THE RELATIONSHIP BETWEEN IRON PARTICLES IN WATER MAINS AND LEAD RELEASE

by

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DEPARTMENT OF CIVIL AND RESOURCE ENGINEERING

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DEDICATION PAGE

Dedicated to my number one supporter (Mrs Mums), you inspire me to aim for nothing but the best and never expect anything less for myself. I love and appreciate you for all you have done for me thus far.

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ABSTRACT

In recent years, significant numbers of projects have investigated lead release sources, mitigation, and health effects. The impact on human health caused by lead release has resulted in stringent lead regulations, which limit the drinking water concentration of lead to 10µg/L. In order to meet regulation guidelines, sources of lead are being removed from the distribution system and premise plumbing. Lead service lines (LSLs) are replaced to minimize the effect of lead release, with LSL contributing as much as 50-75% of total lead at the tap. Adsorption of lead on galvanized iron corrosion scales have been shown to increase lead release in LSL replacements, which is very concerning for utilities considering replacing the LSLs. Adsorption of lead on to iron minerals has been hypothesized as a mechanism for lead exposure. With the significant presence of unlined cast iron pipes in Halifax, the objective of this thesis was to determine the relationship between the iron particles found in cast iron pipes and lead release at the tap.

Bench-scale adsorption experiments were conducted to investigate the adsorption of lead on iron corrosion scales (magnetite and goethite) in reverse osmosis (RO) water and finished water from the JD Kline Water Supply Plant. A pilot-scale study was also conducted to investigate the effects of water mains on lead release with a focus on the comparison between polyvinyl chloride (PVC) pipe and unlined cast iron pipe. Water samples from full scale LSL replacement program were analyzed to determine the amount of lead released between full and partial replacements. Also, the effect of the water main material on lead release when the service lines were connected to tuberculated cast iron water mains and ductile iron water mains was compared.

Results from the bench-scale adsorption experiments showed that lead adsorbs on the iron corrosion scales and that the adsorption capacity of magnetite and goethite increased with increasing pH. Adsorption of lead on magnetite and goethite in RO water and finished water demonstrated the probable adsorption of lead on the iron corrosion scales that detach from the walls of the water mains in a distribution system. Additionally, the results from the pipe loop and copper pipe rack study showed that the copper pipe racks connected to the pipe loops with the cast iron test section produced the most lead release compared to the copper pipe racks connected to the pipe loops with the PVC test section. Longer stagnation time increased lead release and a high chlorine concentration resulted in a decrease in lead release compared to a low chlorine concentration. Finally, analysis of the results from the LSL replacement program showed that full replacements had the least lead release compared to partial replacements. Also, service lines connected to turberculated cast iron water mains released the most lead irrespective of the type of service line replacement conducted. Service lines connected to ductile iron water mains had the least amount of lead released in both partial and full replacements compared to service lines connected to cast iron water mains.

In conclusion, this research demonstrates that there is a relationship between the iron particles in water mains and lead release. The adsorption of lead on the iron particles results in an increase in lead release.

LIST OF ABBREVIATIONS & SYMBOLS USED

Al	Aluminum
ANOVA	Analysis of Variance
b_A	Langmuir adsorption constant
$CaCO_3$	Calcium Carbonate
C_e	Equilibrium concentration
CIPP	Cured In Place Piping
Cl_2	Chlorine
CO_2	Carbon dioxide
Cu	Copper
DO	Dissolved Oxygen
Fe	Iron
HCl	Hydrochloric Acid
HW	Halifax Water
HRM	Halifax Regional Municipality
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
JDKWSP	James Douglas Kline Water Supply Plant
K_A	Freundlich adsorption capacity parameter
$KMnO_4$	Potassium Permanganate
LCR	Lead and Copper Rule
LSL	Lead Service Line
LSLR	Lead Service Line Replacement
MAC	Maximum Acceptable Concentration
$NaHCO_3$	Sodium Bicarbonate
NaOH	Sodium Hydroxide
NASTT	North American Society For Trenchless Technology
Ntu	Nephelometric Turbidity Unit
ORP	Oxidation Reduction Potential
Pb	Lead
PbO_2	Lead Oxide
PO_4	Phosphate

Pb-Sn	Lead-Tin
PVC	Polyvinyl Chloride
PZC	Point of Zero Charge
q_A	$_A$dsorption density
Q_M	Maximum adsorption density
RO	Reverse Osmosis
SO_4	Sulphate
Sn	Tin
USEPA	United States Environmental and Protection agency
µg/L	micrograms/Liter

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CHAPTER 1 INTRODUCTION

The quality of treated water in distribution systems remains a serious concern for water utilities. For instance, the leaching of lead into potable water from corrosion of lead bearing plumbing materials has been managed nationwide by Health Canada using the Guidelines for Canadian Drinking Water Quality (Health Canada 2012). The significant presence of corroded unlined cast iron pipes is also of particular concern in the northeastern region of North America (Cromwell *et al.* 2001).

The occurrence of high levels of lead in the distribution system is very concerning because it is well known that lead in drinking water has adverse impacts on human health and on the cognitive development of children (Fewtrell *et al.,* 2004; Bellinger *et al.,* 1991; Triantafyllidou *et al.,* 2007). Additionally, the improved control of lead paint and dust, a national ban on leaded gas, and the success of the Lead and Copper Rule (LCR) managed by the United States Environmental Protection Agency (USEPA) has resulted in actual levels of lead in children's blood dropping by 80% (Edwards & Dudi 2004). The average national contribution of drinking water to blood lead in the United States is currently believed to be on the order of 7-20% (Edwards *et al.* 2004). In light of these trends, serious problems with lead contamination of potable water were largely considered historical (Edwards & Dudi 2004). However, to further reduce the contribution of drinking water to blood lead concentrations, the Guidelines for Canadian Drinking Water Quality limit lead concentrations in drinking water to a maximum acceptable concentration (MAC) of 10 micrograms/litre (µg/L), measured at the tap (Health Canada 2012).

Lead service line replacement (LSLR) in which the portion or the whole lead service line is replaced is used to reduce the amount of lead leached in the distribution system. Partial and full replacements are conducted in a LSLR. Partial replacement is the replacement of the lead service line from the water main to the properly line. Full replacement is the replacement of the lead service line (LSL) from the water main to the home. Partial replacements are practiced across Halifax due to the ongoing long-term distribution main renewal program. The distribution main renewal program aims to ensure long-term integrity and reliability of the distribution system by replacing the corroded unlined cast iron water mains present in the distribution system. Corroded cast iron pipes have been shown to consist of various iron compounds, including the two dominant species goethite and magnetite (Sarin et. al 2004; McNeill & Edwards 2001). During the main renewal program, LSLs are partially replaced from the new water main to the property line. Partial replacements of LSLs in other studies have been attributed to elevated lead release after replacement due to dislodging of particulate lead from the remaining service line (Boyd et al., 2004; Sandvig et al, 2009), galvanic corrosion (Nguyen et al, 2010; Edwards & Triantafyllidou, 2007) and in some cases, water hammer or sudden flow changes, which can also cause the dislodging of iron corrosion scales from the distribution system (Schock et al, 1996).

Additionally, iron can be released from cast iron pipes that have not been replaced through the dissolution of the corrosion scales or the dislodging of the scales due to pressure changes. Adsorption of lead on iron sulphate has been shown to be responsible for high lead levels in homes with galvanized iron pipes (McFadden et. al 2011). However, the adsorption of lead on iron minerals (e.g. goethite; magnetite) is poorly understood, which is particularly relevant for water utilities that are conducting LSLR in water distribution systems containing corroded cast iron pipe. The adsorption of lead on goethite and magnetite can contribute to high lead releases observed at homes with service lines connected to corroded unlined cast iron pipes. This process occurs by the dislodging of the iron corrosion scale in the water main, followed by the adsorption of lead on the iron corrosion scale, and then the flow of the lead coated iron mineral from the service line to the tap. A correlation between high iron concentration and high lead release has been hypothesized by other researchers (Deshommes et al. 2010; Cartier et al. 2011). Also, some empirical evidence suggests that the interaction between iron corrosion scales and lead particles may exist even following a LSL replacement.

Hence, the hypothesis of this thesis is that lead adsorption onto iron particles is a mechanism for lead release at customers' taps.

1.1 OBJECTIVES

The thesis hypothesis was tested with the overall objective of determining the relationship between iron particles found in water mains and lead release through bench, pilot, and full-scale experiments. It is anticipated that meeting this objective will advance corrosion control strategies in Halifax and locations with soft water. These experiments were designed to satisfy the following research sub-objectives:

Objective 1

Investigate the adsorption of lead on different iron minerals (magnetite and goethite) using RO water and water treatment plant finished water, and evaluate the effect of pH on the adsorption process.

Objective 2

Determine the relationship between lead adsorption to goethite and magnetite and overall lead release in a lead service line replacement program conducted in Halifax, Nova Scotia and determine which type of service line replacement is beneficial for Halifax.

Objective 3

Determine the effects of a corroded cast iron distribution system on lead release in a pilot study, and examine the role of stagnation as a factor in lead release when the service line is connected to a cast iron distribution system.

1.2 ORGANIZATION OF THESIS

The investigation of this research work covers three independent, but related, subject areas. This led to a publication format where every chapter covers a specific experiment. Abstract, introduction, materials and methods, results and discussion, and conclusion for each experiment is included in the separate chapters. Each of the experiment chapters will discuss the relevance of the experiments, how it relates to the other chapters, and how it demonstrates the relationship between the iron particles in the water main and lead release. Chapter 2 outlines the relevant topics for lead corrosion in drinking water and water distribution system corrosion. Chapter 3 includes the materials and methods section that is common to all the different experiments. Chapter 4 presents the various components of the bench-scale experiment, Chapter 5 presents the findings of the full-scale experiment, and Chapter 6 presents the results of the pilot-scale study. Chapter 7 provides recommendations on how to best carry out all the experiments, best practices learned through the operation of the experiments and opportunities for additional research to better understand the relationship the iron particles play in lead release. Chapter 8 provides a summary and conclusions of the entire project, which includes the different experiments.

CHAPTER 2 BACKGROUND

2.1 CORROSION IN LEAD SERVICE LINES, PREMISE PLUMBING AND CAST IRON WATER MAINS

Corrosion of the distribution system and premise plumbing is a problem experienced by drinking water utilities. Corrosion is the physicochemical interaction between a metal and its environment, which results in changes in the properties of the metal (Snoeyink and Wagner 1996). In the waterworks industry, the metal is cast iron, lead, brass or copper and the environment is the water (Schock, 1999).

Internal corrosion of water distribution systems leads to the failure of the distribution system and the deterioration of the water quality in the distribution system (Snoeyink and Wagner 1996). The majority of distribution system pipes across North America are composed of iron materials: cast iron (38%), ductile iron (22%), and steel (5%) (McNeill and Edwards 2001). The corrosion of cast iron pipes is well documented and researched (McNeill and Edwards 2001, Sarin et. al 2004). An increase in the concentration of lead and copper in drinking water, which is released from pipes and solder, are a consequence of corrosion in the distribution system.

The release of lead poses a health concern and the release of iron, copper, manganese and zinc can produce aesthetic problems, such as staining and red water issues, which affect the public's perception of the water (Eisnor 2002). The creation of the Lead and Copper Rule (LCR) by the USEPA in 1991 is meant to identify problems with corrosion in distribution system and emphasize on corrosion control (Schock, 1999).

Lead service lines (LSLs) were installed in drinking water distribution systems prior to the 1950's and, therefore, homes built before the 1950's often have LSLs. Sources of lead in drinking water mainly include LSLs, leaded solder, and brass material devices (Schock, 1990). In studies by Cartier *et al.* (2011) and Sandvig *et al.* (2008), LSLs were shown to contribute as much as 50-75% of the total lead at the tap after an extended stagnation time.

Premise plumbing is defined as the point from the connection of the service line to the distribution system, extending through homes, schools, hospitals and other types of buildings.

Due to the split in financial responsibility between homeowners and utilities, beyond the property line is the responsibility of the property owner. Premise plumbing can also contribute a significant amount of lead at the tap due to the presence of brass fittings, leaded solders, and, in some cases, lead premise pipes.

2.1.1 Corrosion Chemistry

Corrosion in water distribution systems, LSLs, and household plumbing is electrochemical. Electrochemical corrosion is the destruction of a metal by electron transfer reactions (Snoeyink and Wagner 1996). In order for an electrochemical corrosion to occur, all components of an electrochemical cell must be present. Components of an electrochemical cell include:

- The anode and cathode, which are sites on the metal that have different electrical potential.
- The connection between the anode and cathode for electron transport (internal circuit).
- The electrolyte solution (water) that will conduct ions between the anode and cathode (external circuit).

If any one of these components is absent, a corrosion cell does not exist and corrosion will not occur (Snoeyink and Wagner 1996). Figure 2.1 shows a schematic of a electrochemical corrosion cell.

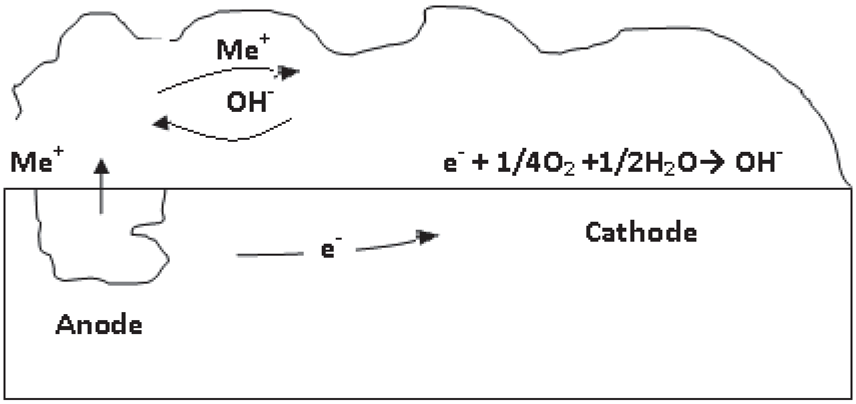

Figure 2.1 Schematic of a corrosion cell (Adapted from Snoeyink and Wagner 1996).

The metal is oxidized when corrosion takes place. This occurs at the anode. At the anode, the metal (Me) corrodes and the electrons generated by the anodic reaction migrate through the internal circuit to the cathode. This reaction is referred to as oxidation, which is the loss of electrons by the metal atoms (Snoeyink and Wagner 1996):

$$\mathrm{Me} \leftrightarrows \mathrm{Me}^{z+} + z\mathrm{e}^{-}, \qquad [2\text{-}1]$$

where z is the number of electrons (e^-) released by the metal. The positive ions generated at the anode will tend to migrate through solution to the cathode, and the negative ions generated at the cathode will tend to migrate to the anode (Snoeyink and Wagner 1996). At the phase boundary of a metal (electrode) in an electrolyte (water) both the forward (oxidation) and reverse (reduction) reactions are occurring at various points on the electrode (Snoeyink and Wagner 1996). The metal corrodes or dissolves in the forward reaction, producing electrons. In the reverse reaction, the metal ions are reduced by combination with electrons (Snoeyink and Wagner 1996).

2.1.2 Types of Corrosion

There are different types of corrosion. The kind of corrosion depends on the material to become corroded, construction of the pipe material, scale and oxide film formation, and hydraulic conditions (Snoeyink and Wagner 1996; Schock 1999). The distribution of anodic and cathodic areas over the corroding material is the primary determinant of the type of corrosion (Snoeyink and Wagner 1996).

2.1.2.1 Uniform corrosion

Uniform corrosion is the most common form of corrosion (Snoeyink and Wagner 1996). Any one site of the metal surface acts as both the anode and cathode. Because anodic sites shift or creep about the surface, the rate of metal loss is relatively uniform over the metal surface (Snoeyink and Wagner 1996). Corrosion cells develop on these heterogenous metals because there are differences in potential existing between different areas due to differences in crystal structure or imperfections in the metal (Snoeyink and Wagner 1996; Schock 1999; Eisnor 2002).

In a distribution system, uniform corrosion will occur within a pipe when the anodic and cathodic areas are very small and close to one another (Snoeyink and Wagner 1996), resulting in a corrosion that may be relatively uniform over the entire surface. Uniform corrosion results from the heterogeneous nature of cast iron, copper, and lead pipes.

2.1.2.2 Galvanic corrosion

Galvanic corrosion results when two different types of metals or alloys contact each other and the elements of the corrosion cell are present (Snoeyink and Wagner 1996). One of the metals serves as the anode and deteriorates, while the other serves as the cathode (Snoeyink and Wagner 1996). The galvanic series represents the arrangement of metals in the order of their tendency to be anodic (Schock 1999). An EMF series of metals is shown in Table 2.1. The rate of galvanic corrosion is increased by greater differences in potential between the two metals.

Table 2.1 Electromotive force (EMF) series.

