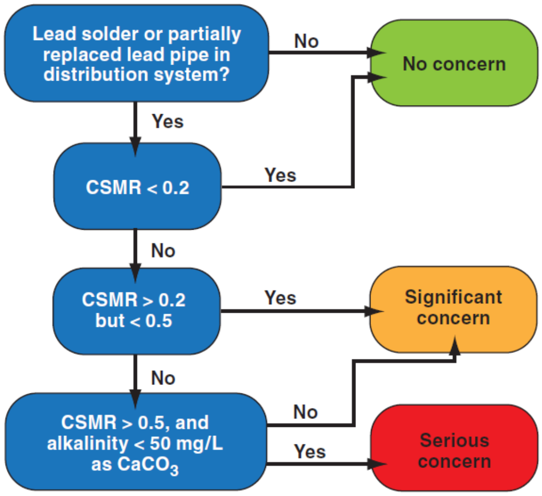

Figure 4.3.1: Level of concern for lead corrosion (Nguyen et al., 2010)

The total and dissolved lead in the effluent is illustrated in Figure 4.3.2. The majority of lead present in water samples analyzed was found to be in the particulate form. Lead particles have been found to be dominant in many studies (Camara et al., 2013; Cartier et al., 2012; Wang et al., 2012). In this study, the experimental conditions of pH 7.5 with 0.5 mg/L phosphate addition resulted in the highest concentration of total lead released (957 µg/L). In contrast, the experimental conditions of pH 9.5 with 2.0 mg/L phosphate addition resulted in the lowest total lead (66.5 µg/L) released compared to all of the other test conditions.

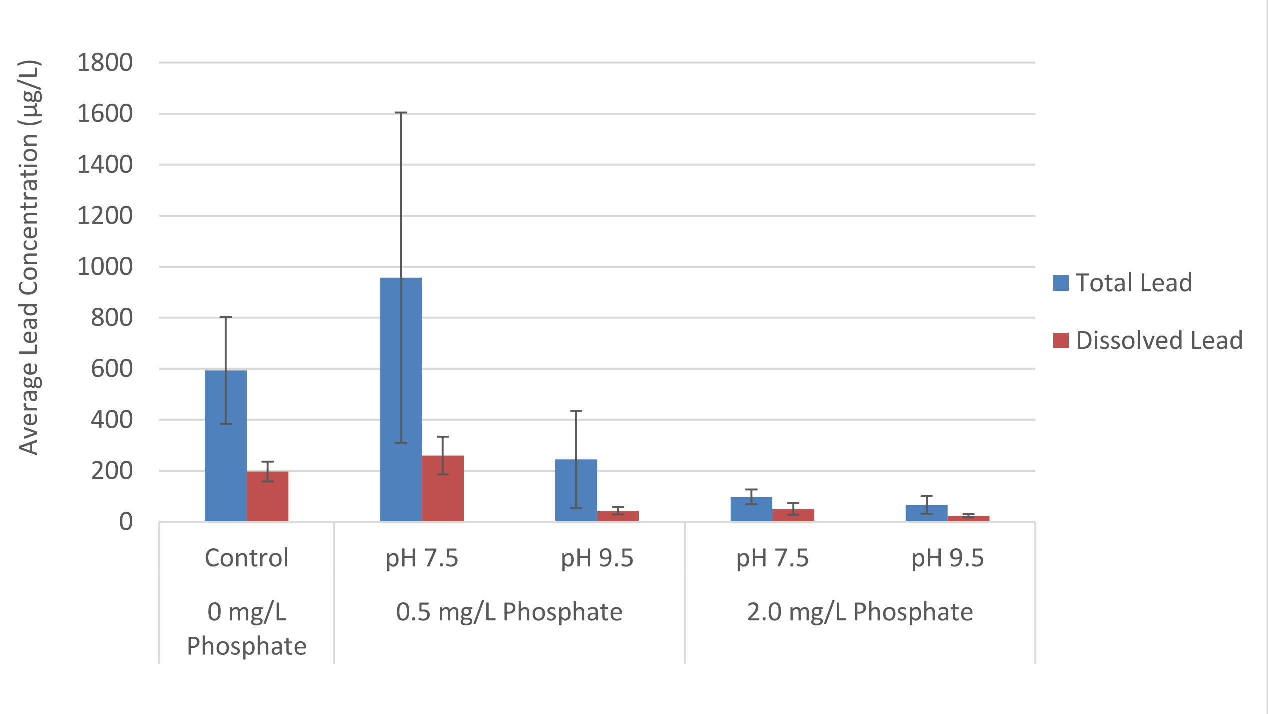

Figure 4.3.2: Effluent total and dissolved lead concentrations (Error bars represent the 95% confidence intervals)

The increase in pH at both doses of phosphate resulted in lower total lead concentrations released (Figure 4.3.2). This is because lower pH favors dissolution of lead while higher pH favors formation of protective scales that prevent corrosion (Crittenden et al., 2012). Research by Dudi and Edwards (2004) demonstrated that lead released at a pH of 7.5 was significantly higher than lead released at a pH of 8.5. Furthermore, Edwards et al. (2002) proved that lead levels decreased up to a pH of 9.5 regardless of pipe age. The lowest levels of lead at the tap have been found in waters with a pH above 8 (Dodrill & Edwards, 1995; Douglas et al., 2004). Hence, results from this bench-scale experiment are consistent with prior research since the lowest lead levels were associated with higher pH treatment.

Figure 4.3.2 also illustrates the increase in phosphate dose from 0.5 mg/L to 2.0 mg/L at both pH levels decreased the amount of total lead released to the bulk water. Addition of phosphate increases passivity of a metal by creating a protective insoluble film on the inside of the pipe surface which can help prevent metals from dissolving in drinking water (United States Environmental Protection Agency, 2011). In this case, phosphate promoted the formation of an insoluble film on the surface of the coupons which aided in reducing corrosion of the 50:50 lead tin solder thus reducing total lead concentrations.

A factorial analysis using the two pH levels (7.5 and 9.5) and two orthophosphate doses (0.5 and 2.0 mg/L) revealed the effect of orthophosphate on total lead was significant ($P = 0.037$). Additionally, one-way ANOVA evaluated the effect of all three doses of orthophosphate on total lead alone to be significant ($P = 0.05$).

A factorial analysis determined that the effect of pH ($P = 0.000$) and orthophosphate ($P = 0.000$) as well as the interaction between the two factors ($P = 0.000$) were all significant in reducing dissolved lead concentrations. Additionally, one-way ANOVA determined the effect of all three doses of orthophosphate on dissolved lead alone to be significant (P = 0.000).

The total and dissolved copper measured in the effluent is illustrated in Figure 4.3.3. The control without phosphate treatment released the highest concentration of total copper (489 µg/L). Treatment of pH 9.5 with 0.5 mg/L phosphate released the lowest amount of total copper (11.1 µg/L). Overall, the increase in pH at each dose of phosphate decreased the total copper concentrations. Research by Dartmann et al. (2010) also determined an increase in pH resulted in a decrease in copper levels.

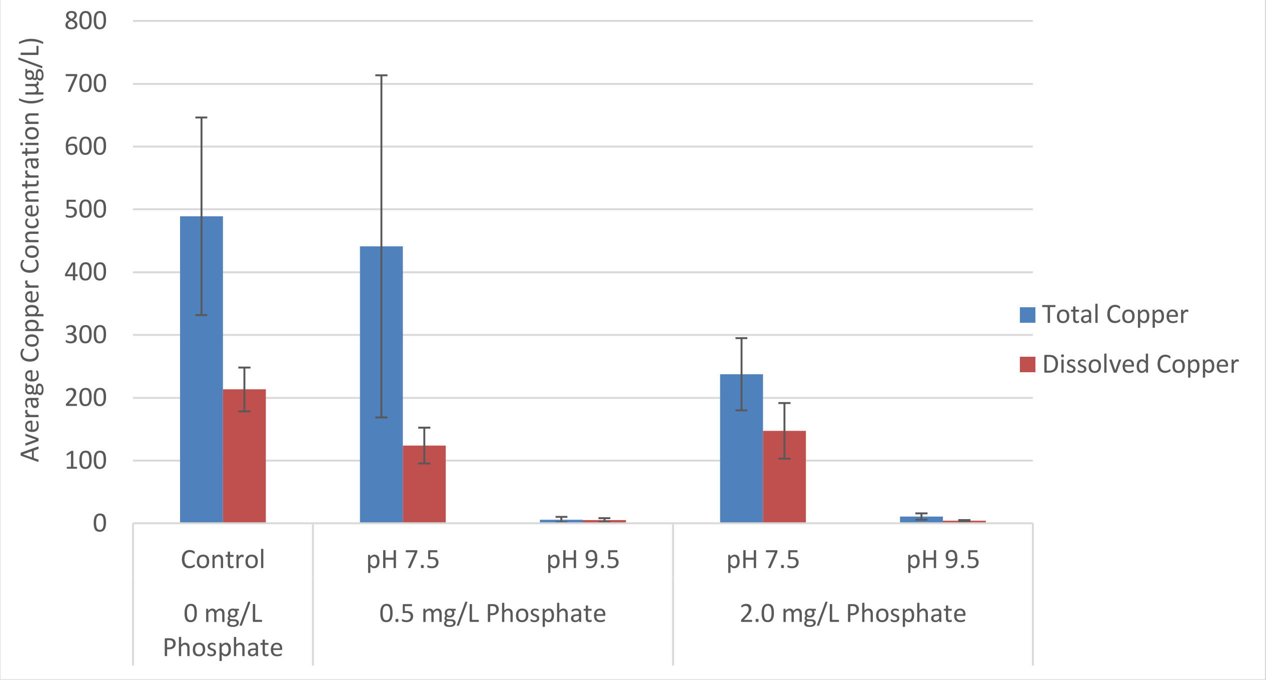

Figure 4.3.3: Effluent total and dissolved copper concentrations (Error bars represent the 95% confidence intervals)

The increase in phosphate dosage resulted in different copper corrosion effects (Figure 4.3.3). An increase in phosphate dose at pH 7.5 decreased the amount of total copper from 441 µg/L to 237 µg/L; however, the increase in phosphate dose at pH 9.5 appeared to have no effect on total copper. Solubility models for copper illustrate the optimal pH for orthophosphate passivity is between 6.5 and 7.5 on copper surfaces (Schock et al., 1995). As a result, the addition of phosphate was more effective in reducing total copper levels at pH 7.5 compared to pH 9.5.

A factorial analysis using two pH levels (7.5 and 9.5) and the two orthophosphate doses (0.5 and 2.0 mg/L) determined that pH ($P = 0.001$) was the only significant factor in reducing total copper concentrations. A one-way ANOVA determined the effect of all three doses of orthophosphate on total lead was not significant.

Furthermore, a similar factorial analysis was completed on the dissolved copper which revealed that pH ($P = 0.000$) played a significant role in reducing dissolved copper concentrations. A one-way ANOVA determined the effect of all three doses of orthophosphate on dissolved copper to be significant ($P = 0.001$).

Figure 4.3.4 displays the bulk water cATP concentrations of the experiment. The highest concentrations of cATP were measured during the acclimation phase in which no chlorine was added. The addition of chlorine reduced the cATP concentration in each annular reactor. Although chlorine reduced the cATP in each reactor, the cATP remained higher at pH 9.5 compared to the pH 7.5 treatment. This is due to the presence of two main oxidants: hypochlorous acid and the hypoclorite ion. Hypochlorous acid (HOCl) is a weak acid (pK_a value of 7.6) and is the predominant form present below pH of 7.6 (Crittenden et al., 2012). However, above pH 7.6, the hypochlorite ion (OCl^-) is the predominant form present (Crittenden et al., 2012). Since hypochlorous acid has faster disinfection kinetics than the hypochlorite ion (Crittenden et al., 2012); the free chlorine present is more effective below a pH of 7.6 and therefore a lower cATP concentration measured at pH 7.5 compared to pH 9.5.