Electrode		Electrode reaction	E°/V
Au	Gold	$Au^{3+} + 3e^{-} \leftrightarrows Au$	+1.43
Ag	Silver	$Ag^{+} + e^{-} \leftrightarrows Ag$	+0.80
Cu	Copper	$Cu^{2+} + 2e^{-} \leftrightarrows Cu$	+0.34
H	Hydrogen	$H^{+} + e^{-} \leftrightarrows H$	0
Pb	Lead	$Pb^{2+} + 2e^{-} \leftrightarrows Pb$	-0.13
Sn	Tin	$Sn^{2+} + 2e^{-} \leftrightarrows Sn$	-0.14
Ni	Nickel	$Ni^{2+} + 2e^{-} \leftrightarrows Ni$	-0.25
Cd	Cadmium	$Cd^{2+} + 2e^{-} \leftrightarrows Cd$	-0.40
Fe	Iron	$Fe^{2+} + 2e^{-} \leftrightarrows Fe$	-0.44
Zn	Zinc	$Zn^{2+} + 2e^{-} \leftrightarrows Zn$	-0.76
Ti	Titanium	$Ti^{2+} + 2e^{-} \leftrightarrows Ti$	-1.63
Al	Aluminium	$Al^{3+} + 3e^{-} \leftrightarrows Al$	-1.66
Mg	Magnesium	$Mg^{2+} + 2e^{-} \leftrightarrows Mg$	-2.37
Na	Sodium	$Na^{+} + e^{-} \leftrightarrows Na$	-2.71
K	Potassium	$K^{+} + e^{-} \leftrightarrows K$	-2.93

Li	Lithium	$Li^+ + e^- \leftrightarrows Li$	-3.05

Within a water distribution system, prime locations for galvanic corrosion are lead/tin soldered joints in copper pipes, or when lead is physically connected to copper. The lead surface is anodic and the rate of lead corrosion is accelerated (Nguyen et al. 2010). The free lead (Pb^{2+}) released to the water by galvanic corrosion in the connection of lead and copper is a Lewis acid. The Lewis acid decreases pH upon removal of OH^- ions from the water via formation of soluble complexes or insoluble precipitates that contain OH^- (Nguyen et al. 2010). However, because tin is a stronger Lewis acid than lead, it will lower the pH more than lead if it is present in a 50:50 (by weight) Pb/Sn solder (Nguyen et al. 2010). Lead contamination due to galvanic attack of lead/tin solder causing corrosive microenvironments can form at lead solder and copper pipe, perpetuating very high lead corrosion (Nguyen *et al.* 2011; Oliphant 1983). Partial replacements, which involve the connection between lead and copper, increase lead corrosion due to galvanic corrosion. Previous research showed that partial replacement promoted galvanic corrosion resulting in higher lead release (Boyd et al. 2004; Sandvig et al.2008; Mcfadden et al. 2011; Triantafyllidou et al. 2011).

2.1.2.3 Localized corrosion

Localized attack resulting in pitting may occur, both with galvanic corrosion and with corrosion of a single metal system. Localized corrosion happens due to imperfections in the metal or in regions of high stress in the metal (Snoeyink and Wagner 1996). Areas of high stress or of metal imperfection are usually anodic, and the potential difference between these regions and the rest of the metal is such that the anode remains at the same locations. Usually the anodic region is small relative to the cathodic area and it results in a rapid corrosion rate compared to uniform corrosion.

In water pipes, localized corrosion leads to the formation of tubercles, which appear as nodules or knob-like prominences on the scale of the corrosion product. In iron or steel pipes, the tubercules are made up of various iron oxides and oxyhydroxides. They are usually rust colored and soft on the outside and are both harder and darker towards the inside (Schock 1999). Uncontrolled tuberculation can double the cost of pumping water through the distribution system due to the increased roughness of the pipe and decrease in pipe diameter (Snoeyink and Wagner 1996).

2.1.2.4 Concentration cell corrosion

Concentration cell corrosion is caused by the difference in the concentration of the aqueous solution species compared to the differences in the metal, which causes uniform corrosion (Snoeyink and Wagner 1996). The corrosion process will always occur in a way that tends to equalize potential at the two locations. Differences in pH, hydrogen ion concentration, metal ion concentration or dissolved oxygen concentrations at different sites on a metal surface induce concentration cell corrosion (Snoeyink and Wagner 1996). Differences in temperature can also induce differences in the solution potential of the same metal (Schock, 1999).

2.1.2.5 Microbially influenced corrosion

Microbes in the water distribution system influence corrosion in many ways. Growth of microorganisms in biofilm can create concentration differentials that promote corrosion (Schock 1990). The microorganisms generally grow in patches along the surface in a way that creates adjacent regions with differentials oxygen, hydrogen ion, and metal ion concentrations. These concentration differentials promote corrosion. Lee *et al.* (1980) found evidence that microbial growth promoted localized corrosion, consistent with concentration cell corrosion.

Microorganisms may catalyze reactions associated with the corrosion process (Snoeyink and Wagner 1996). Microorganisms that can oxidize or reduce different forms of iron and lead, which promotes the depolarization of the anode and further the corrosion process (Emde *et al.* 1992). Iron precipitating bacteria can convert divalent iron to trivalent iron, which also results in the formation of the corrosion by - products (Snoeyink and Wagner 1996).

2.1.3 Factors Affecting Corrosion in Drinking Water

The factors affecting the corrosion of metals in drinking water can be categorized into physical, chemical, and biological characteristics (Snoeyink and Wagner 1996). However, in most cases, corrosion is caused by a complex interaction among several factors. The important factors that affect corrosion in water distribution systems are outlined in Table 2.2 and the factors that were considered in this research thesis are discussed in further detail in the following sections.

Table 2.2 Factors affecting corrosion in drinking water.

Factor	Effect of Corrosion
	Physical Characteristics
Flow	Affects the corrosion of lead and brass devices (Schock 1999; Sarver et al. 2011; Cartier et al. 2012; Xie and Giammar 2011)
Temperature	Generally increases corrosion (Droste 1997; Schock 1999; Sarver *et al* 2011)
Stagnation time	Metal concentration increases with stagnation (Lytle and Schock 2000; Lasheen *et al.* 2008; Gagnon and Doubrough 2011; Xie and Giammar 2011).
	Chemical Characteristics
pH	Lower pH values tend to increase corrosion; high pH values aid in the formation of protective scales (Droste 1997; McNeill and Edwards 2001; Lasheen *et al.* 2008; Tam and Elefsiniotis 2009)
Alkalinity	Alkalinity helps to buffer the pH of the water, thus at lower alkalinities there is more pH fluctuations and an increase in corrosion rate (Droste 1997; McNeill and Edwards 2001; Tam and Elefsiniotis 2009).
Disinfectant Residual	Studies have shown that there is more lead corrosion when comparing chlorine with chloramines, however, high chlorine in the distribution system can lower lead release by the formation of metallic lead oxides (Edwards and Dudi 2004; Lytle and Schock 2005; Davidson *et al.* 2004; Xie and Giammar 2011).
Total Dissolved Solids	An increase in total dissolved solids will increase conductivity and thus increase the corrosion rate (Droste 1997).
Hardness	High hardness may cause the $CaCO_3$ to precipitate to form a protective coating that lowers metal release (McNeill and Edwards 2001; Schock 1999).
Natural organic matter	Depending on the amount of natural organic matter, it may form a protective coating or react with corrosion products and increase corrosion (Schock 1999; Korshin et al. 2005).

2.1.3.1 Stagnation time

Lead and copper sampling under the USEPA LCR and Health Canada require that first draw samples must be taken following at least six hour stagnant contact with the plumbing material. Studies conducted by Lytle and Schock (2000) to evaluate the impact of stagnation on metal dissolution from plumbing materials (lead, copper, brass) showed that metal levels increase exponentially with time. In their study, Gagnon and Doubrough (2011) showed that lead concentrations were 2.5 times greater in a 23 hours stagnation compared to 30 minutes stagnation. Lasheen et al. (2008) also concluded that a longer stagnation resulted in a higher lead and iron release in their study. In addition, Lytle and Schock (2000) determined that metal concentrations will continue to increase following well beyond 24 hours of stagnation. However, copper concentrations will increase until dissolved oxygen falls below 1 mg/L after which copper concentrations will drop asymptotically. Additionally, the results from Lytle and Schock (2000) showed that stagnation behavior is complex in nature, difficult to predict, and dependent on water chemistry. Therefore, understanding stagnation profile is important when determining corrosion control strategies and conclusions in research (Lytle and Schock 2000). Furthermore, a recent study by Xie and Giammar (2011) determined that, even in the presence of orthophosphate corrosion inhibitor, dissolved lead concentrations exceeded the action level of lead (15µg/L) following 24 hour stagnation. However, 8 hour stagnation results from the same study resulted in dissolved lead concentrations below the 15 µg/L action level.

2.1.3.2 pH

The pH of the water is an important factor in corrosion because low pH may increase corrosion rate, and high pH may protect pipes and decrease corrosion rates or can also cause dezincification of brasses (Droste 1997; Schock 1999). At pH values below 5, metals corrode rapidly and at pH values greater than 9, metals are usually protected (Eisnor 2002). Studies show that lead and iron concentrations increase with pH decrease (Lasheen *et al.* 2008; Tam and Elefsiniotis 2009). This can be explained by the fact that the solubility of lead is governed by the formation of lead carbonates as pipe deposits. However, below pH of 8 there is a substantial decrease in the equilibrium carbonate concentration and the primary form of lead in water at low pH is predominantly Pb^{2+} and less abundant inorganic forms ($Pb(SO_4)_2^{2-}$, $PbCO_3$, $Pb_3(OH)_2(CO_3)_2$) (Lasheen et al. 2008). Lead dissolution in drinking water tends to be at a maximum in waters with a low pH.

2.1.3.3 Disinfectant residual

Chlorine is widely used in water treatment for chemical disinfection. In Halifax, chlorine is used for disinfection and a minimum chlorine residual of 1 mg/L is maintained in the distribution system. Most of the guidance for lead control in drinking water is based on the presumption that Pb(II) solids control lead solubility, although recent research has shown that Pb(IV) oxides (PbO_2) play a significant geochemical role in drinking water (Lytle and Schock 2005).

Free chlorine can raise the redox potential of lead, inhibit PbO_2 dissolution, and oxidize Pb(II) released from hydrocerrusite to PbO_2 which reduces lead in water (Xie and Giammar 2011; Lytle and Schock 2005; Davidson et al. 2004). In addition, the presence of PbO_2 is associated with water of persistently high Oxidation Reduction Potential (ORP), which is only possible by maintaining sufficient levels of free chlorine in water in contact with lead service lines and other lead materials (Lytle and Schock 2005). The high redox potential necessary to achieve PbO_2 formation in water can only be met with the use of strong oxidants (e.g. free chlorine, chlorine dioxide) and their persistence into the distribution system (Lytle and Schock 2005). Furthermore, the formation of PbO_2 in chlorinated water requires time to overcome kinetic barriers and may require precursor Pb (II) mineral phases (Lytle and Schock 2005). The rate of PbO_2 formation and chlorine consumption increases when pH increases.

Distribution systems that have historically maintained high chlorine residuals could have PbO_2 functioning to limit lead release, while hydrocerussite or cerussite are presumed to be the main components of the passivating films or other diffusion barriers (Lytle and Schock 2005). The effects of changes in ORP have been linked to instances of erratic lead release in some distribution systems caused by the destabilization of the PbO_2 scales (Lytle and Schock 2005).

2.1.4 Corrosion of Cast Iron Water Mains and Corrosion Scales

The corrosion of cast iron water mains can be either uniform or localized (Benjamin et al. 1996). Localized corrosion of ferrous materials often leads to tuberculation. Tuberculation reduces the effective pipe size and increases the roughness of the pipe inside diameter (Benjamin et al. 1996). Microorganisms may also attach and grow on the tubercles. The corrosion of cast iron water mains and scale formation is well researched (McNeill and Edwards 2001; Sarin et al. 2001; Sarin et al. 2004). In Halifax, due to the age of the distribution system, the majority of the distribution system consists of cast iron pipes. However, ongoing water main replacements programs are replacing about 4.5 km of cast iron pipe annually (Halifax Water 2012).

The iron release rate is influenced by a complex combination of water quality parameters (DO, pH, alkalinity, buffer intensity, temperature, application of an inhibitor) and physical (water flow characteristics) factors (Benjamin et al. 1996; Sarin et.al 2004; McNeill and Edwards 2001). As a result, the iron release rate often bears no simple relationship to the instantaneous overall corrosion rate, which is the rate at which metallic iron is being converted to an oxidized form (Benjamin et al. 1996). Since iron corrosion and iron release are independent processes, measures that limit iron release might not be effective at controlling the iron corrosion rate (McNeill and Edwards 2001; Benjamin et al. 1996).

Metallic iron cannot coexist in an equilibrium system with water containing a measurable concentration of DO or free chlorine, as explained by the Pourbaix diagram (Figure 2.2) (Benjamin et al. 1996).

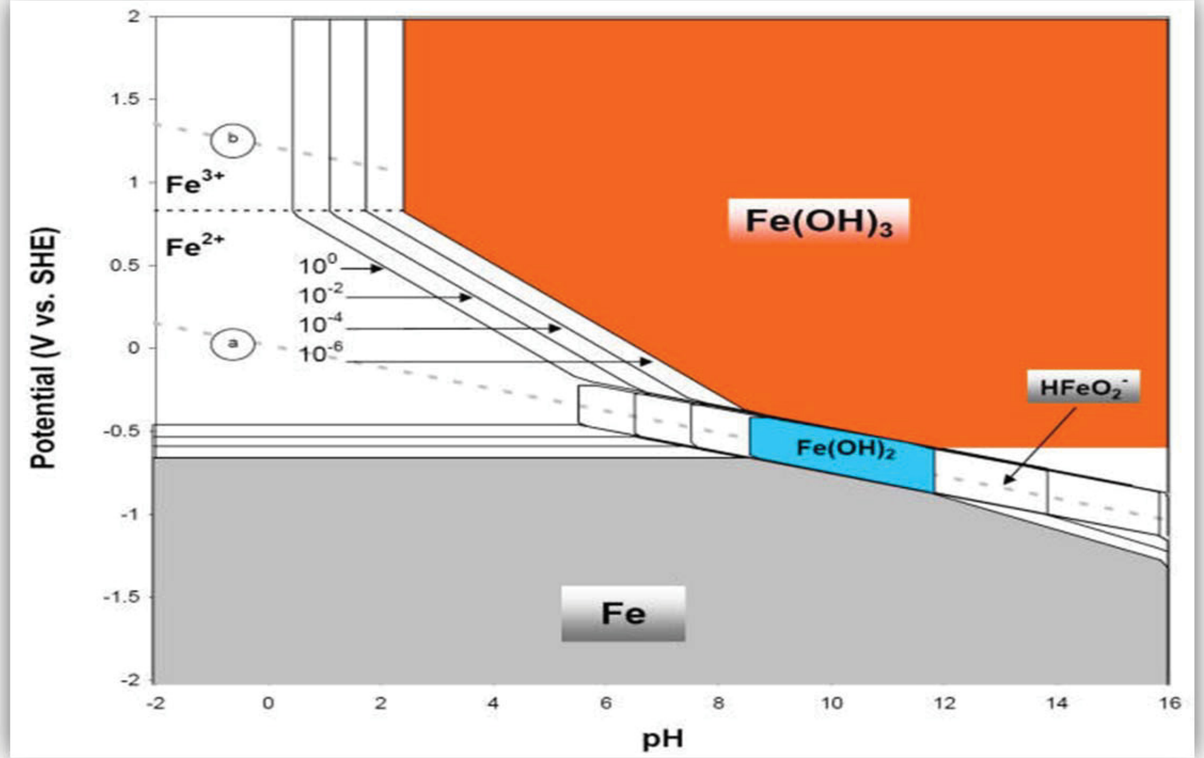

Figure 2.2 Pourbaix diagram for iron in water at 25°C (http://corrosion-doctors.org/Corrosion-Thermodynamics/Potential-pH-diagram-iron.htm)

Corrosion of the cast iron pipe leads to scale formation on the walls of the pipe. Iron scales originate at the pipe wall and grow radially inward towards the pipe center (Eisnor 2002). The iron scale is composed of many iron compounds (Table 2.3). However, research on the characterization of iron pipe scales found that goethite and magnetite are present in a larger percentage (Sarin *et al.* 2001). Additionally, more recent research from the same authors found high concentrations of readily soluble Fe(II) content present in the pipe scales and a dense shell-like layer has been observed near the top of the scale that is in contact with water (Sarin *et al.* 2004).

Table 2.3 Corrosion scales present in cast iron pipes (adapted from McNeill and Edwards 2001).