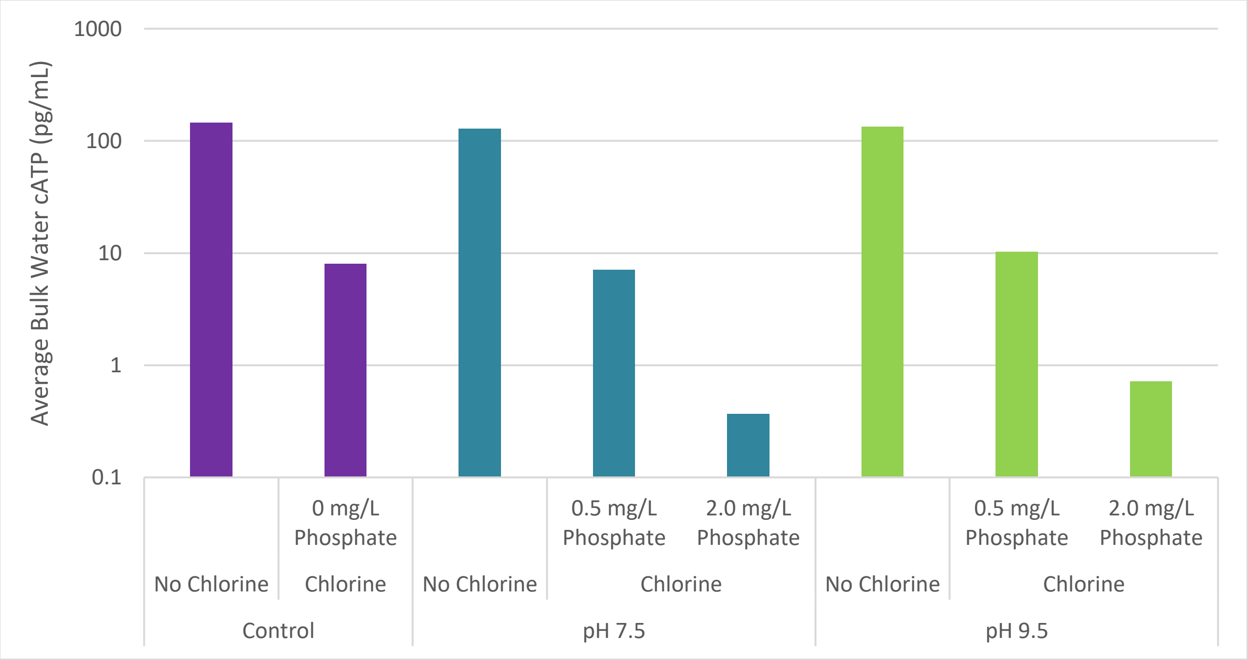

Figure 4.3.4: Average bulk water cATP

The addition of phosphate generally decreased the cATP concentration in the bulk water when compared to the control with no phosphate addition. The increase in phosphate dose from 0.5 mg/L to 2.0 mg/L at both pH treatments decreased the bulk water cATP concentration (Figure Figure 4.3.4).

A one-way ANOVA was completed on each annular reactor to determine the effects of chlorine compared to no chlorine. Each analysis resulted in chlorine ($P = 0.000$) having a significant effect on reducing bulk water cATP concentrations. A factorial analysis using two pH levels (7.5 and 9.5) and two orthophosphate doses (0.5 and 2.0 mg/L) resulted in the effect of orthophosphate ($P = 0.006$) being significant in reducing bulk water cATP concentrations. However, a one-way ANOVA using all three doses of orthophosphate determined that the effect of phosphate alone on bulk water ATP concentrations was not significant.

The average biofilm cATP is shown in Figure 4.3.5. The highest concentrations of biofilm on the coupons were associated with the acclimation phase in which no chlorine was added. The amount of biofilm decreased after chlorine addition which was similar to the results obtained from the bulk water. There were slightly higher biofilm concentrations at pH 9.5 compared to pH 7.5 due to the fact that free chlorine is not as effective above a pH of 7.6 (Crittenden et al., 2012) which is also similar to the bulk water results. Overall, the addition of phosphate increased the amount of biofilm present on the coupons compared to the control with no phosphate treatment which had the lowest biofilm concentration. Other studies by Chu et al. (2005) and Fang et al. (2009) used a different method to measure biofilm (Heterotrophic Plate Count) and also found an increase in microbial population with the addition of phosphorous In this study, the increase in biofilm associated with the addition of phosphate is the opposite trend than that found in the bulk water cATP concentrations.

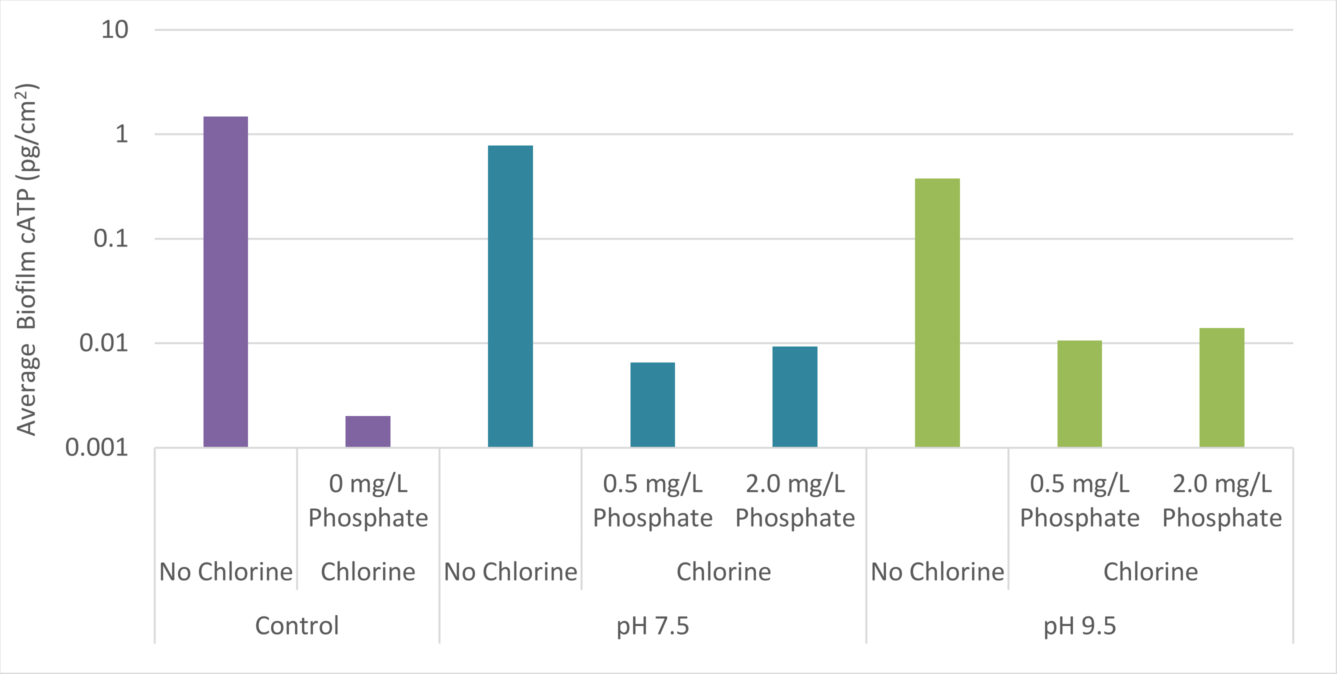

Figure 4.3.5: Average Biofilm cATP

A one-way ANOVA was completed on each annular reactor to determine the effects of chlorine compared to no chlorine. ANOVA results showed that chlorine did have a significant effect ($P = 0.000$) on reducing biofilm cATP concentrations. A factorial analysis using two pH levels (7.5 and 9.5) and two orthophosphate levels (0.5 and 2.0 mg/L) determined that neither pH or orthophosphate played a significant role in the increase in biofilm cATP concentrations. A one-way ANOVA using the three doses of phosphate determined that phosphate alone had a significant impact ($P = 0.002$) on the increase in biofilm cATP.

Biofilm accumulated on the surface of each coupon which permitted lead to accumulate within the biofilm. The total and dissolved lead within the biofilm is shown in Figure 4.3.6. The majority of lead present within the biofilm was in particulate form similar to the bulk water total lead results (Figure 4.3.2). Many studies have found that lead particles play a dominant role at neutral pH with phosphate corrosion inhibitors (Cartier et al., 2012; Woszczynski et al., 2013). Figure 4.3.6 illustrates that treatment of pH 7.5 with 0.5 mg/L phosphate contained the highest amount of total lead within the biofilm (253.6 $\mu g/cm^2$) while treatment of pH 9.5 with 2.0 mg/L phosphate contained the lowest concentration of total lead within the biofilm (25 $\mu g/cm^2$) which is similar to the results obtained from the bulk water. Overall the increase in pH at both doses of phosphate decreased the amount of total lead within the biofilm. Additionally, the increase in phosphate dose at each pH decreased the amount of total lead within the biofilm. Thus an increase in both pH and phosphate dose appear to have played a significant role in reducing total lead within the biofilm. Overall, the biofilm total lead results display similar trends as the bulk water total lead results.

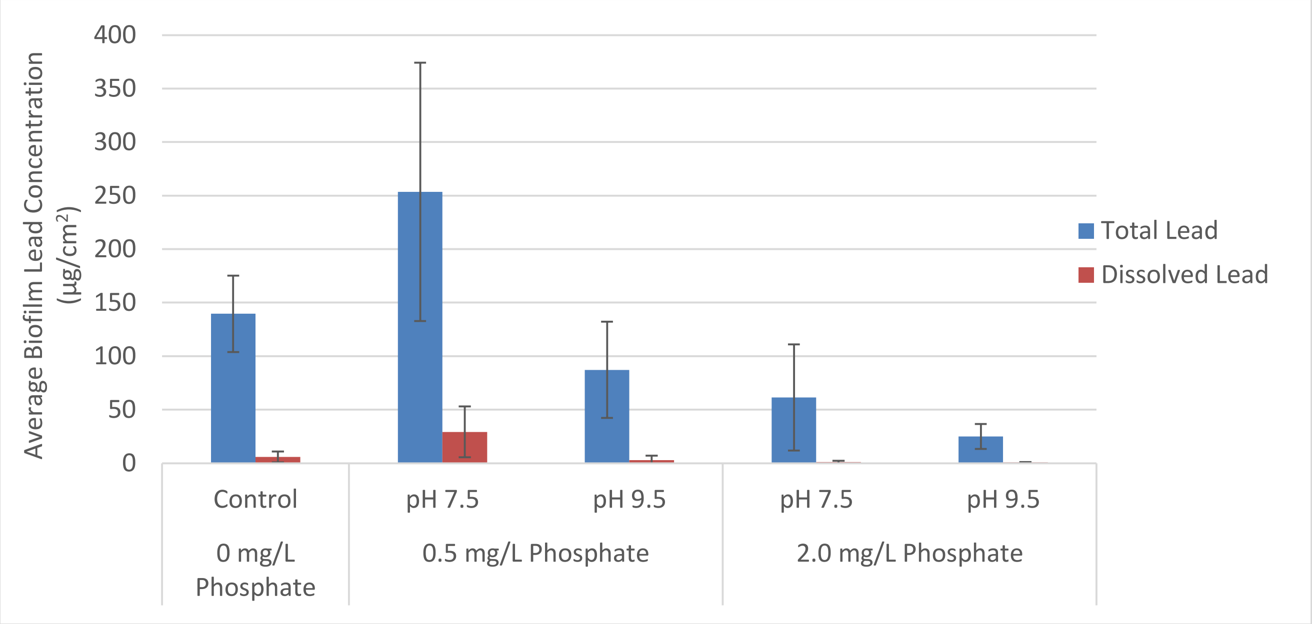

Figure 4.3.6: Biofilm total and dissolved lead concentrations (Error bars represent the 95% confidence intervals)

A factorial analysis using two pH levels (7.5 and 9.5) and two orthophosphate doses (0.5 and 2.0 mg/L) resulted in both pH ($P = 0.001$) and orthophosphate ($P = 0.002$) having a significant effect in reducing biofilm total lead concentrations. Furthermore, a one-way ANOVA using all three doses of orthophosphate determined that phosphate ($P = 0.005$) alone played a significant role in reducing the concentration of total lead within the biofilm.

Factorial analysis also resulted in both pH ($P = 0.019$) and orthophosphate ($P = 0.009$) significantly reducing biofilm dissolved lead levels while the interaction between the two factors ($P = 0.021$) significantly increased biofilm dissolved lead levels. Additionally, a one-way ANOVA using all three doses of phosphate determined that phosphate ($P = 0.003$) alone played a significant role in reducing biofilm dissolved lead concentrations.

The accumulation of biofilm on the surface of each coupon also promoted the accumulation of copper within the biofilm. Figure 4.3.7 displays the results for total and dissolved copper accumulation within the biofilm; the majority of copper present was in particulate form which was also the case for the bulk water. Treatment of pH 7.5 with 2.0 mg/L contained the highest concentration of total copper while treatment of pH 9.5 with 0.5 mg/L contained the lowest concentration of total copper. Overall the increase in pH at both doses of phosphate decreased the amount of total copper within the biofilm similar to the results obtained from the bulk water. The increase in phosphate dosage at pH 7.5 increased the amount of total copper within the biofilm from 8 to 39 μg/L which is the opposite trend than that of the bulk water. The increase in phosphate dosage at pH 9.5 had no effect on the total copper present within the biofilm which is also similar to the trend obtained from the bulk water.