Name	Chemical Formula	Iron Oxidation State
Ferrous hydroxide	$Fe(OH)_2$	II
Ferric hydroxide	$Fe(OH)_3$	III
Wustite	FeO	II
Goethite	α- FeOOH	III
Akaganeite	β - FeOOH	III
Lepidocrocite	γ - FeOOH	III
Hematite	α- Fe_2O_3	III
Maghemite	γ - Fe_2O_3	III
Magnetite	$Fe_3O_4(FeO \bullet Fe_2O_3)$	II and III
Ferric oxyhydroxide	$FeO_x(OH)_{3-2x}$	III
Siderite	$FeCO_3$	II
Iron hydroxycarbonate	$Fe_x(OH)_y(CO_3)_z$	III
“Green rust”	$Fe(III)_{x1}Fe(II)_{x2}(OH)_y(CO_3 \bullet SO_4)_z$	II and III
Vivianite	$Fe_3(PO_4)_2 \bullet 8H_2O$	II
Strengite	$FePO_4$	III
Schreibersite	Fe_3P	Not known

Iron may be released from the corroded iron surfaces by the corrosion of iron, dissolution of ferrous components of the scales, and hydraulic scouring of particles from the scales (Sarin et. al 2001; Sarin et al. 2004). The release of iron in the distribution system can adversely affect water quality, and the adsorption and accumulation of substances, such as arsenic and radium, on the iron particles has been demonstrated in prior research (Gimenaz *et al.* 2007; Field *et al.* 1995).

2.1.5 Corrosion Inhibition with Phosphates

Elevated lead in the distribution system has occurred while utilities practiced optimized corrosion control using orthophosphate inhibitors (Edwards and Triantafyllidou 2007).

In a survey of water utilities conducted by Dodrill & Edwards (1995), it was discovered that corrosion inhibitors are beneficial only in low alkalinity water sources (< 30 mg/L as $CaCO_3$) at all pH values with all results being significant at a 95% confidence interval. Inhibitors did not produce a statistically significant reduction in lead release in any other pH-alkalinity category tested (Dodrill & Edwards 1995). It was also found that use of inhibitors exacerbates lead release when used in waters with pH < 7.40 and alkalinity 30-74 mg/L as $CaCO_3$ (Dodrill & Edwards 1995). Many of these effects were directly attributed to polyphosphates and not orthophosphates (Dodrill & Edwards 1995). Recent research by Tam and Elefsiniotis (2009) showed that the addition of orthophosphate was effective at pH > 7.5, resulting in an approximately 70% reduction in both lead and copper release.

In the galvanic corrosion of lead-tin solder in contact with copper pipe, there is a tendency for phosphate to increase lead release if the sulphate concentrations are low (<10 mg/L SO_4) or if less than 30% of the carrying current is carried by sulphate ions (Nguyen *et al*. 2011). The galvanic current sacrificing the Pb-Sn solder anode is increased due to orthophosphate in some cases, which in turn translates to lower pH and higher concentrations of aggressive anions, such as Cl^- at Pb-Sn solder surfaces (Nguyen *et al*. 2011). Dosing of orthophosphate occasionally creates significant adverse consequences on galvanic corrosion of lead bearing plumbing materials connected to copper tube (Nguyen *et al*. 2011). Additionally, because orthophosphate often has profound benefits in reducing lead release during uniform corrosion, the net impacts of orthophosphate on overall lead release to water in individual buildings can be complicated. In cases where orthophosphate exacerbates galvanic corrosion of 50:50 Pb–Sn solder, tin release is more strongly affected than lead (Nguyen *et al*. 2011). Therefore, even in the presence of an orthophosphate corrosion inhibitor and lead phosphate (Pb_3PO_4) surface scales, soluble lead is expected to increase rapidly if the pH at the lead solder anode surface drops below pH 4.6 (Nguyen *et al*. 2011).

In controlling lead leaching from solder galvanically connected to copper, orthophosphate alone is most effective in reducing the concentration of lead leached (Edwards and Triantafyllidou 2007). Zinc orthophosphate is the second most effective corrosion inhibitor, whereas zinc alone is the least effective corrosion inhibitor (Edwards and Triantafyllidou 2007). A comparison of the different corrosion inhibitors regardless of coagulation chemical indicates that addition of zinc orthophosphate is the most effective lead corrosion strategy for brass connected to copper followed by zinc alone (Edwards and Triantafyllidou 2007).

2.2 WATER MAIN MAINTENANCE

Water mains are an important component of the water supply system. If the water mains lack proper and timely maintenance, the incidences of leaks and water main breaks will increase, water quality will deteriorate, and hydraulic capacity will decrease. Water main maintenance and renewal solves these problems and prolongs their useful life (Deb 1991). Trenchless technologies are commonly used for water main maintenance because they reduce the obstruction to traffic, thereby making it feasible to repair or conduct maintenance on a water main with little or no effect to the flow of traffic and people in that area.

2.2.1 Epoxy Lining

Epoxy lining is a trenchless technology used to restore pipe and water quality. Epoxy lining does not strengthen the structural integrity of the pipe nor reduce it. Entry and exit pits are dug, as in all trenchless methods. The epoxy is then applied after the water main has thoroughly been cleaned of corrosion and the remnants of tuberculation.

The cleaning process is conducted using metal wire brushes and scrapers (pigs) that are pulled through the length of the water main being lined (Figure 2.3). Following the cleaning process, the water main is thoroughly flushed with water. The sediments are collected in a barrel, left to settle, and later disposed of in an environmentally friendly manner. The epoxy lining is then applied to the water main using an advanced control radial spray-on technique ensuring uniform coating on the inside of the pipe. The epoxy lining inhibits further corrosion and oxidation of the pipe interior (Figure 2.4).

a.) Criss-Cross Wire Brush (Pig). b.) Metal brush used for pipe cleaning.

Figure 2.3 Pig and Metal used in water main cleaning (Courtesy of Halifax Water).

Figure 2.4 Excavated water main showing epoxy lining (Courtesy of Halifax Water).

2.2.2 Cure In Place Piping (CIPP)

CIPP is a structural liner used to improve the structural integrity of the water main. As in all water main rehabilitations, before any work is started, the customers are switched to a temporary line for the duration of the project. The temporary line is chlorinated, de-chlorinated, and tested before any of the customers start using the water. Access pits are dug at strategic locations in the water main to minimize the interruption to traffic and also to reduce the number of pits that have to be excavated. The water main is then cut and drained to allow the cleaning crew access to the host pipe.

Cleaning the pipe is a critical step in the rehabilitation of a water main using CIPP. The rust and scale have to be removed to allow the new composite liner to adhere to the wall of the host pipe and also restore the flow capacity of the pipe (NASTT 2005). The cleaning is done using water pressure and a rotary chain boring tool (pigs). Following the completion of the cleaning, the pipe is inspected with a camera to ensure all the rust and scales have been removed. The service connections are then plugged to prevent the resin from blocking the service. The plugs are also used to make visible any non-penetrating services in the lined pipe. These special plugs allow the operators to locate the non-penetrating services after they have been covered with the composite liner. A log is kept of the location of all the services so that they will be re-opened after the liner cures.

The lining and curing involves three main activities: wetting of the liner, insertion in the host pipe, and curing the liner inside the host pipe. The impregnation of the material is done on site in a refrigerated atmosphere (NASTT 2005). Insertion is the method for placing the structural liner inside the host pipe. Two methods of insertion are commonly used: pulling-in-place and inversion. The pulling-in-place method is the most commonly used method in smaller diameter water mains that have many services. This method is carried out without the use of specialized equipment (NASTT 2005).

The curing of the liner involves heating the impregnated liner to initiate a reaction between the reactants of the polymer resin. The reaction causes the polymer resin to reticulate and harden to confer mechanical rigidity to the liner. The heat is supplied by hot water being pumped into the pipe. After the liner has cured, a remote control robot is sent into the pipe to remove the plugs on all the services, cutting through the liner and permitting free flow of water.

The reinstatement of all the services is followed by chlorination and de-chlorination of the water main. In addition, water samples are collected to test for the presence of total coliform and e-coli. If all the water samples are clean of total coliform and e-coli, the water main is put back in service (Figure 2.5).

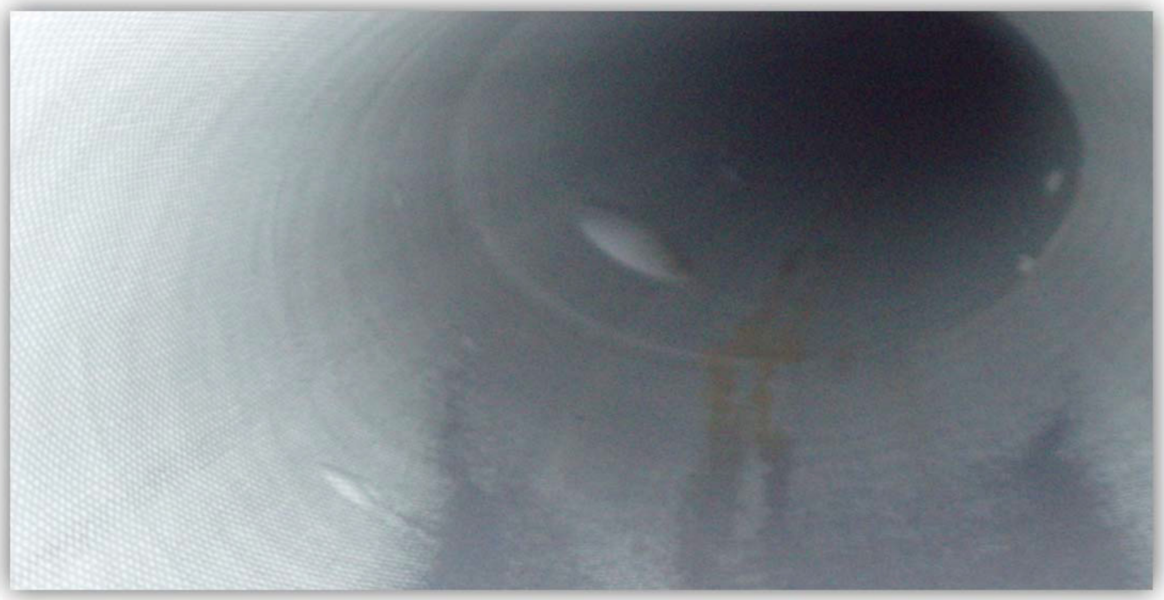

Figure 2.5 Internal view of a completed CIPP (photo by author)

2.3 ADSORPTION THEORY

Adsorption is a mass transfer operation in which substances present in a liquid phase are adsorbed or accumulated on a solid phase and thus removed from the liquid (Crittenden *et al.* 2005). Adsorption processes are used in drinking water treatment for the removal of organic and inorganic constituents. Arsenic for example can be removed by adsorption with magnetite (Raven *et al.* 1998). The constituent that undergoes adsorption is referred to as the adsorbate, and the solid onto which the constituent is adsorbed is referred to as the adsorbent (Droste 1997; Crittenden *et al.* 2005). In the adsorption process, dissolved species are transported into the porous solid adsorbent granule by diffusion and are then adsorbed onto the extensive inner surface of the adsorbent (Crittenden *et al.* 2005). Adsorption occurs by either chemical reaction (chemisorption) or physical attraction (physical adsorption).

Chemisorption happens due to a chemical reaction that entails the transfer of electrons between the adsorbent and the adsorbate and a chemical bond with the surface occurs. Chemisorption is usually not reversible because the adsorbate is chemically bonded to the surface.
Physical adsorption is the most common mechnanism by which adsorbates are removed in water treatment. Physical adsorption is a rapid process caused by nonspecific binding mechanisms, such as van der Waals forces (Crittenden *et al.* 2005). Physical adsorption is reversible, that is, the adsorbate desorbs in response to a decrease in solution concentration.

2.3.1 Interfacial Equilibria for Adsorption

In aqueous solution, three interactions compete when considering physical adsorption:

- Adsorbate – water interactions,
- Adsorbate – surface interactions,
- Water- surface interactions.

The extent of adsorption is determined by the strength of adsorbate-surface interactions as compared to the adsorbate-water and water-surface interactions (Crittenden *et al*. 2005). Furthermore, adsorbate-surface interactions are determined by surface chemistry, and adsorbate-water, and water-surface interactions are related to the solubility of the adsorbate (Crittenden *et al.* 2005). In chemisorption, however, the primary factor controlling the extent of reaction is the type of reaction that occurs on the surface. In both physical adsorption and chemisorption, the surface area and pore size are important factors that determine the number of adsorption sites and the accessibility of the sites for adsorbates. An inverse relationship between the pore size and surface area exist. In a given pore volume, the smaller the pores, the greater the surface area that is available for adsorption. Likewise, the size of the adsorbate that can enter a pore is limited by the pore size of the adsorbent, and is referred to as steric effects (Crittenden *et al.* 2005).

2.3.2 Surface Chemistry and Forces Involved in Adsorption

There are three interfaces involved in adsorption:

- Adsorbate-adsorbent,

- Adsorbate- water, and
- Water – adsorbent.

The forces active at each of these interfaces are summarized in Table 2.4.

Table 2.4 Forces that are active at the three interfaces involved in adsorption (Crittenden et al. 2005).

Force	Approximate Energy of Interaction, kJ/mole	Interface		
		Absorbates/ Adsorbent	**Adsorbates/ Water**	**Water/ Adsorbent**
Coulombic repulsion	>42	Yes	No	No
Coulombic attraction Ionic species –neutral species attraction	>42	Yes	No	No
Covalent bonding	>42	Yes	No	No
Ionic species – dipole attraction	<8	Yes	No	No
Dipole – dipole attraction	<8	Yes	Yes	Yes
Dipole –induced dipole attraction	<8	Yes	Yes	Yes
Hydrogen bonding	8 – 42	Yes	Yes	Yes
van der Waal's attraction	8 – 42	Yes	Yes	Yes

2.3.2.1 Chemical adsorption

Chemical adsorption (chemisorption) occurs when the adsorbate reacts with the surface to form a covalent bond or an ionic bond. Adsorbates bound by chemisorption to a surface generally cannot accumulate at more than one molecule layer, because of the specificity of the bond between adsorbate and surface (Crittenden *et al.* 2005). The bond may also be specific to particular sites or functional groups on the surface of the adsorbent. The charged surface groups attract the opposite charges and repel like charges according to Coulomb's law (Crittenden *et al.* 2005). For adsorption of ionic species to surfaces, the most important mechanism is electrostatic attraction, which is highly dependent on pH and ionic strength (Crittenden *et al.* 2005).

2.3.2.2 Physical adsorption

Adsorbates undergo physical adsorption if the forces of attraction include only physical forces that exclude covalent bonding with the surface and coulombic attraction of unlike charges (Crittenden *et al.* 2005). In certain cases, the difference between physical and chemical adsorption may not be that distinct. Compared to chemical adsorption, physical adsorption is less specific for which compounds absorb to surface sites, has weaker forces and energies of bonding, operates over longer distances (multiple layers), and is more reversible (Crittenden *et al.* 2005).

2.3.3 Adsorption Isotherms

Adsorption isotherms describe the relation between the amount or concentration of adsorbate that accumulates on the adsorbent and the equilibrium concentration of dissolved adsorbate (Droste 1997). Adsorption isotherms are obtained by exposing a known quantity of adsorbate in a fixed volume of liquid to various dosages of adsorbent. Approximately 12 headspace bottles/flasks are used with various dosages of adsorbent and allowed to equilibrate on a shaker table for five days. At the end of the equilibration period, the aqueous-phase concentration of the adsorbate is measured and the adsorption equilibrium capacity is calculated for each bottle/flask using the mass balance equation shown below.

$$q_e = \frac{V}{M}(C_o - C_e) \qquad [2\text{-}2]$$

where,

q_e = equilibrium adsorbent- phase concentration of adsorbate, mg adsorbate / g adsorbent
Co = initial aqueous- phase concentration of adsorbate, mg/L
Ce = equilibrium aqueous – phase concentration of adsorbate, mg/L
V = volume of aqueous – phase added to bottle, L
M = mass of adsorbent, g

Equations developed by Freundlich and Langmuir are used to describe the equilibrium capacity of adsorbents.

2.3.3.1 Freundlich equation

The Freundlich adsorption isotherm is used to describe the data for heterogeneous adsorbents, a quality which can be assumed for magnetite and goethite. The Freundlich adsorption isotherm equation is expressed as:

$$\mathrm{q_A} = \mathrm{K_A} \mathrm{C_A}^{1/\mathrm{n}} \qquad [2\text{-}3]$$

where

$\mathrm{K_A}$ = Freundlich adsorption capacity parameter, (μg/g) (L/μg)$^{1/n}$

1/n = Freundlich adsorption intensity parameter, unitless

The linear form of the Freundlich equation is:

$$\log(\mathrm{q_A}) = \log(\mathrm{K_A}) + \left(\frac{1}{\mathrm{n}}\right)\log(\mathrm{C_A}) \qquad [2\text{-}4]$$

A linear regression of log q_A vs log C_A gives the Freundlich parameters.

2.3.3.2 Langmuir equation

The Langmuir adsorption isotherm is used to describe the equilibrium between surface and solution as a reversible chemical equilibrium between species (Crittenden et al. 2005). The Langmuir model allows accumulation only up to a monolayer, which is a suitable assumption for liquids (Droste 1997). The Langmuir adsorption isotherm equation is expressed as:

$$\mathrm{q_A} = \frac{\mathrm{Q_M b_A C_e}}{\mathrm{b_A C_e} + 1} \qquad [2\text{-}5]$$

where,

q_A = adsorption density achieved in μg lead/g solid,

C_e = equilibrium concentration in μg lead/L,

Q_M = maximum adsorption density when the surface sites are saturated with the adsorbate mg lead/ g solid

b_A = Langmuir adsorption constant of adsorbate, L /mg

It is always convenient to rearrange equation 2-5 in linear form:

$$\frac{C_e}{q_A} = \frac{1}{b_A Q_M} + \frac{C_e}{Q_M} \qquad [2\text{-}6]$$

Plots of C_e/q_A versus C_e using Equation 2-6 result in respective straight lines with slope of $1/Q_M$ and intercept $1/b_AQ_M$. The values of b_A and Q_M are determined from the line of best fit.

The Freundlich and Langmuir equations were both used to analyze the collected adsorption batch results. Both equations were used because the both equations could describe adsorption of lead on the iron minerals and no guidance on which equation to use was available.

2.4 PIPE LOOPS/PIPE RIGS

Water distribution and premise plumbing simulators usually use pipe loops, or what are more generally referred to as pipe rigs. Different researchers use several types of pipe loops (pipe rigs) depending on their research objective. The three main types of pipe loops (pipe rigs) are once through, stagnation, and recirculating. The Dalhousie Pipe Loop© was designed by Rutledge (2003) to be a research standard because there were no universal pipe loop standards at that time (Eisnor and Gagnon 2003). The Dalhousie Pipe Loop© is a recirculating pipe loop that connects to a copper pipe rack. Pipe loops can be either open or closed loop depending on the type of testing that is simulated. However, the Dalhousie Pipe Loop© was designed as a closed loop (Rutledge 2003). Past standard pipe loop (pipe rig) setups focused only on evaluating water quality with no consideration to simulating the hydraulic conditions (Rutledge 2003). However, recent research has focused more on hydraulic conditions affecting water quality and metal release (Woszczynski 2011; Wang *et al.* 2012; Gagnon and Doubrough 2011).

Once through and stagnation pipe loops (pipe rigs) have been used with success in previous research conducted by Dr. Gagnon's research group (Maddison *et. al* 2001). Maddison *et al.* (2001) found that with short pipe sections and high velocities there is no measurable change in the water quality of once through rigs. However, the length of the pipe section can impact the water quality if there is sufficient retention time, which was shown by McMath (1997) where a 1.3km length pipe section was used. In order to increase the retention time using short pipe sections, the water is recirculated or a stagnation time is provided to promote pipe wall interactions and water chemistry reactions (Maddison 2002). The benefit of using a recirculating pipe loop (pipe rig) is that the retention time can be adjusted to match a typical distribution system retention time with minimal cost of acquiring long length pipes (Rutledge 2003).

Pipe loops are used to investigate various research topics related to water distribution. The effects of pipe material, disinfectant type, retention time, corrosion control, flow rate, and basic water quality parameters are easily investigated using pipe loops (pipe rigs) (Rutledge 2003). The use of pipe loop (pipe rig) by researchers over the years has seen a dramatic increase due to the benefits of pipe loop (pipe rig) studies. In the effort to minimize lead release in premise plumbing, understanding the impacts of physical and chemical changes in the distribution system on lead release in premise plumbing is pertinent. A review of research related to recirculation pipe loops (pipe rigs) was presented by Eisnor and Gagnon (2003). A modification of the review is presented in Table 2-5.

Table 2.5 Review of Recirculation Pipe loops (Pipe rigs) (Adapted from Eisnor and Gagnon 2003).

Purpose	Stagnation Time	Pipe Length	Pipe Diameter	Pipe Material	Duration	Velocity	Author
Biofilm	n.r.[1]	31 m/loop[2]	100 mm	Cement-lined Cast Iron	n.r.	1m/s	Haudidier et al. 1989
Corrosion	n.r.	Coupons	n.r.	Mild Steel, Copper, Brass, Solder Coating	3 -4 months	0.03m/s	Reiber 1993
Corrosion	Varied	1.2 m	12.5 mm	Copper	n.r.	0.36m/s	Schock et al. 1995
Biofilm	n.r.	0.6 m	100 mm	Mild Steel	n.r.	0.3m/s	Camper, 1996
Corrosion Control	22 & 72 h	Coupons	12.5 mm	Brass, Copper, Zinc, & Lead	30 months	0.36m/s	Lytle and Schock 2000
Corrosion Control	n.r.	3.2 m	100 mm	Old Cast Iron	24 months	n.r.	Lohmann et al. 1997
Corrosion	12 h	n.r.	n.r.	Old Cast Iron	n.r.	n.r.	Price and Jefferson, 1997
Disinfectant efficacy	6 & 24 h	1.8 m	150 mm	Concrete line ductile iron, Polyvinyl Chloride.	6 months	0.3 m/s	Rutledge 2003
Corrosion	12 h	1.8 m	150 mm	Polyvinyl Chloride, Copper, Lead/tin solder	100 d	0.3 m/s	Gagnon and Doubrough 2011
Corrosion	Varied	0.06 m & 0.91m	19 mm	Copper & Brass	n.r.	2.1 m/s	Sarver and Edwards 2011
Corrosion	6 & 17.5 h	0.6 m	25 mm	Lead & Copper	19 weeks	0.3 m/s	Wang et al. 2012

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[1] n.r. represents not reported

CHAPTER 3 MATERIALS AND METHODS

The main purpose of this chapter is to describe the finish water characteristics leaving the plant, to describe the water distribution system in the study area and to provide a description of the Dalhousie Pipe Loop© and Copper Pipe Rack situated at the James Douglas Kline Water Supply Plant. Analytical procedures that are common to all the experiments will also be described in this chapter. In addition, materials and methods that are chapter specific, statistical analysis and quality control/assurance will be described in their respective chapters.

This research involved the analysis of Lead Service Line Replacement (LSLR) water samples and the tendency of lead to adsorb on iron particles in the Halifax Water distribution system which supplies customers in Halifax, Nova Scotia.

3.1 JAMES DOUGLAS KLINE WATER SUPPLY PLANT

The James Douglas Kline Water Supply Plant (JDKWSP) is a direct filtration plant operated and maintained by Halifax Water that treats water from Pockwock Lake. The plant uses pre-screening, oxidation, pre-chlorination, coagulation, hydraulic flocculation, filtration, and chlorination. Pre-screening of the raw water removes all large impurities in the water, which is followed by a potassium permanganate ($KMnO_4$) addition for the oxidation of manganese and iron. Next, pH adjustment is done by adding carbon dioxide (CO_2) followed by the addition of alum at a concentration of 8 mg/L. Cationic polymers are added during the cold weather months (November to June) to aid floc strengthening and to ensure the removal of natural organic matter (NOM). Pre-chlorination, which follows the addition of the coagulant, prevents the growth of bio- film in the filters. Hydraulic flocculation, direct filtration, and chlorination of the filtered water follow in the respective sequence. Finished water from the treatment process has a total chlorine residual of 1.0 mg/L, pH of 7.4, zinc/ortho polyphosphate of 0.5 mg/L as PO_4 for corrosion control, and hydrofluosilicic acid is added to provide fluoride in the finished water (Knowles 2011). Figure 3.1 shows the process diagram at the JDKWSP and Table 3.1 details the finished water characteristics during the study period.

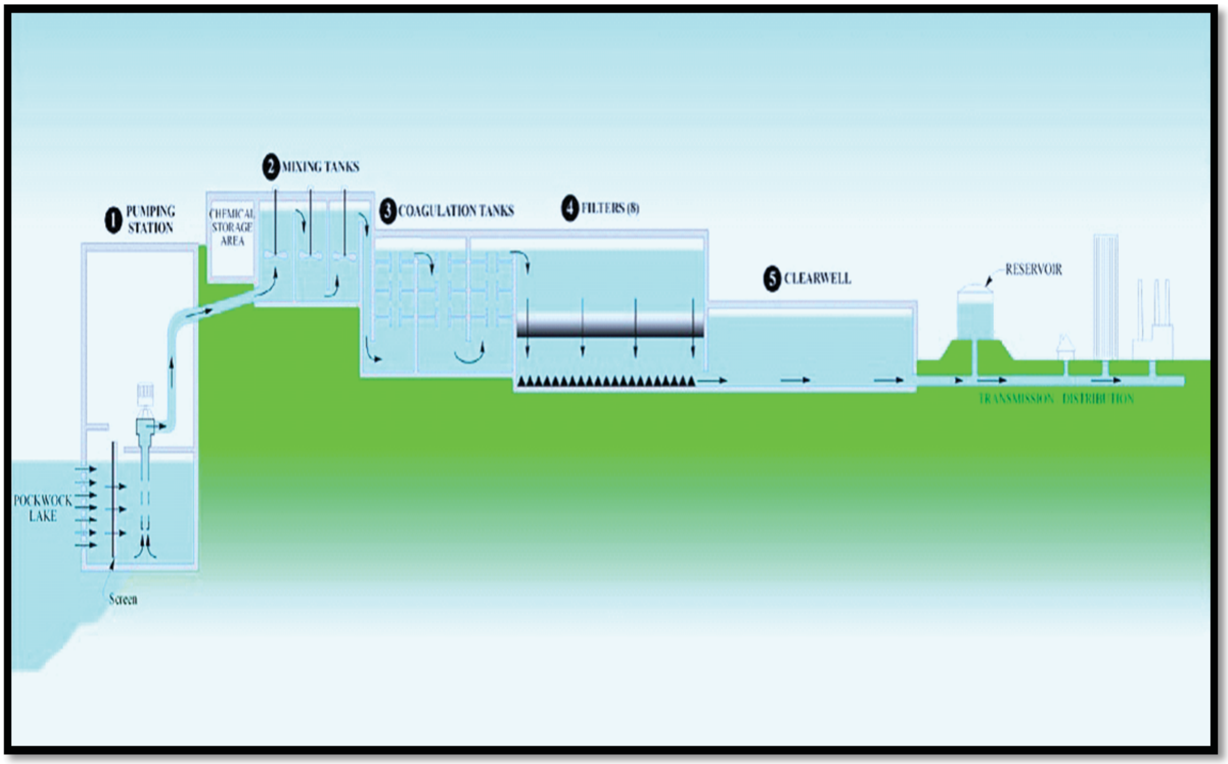


Figure 3.1 Process diagram for the JDKWSP (Adapted from Halifax Water 2012).

Table 3.1 Finished water characteristics from August 2011 to August 2012.

Parameter	**Average ± Standard deviation**
pH	7.4 ± 0.1
Turbidity (NTU)	0.1 ± 0.0
Alkalinity	16.0 ± 2.9
Total Cl_2 (mg/L)	1.2 ± 0.3
Free Cl_2 (mg/L)	1.1 ± 0.3
Phosphate as PO_4 (mg/L)	0.5 ± 0.1
Iron (mg/L)	0.0 ± 0.1
Aluminum (mg/L)	0.1 ± 0.9
Number of samples	460

3.2 HALIFAX WATER DISTRIBUTION SYSTEM

The water distribution system in Halifax consists of a mixture of cast iron, ductile iron, polyvinyl chloride (PVC) water mains, which are mainly used for areas close to the shore due to the corrosivity of the soil, and other pipe materials (Table 3.2). Like most North American cities with aging buried infrastructure, the condition of the water distribution system varies from tuberculated water mains, newly replaced water mains, to recently pigged and lined water mains. Halifax Water employs an ongoing long-term distribution main renewal program that aims to ensure long-term integrity and reliability of the distribution system. The distribution main replacement program replaces structurally deficient pipes that have increasing maintenance costs and reduced reliability, which is common in cast iron pipes installed before 1960 (Halifax Water 2012). These cast iron pipes are replaced with new Ductile Iron pipes. The majority of the distribution main replacement projects are undertaken in partnership with Halifax Regional Municipality (HRM) road or sewer renewal projects in order to reduce public disruption and to improve cost benefit. Currently, approximately 4.5 kilometers of cast iron pipes are replaced annually (Halifax Water 2012).

Table 3.2 Water main material and percentage in the HRM.

Pipe material	Total Pipe Length (m)	%
Asbestos Cement	1176.41	0.2
Brass	73.42	0.0
Cast Iron	**253143.91**	**33.7**
Copper	945.56	0.1
Ductile Iron	**368265.15**	**49.0**
Ductile Iron Hyprotec	5382.02	0.7
Galvanized Steel	2.6	0.0
HDPE	1169.61	0.2
Hyprescon	38268.76	5.1
Hyprescon C-301	7366.37	1.0
Hyprescon C-303	4350.33	0.6
PVC	**39866.51**	**5.3**
Stainless Steel	713.1	0.1
Unknown	30759.67	4.1

3.3 DALHOUSIE PIPE LOOP AND COPPER PIPE RACK DESCRIPTION

The Dalhousie Pipe Loop© is a recirculating pipe loop with variable flow rate and retention time designed by Rutledge (2003) to be a research standard for water distribution system simulation. Hydraulic and computational analysis were conducted by Rutledge (2003) to confirm that the Dalhousie Pipe Loop© indeed simulated a distribution system. The basic form of the Dalhousie Pipe Loop© can be altered for various research objectives. There were four Dalhousie Pipe Loops© used in this study. The pipe loops are operated independently of each other so chemical dosage and operation differs from one pipe loop to the next. A schematic and pictures of the Dalhousie Pipe Loop© and components are presented in Figure 3.2 through Figure 3.6. The Dalhousie Pipe Loop© consists of five major components:

- The test section,
- The recirculation pump,
- The return section,
- The transition section ,
- The steel support frame.

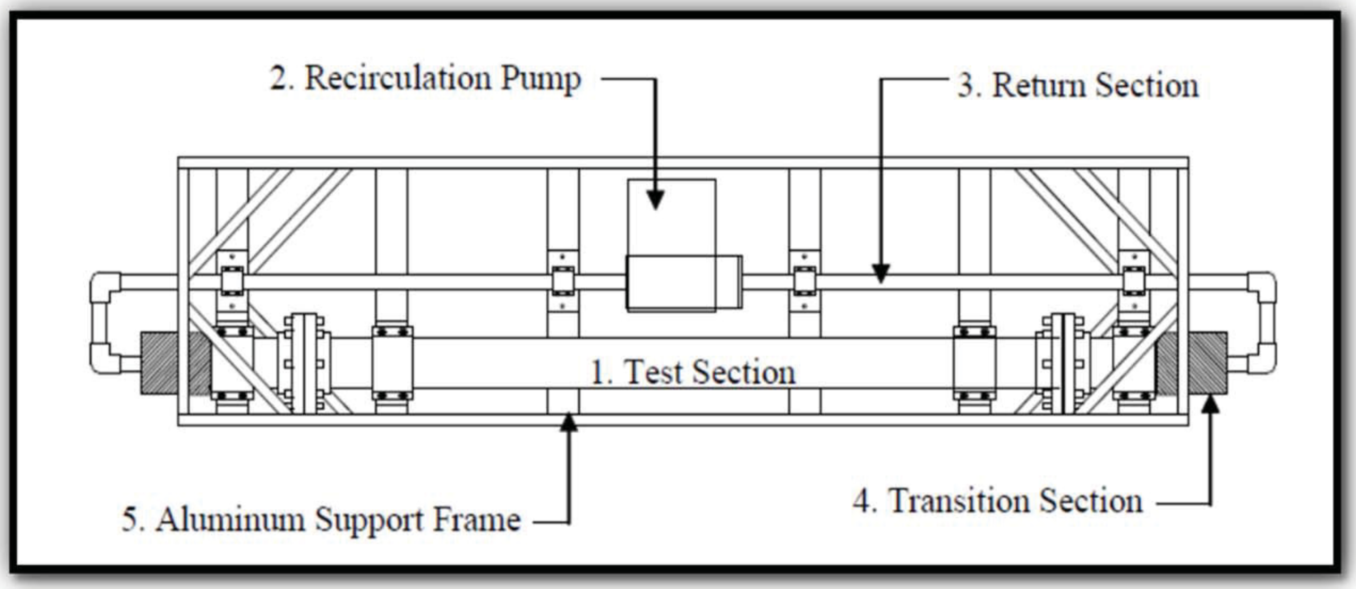


Figure 3.2 Top view of the Dalhousie Pipe Loop©.