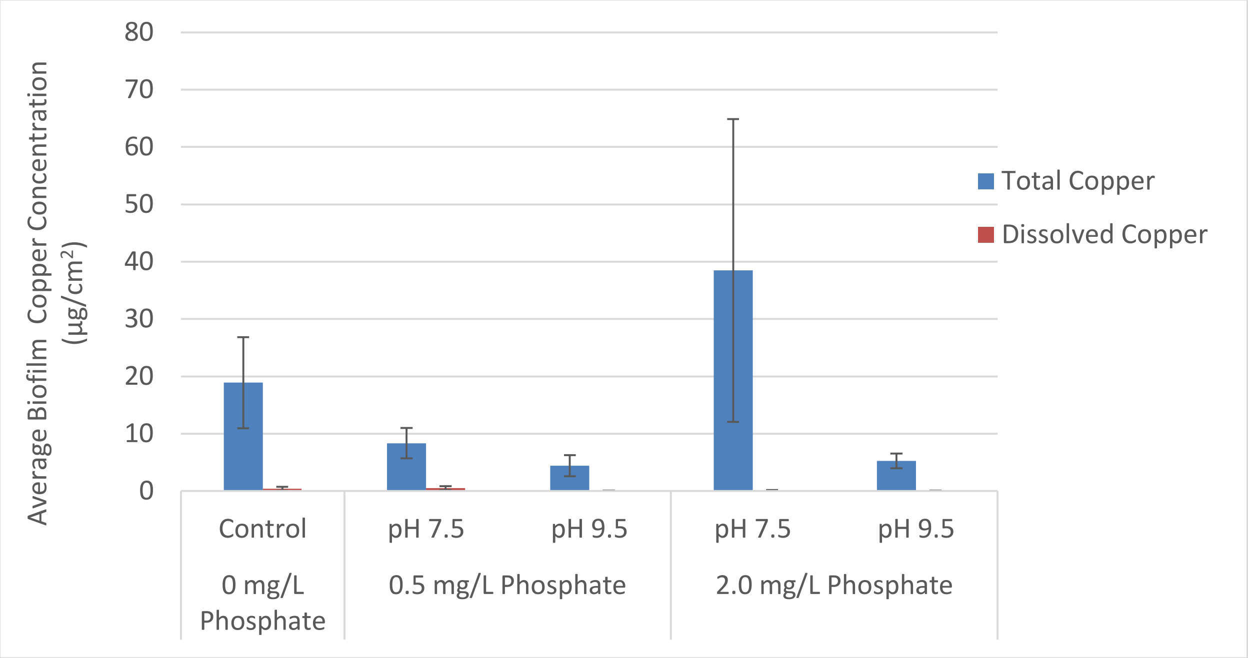

Figure 4.3.7: Biofilm total and dissolved copper concentrations (Error bars represent the 95% confidence intervals)

A factorial analysis using two pH levels (7.5 and 9.5) and two orthophosphate levels (0.5 and 2.0 mg/L) resulted in pH (P = 0.004) significantly decreasing total copper while orthophosphate (P = 0.014) significantly increased total copper and the interaction between the two factors (P = 0.020) significantly decreased total copper concentrations within the biofilm. A one-way ANOVA using the three doses of orthophosphate revealed that phosphate (P = 0.016) alone was significant in increasing biofilm total copper levels.

Factorial analysis also determined that pH (P = 0.001) and orthophosphate (P = 0.020) played a significant role in reducing biofilm dissolved copper concentrations, however the interaction between the two factors (P = 0.013) significantly increased dissolved copper concentrations. However, a one-way ANOVA determined that phosphate alone was not significant in reducing biofilm dissolved copper concentrations.

An analysis of the corrosion product on the surface of a coupon from each annular reactor was completed by EDS and the results are displayed in Table 4.3.3. Analysis was completed at the end of the bench scale experiment, thus after both doses of phosphate were applied to treatments of pH 7.5 and pH 9.5. Phosphate was detected in treatments with pH 7.5 and pH 9.5 at percent atomic compositions of 2.7 and 1.4 (Table 4.3.3) indicating the presence of a phosphate corrosion scale. Research by Nadagouda et al. (2009) determined that scales with percent atomic compositions up to 7% phosphorus are achievable when dosing with phosphate based corrosion inhibitors. When the coupons were removed, they appeared to contain blue-green copper oxides (Figure 4.2.4b) and EDS confirmed the presence of both copper and oxygen thus indicating possible copper oxide corrosion scales.

Table 4.3.3: Percent atomic composition for each treatment after the duration of the experiment

% atomic composition											
Treatment	C	O	P	Cl	Ca	Cu	Sn	Pb	Si	Mg	Cr
Control	16.2	67.5	0.09	0.2		3.0	8.36	4.7	1.0		
pH 7.5	24.4	57.1	2.7	0.7	2.0	1.3	5.0	6.2			
pH 9.5	11.8	54.6	1.4	16.4	7.6	0.69	21.1	1.6	2.2	1.9	3.6

Figures 4.3.8, 4.3.9 and 4.3.10 below display the SEM photos of 50:50 lead tin solder on copper coupons exposed to various treatments. Figure 4.3.8 shows that corrosion occurred as there are visible areas where material is lost (small holes or gaps in the photo). Figure 4.3.9 appears to be more smooth with less gaps or holes present indicating that less corrosion occurred. Furthermore, Figure 4.3.10 appears to be the smoothest with little loss of material or corrosion that occurred. These visual SEM results can be compared to the total lead data presented in Figure 4.3.2. The bulk water obtained from the control of pH 7.6 with 0 mg/L phosphate measured a total lead concentration of 580.8 µg/L, the bulk water obtained from the treatment of pH 7.5 with 2.0 mg/L phosphate measured a total lead concentration of 95.2 µg/L and the bulk water obtained from the treatment of pH 9.5 with 2.0 mg/L phosphate measured a total lead concentration of 66.5 µg/L. SEM results visually proved the most material lost from corrosion was in the control with no phosphate, which coincides with the fact that the control measured the highest total lead levels in the bulk water. Thus the most lead leaching occurred in this environment. The SEM results for the other two treatments, as discussed above, visually proved less material lost compared to the control, hence lower lead levels measured in the bulk water compared to the control. Additionally, SEM photo in Figure 4.3.10 appeared to have the least amount of material lost, thus the lowest lead leaching and most efficient treatment which was verified by data in Figure 4.3.2.

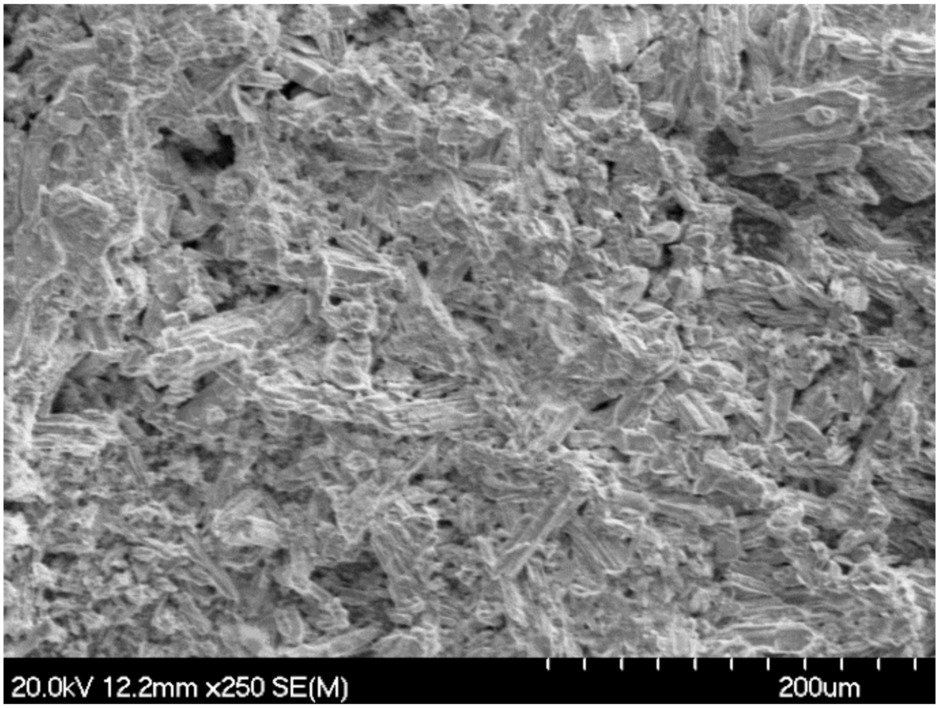

Figure 4.3.8: SEM photo of 50:50 lead tin solder on a copper coupon that was exposed to pH 7.6 and 0 mg/L phosphate

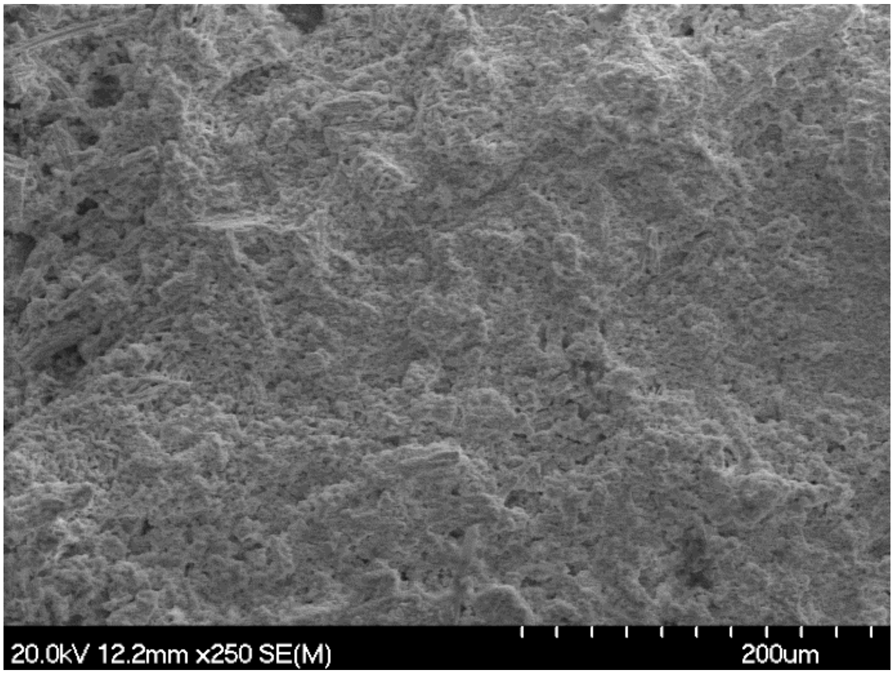

Figure 4.3.9: SEM photo of 50:50 lead tin solder on a copper coupon that was exposed to a treatment of pH 7.5 and 2.0 mg/L phosphate

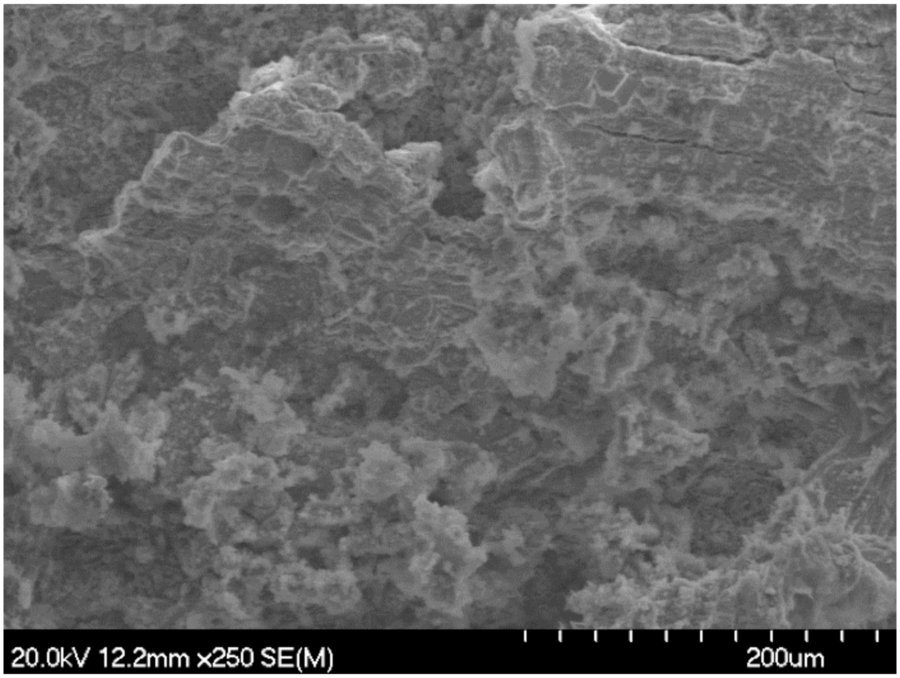

Figure 4.3.10: SEM photo of 50:50 lead tin solder on a copper coupon that was exposed to a treatment of pH 9.5 and a phosphate dose of 2.0 mg/L

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4.4 Conclusions

Each annular reactor had a CSMR between 7 and 8 which posed serious concern for lead corrosion which indicated that a corrosive environment was present. Thus, there was a need for corrosion control within the reactors. The adjustment of pH and addition of orthophosphate led to the following conclusions:

- The presence of orthophosphate significantly reduced bulk water total lead and increased orthophosphate dose led to lower lead concentrations in the bulk water.
- The effect of pH and orthophosphate as well as the interaction between the two factors were all significant in reducing bulk water dissolved lead concentrations.

- A factorial analysis determined that pH was the only significant factor in reducing bulk water total copper concentrations.
- Factorial analysis determined that pH played a significant role in reducing bulk water dissolved copper concentrations. ANOVA determined the effect of orthophosphate alone on bulk water dissolved copper was significant.
- Chlorine had a significant effect on reducing both bulk water and biofilm cATP concentrations. Additionally, a factorial analysis resulted in the effect of orthophosphate significantly reducing bulk water cATP concentrations.
- Orthophosphate had a significant impact on the increase in biofilm cATP, however this can be controlled through the addition of chlorine.
- Both pH and orthophosphate played a significant role in reducing biofilm total lead concentrations.
- Both pH and orthophosphate as well as the interaction between the two factors had a significant effect in reducing total copper concentrations within the biofilm.

CHAPTER 5 LEAD AND COPPER MONITORING PROGRAM

5.1 Introduction

Health Canada (1996) developed standards for drinking water suppliers in the document "Guidelines for Canadian Drinking Water Quality" which is employed in Nova Scotia. The guidelines state the Maximum Acceptable Concentration for lead is 10 µg/L but they do not provide a monitoring method. Health Canada (2009) developed another document "Guidance on Controlling Corrosion in Drinking Water Distribution Systems" to provide information and guidance on the development of corrosion control and monitoring programs. This document discusses both protocols and corrective measures to undertake when lead levels are above action levels.