Three other components of relevance to the Dalhousie Pipe Loop© are:

- The feed pump
- The influent and effluent ports
- The chemical feed jugs

A description of each component is provided below.

3.3.1 Test Section

The Test Section for the pipe loop is typically a 1.83m (6') length, 100mm (4") diameter PVC pipe measured from flange face to flange face. For this research work, two of the Test Sections on two Dalhousie Pipe Loops© were replaced with two 250 mm (6") cast iron water mains harvested from the Halifax Water distribution system. These cast iron Test Sections were retrofitted at Dalhousie University for the pipe loop setup (Figure 3.3).

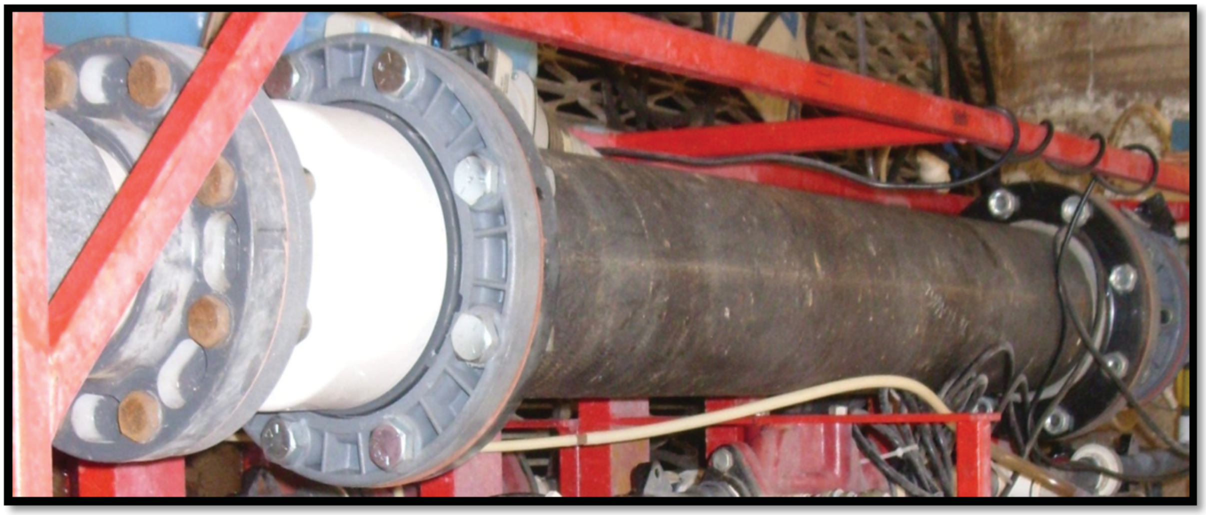


Figure 3.3 Retrofitted cast iron test section mounted on the Dalhousie Pipe Loop©.

3.3.2 Recirculation Pump

The recirculation pump ensures the continual flow of water through the pipe loop to provide the desired flow rate across the Test Section. The recirculation pump is a Grundfos (Grundfos Canada Inc, Burlington, ON) centrifugal pump rated at 146 L/min at 2.1m (7') of head and operated at approximately 141L/min and 0.0m (0.0') of head. The pump is a three speed single phase pump. The pump's cast iron housing has stainless steel and Teflon lined inner workings to ensure that no iron is leeched into the pipe loop by the pump. At every sample collection, the recirculation pump is felt by hand to check for overheating, which is an indication of the pump not circulating the water. A manual start of the pump is then required when overheating of the recirculation pump occurs (Figure 3.4).

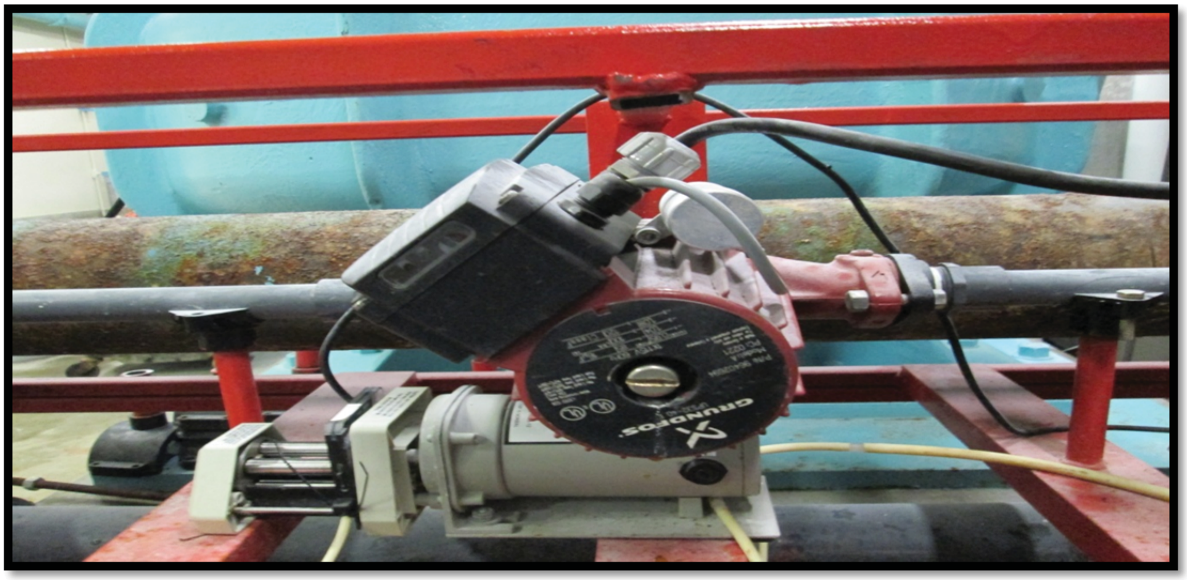


Figure 3.4 Recirculation pump in the pipe loop setup.

3.3.3 Return Section

The Return Section ensures the continual flow of water in the pipe loop by providing a connection between the various components. It consists of a series of 25mm (1 inch) PVC pipe and pipe fittings. The Return Section takes water from the effluent end of the Test Section to the influent side of the recirculation pump and from the effluent side of the recirculation pump to the influent end of the Test Section to ensure the continual loop of the water.

3.3.4 Transition Section

The Transition Section provides the connection between the Test Section and the Return Section and facilitates the change in pipe diameter from 25 mm (1") to 100 mm (4") pipe via a series of PVC couplings (Rutledge 2003). The Transition Section is mounted to the Steel Support Frame and the 250mm (10") long section also contains the Effluent Port for sample collection.

3.3.5 Steel Frame

The steel frame of the pipe loop provides a support for the major components of the pipe loops. The weight of the pipe loop in the support frame without the Test Section is 120 kg (260 lbs). The pipe loops were designed for easy transport and can be stacked to minimize the footprint.

3.3.6 Feed Pump

A ProMinent (ProMinent, Guelph, ON) diaphragm chemical feed pump pumps clearwell water from a continuously feed container into the loop. The pump has variable stroke length and speed, which allows for the adjustment of the flow rate. Furthermore, the pump is chemically inert which prevents the contamination of the water quality (Figure 3.5).

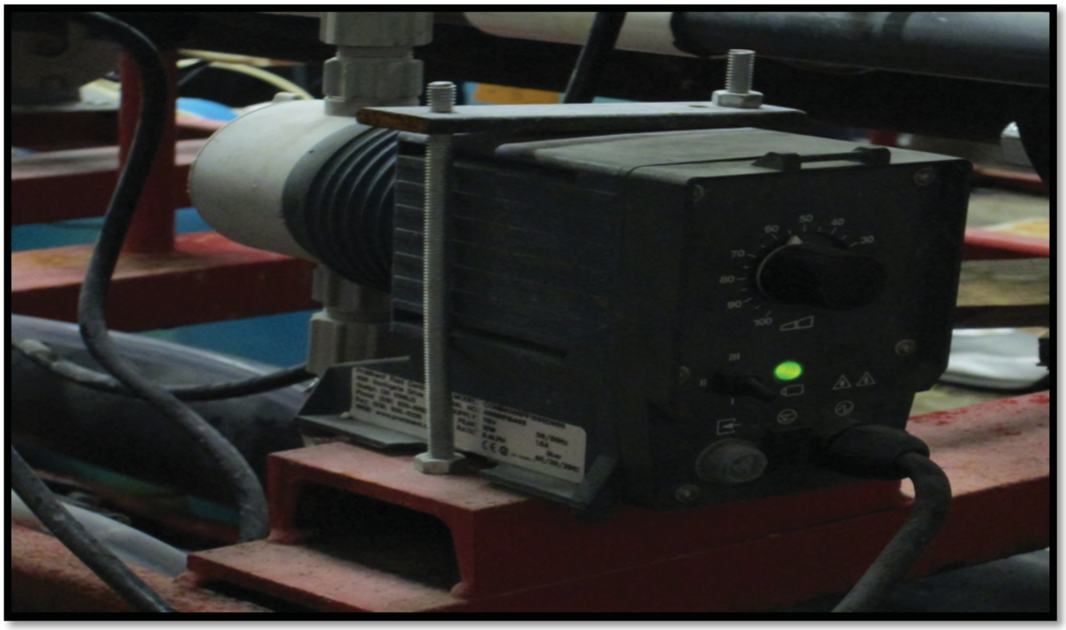
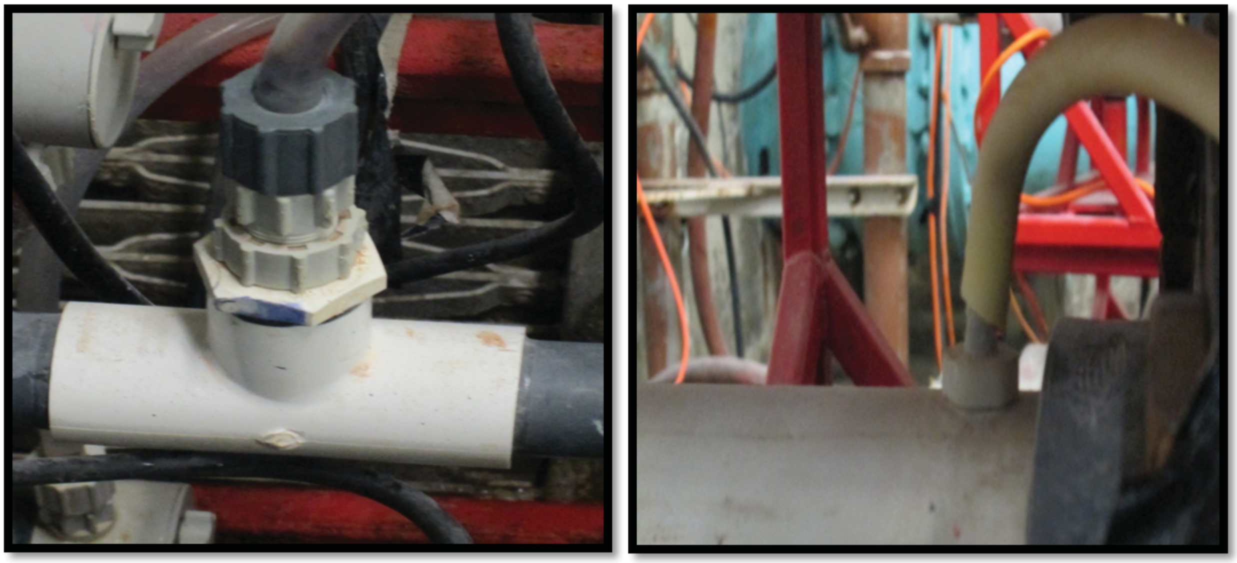


Figure 3.5 ProMinent feed pump used in the pipe loop set up.

3.3.7 Influent and Effluent Ports

The Influent and Effluent Ports are located on the Return and Transition Section respectively. The Influent Port is the connection point for the feed pump to provide the new water to the pipe loop. The Effluent Port acts as both a sample collection point and the outflow for the water, which is then collected in a reservoir bin and then pumped through the copper pipe racks.



a.) Influent Port b.) Effluent Port

Figure 3.6 Influent and Effluent ports on the pipe loop**.**

3.3.8 Chemical feed jugs

To investigate the effects of cast iron on lead release, chemicals were added to the pipe loop by pumping the chemicals from 20L blue jugs by using a variable speed peristaltic pump (Masterflex, Vernon Hill, IL) with a 1 to 100rpm motor and L/S 14 PHAR-MED tubing with an inner diameter of 1.6mm. The flow rate used was 3mL/min to ensure enough chlorine residual in the pipe loop on the sampling days. Chlorine was added to maintain total chlorine residual, zinc/ortho polyphosphate was added for corrosion control, and 1 M Sodium Hydroxide (NaOH) or 1 M Hydrochloric Acid (HCl) was added for pH adjustment. Due to the variability of the feed water and the chemical concentration in the effluent of the pipe loops, the volume of chlorine, the volume of phosphate and the volume of acid or base was adjusted on a trial and error basis to maintain the required testing conditions.

3.3.9 Copper Pipe Rack

Copper Pipe Racks were used in connection with the Dalhousie Pipe Loop© to simulate premise plumbing. The Copper Pipe Racks consists of seven 12’ length ½” diameter Class M copper pipe. There are 24 50:50 lead:tin solder joints connecting the seven 12’ pieces together. At one end of the Copper Pipe Rack, there is a brass fitting that connects the tubing between the reservoir bin and the Copper Pipe Rack. At the other end of the Copper Pipe Rack, the brass fitting connects the Copper Pipe Rack to tubing for sample collection. The flow rate through the Copper Pipe Rack is 5.6L/min. The only source of lead from the Copper Pipe Rack is the 24 50:50 lead:tin solders.

3.4 ANALYTICAL PROCEDURES

Experimental parameters that were monitored throughout this research include pH, turbidity, chlorine, phosphate, lead, iron, aluminum, copper, and tin.

3.4.1 General Water Quality Parameters

In all the experiments, reverse osmosis (RO) water was used for all cleaning and chemical stock preparation. All glassware and sampling bottles were rinsed a couple of times using RO water following a cleaning with neo disher® LaboClean UW detergent in the dish washer. The RO water was obtained from a Milli-Q® purification system. Combination pH/mV/Temperature/ DO and Conductivity meters (Accumet XL 25 and XL 60 models) with plastic bodied, gel-filled, combination pH electrodes (Accument Accu-Cap) were used for pH readings. Three-point calibration (pH 4, 7, 10) was conducted prior to any pH measurement on the Accumet. A Hach 2100AN laboratory turbidity meter was used for all full scale LSL replacement sample turbidity measurements. A HACH DR/4000 UV/VIS spectrophotometer (Hach Company, Loveland, CO) was used to measure chlorine and phosphate concentrations for the pipe loop effluent.

3.4.2 Metal Analysis

Total and dissolved metals were measured using the inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific X-Series 2). The method detection limit (MDL) for the ICP-MS was: Aluminum – 2µg/L, Iron– 6µg/L, Copper – 0.7µg/L, Lead – 0.4µg/L, and Tin – 0.6µg/L. 10ml of the water samples were acidified using three drops of concentrated nitric acid and stored in 4°C until analysis. Before the water samples were acidified, the water sample was filtered through a 0.45µm polsulfone filter membrane (GE Water & Process Technologies) that had been pre rinsed with 500ml of RO water. The filtered sample was then acidified before the metal analysis on the ICP-MS to measure the dissolved metals.

CHAPTER 4 BENCH SCALE ADSORPTION OF LEAD ON IRON CORROSION SCALES

4.1 ABSTRACT

This study investigated the adsorption of lead on iron corrosion scales (magnetite and goethite) using buffered reverse osmosis (RO) water and finished water from the JD Kline Water Supply Plant. Adsorption experiments were conducted using the lead spiked RO water and lead spiked finished water containing different amounts of the iron corrosion scales centrifuged on a laboratory shaker table for five days. The iron corrosion scales were filtered and the solution was analyzed for lead and iron. Freundlich and Langmuir adsorption isotherm models were used to model the collected data from the adsorption experiments. Results from the adsorption studies showed that lead adsorbs on the iron corrosion scales and that the adsorption capacity of magnetite and goethite increased with increasing pH. Generally, magnetite had a higher adsorption density for lead at all pH conditions except a solution of pH 7.5. In finished water, magnetite had a higher adsorption density than goethite. Adsorption of lead on magnetite and goethite in RO water and finished water indicates the potential for lead adsorption on iron corrosion scales that detach from the walls of the water mains in a distribution system.