Sampling protocols for non-residential sites such as child care centres, schools and offices pinpoint lead sources within the plumbing system in buildings. Lead found in drinking water may be due to lead containing material within the faucet itself, plumbing within the building and/or from the main distribution line (Health Canada, 2009). More specifically, potential sources of lead for non-residential buildings shown in Figure 5.1a include lead solder, lead fluxes, lead pipe and fittings, fixtures, valves, meters and components containing brass (USEPA, 2006). Even though the water supplier may deliver water that meets all standards, the plumbing in non-residential buildings may elevate lead concentrations above action levels. Figure 5.1a also displays types of outlets that may be sources of lead such as coolers, bubblers and faucets. Cold water faucets (Figure 5.1b) were the focus for this study since drinking water fountains within the building contained a lead filter.

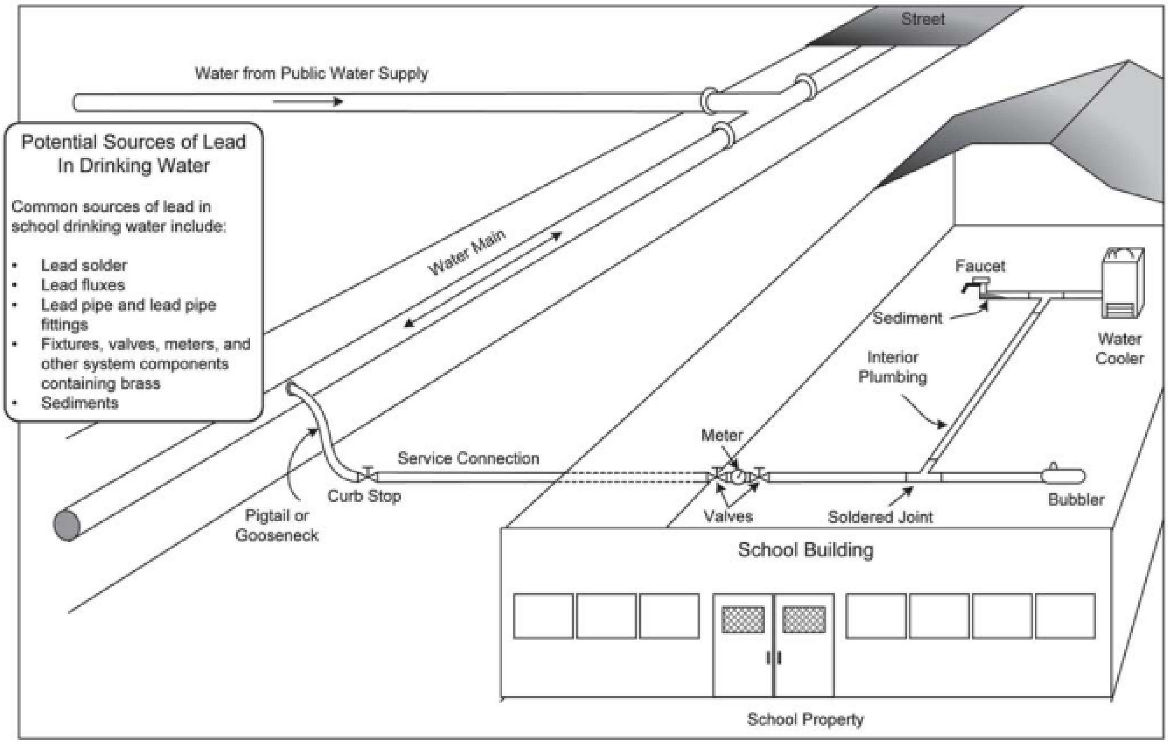

Figure 5.1a: Potential sources of lead within the plumbing system of a non-residential building (USEPA, 2006)

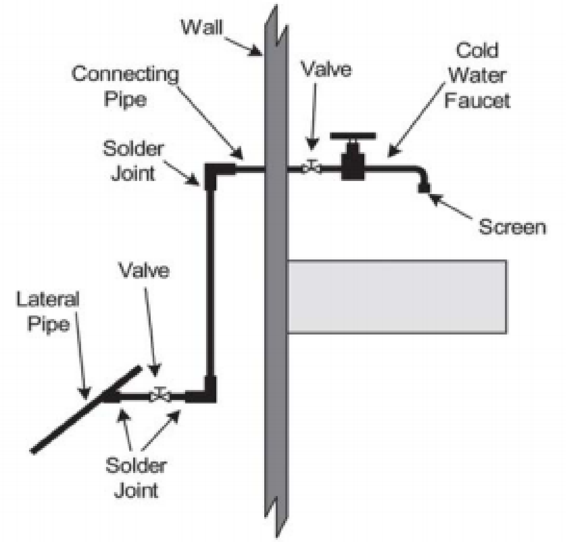

Figure 5.1b: Plumbing system of a cold water tap (USEPA, 2006)

Although there are many direct sources of lead within the plumbing system, there are other factors that contribute to an increase in lead concentrations at the tap. Water use within buildings will likely be intermittent, meaning there will be several periods of stagnation throughout the day, evenings and on weekends. These stagnation periods will likely increase lead levels monitored at the tap. Factors such as the frequency of use of the outlet, the amount of time the building is occupied per day as well as number of occupants are all factors that affect stagnation periods (Health Canada, 2009).

A two-tier sampling approach is used to identify the source of lead within non-residential settings. Tier 1 sampling detects cold water outlets that have higher lead levels following stagnation. Tier 2 sampling is used in combination with results obtained from Tier 1 to help detect the source of lead in the plumbing. Table 5.1 discusses the two sampling protocols along with corrosion control recommendations (Health Canada, 2009).

Table 5.1: Sampling protocols and corrosion control recommendations

Sampling Protocol	Sampling and Corrosion Control Recommendations
Tier 1	• A first draw 250 mL sample is collected following a stagnation time between 8 to 24 hours. • If lead concentration exceeds 20 µg/L at any of the outlets, conduct further sampling (Tier 2). Furthermore, interim corrective measures will need to be implemented. Corrective measures may include cleaning debris from screens or aerators of the outlet, flush the plumbing system, rendering the outlet out of service, use of certified drinking water treatment devices such as lead filters, etc. • Educate the occupants within the building on the outcome of the monitoring program and any interim measures that to be implemented.
Tier 2	• Outlets that exceeded 20 µg/L lead for Tier 1 require a second 250 mL flushed sample collected after the water has been stagnated (between 8 to 24 hours) and flushed for 30 seconds. • If lead levels in any of the second samples exceeds 20 µg/L corrective measures need to be implemented immediately. Corrective measures can include interim measures mentioned in Tier 1 until a permanent solution is implemented. Additionally, other control measures may include flushing outlets, replacing outlets, fountains, pipes, leaded brass fittings and leaded brass components and working with the water supplier to ensure water supplied is not corrosive prior to entering the plumbing system within the building. • Educate the occupants within the building on the results obtained from the monitoring program as well as temporary and permanent corrective measures that will be implemented. They will need to understand the issue and learn how to participate in carrying out interim measures such as flushing the outlet in order to protect their health.

Monitoring programs are part of a multi-barrier approach to ensure safe and reliable drinking water from the source to the consumer's tap (Health Canada, 2009). It is the responsibility of the building owner or manager, school boards, child care centres, etc. to ensure monitoring programs are carried out for public safety (Health Canada, 2009). The protocols may also be carried out by utilities that wish to include non-residential buildings in their corrosion control monitoring programs. Although water utilities may not be responsible for the plumbing within a non-residential building, utilities are expected to ensure water delivered to the internal plumbing system is non-corrosive (Health Canada, 2009). Buildings may be supplied with non-corrosive water but contain high lead levels at the tap due to the internal plumbing system. Authorities such as building owners, school boards, etc. would then address the issue and determine corrective measures (Health Canada, 2009). The overall goal of a monitoring program is to assess lead levels at the outlet and determine corrective measures when needed.

Since the previous bench scale experiments discussed throughout this thesis determined the groundwater to be corrosive, an at the tap monitoring program was carried out to measure concentrations of lead and copper. The objective of the study was to determine whether or not lead and/or copper were contaminants of concern in the non-residential building's drinking water. A second objective was to determine possible sources of each contaminant within the plumbing system of the building. The monitoring program was conducted during the summer and fall months to include seasonal effects of higher temperatures.

5.2 Materials and Methods

5.2.1 Source Water

Since this was a monitoring program completed at the tap, the water quality results are displayed and discussed in Section 5.3.

5.2.2 Experimental Design

Five faucets in a non-residential building were chosen for sequential sampling: (1) kitchen, (2) bathroom, (3) equipment room, (4) lab (Figure 5.2.2) and (5) raw groundwater (Figure 5.2.2). All faucets were flushed for approximately 5 minutes and then covered the day before sampling. Water was stagnated for 16 hours since Health Canada recommends a minimum stagnation time of 8 hours and no more than 24 hours (Health Canada, 2009). Following the stagnation period, sequential sampling was conducted. Four consecutive samples of 250 mL were collect followed by two 1 L volume samples for a total of 3 L (McIlwain et al., 2015). All sites were sampled during the one sampling event on a weekly basis. Sampling began July 15th, 2015 and continued until the end of October, 2015.

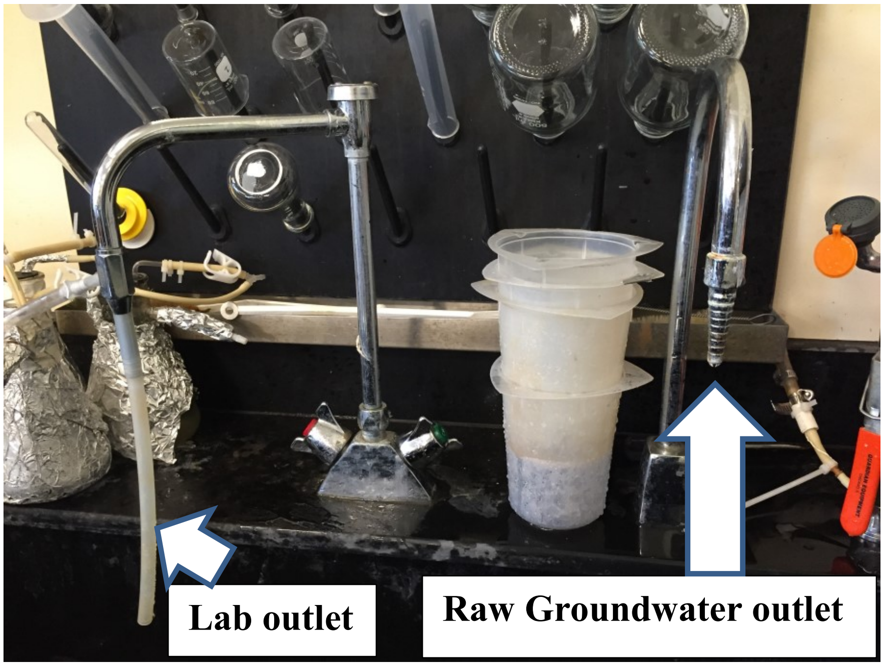

Figure 5.2.2: Lab and groundwater outlet

5.2.3 Sampling

All consecutive samples were analyzed for both dissolved and total lead and copper. First, third and fifth draw samples were analyzed for pH, temperature, turbidity, chloride and sulphate for each location. Polypropylene 250 mL and 1 L bottles were rinsed in a concentrated nitric acid bath, then rinsed with milli-Q three times and dried in a dust free area prior to collecting samples for metals analysis. Once all 250 mL and 1 L samples were collected, a 10 mL aliquot was immediately syringe filtered using a 0.45 µm cellulose nitrate filter for dissolved metals analysis. Then, additional aliquots were collected from first, third and fifth draw samples for pH, turbidity, chloride and sulphate measurements. The rest of the sample was preserved with concentrated nitric acid for at least 24 hours before a 10 mL sample was collected for total metals analysis. Ion chromatography vials were rinsed with milli-Q three times and used to collect samples for chloride and sulphate for ion chromatography analysis.

5.2.4 Analytical Methods.

The pH was analyzed using an Accumet XL50 dual channel probe (Fisher Scientific, U.S.A.) according to the manufacturer's instructions. Temperature was measured using a thermometer. Turbidity was measured using the HACH 2100N Turbidimeter (HACH, CO, U.S.A.) according to the manufacturer's instructions. Sulphate and chloride were measured using a 761 Compact IC (Metrohm, Herisau, Switzerland). The concentration of metals was analyzed using an X-Series 2 Inductively Coupled Mass Spectrometry (ICP-MS) (Thermo Fisher Scientific, MA, U.S.A.). The limit of detection for copper and lead was 0.7 µg/L and 0.4 µg/L, respectively.

5.3 Results and Discussion

Table 5.3.1 displays the average water quality parameters for each location. The average CSMR displayed in Figure 5.3.1 ranged from 7.0 to 7.9 for the bathroom, equipment room, kitchen and lab but was slightly higher for the raw groundwater with an average of 8.1. The CSMR was much larger than the recommended criteria of 0.7 which indicated a corrosive environment was present (Nguyen et al., 2011). In general, the CSMR measured was consistent among each of the samples with the raw groundwater slightly higher than all other locations. The CSMR was slightly higher for the raw groundwater due to higher concentrations of both chloride and sulphate (Table 5.3.1). It is important to note the raw groundwater was drawn from the same aquifer as the other locations but from a different well head. The raw groundwater was not treated drinking water from the town while all other locations were treated drinking water.

Table 5.3.1: Water quality for each location with standard deviation

Location	Sample Volume (mL)	pH	Turbidity (NTU)	Temperature (ºC)	Chloride (mg/L)	Sulphate (mg/L)	CSMR
Bathroom	250	7.0 ± 0.3	0.39 ± 0.14	21.4 ± 0.5	90.79 ± 4.70	12.68 ± 3.79	7.74 ± 1.98
	750	6.8 ± 0.4	0.35 ± 0.11	20.7 ± 0.9	92.45 ± 4.90	12.89 ± 3.88	7.73 ± 1.94
	2000	6.8 ± 0.4	0.39 ± 0.10	20.2 ± 1.1	92.98 ± 4.39	13.11 ± 3.99	7.55 ± 1.75
Equipment Room	250	7.0 ± 0.4	0.50 ± 0.10	21.2 ± 0.5	90.85 ± 3.93	12.52 ± 3.63	7.95 ± 2.30
	750	6.9 ± 0.5	0.37 ± 0.11	21.0 ± 0.5	90.61 ± 3.41	12.74 ± 3.73	7.64 ± 1.91
	2000	6.8 ± 0.4	0.37 ± 0.05	20.9 ± 0.5	91.79 ± 3.96	12.68 ± 3.73	7.81 ± 2.01
Kitchen	250	6.8 ± 0.5	0.42 ± 0.11	22.0 ± 0.5	91.91 ± 4.00	12.8 ± 3.92	7.81 ± 2.09
	750	6.7 ± 0.5	0.38 ± 0.12	22.3 ± 0.8	90.52 ± 4.12	12.72 ± 3.65	7.68 ± 2.01
	2000	6.6 ± 0.5	0.35 ± 0.06	22.0 ± 0.7	90.96 ± 2.89	14.04 ± 3.97	7.04 ± 2.03
Lab	250	6.9 ± 0.4	0.43 ± 0.13	21.5 ± 0.9	91.70 ± 4.89	13.22 ± 4.25	7.62 ± 2.20
	750	6.9 ± 0.4	0.36 ± 0.07	21.4 ± 0.8	90.94 ± 3.23	12.73 ± 3.85	7.79 ± 2.11
	2000	6.8 ± 0.5	0.42 ± 0.13	21.3 ± 0.8	92.11 ± 4.03	13.13 ± 3.92	7.65 ± 2.16
Raw Groundwater	250	7.1 ± 0.4	0.37 ± 0.06	21.6 ± 0.6	147.97 ± 6.21	18.89 ± 3.38	8.09 ± 1.44
	750	6.9 ± 0.4	0.36 ± 0.13	22.3 ± 0.9	149.53 ± 6.99	19.01 ± 3.58	8.15 ± 1.50
	2000	6.8 ± 0.4	0.35 ± 0.07	22.7 ± 1.0	148.88 ± 7.21	19.0 ± 3.77	8.11 ± 1.52

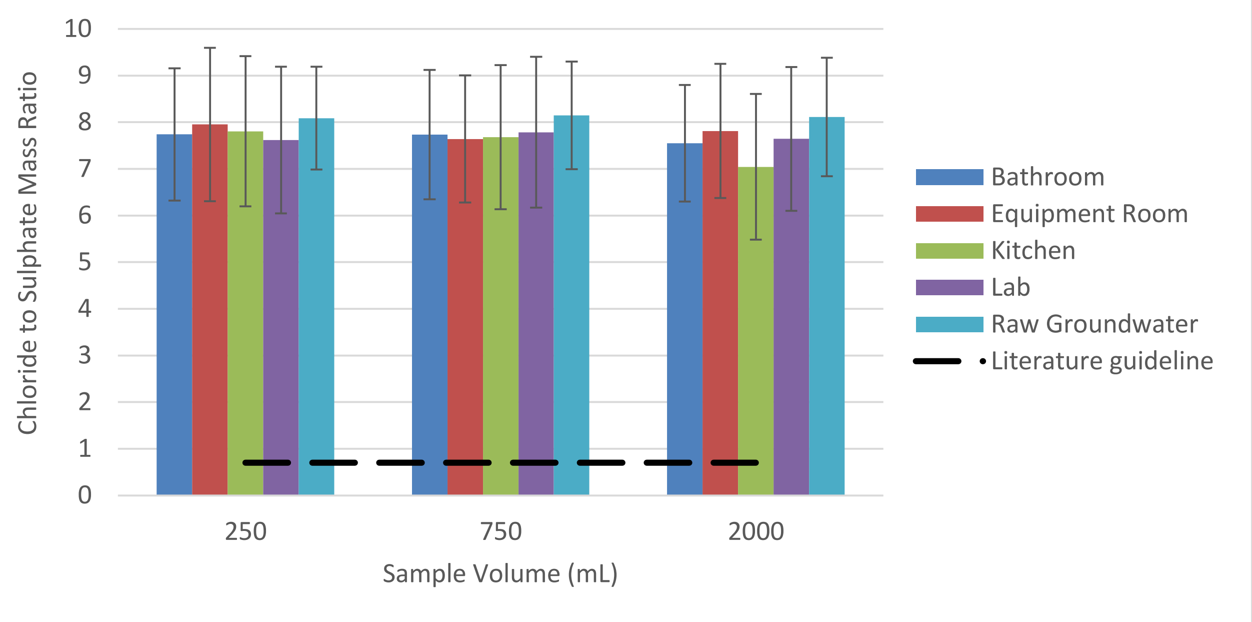

Figure 5.3.1: CSMR for each sampling location (Error bars represent the 95% confidence intervals)

Figure 5.3.2 displays the average total lead for each sampling location. The majority of the locations had an average total lead of less than 20 µg/L (Figure 5.3.2); the only location above the action level was the raw groundwater which is not used for drinking water purposes. Although the raw groundwater is not used as drinking water, this location was chosen in order to compare against the drinking water locations because of the difference in piping. The raw groundwater piping was composed of PVC with a brass faucet while piping at the other locations was composed of copper with brass faucets and valves. The highest average total lead concentration was the raw groundwater first draw sample measured at 48.8 µg/L and illustrated in Figure 5.3.2. This is due to the brass containing faucet. The second highest total lead concentration was the first draw lead sample for the bathroom measured at 11.5 µg/L. This was also due to the presence of a brass containing faucet. The average total lead decreased as sample volume increased for each location due to water being flushed through the system. The kitchen contained the lowest overall total lead concentrations due to the presence of a lead filter at the tap. Building staff stated that faucets and valves throughout the plumbing system were made of brass which were the sources of lead throughout this study.

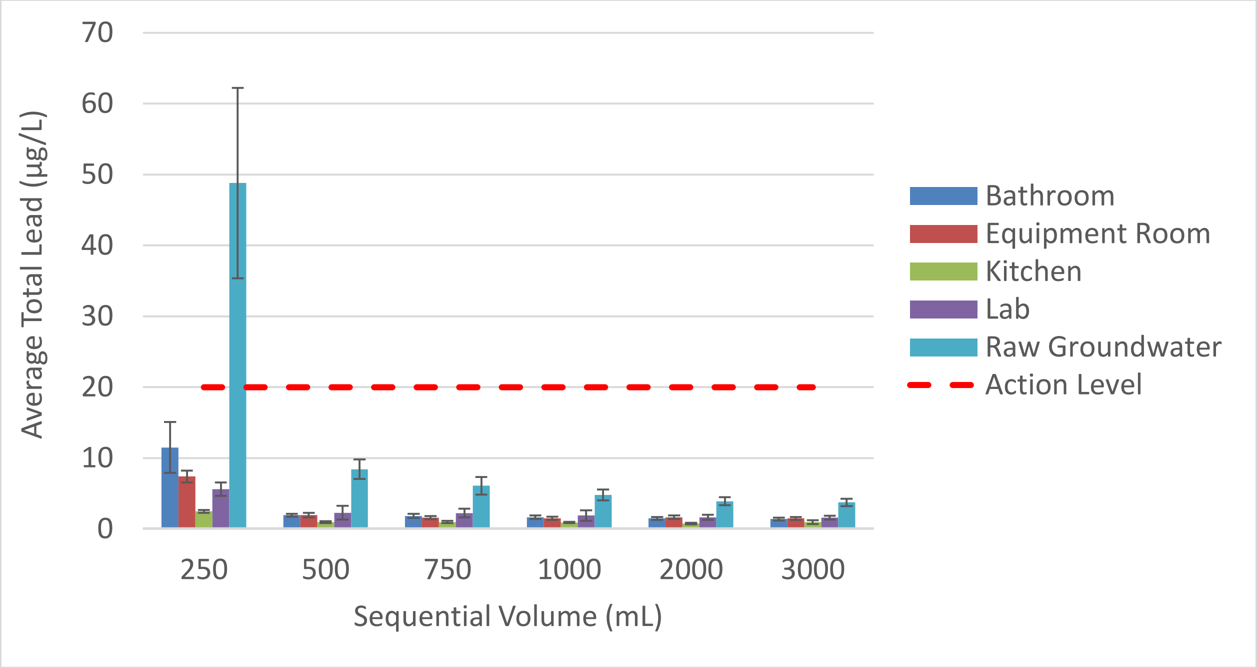

Figure 5.3.2: Average total lead concentrations for all locations (Error bars represent the 95% confidence intervals)

Figure 5.3.3 displays all of the first draw total lead samples from the monitoring program; 12 out of 13 samples for the raw groundwater were above the action level, two bathroom samples were near or above the action level while all other locations were under the action level. The kitchen had the lowest lead concentration due to the presence of a lead filter installed at the tap. Additionally, the equipment room, kitchen and lab had a lower variability of first draw total lead concentrations.

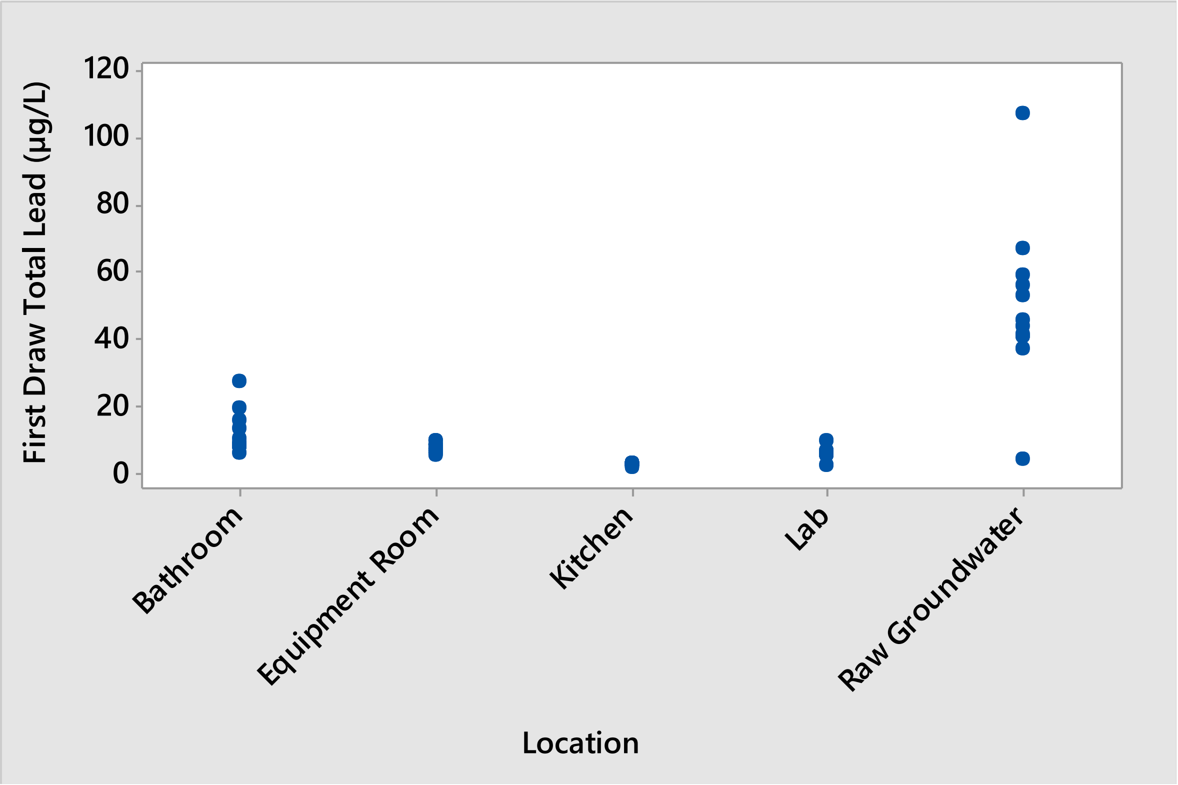

Figure 5.3.3: First draw total lead for each location

Since the bathroom and raw groundwater locations contained higher total lead concentrations, these two locations were chosen to display the total lead compared with dissolved lead. Figures 5.3.4 and 5.3.5 illustrate the first draw sample contained more particulate lead than all other samples due to the brass containing faucet. The majority of lead was in dissolved form for samples of sequential volume 500 mL through 3000 mL. Although only two locations are displayed, all other locations revealed similar results (See Appendix).