4.2 INTRODUCTION

Corroded unlined cast iron pipes are present in many water distribution systems but are of particular concern in the northeastern region of North America due to aging buried infrastructure (Cromwell *et al.* 2001; McNeill & Edwards 2001). The corrosion scales present in iron pipes consist of various iron compounds, including the two dominant species goethite and magnetite (Sarin et. al 2001). Iron can be released from cast iron pipes through the dissolution of the corrosion scales or the dislodging of the scales due to pressure changes (Sarin *et al.* 2004). A possible process of dislodging iron corrosion scale in the water main, followed by the adsorption of lead on the iron corrosion scale, and then subsequent release of lead coated iron mineral from the service line to the tap is provided as a schematic in Figure 4.1.

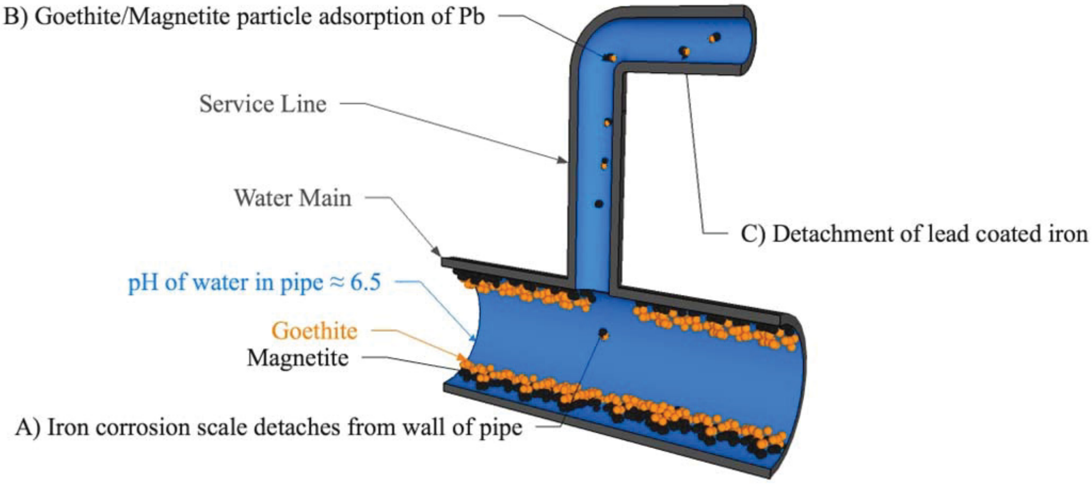


Figure 4.1 Schematic of the flow of the iron corrosion scale from the wall of the pipe to the tap.

Adsorption of lead on iron sulphate found in galvanized iron pipes can be responsible for high lead levels (McFadden et. al 2011). However, the adsorption of lead on iron minerals (e.g., goethite; magnetite) is poorly understood, which is of concern for water utilities that have corroded unlined cast iron pipes in their water distribution systems. A correlation between high iron concentration and high lead release has been hypothesized by various researchers (Deshommes et al. 2010; Cartier et. al 2011). However, there studies have been largely empirical and specific to the distribution system conditions studied. The adsorption of lead on goethite and magnetite may contribute to high lead concentrations at homes with service lines connected to corroded unlined cast iron pipes.

The zero point of charge (ZPC) is the pH at which the positive and the negative sites are in equal amount (i.e. net surface charge is zero). At pH values greater than the ZPC, the iron oxide becomes more negative, hence adsorption increases. Researchers have found varying ranges of the ZPC for magnetite from pH 6.8 to pH 8.0 (Yean et al. 2005; Illes & Tombacz 2005). The ZPC of goethite was 6.01 measured on the Nano-zetasizer in the water quality laboratory. Additionally, the ZPC for magnetite is different depending on the water quality parameters of the solution the iron particles are in. Illes and Tombacz (2005) showed that at a pH greater than the

ZPC of magnetite (pH 8.0), the pure oxide surface has a negative charge. The results from Illes and Tombacz (2005) indicated a possibility of the adsorption of lead on magnetite and also the possibility of an increase in adsorption capacity at higher pH values. Finally, in order to understand the sources of lead in tap water, determining how the iron minerals from the walls of the water main affect lead release is very important.

This chapter aims to understand the adsorption of lead onto iron minerals. In particular, the objectives of this study were to investigate the adsorption of lead on different iron minerals (magnetite and goethite) using reverse osmosis (RO) water and finished water from the JD Kline Water Supply Plant, and to evaluate the effect pH has on the adsorption process.

4.3 MATERIALS AND METHODS

4.3.1 Preparation of Iron Corrosion Scales

Magnetite and goethite were synthesized at the water quality laboratory at Dalhousie University. Magnetite was prepared by the oxidation of Fe^{II} solution using a method described in Schwertmann and Cornell (2000). The process synthesized magnetite particles with a size range of 0.05 to 0.2 µm and surface area of 4 m^2/g, which was indicated in Schwertmann and Cornell (2000). Goethite was prepared using a method modified by Schwertmann and Cornell (2000). The process synthesized goethite particles with a size of 0.75 µm measured on the Nano-Zetasizer (Malvern nano series) and surface area of 20 m^2/g, which is the surface area obtained using the method outlined in Schwertmann and Cornell (2000). Metal analysis to determine the concentration of iron in both magnetite and goethite were carried out using the atomic absorption graphite furnace (PerkinElmer Analyst 200). The concentrations of iron determined from the metal analysis were used to calculate the amount of magnetite and goethite needed in the following experiment.

4.3.2 Experimental Procedures

The experimental setup was based on adsorption studies described in Crittenden *et al.* (2005). In these studies, 100 mg of sodium bicarbonate ($NaHCO_3$) was added to two conical flasks containing one litre RO water obtained from a Milli-Q® purification system and pH adjusted to the required pH (5.5, 6.5, 7.5, 8.5) using 1M HCl or 1M NaOH solution. 150 ml of the buffered and pH adjusted solution was then poured into 12 X 250 ml flasks. Initial adsorption experiments used an initial lead concentration of 100µg/L, which was the concentration used in McFadden *et al.* (2011). Either magnetite or goethite was then added to the flasks, which were then put on the laboratory shaker table (Barnstead Lab-line) for five days at 150 rpm. Two of the flasks were used as the control. At the end of the five days, the contents of the flask were centrifuged (Centra CL2 Thermo IEC) at 2500 rpm from five minutes to 15 minutes, depending on how much magnetite or goethite was added. 10ml of the solution was collected in an inductively coupled plasma mass spectrometry (ICP-MS) tube and acidified with concentrated nitric acid for lead and iron analysis. In addition, the remaining solution was filtered through a 0.45µm polsulfone filter membrane (GE Water & Process Technologies) to remove all the remaining iron corrosion minerals in solution. 10 ml of the filtrate was then collected and acidified for lead and iron analysis.

4.3.2.1 Factorial design adsorption experiment

The factors considered in the factorial design were pH and iron mineral mass. A two level factorial design was used for the first adsorption experiment to determine the statistically significant factors. A pH of 5.5 and 8.5 was used because these were the minimum and maximum pH measured from the samples in the lead service line replacement program. The mass of magnetite and goethite were calculated using an assumption of a 2mm corrosion scale, with 75% goethite and 25% magnetite, and a 100:1 ratio of iron to lead, as used in McFadden *et al.* (2011) (Table 4.1). Studies conducted by Sarin *et al.* (2001) showed that iron corrosion scales in iron pipes can vary from 2mm to 5mm containing 75% goethite and 25% magnetite.

Table 4.1 Initial factors used in the factorial design of the bench experiment.

Factors		
pH	5.5	8.5
Magnetite (mg)	2.25	4.5
Goethite (mg)	1.5	15

The adsorption experiment was conducted using the method outlined above and the samples were analyzed at the end of the adsorption period.

4.3.2.2 Adsorption Isotherm experiment

The adsorption experiment was repeated with the same procedure but with different masses of magnetite and goethite to create adsorption isotherms for magnetite and goethite at a pH of 5.5, 6.5, and 7.5 (Table 4.2). The initial lead concentration for the adsorption isotherm experiments was 100µg/L. However, subsequent adsorption experiments used an initial lead concentration of 500µg/L because of the higher adsorptive capacity observed at higher pH values.

Table 4.2 Factors used to create adsorption isotherms.

pH	**5.5**	**6.5**	**7.5**
Magnetite & Goethite (mg)	2.25	2.25	2.25
Magnetite & Goethite (mg)	4.5	4.5	4.5
Magnetite & Goethite (mg)	7.5	7.5	7.5
Magnetite & Goethite (mg)	15	15	15
Magnetite & Goethite (mg)	30	30	30

Adsorption experiments were also conducted on the plant finished water (total chlorine residual of 1.0mg/L, pH of 7.4, and zinc/ortho polyphosphate of 0.5mg/L as PO_4). The plant finished water was also spiked with lead because the plant finished water does not contain lead. The initial adsorption trials used an initial lead concentration of 100µg/L but this was shown to be a low concentration so subsequent trials for the adsorption experiment in finished water used an initial lead concentration of 500µg/L. The same procedure described above was used for the finished water trials.

4.3.3 Analytical Procedures

In the adsorption study, reverse osmosis (RO) water was used for all cleaning and rinsing of the glassware. All glassware was soaked in a nitric acid bath for at least 16 hours prior to the start of the adsorption experiment. The glassware was rinsed several times using RO water obtained from a Milli-Q® purification system. A combination pH/mV/Temperature/ DO and Conductivity meters (Accumet XL 25 and XL 60 models) with plastic bodied, gel-filled, combination pH electrodes (Accument Accu-Cap) were used for the pH adjustment. Three-point calibration (pH 4, 7, 10) was conducted prior to any pH measurement on the Accumet.

Lead and iron samples for analysis were prepared by acidifying the solution with a few drops of concentrated nitric acid and then storing at 4ºC until analysis. All the lead and iron analyses were conducted using the ICP-MS which has built in quality control checks to ensure the accuracy of the results. The ICP-MS had a method detection limit (MDL) of 0.4μg/L for lead and 6μg/L for iron. Scanning Electron Microscopy (SEM) (Hitachi S4700 Field Emission-SEM) and Energy Dispersive X-Ray Spectrometer (EDS) (Oxford X-Max EDS) were used to obtain before and after adsorption images and to determine the chemical composition of the iron oxides. The nano-zetasizer (Malvern nano series) was used for size and zeta potential measurements of the samples. All of the adsorption trials were duplicated to increase accuracy and to show reproducibility of the data generated.

4.3.4 Adsorption Data Analysis

The data generated from the batch experiments were fitted to the Freundlich and Langmuir isotherm equations to determine coefficients and isotherm curves for all experiments.

4.3.4.1 Freundlich equation

The Freundlich adsorption isotherm is used to describe the data for heterogonous adsorbents, a quality which can be assumed for magnetite and goethite. The Freundlich adsorption isotherm equation is expressed as

$$q_A = K_A C_A^{1/n} \qquad [4\text{-}1]$$

where

K_A = Freundlich adsorption capacity parameter, (μg/g) (L/μg)$^{1/n}$

1/n = Freundlich adsorption intensity parameter, unitless

The linear form of the Freundlich equation is:

$$\log(q_A) = \log(K_A) + \left(\frac{1}{n}\right)\log(C_A) \qquad [\,4\text{-}2]$$

A linear regression of log q_A vs log C_A gives the Freundlich parameters.

4.3.4.2 Langmuir equation

The Langmuir adsorption isotherm is used to describe the equilibrium between surface and solution as a reversible chemical equilibrium between species (Crittenden et al. 2005). The Langmuir model allows accumulation only up to a monolayer which is a suitable assumption for adsorption in liquids (Droste 1997). The Langmuir adsorption isotherm equation is expressed as:

$$q_A = \frac{Q_M b_A C_e}{b_A C_e + 1} \qquad [4\text{-}3]$$

where

q_A = adsorption density achieved in μg lead/g solid,

C_e = equilibrium concentration in μg lead/L,

Q_M = maximum adsorption density when the surface sites are saturated with adsorbate,

b_A = Langmuir adsorption constant of the adsorbate.

It is always convenient to rearrange equation 4-3 in linear form:

$$\frac{C_e}{q_A} = \frac{1}{b_A Q_M} + \frac{C_e}{Q_M} \qquad [4\text{-}4]$$

Equation 4-4 in the linear form of the Langmuir model with slope of $1/Q_M$ and intercept $1/b_AQ_M$. The values of b_A and Q_M were determined from a linear regression analysis.

4.4 RESULTS AND DISCUSSION

4.4.1 Lead adsorption in RO water

Lead adsorption on magnetite and goethite was generally high (over 50% removal) and reached 99% removal in some experimental trials. Magnetite yielded a higher adsorption density than goethite in all of the experimental trials except in the pH 7.5 solution. The higher adsorption density is due to the presence of ferrous-ferric ions in magnetite compared to just ferric ions in goethite. Ferric ions are more stable than ferrous ions. Hence, the adsorption on lead on ferric and ferrous ions will be different. The adsorption density for magnetite and goethite is shown in Table 4.3.

Table 4.3 Adsorption densities of magnetite and goethite at the various pH values.

	5.5	**6.5**	**7.5**
Magnetite	2530 ± 0.00µg/g	17000 ± 4600µg/g	18000 ± 5000µg/g
Goethite	2480 ± 1.41µg/g	13000 ± 6400µg/g	19000 ± 4200µg/g

In the experiments for lead adsorption on magnetite, there is little difference between the pH 6.5 and pH 7.5 adsorption densities but a great difference can be noted in the lead adsorption on goethite. Illes and Tombacz (2005) and Wu et al. (2003) determined that the adsorption rate in magnetite and goethite increased with increasing pH. Goethite and magnetite have different ZPC pH values (6.01 for goethite measured on the Nano-zetasizer and 6.8 – 8.0 for magnetite (Yean et al. 2005; Illes & Tombacz 2005), hence, the effects of a pH 6.5 and 7.5 solution will be experienced differently in the adsorption process. Zeta potential measurements of the samples at the different pH conditions were collected to determine the surface charge of the goethite and magnetite particles used in this study (Table 4.4). As observed in Table 4.4, the ZPC for goethite is between pH 5.5 and pH 6.5. The more negative the surface charges on the iron mineral, the greater the adsorption capacity of the iron mineral. The ZPC of magnetite could not be determined from the table. Although studies by Illes and Tombacz (2005) demonstrated that the ZPC of magnetite is dependent on the solution the magnetite particles are in.

Table 4.4 Zeta potential measurements for goethite and magnetite at the test pH values.

pH	**Magnetite (mV)**	**Goethite (mV)**
5.5	-42.0	14.2
6.5	-27.0	-19.0
7.5	-34.1	-20.4

Freundlich and Langmuir isotherm models were used to describe lead adsorption on the magnetite and the goethite. The linearized Freundlich model was a better fit for the data than the linearized Langmuir adsorption model which was also observed in Crittenden et al. (2005). The best fit for Freundlich isotherm model for a pH of 5.5, 6.5, and 7.5 had R^2 (0.89, 0.86, 0.9) respectively for magnetite and R^2 (0.87, 0.56, 0.95) respectively for goethite. The best fit Langmuir isotherm model for a pH of 5.5, 6.5, and 7.5 had R^2 (0.99, 0.51, 0.55) respectively for magnetite and R^2 (0.81, 0.41, 0.43) respectively for goethite. Langmuir isotherm model results for goethite at a pH of 6.5 was comparable to previous research conducted on the adsorption of lead on goethite by Wu *et al.* (2003) (Table 4.5 and Table 4.6). In the table, pH = 7.2 corresponds to the finished water from the JDKWSP.

Table 4.5 Freundlich isotherm constants for lead spiked solutions.

	Iron Mineral							
	Magnetite				**Goethite**			
Initial pH	5.5	6.5	7.2	7.5	5.5	6.5	7.2	7.5
Initial C (µg/L lead)	74.6	302.1	488	314.3	101.5	295.0	465.1	314.3
Freundlich K (µg/g)	850	2600	1156	2200	210	710	576	1000
1/n	0.36	0.36	0.32	0.44	0.54	0.44	0.44	0.81
Freundlich R^2	0.89	0.86	0.82	0.90	0.87	0.56	0.98	0.95

Table 4.6 Langmuir isotherm constants for lead spiked solutions.

	Iron Mineral							
	Magnetite				**Goethite**			
Initial pH	5.5	6.5	7.2	7.5	5.5	6.5	7.2	7.5
Initial C (µg/L lead)	74.56	338.2	488	275.1	101.5	295	465.1	272.4
Q_{max} (µg Lead/g solid)	2500	10000	10000	10000	1100	10000	10000	16700
b_A	0.57	0.03	0.01	0.08	0.01	0.02	0.01	0.001
Langmuir R^2	0.99	0.74	0.67	0.85	0.81	0.41	0.94	0.8

The results of both the Freundlich and Langmuir models also alluded to the possibility of a higher adsorption capacity at a higher pH. The R^2 values for the isotherm models for the initial lead concentration of 100µg/L in the pH 6.5, pH 7.5, and finished water were extremely low (i.e. less than zero in some cases) (Table 4.7). In the trials with the low initial lead concentrations the Langmuir model had a poor fit for the data.