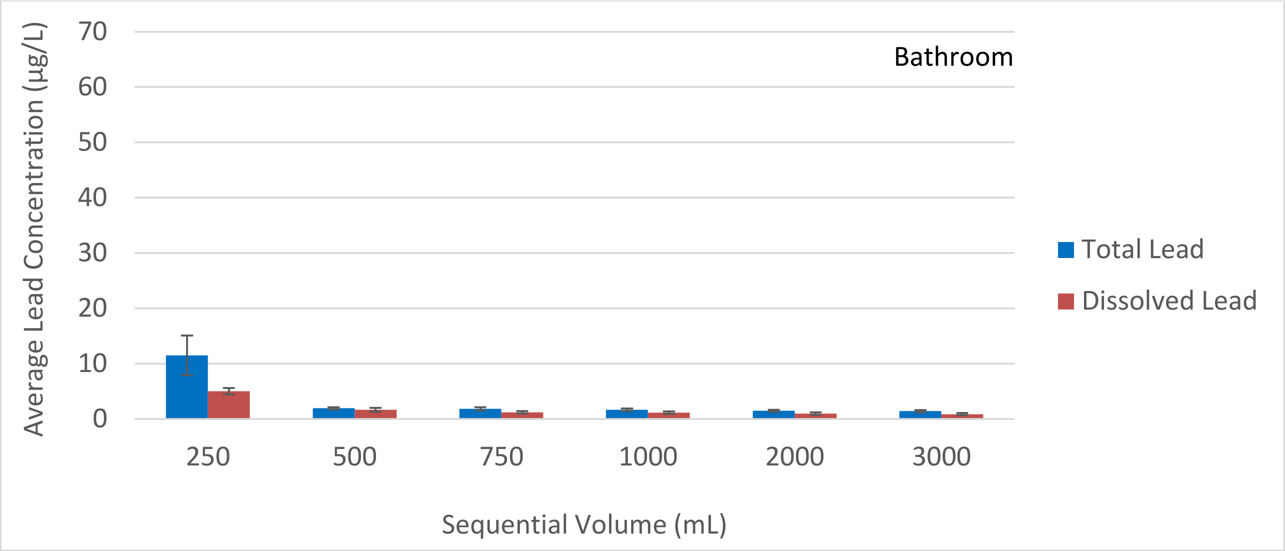

Figure 5.3.4: Total and dissolved lead concentrations for the bathroom (Error bars represent the 95% confidence intervals)

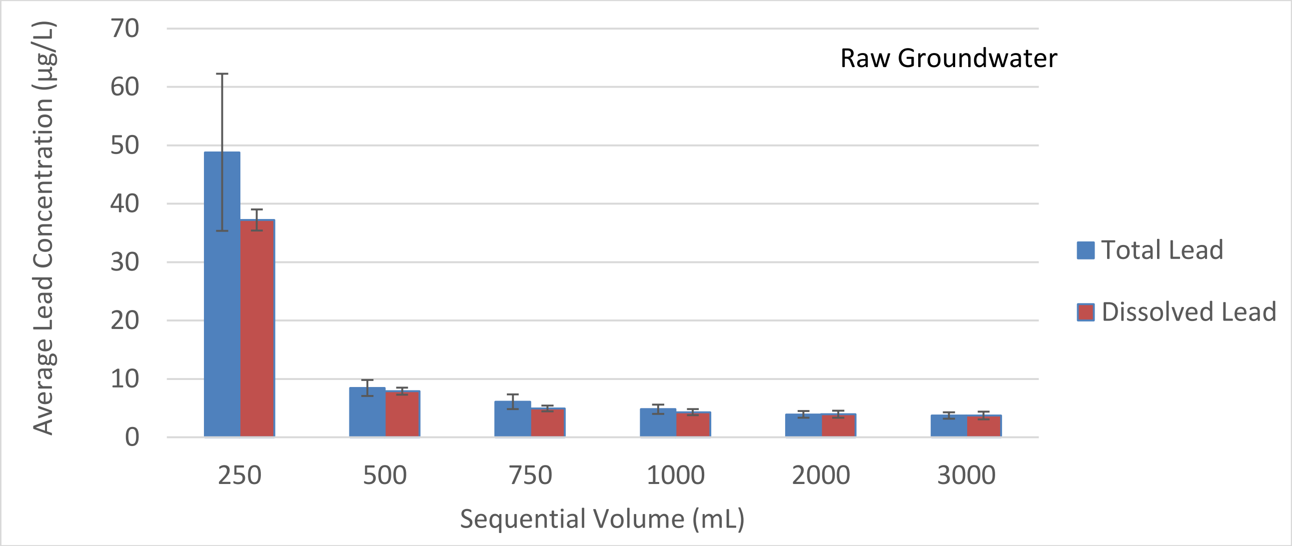

Figure 5.3.5: Total and dissolved lead concentrations for the raw groundwater (Error bars represent the 95% confidence intervals)

Since the bathroom and raw groundwater contained higher lead samples, the concentration of both aluminum and iron were measured on six samples from September 11, 2015 to October 30, 2015 in order to determine if other metals were present. All dissolved aluminum samples were below the detection limit of 4 µg/L and only one total aluminum sample was above the detection limit measuring at 6 µg/L. Thus, aluminum concentrations were low and all well below Health Canada's operational guidance value of 100 µg/L. Additionally, all dissolved iron samples were less than the detection limit of 7 µg/L. The majority of total iron concentrations were below the detection limit as shown in Figure 5.3.6. However, the bathroom and raw groundwater first draw samples contained higher iron concentrations than the other samples. Although these locations contained higher iron, the concentration was well below the aesthetic objective of 300 µg/L. Furthermore, samples two through six for all locations measured consistent total iron concentrations.

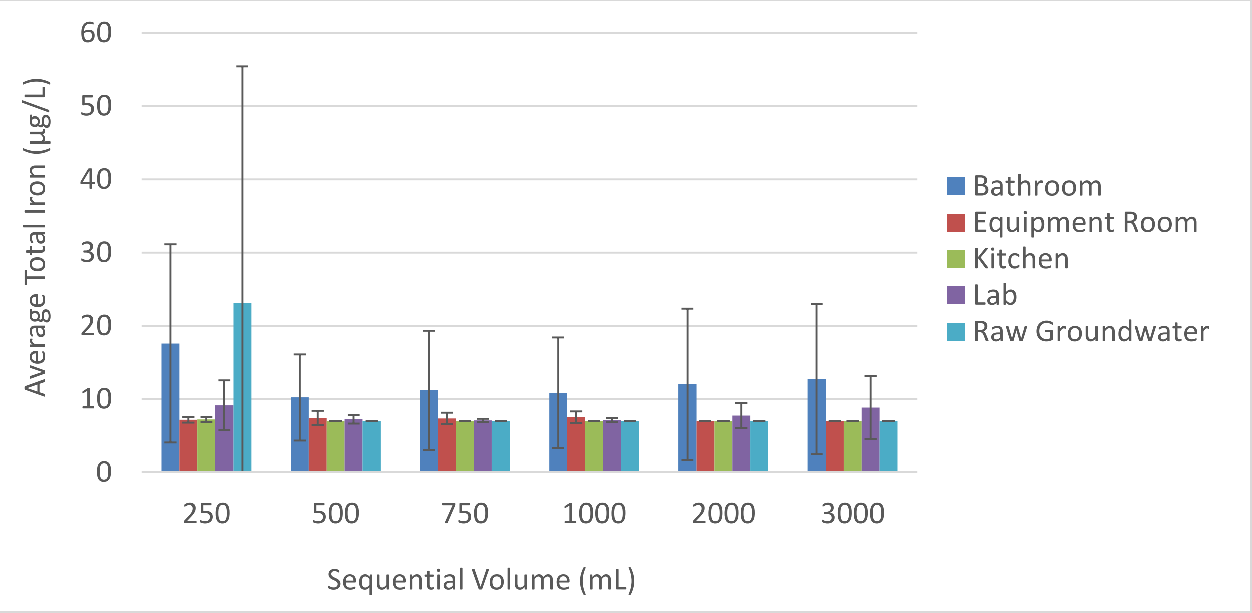

Figure 5.3.6: Average total iron concentrations for all locations (Error bars represent the 95% confidence intervals)

The sampling program produced high copper concentrations at four of the five locations. Average copper concentrations illustrated in Figure 5.3.7 ranged from 46.9 µg/L to 3803.9 µg/L. The raw groundwater was the only location under the aesthetic objective of 1000 µg/L, ranging from 46.9 to 365.7 µg/L. All other locations were above the aesthetic objective due to the presence of copper piping and components along with corrosive water at a high CSMR greater than 7 (Figure 5.3.1). A high percentage of the samples were above Health Canada's aesthetic objective; 71.8 % of the bathroom samples, 79.5 % of the equipment room samples, 43.6 % of the kitchen samples and 89.7 % of the lab samples. Since the majority of samples were above Health Canada's aesthetic objective, other guidelines such as the EPA and the WHO were considered. The EPA's action level is 1300 µg/L (EPA, 2016) whereas the WHO Guidelines for Drinking Water Quality state the guideline for copper is 2000 µg/L (WHO, 2011). The percentage of samples above each objective and/or guideline is displayed in Table 5.3.2 below. Over half of the samples were also above the EPA guideline for the bathroom, equipment room and lab at 71.8 %, 60.3 % and 73.1 %, respectively. Additionally, 57.7 % of the bathroom samples were above the WHO guideline.

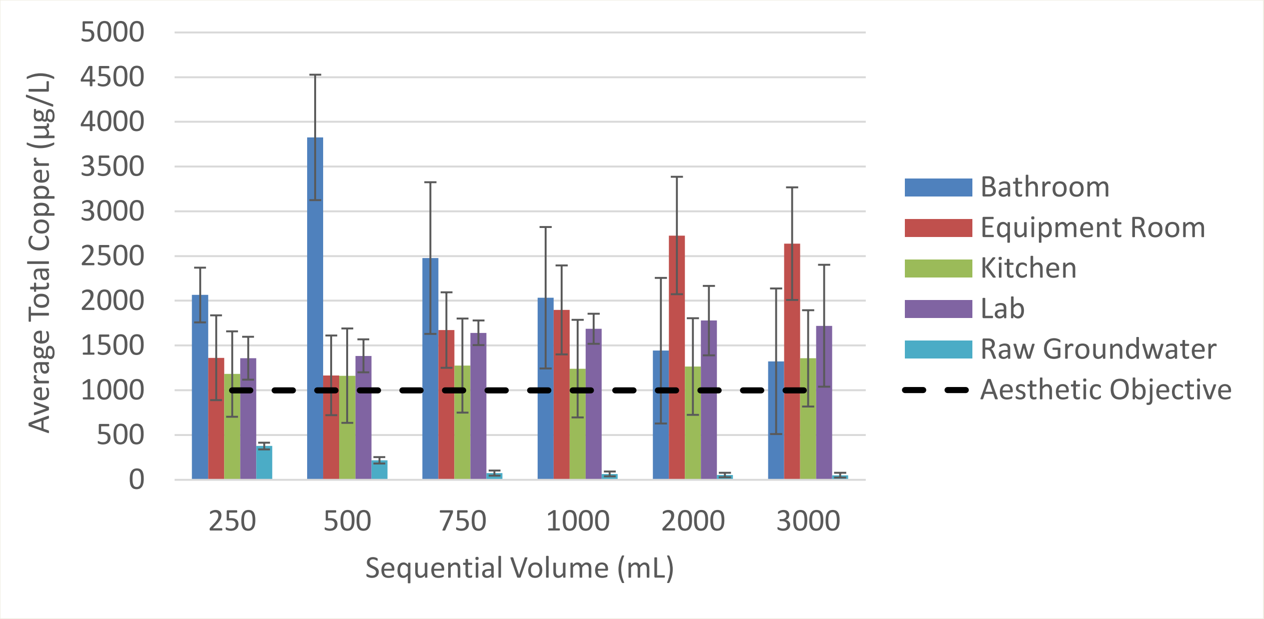

Figure 5.3.7: Average total copper concentrations for all locations (Error bars represent the 95% confidence intervals)

Table 5.3.2: Percentage of samples above Copper objectives and guidelines

Objective/Guideline	Bathroom	Equipment Room	Kitchen	Lab	Raw Groundwater
Health Canada (AO: >1000 µg/L)	71.8	79.5	43.6	89.7	0.0
EPA (AL: >1300 µg/L)	71.8	60.3	17.9	73.1	0.0
WHO (Guideline: >2000 µg/L)	57.7	37.2	7.7	16.7	0.0

Since the bathroom contained the highest total copper concentrations and the raw groundwater contained the lowest total copper concentrations, these two locations were chosen to display the total copper compared with dissolved copper. Figures 5.3.8 and 5.3.9 illustrate the majority of copper was in dissolved form for all samples Although only two locations are displayed, all other locations revealed similar results in that the majority of copper was in dissolved form (See Appendix).