Table 4.7 Langmuir isotherm constants for lead spiked RO water with the low initial concentration.

	Iron Mineral					
	Magnetite			**Goethite**		
Initial pH	6.5	7.5	7.2	6.5	7.5	7.2
Initial C (µg/L lead)	28.85	32.39	56.99	96.99	45.13	39.28
Q_{max} (µg Lead/g solid)	200000	1250	3333.3	33333.3	10000	1666.7
b_A	0	0.89	0.09	0.0006	0.08	0.05
Langmuir R^2	2.00E-05	0.39	0.19	0.0008	0.17	0.1

In the adsorption experiments with an initial lead concentration of 100µg/L, it was observed that there is a higher adsorptive capacity of lead on magnetite and goethite at higher pH values. Latter trials which used an initial lead concentration of 500µg/L produced better results and showed the maximum adsorption of the lead on the magnetite and goethite (Figure 4.2).

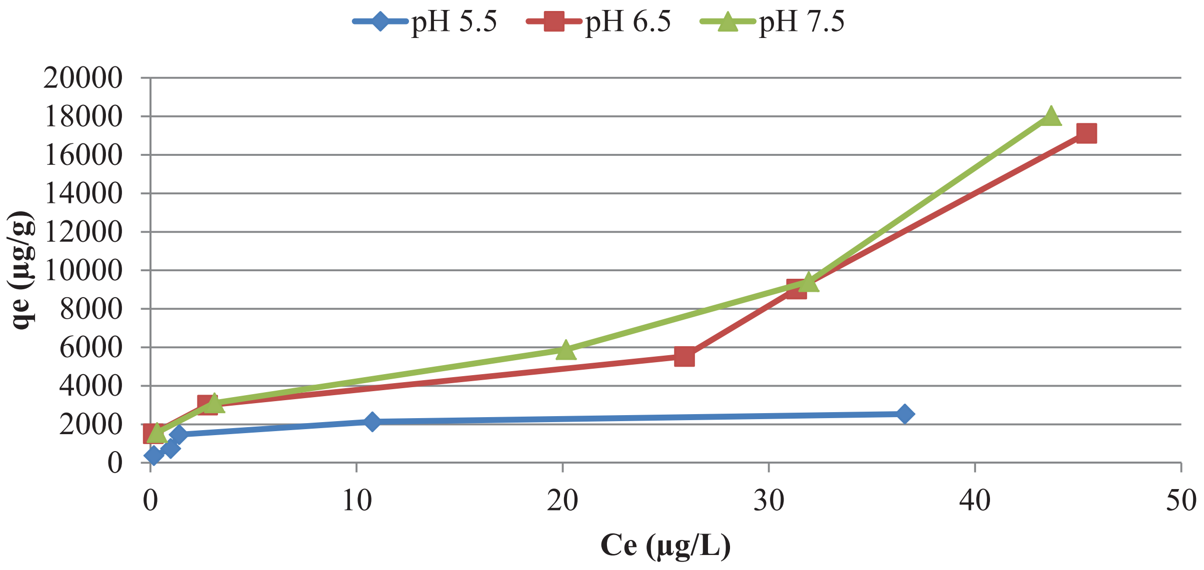


Figure 4.2 Adsorption density and equilibrium concentration for magnetite.

4.4.2 Lead Adsorption in Finished Water

Lead adsorption on magnetite and goethite in finished water was also generally high (Q_{max} = 10,000 µg/g for both magnetite and goethite). Magnetite yielded higher adsorption densities than goethite in finished water, 10,700µg/g for magnetite compared to 8,000µg/g for goethite. The same observation of a higher adsorptive capacity at higher pH values was made. This observation was confirmed using both the Freundlich and Langmuir isotherm models. Subsequent adsorption experiments using a higher initial lead concentration showed a better fit for the data.

Using the Langmuir model, magnetite and goethite had the same Q_{max} (10000 µg/g) value. However, when the Freundlich model was used on the data, magnetite had a K value of 1156 and goethite had a K value of 576. These observations were made for adsorption in finished water for a pH of 7.2.

The general iron mineral morphology of magnetite and goethite was characterized by SEM to determine whether observable changes could be identified before and after adsorption. Prior to the adsorption process, the morphology of the goethite was a smooth needle as was also seen in previous characterization studies (Schwertmann and Cornell 2000). Following the adsorption process, the needle surfaces were more pronounced with a thin coating on the surface, which was likely lead (Figure 4.3).

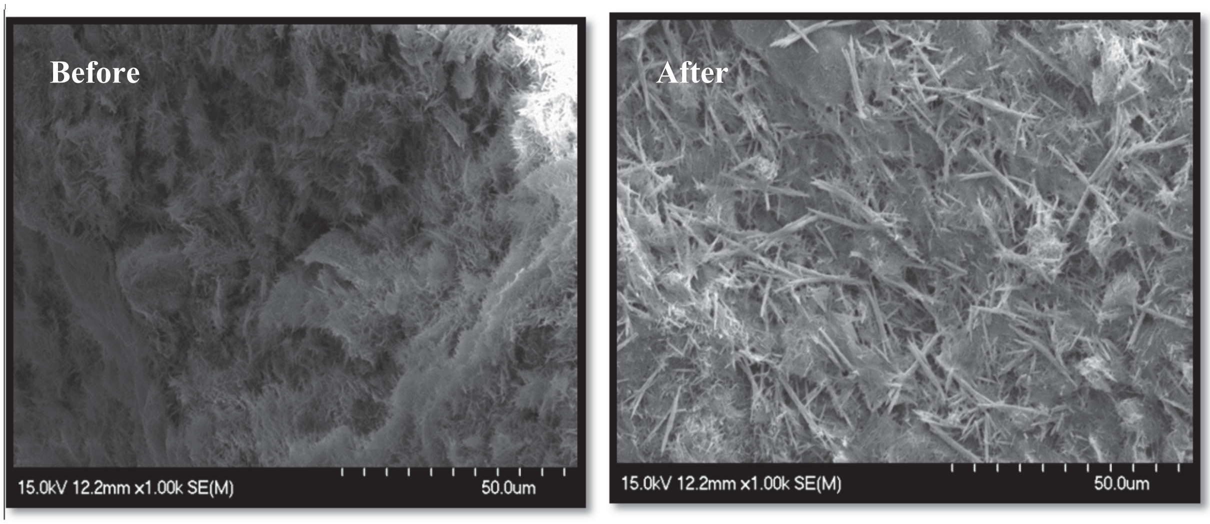


Figure 4.3 SEM image showing before and after adsorption images of goethite.

The morphology of the magnetite before adsorption is a spheroidal or cube like structure which agglomerated into clusters. This observation is consistent with previous characterization research conducted for magnetite (Giri *et al.* 2011, Wei and Viadero 2007). After adsorption, the clusters were found to be less pronounced on the surface of the mineral (Figure 4.4).

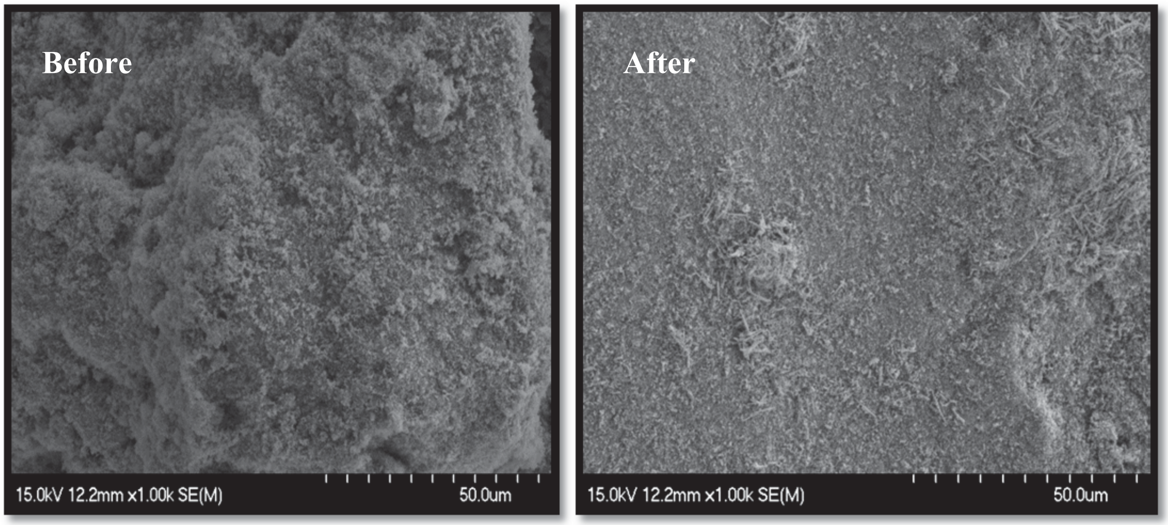


Figure 4.4 SEM image showing before and after adsorption images of magnetite.

The chemical composition of the magnetite and goethite were analyzed on EDS. The results of the EDS analysis clearly demonstrate the absence of lead in the "before adsorption" analysis and the presence of lead in the "after adsorption" analysis (Tables 4.8 and 4.9).

Table 4.8 EDS results of the before and after adsorption chemical composition on goethite.

All results in weight%							
Before Adsorption				After Adsorption			
C	O	Fe	Pb	C	O	Fe	Pb
13.2	57.8	29.0	0	6.5	15.2	61.2	17.1

Table 4.9 EDS results of the before and after adsorption chemical composition on magnetite.

All results in weight%							
Before Adsorption				After Adsorption			
C	O	Fe	Pb	C	O	Fe	Pb
13.9	44.8	41.3	0	9.8	15.2	39.3	35.7

4.5 CONCLUSIONS

In general, magnetite and goethite were capable of absorbing lead from both lead spiked RO water and lead spiked finished water. Results indicates that pH of the water is a key factor in the adsorption of lead on either magnetite or goethite. A higher pH favored the adsorption of lead on magnetite more than the adsorption of lead on goethite. Adsorption of lead in finished water shows that the adsorption of lead on magnetite and goethite that detach from the walls of the water mains is a possibility in the field. Additional work is required to better understand the adsorption of lead on magnetite and goethite in a full scale setup. Adsorption experiments using a different lead source or tap water with a known lead concentration will be a valuable next step in understanding the adsorption of lead on iron particles.

CHAPTER 5 LEAD SERVICE LINE REPLACEMENT PROGRAM IN HALIFAX,NS

5.1 ABSTRACT

Lead samples from a lead service line replacement (LSLR) program were collected from tap water of 28 homes in Halifax, Nova Scotia. Tap water samples were collected after a minimum six hour stagnation. The tap water samples were collected to determine the amount of lead and iron released following the LSLR. Analysis of the results showed that full replacements had the least lead released as compared to partial replacements, in the low alkalinity water present in Halifax. In addition, a relationship between the condition of the cast iron water main and lead release was established. Service lines connected to turberculated cast iron water mains released the most lead irrespective of the type of service line replacement conducted. In full replacements, the average lead concentration of service lines connected to cast iron water mains was 9µg/L compared to 1µg/L for service lines connected to ductile iron water mains. In the partial replacement scenario, the average lead concentration was 12µg/L for service lines connected to cast iron water mains compared to 3.5µg/L for service lines connected to a ductile iron water main. Adsorption of lead on the iron corrosion scales that dissolved or dislodged from the tuberculated water mains could account for the higher lead release observed. Service lines connected to ductile iron water mains had the least amount of lead concentrations in both partial and full replacements compared to service lines connected to cast iron water mains. Finally, samples that had iron concentrations below the method detection limit (6µg/L) of the ICP-MS also had low lead concentrations. Correspondingly, higher iron concentrations were associated with high lead concentrations.

5.2 INTRODUCTION

The occurrence of high levels of lead in the distribution system remains a serious concern for water utilities because lead has adverse impacts on human health and on the cognitive development of children (Fewtrell *et al.,* 2004; Bellinger *et al.,* 1991; Triantafyllidou *et al.,* 2007). The Guidelines for Canadian Drinking Water Quality limit lead concentrations in drinking water to a maximum acceptable concentration (MAC) of 10 micrograms/Liter (µg/L), measured at the tap.

In order to reduce the amount of lead in the distribution system, some utilities have adopted lead service line replacement (LSLR) in which a portion or the whole lead service line is replaced. A schematic of a typical home showing the service line, financial responsibility, and the mechanism of adsorption of the lead on iron minerals is shown

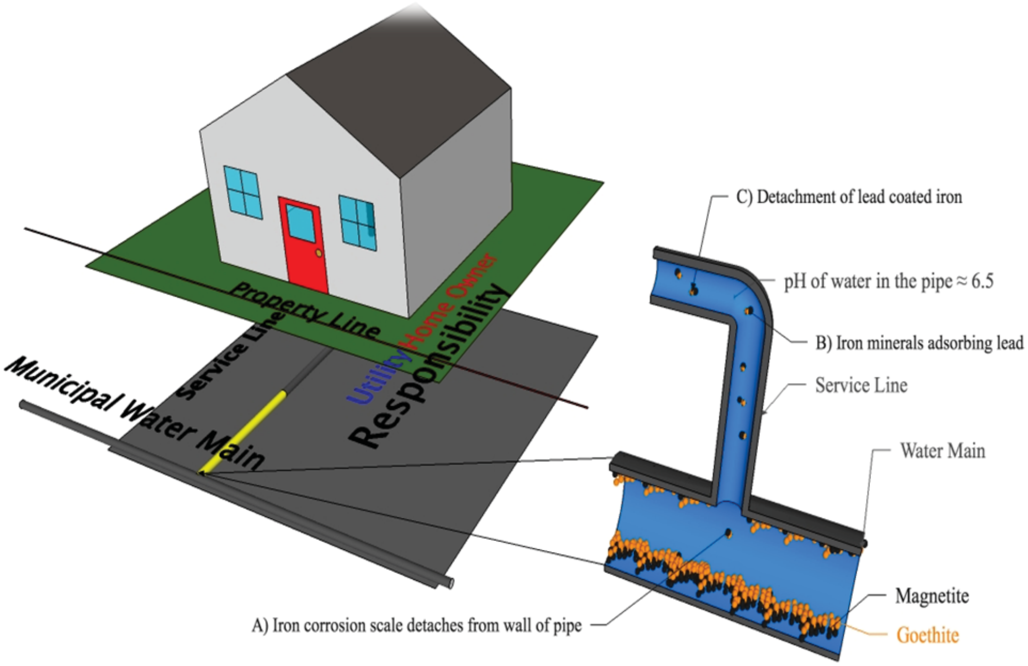


Figure 5.1 Schematic representation of the lead service line showing responsibility and flow of the iron corrosion scale from the wall of the pipe to the tap.

The public side of the service line is the responsibility of the utility, and the private side is the responsibility of the home owner. Partial replacement is the replacement of the lead service line (LSL) from the water main to the property line. A full replacement is the replacement of the LSL from the water main to the home. Partial lead replacements are practiced in Halifax due to the ongoing long-term distribution main renewal program. The distribution main renewal program aims to ensure long-term integrity and reliability of the distribution system by replacing the corroded unlined cast iron water mains present in the distribution system. The corroded cast iron pipes consist of various iron compounds including the two dominant species goethite and magnetite (Sarin et. al 2001; McNeill & Edwards 2001). During the water main renewal program, LSLs are partially replaced from the new water main to the property line. Partial replacements have been attributed to elevated lead release after replacement due to dislodging of particulate lead from the remaining service line (Sandvig et al, 2008), galvanic corrosion

(Nguyen et al, 2010; Edwards & Triantafyllidou, 2007), and in some cases water hammer or sudden flow changes which can also cause the dislodging of iron corrosion scales from the distribution system (Schock et al, 1996).

Recent research demonstrated the adsorption of lead on iron sulphate leading to high lead levels (McFadden et. al 2011). However, the adsorption of lead on iron minerals (e.g. goethite; magnetite) is poorly understood. This is particularly relevant for Halifax which has a significant number of corroded unlined cast iron pipes in the water distribution system. A correlation between high iron concentration and high lead release has been hypothesized by various researchers (Deshommes et. al 2010; Cartier et. al 2011). LSLR profiles are useful for determining the effectiveness of a LSLR. The lead profile can verify the removal of all the lead sources at a location.

The main objective of this research was to determine the relationship between lead adsorption to goethite and magnetite and overall lead release in a lead service line replacement program conducted in Halifax, Nova Scotia, Canada. Based on these results, this research aims to determine which type of lead service line replacement (full or partial) was beneficial for Halifax.