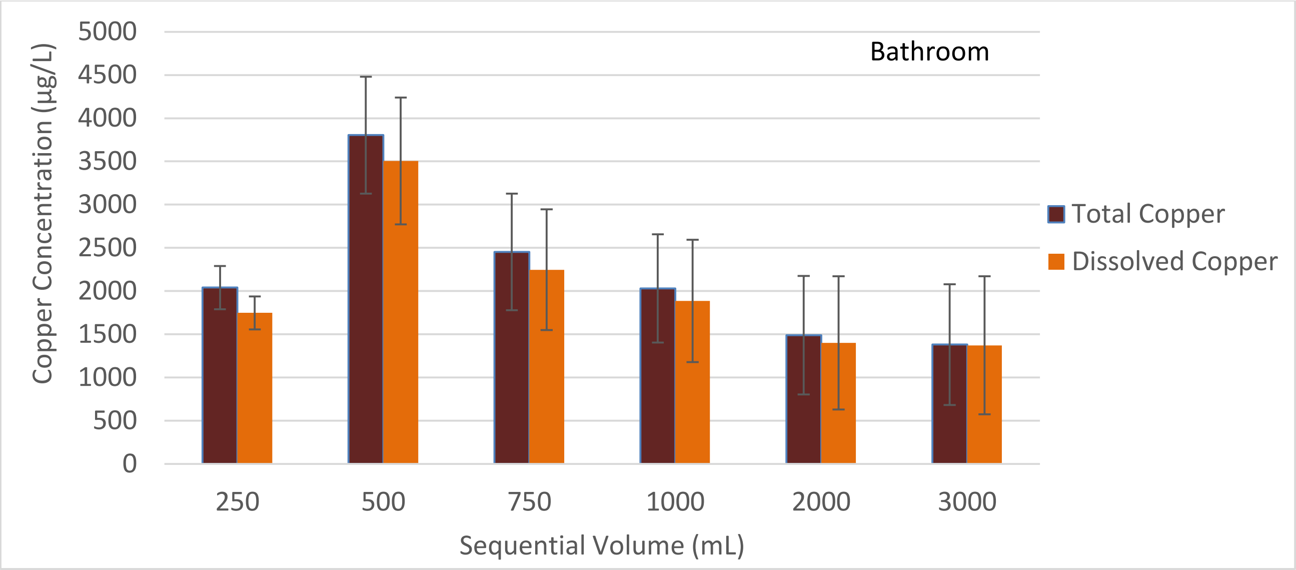

Figure 5.3.8: Total and dissolved copper concentrations for the bathroom (Error bars represent the 95% confidence intervals)

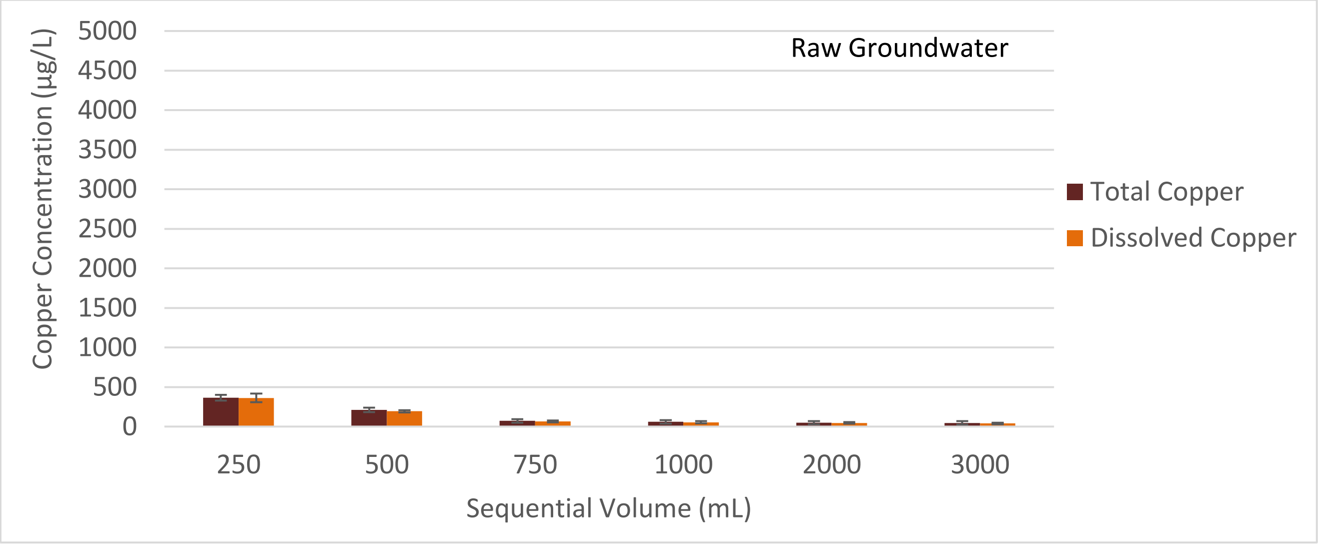

Figure 5.3.9: Total and dissolved copper concentrations for the raw groundwater (Error bars represent the 95% confidence intervals)

5.4 Conclusions

An initial assessment of the materials used within the distribution system along with water quality data can help identify the level of lead corrosion concern for utilities. Figure 5.4.1 below was used to initially identify the concern for lead corrosion. Throughout the distribution system, lead solder was used along with brass faucets and valves with a measured CSMR above 7. This assessment lead to a serious concern for the level of lead corrosion, hence the implementation of a monitoring program for the groundwater source.

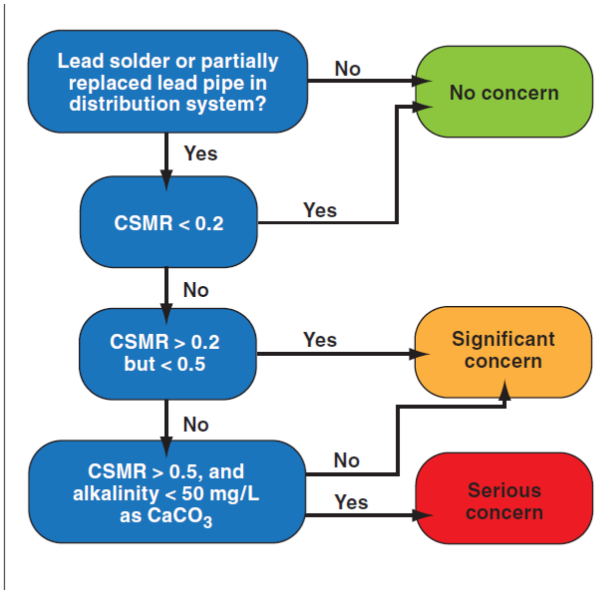

Figure 5.4: Level of concern for lead corrosion (Nguyen et al., 2010)

The monitoring program led to the following conclusions:

- Average CSMR was between 7 and 8 for all locations which indicated a corrosive environment was present.
- The raw groundwater location which was not used for drinking water purposes was the only location with an average total lead concentration above the action level of 20 µg/L.

- First draw total lead samples resulted in two locations being above the action level: raw groundwater and bathroom. The raw groundwater contained 12 out of 13 samples above the action level while the bathroom contained two samples near or above the action level. The source of lead throughout the distribution system in this case were brass faucets and valves. The kitchen tap contained a lead filter with and all samples for lead were well below the action level. Thus, it is recommended that a lead filter also be installed in the bathroom location to help reduce lead levels.
- As sample volume increased, the average total lead decreased due to the water being flushed through system.
- High copper concentrations were found at four out of the five locations throughout the monitoring program. The raw groundwater was the only non-drinking water location and also the only location under the aesthetic objective of 1000 µg/L. All other locations were above the aesthetic objective due to the presence of copper piping and components along with corrosive water at a high CSMR greater than 7. A high percentage of samples were not only above Health Canada's aesthetic objective, but also above the EPA action level and the WHO guideline.

CHAPTER 6 CONCLUSION

6.1 Summary

Three experimental approaches were used in order to monitor and understand the effect of orthophosphate on both metals release and biofilm formation within the drinking water distribution system. Table 6.1 summarizes the findings from each experiment.

Table 6.1: Conclusions from each experiment

Chapter	**Experimental Approach**	**Conclusions**
Chapter 3: Effect of orthophosphate on metals release in bench scale partial lead service line replacements	Bench scale stagnant dump-and-fill experiment using harvested lead-copper pipe sections	• Total lead concentrations were higher for the groundwater source due to a high CSMR of 7.7 to 8.3. • Neither pH or orthophosphate alone had a significant effect on total lead released, but the interaction was statistically significant for both water sources. • Although the effects of pH and/or phosphate on the dissolved lead for both the surface water and groundwater source were not significant, the dissolved lead concentrations in the pipe effluent were generally lower in the presence of orthophosphate. • The average total copper concentrations after stagnation for both water sources were all below 25 µg/L which was below Health Canada's aesthetic objective of 1000 µg/L (Health Canada, 2014). Neither pH or orthophosphate had a significant effect on total copper concentrations for the surface water, but the interaction between pH and orthophosphate significantly reduced total copper for the groundwater. • Dissolved copper concentrations were all under 10 µg/L. No significant effects of pH and/or phosphate were found on dissolved copper concentrations for the surface water, however, pH significantly reduced dissolved copper concentrations for the groundwater source.

Chapter 4: Effect of orthophosphate on metals release and biofilm formation in simulated drinking water systems	Annular reactors	• The presence of orthophosphate significantly reduced bulk water total lead and increased orthophosphate dose led to lower lead concentrations in the bulk water. • The effect of pH and orthophosphate as well as the interaction between the two factors were all significant in reducing bulk water dissolved lead concentrations. • Increase in pH significantly reduced bulk water total copper concentrations. • Increase in pH significantly reduced bulk water dissolved copper concentrations. ANOVA determined that the effect of orthophosphate alone on bulk water dissolved copper was significant. • Chlorine significantly reduced both bulk water and biofilm cATP concentrations. • Orthophosphate significantly reduced bulk water cATP concentrations. • Orthophosphate significantly increased biofilm cATP. • Both pH and orthophosphate significantly reduced biofilm total lead levels. • Both pH and orthophosphate as well as the interaction between the two factors significantly reduced total copper concentrations within the biofilm.
Chapter 5: Lead and copper monitoring program	Monitoring completed at the tap	• Average CSMR at the tap was between 7 and 8 which indicated a corrosive environment was present. • The raw groundwater location which was not used for drinking water purposes was the only location out of a total of five locations with an average total lead concentration above the action level of 20 µg/L. • First draw total lead samples resulted in two locations being above the action level: raw groundwater and bathroom. The source of lead throughout the distribution system in this case were brass faucets and valves. • As sample volume increased, the average total lead decreased due to the water being flushed through system.

		- High copper concentrations were found at four out of the five locations throughout the monitoring program. The raw groundwater was the only non-drinking water location and also the only location under the aesthetic objective of 1000 µg/L. All other locations were above the aesthetic objective due to the presence of copper piping and components along with corrosive water at a high CSMR greater than 7. A high percentage of samples were not only above Health Canada's aesthetic objective, but also above the EPA action level and the WHO guideline.

6.2 Recommendations

Further monitoring at the tap should be conducted in order to determine if lead and/or copper are of concern in other non-residential buildings in the same area. It is also recommended that residential testing be conducted to determine whether consumers are at risk for health effects as the CSMR indicated that a corrosive environment was present. The kitchen tap contained a lead filter and all samples for lead were well below the action level. Thus, it is recommended that a lead filter also be installed in the bathroom tap to ensure lead levels remain below the action level. The raw groundwater location piping was composed of PVC, while piping at the other locations was composed of copper. Since the majority of copper samples were above Health Canada's aesthetic objective except for the raw groundwater location, it is recommended to install PVC tubing.

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APPENDIX

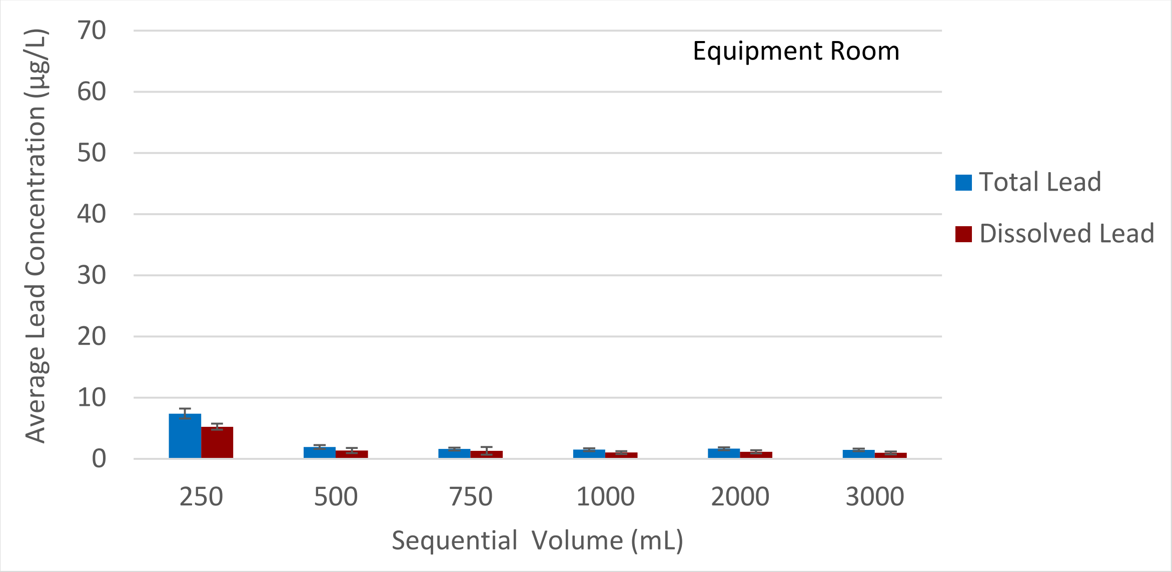

Figure A.1: Total and dissolved lead concentrations for the equipment room (Error bars represent the 95% confidence intervals)

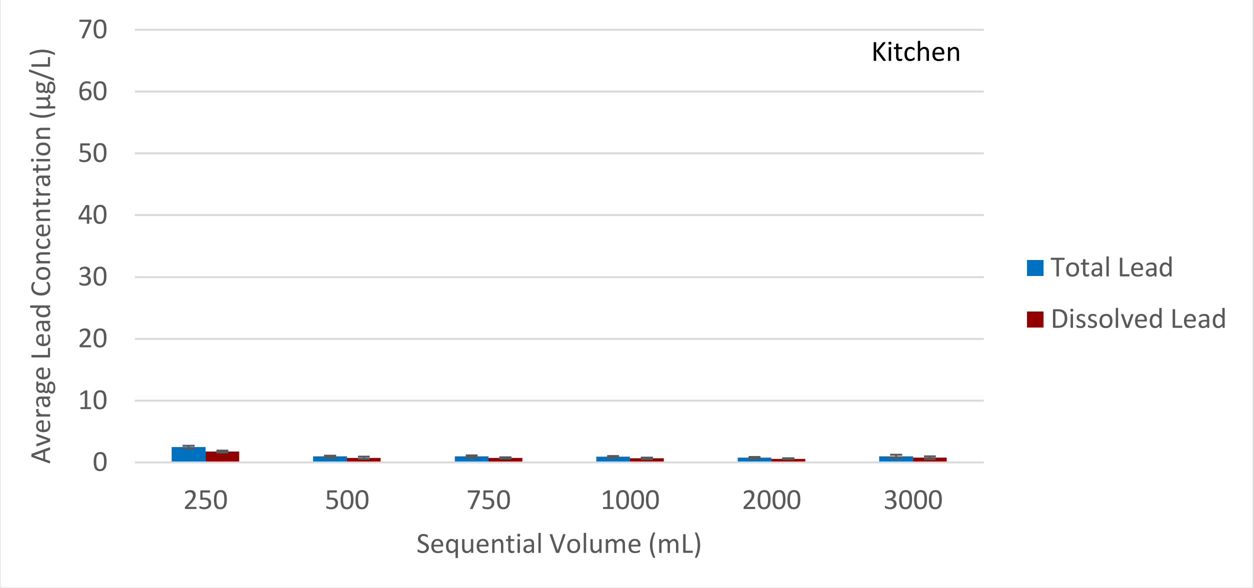

Figure A.2: Total and dissolved lead concentrations for the kitchen (Error bars represent the 95% confidence intervals)

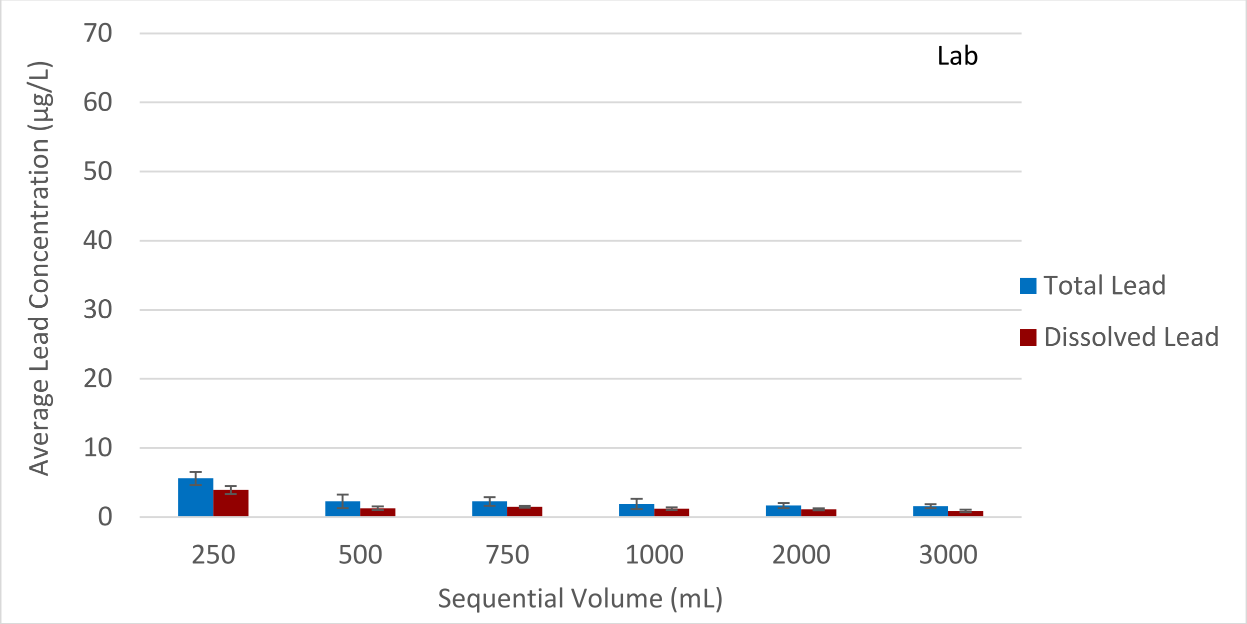

Figure A.3: Total and dissolved lead concentrations for the lab (Error bars represent the 95% confidence intervals)

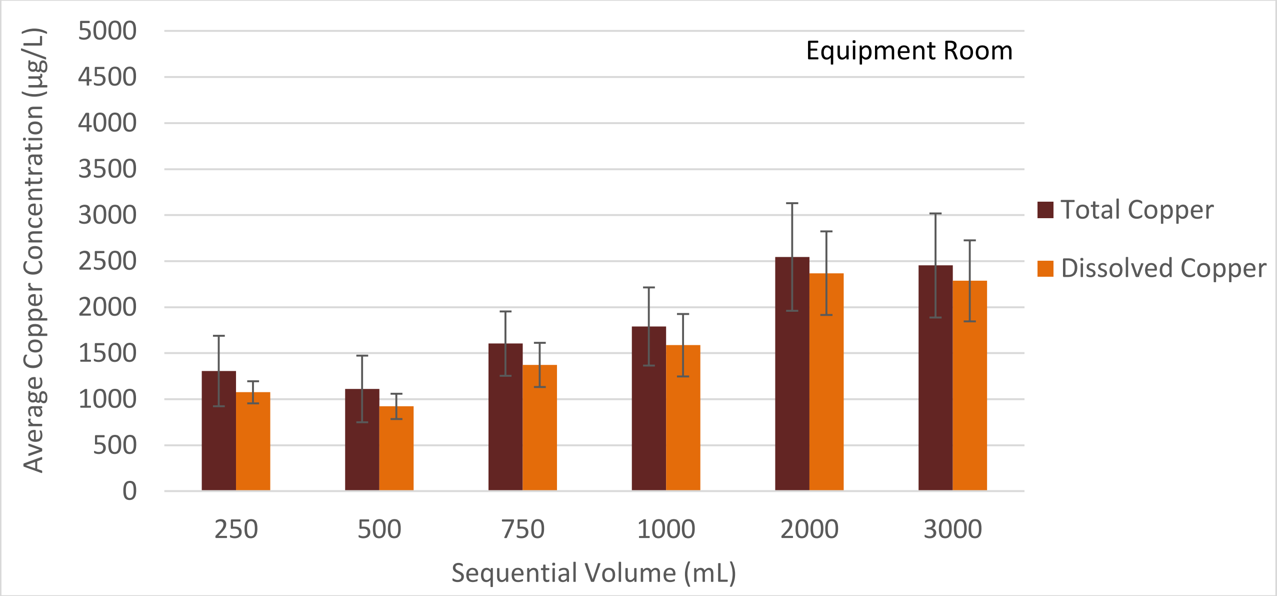

Figure A.4: Total and dissolved copper concentrations for the equipment room (Error bars represent the 95% confidence intervals)

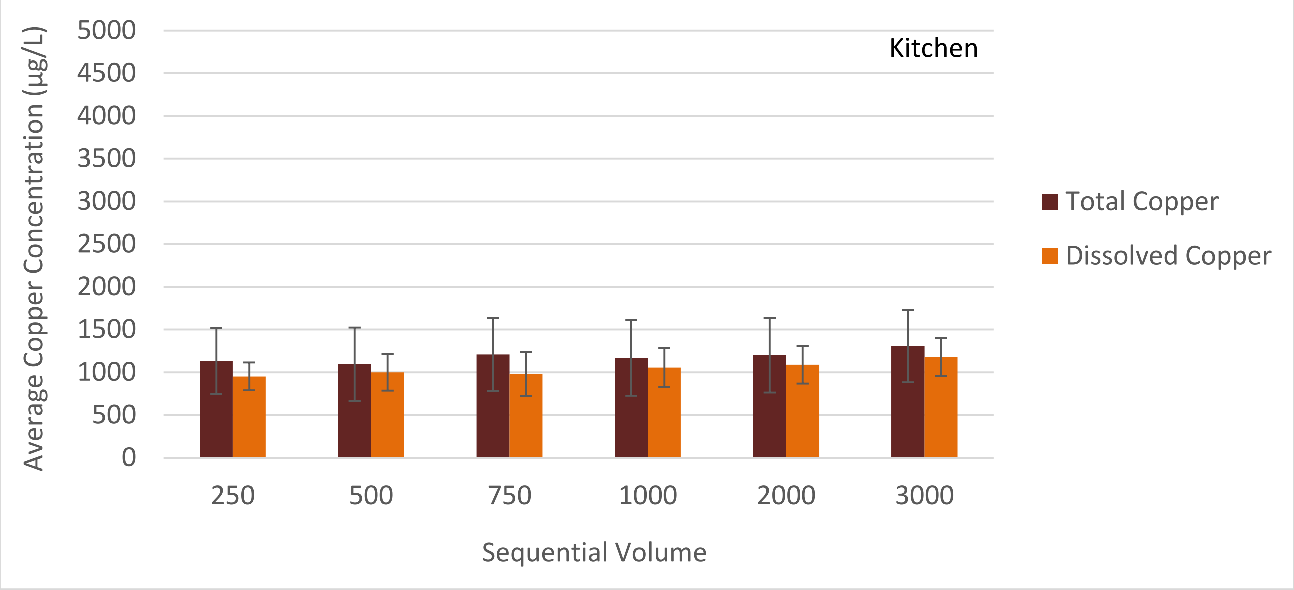

Figure A.5: Total and dissolved copper concentrations for the kitchen (Error bars represent the 95% confidence intervals)

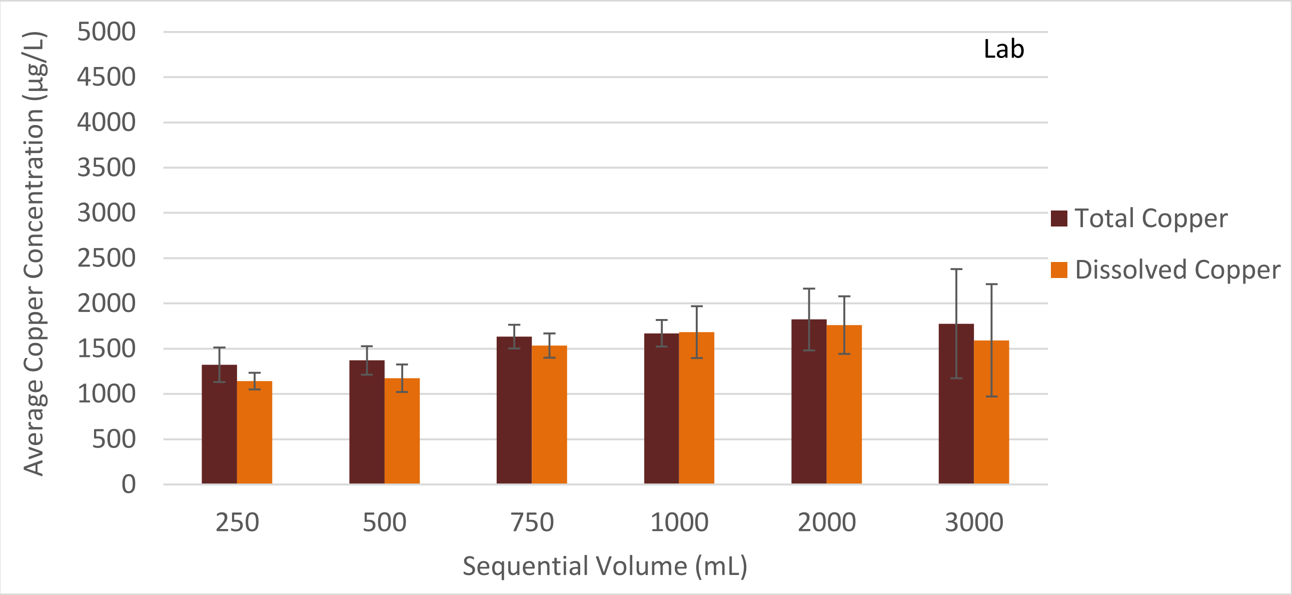

Figure A.6: Total and dissolved copper concentrations for the lab (Error bars represent the 95% confidence intervals)