5.3 MATERIALS AND METHODS

5.3.1 Description of Treatment Plant

Halifax is supplied by the James Douglas Kline Water Supply Plant (JDKWSP). The JDKWSP is a direct filtration plant that treats water from Pockwock Lake and is operated and maintained by Halifax Water. Pre-screening of the raw water removes all large impurities in the water, which is followed by a potassium permanganate ($KMnO_4$) addition for the oxidation of manganese and iron. Next, pH adjustment is done by adding carbon dioxide (CO_2) followed by the addition of Alum at a concentration of 8mg/L. Cationic polymers are then added during the cold weather months (November to June) to aid floc strengthening and to ensure the removal of natural organic matter. Pre-chlorination, which follows the addition of the coagulant, prevents the growth of bio film on the filters. Hydraulic flocculation, direct filtration, and chlorination of the filtered water follow in the respective sequence. Finished water from the treatment process has a total chlorine residual of 1.0mg/L, pH of 7.4, and zinc/ortho polyphosphate concentration of 0.5mg/L as PO_4 for corrosion control, and hydrofluosilicic acid is added to provide fluoride in the finished water (Knowles 2011). Table 5.1 shows the characteristics of the finished water during the duration of the LSLR program.

Table 5.1 Finished water characteristics from April 2011 to June 2012.

Parameter	**Average ± Standard deviation**
pH	7.4 ± 0.1
Turbidity (NTU)	0.1 ± 0.0
Alkalinity	16.0 ± 2.9
Total Cl_2 (mg/L)	1.2 ± 0.3
Free Cl_2 (mg/L)	1.1 ± 0.3
Phosphate as PO_4 (mg/L)	0.5 ± 0.1
Iron (mg/L)	0.0 ± 0.1
Aluminum (mg/L)	0.1 ± 0.9
Number of samples	460

5.3.2 Site Description

LSLs, solder, and brass devices are all documented sources of lead in drinking water (Kimbrough 2001). Homes built prior to the 1950’s in Halifax may have LSLs and homes with plumbing installed prior to 1986 may have leaded solder joints. Leaded solder use was discontinued in 1986 by the National Plumbing Code of Canada (Health Canada 2012). In the study area, some of the homes have LSLs, lead soldered joints, and brass devices with a high percentage of lead. Within the Halifax Regional Municipality (HRM), 4,000 homes are estimated to have either full or partial lead service lines. In the LSL replacement program, 53.5% of the homes that volunteered for the program had full replacements and 46.5% had partial replacements. Plumbing in the homes were mostly polyvinyl chloride (PVC) and copper. Eight homes had both PVC and copper plumbing, six homes had only PVC plumbing, and 14 homes had only copper plumbing.

5.3.3 Sampling Protocol

Sample collection was done on a volunteer basis. Customers volunteered to take part in the LSL replacement program by collecting samples at different periods following the LSL replacement. Customers collected five – one liter samples before the replacement of the LSL, 72 hours following the replacement, 1 month after the replacement, 3 months after the replacement, and 6 months after the replacement. All of the samples were collected after a minimum six-hour stagnation time, which was outlined in the proper sample collection instructions given to the customer (Appendix B). Four consecutive liters were collected and the fifth liter was collected after five minutes of flushing. The fifth liter represented the flushed sample, which is an indication of the water in the water main. Although in certain homes with longer LSLs the fifth liter still represents the water in the LSL (Cartier et al. 2011). Sample collection following a six-hour stagnation period detects many lead sources and tracks corrosion control effectiveness; however, it does not detect peak lead concentrations observed in LSLs (Sandvig et al, 2008; Cartier et al 2011). Nevertheless, collecting more than three liters of samples can give an indication of the effects of the service line. Following sample collection, the customer called the water quality inspector at Halifax Water who then picked up the five – one liter samples and dropped them off at the water quality laboratory at Dalhousie University where the samples were then prepared for metal analysis.

5.3.4 Water Distribution Condition

The water distribution system in the study area consists of a mixture of cast iron water mains and ductile iron water mains. Unlined cast iron pipes are prone to tuberculation. Tuberculation is formation of small mounds of iron corrosion products on the inside of the iron pipe. Tuberculated pipes are maintained by mechanically cleaning the inside of the water main with pigs (pigged) and lining the inside of the pipe with either epoxy of cured in place liners (lined). Lining of the water main prevents the direct contact of the water with the wall of the pipe. In the study area, the condition of the cast iron water main varies from tuberculated water mains to recently pigged and lined water mains. Information on the water main was obtained by Halifax Water using ArcGIS®. ArcGIS® is a geographic information system that Halifax Water uses to compile maps and geographic information on their distribution system. The information from

ArcGIS® determined the condition of all the water mains from the volunteer sites. Table 5.2 details the conditions of the water main for all the LSL replacement sites.

Table 5.2. Water main material and condition in the LSL replacement program.

Pipe Material	Partial Replacement (# of sites)	Full Replacement (# of sites)
Ductile Iron	3	2
Cast Iron		
Pigged	2	2
Pigged and Lined	2	3
Not pigged or lined	6	8

5.3.5 Experimental Procedures

The five 1-L water samples from the LSL replacement program were prepared and acidified for metal analysis (lead and iron) within 24 hours of the sample collection date. The samples were acidified within 24 hours to prevent any metals from adhering to the sampling bottles (Edwards and Dudi 2004; Deshommes et al, 2010). The pH and turbidity of the water samples were measured before the samples were prepared. After the pH and turbidity measurements, the samples were vigorously shaken and 10mL of sample was collected in an inductively coupled plasma mass spectrometry (ICP-MS) tube and acidified with concentrated nitric acid. For the dissolved metal analysis, 250mL from each of the five-one liter samples were filtered through a 0.45µm polysulfone filter membrane (GE Water & Process Technologies). 10mL of the filtered sample was acidified in the ICP-MS tube and stored. However, if the turbidity of the water samples was >1NTU, acid digestion of the water sample was conducted. In the acid digestion, the water sample was acidified for at least 16 hours at pH < 2, following that, 10 mL of the sample was poured into an acid digester tube with the addition of 0.5 mL of concentrated nitric acid. The sample was put on the acid digester at 105ºC for two hours as indicated in Standard Methods (Section 3030 Nitric Acid Digestion) (Jarvis et al, 1992). At the end of the two hours, the sample was topped up to the 10mL mark using reverse osmosis (RO) water and then poured in the inductively coupled plasma mass spectrometry (ICP-MS) tube and stored at 4ºC for analysis with the ICP-MS.

The remaining water samples for the total and dissolved metals were also acidified and stored in the fridge at 4ºC. All metal analysis samples were stored at 4ºC before analysis with the ICP-MS was conducted.

5.3.6 Analytical Procedures

In the LSLR study, RO water was used for all cleaning and rinsing of the glassware. All sampling bottles were soaked in a nitric acid bath for at least 16 hours before use. The glassware were rinsed a couple of times using RO water obtained from a Milli-Q® purification system. Combination pH/mV/Temperature/ DO and Conductivity meters (Accumet XL 25 and XL 60 models) with plastic bodied, gel-filled, combination pH electrodes (Accument Accu-Cap) were used for the pH measurement. Three-point calibration (pH 4, 7, 10) was conducted prior to any pH measurement on the Accumet. A Hach 2100AN laboratory turbidity meter was used for all full LSLR samples turbidity measurements.

Lead, iron, copper, aluminum, and tin samples for analysis were prepared by acidifying the solution with a few drops of concentrated nitric acid and then storing at 4ºC until analysis. Total and dissolved metal analyses were conducted for all the samples received. The dissolved metals were the metals present after the water sample was filtered through a 0.45µm filter membrane.

The metal analysis was conducted using the ICP-MS which has built in quality control checks to ensure the accuracy of the results. The method detection limit (MDL) for the ICP-MS was: Aluminum – 2µg/L, Iron– 6µg/L, Copper – 0.7µg/L, Lead – 0.4µg/L, and Tin – 0.6µg/L. If the quality control standards and blanks were inaccurate the samples were reanalyzed using the remaining water samples in storage.

5.3.7 Statistical Analysis

Paired t-test statistical analysis compared the results from the digested and non digested samples that had turbidity <1NTU.

5.4 RESULTS AND DISCUSSION

Water quality parameters measured in the LSLR program were turbidity and pH. The average pH for the samples received was 6.5 with the maximum and minimum pH being 5.5 and 8.5, respectively. In the pH range of 7 to 9 inclusive, weight loss and degree of tuberculation in cast iron pipes increases with increasing pH (McNeill & Edwards 2001). Turbidity in the samples collected was generally low, except in a single sample where the turbidity was > 1NTU. Turbidity can be an indicator of iron in the water (Sarin et al. 2001). The turbidity of the sample was also used to determine whether particulate lead was present, in which case an acid digestion of the sample was needed.

The length of the service line and plumbing characteristics of the home varied from site to site, and the lead concentration of the first and second liters was also found to vary (Figure 5.2) as was shown by previous research on a LSLR program (Cartier *et al.* 2011).

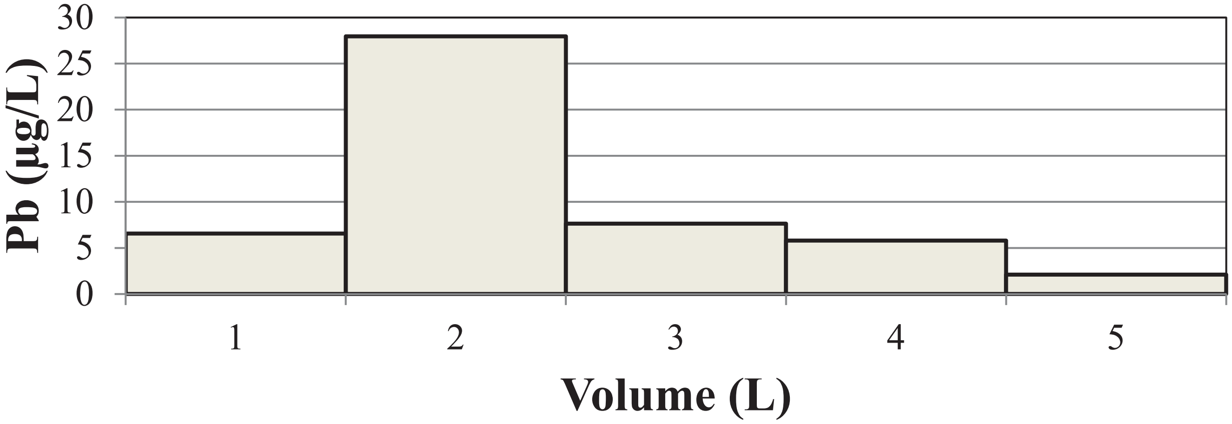


Figure 5.2 Sequential volume samples 72 hours after replacement showing variation in lead concentration.

5.4.1 Full Replacements

Results in the full replacement scenario indicated decreases in lead concentrations after the complete removal of the lead service line (Figure 5.4). This result is in agreement with previous research on full replacements (Cartier *et al.* 2011). Overall, the lead concentrations were much lower in locations that contained only PVC in their household plumbing. However, the presence of brass fittings, which has been shown to contain up to 8% lead by mass (Kimbrough 2001), can explain the variability in the lead concentrations in some of the volunteer sites used in the LSLR program and also the premise plumbing of the home. Homes with copper and brass devices experienced lead concentrations above the 10 µg/L limit even though it was a full replacement.

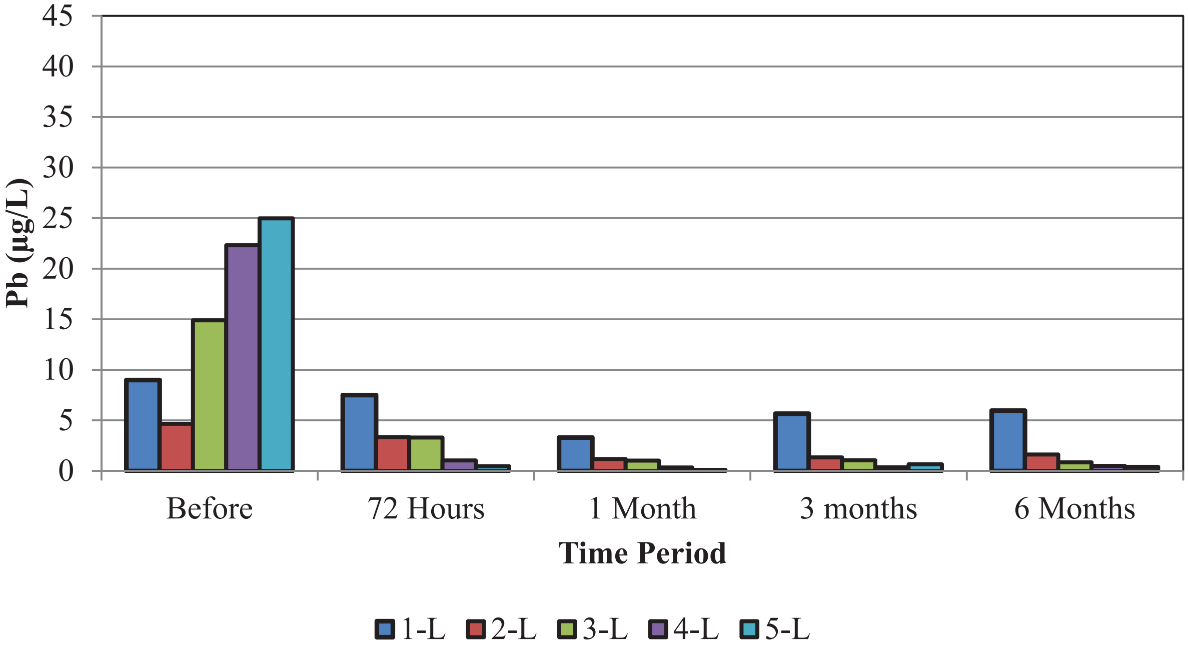


Figure 5.3 Full replacement results in the LSL replacement program.

5.4.2 Partial Replacements

Partial replacements resulted in an increase in lead concentration after the removal of the lead service on the public side (Figure 5.5). Dislodging of particulate lead from the remaining service line (Sandvig et al, 2008) and galvanic corrosion have been shown to be causes of elevated lead observed after partial replacements (Schock et al, 1996; Nguyen et al, 2010; Edwards & Triantafyllidou, 2007; Wang et al, 2012). In most of the sites with a partial replacement, the

MAC was exceeded. Although the lead concentrations decreased over time, at the end of the 6 months period certain homes still had exceedance.

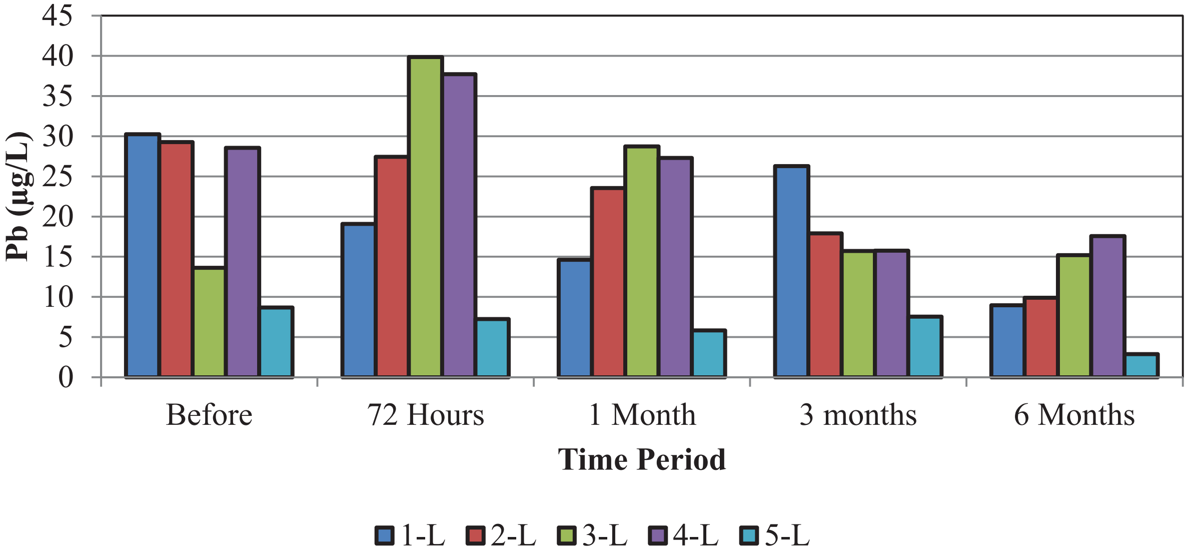


Figure 5.4 Partial replacement result seen in the LSL replacement program.

Results of the full and partial replacements for a few sites are shown in Table 5.3. As with full replacements, the initial lead concentrations were above the MAC for location A and H. 72 hours after the full replacement, the concentrations were well below the MAC and a decrease was observed over time. In the partial replacement scenario, there was an increase between the initial lead concentration and 72 hours samples. The increase in lead concentration can be attributed to galvanic corrosion, or the dislodging of particulate lead from the remaining service line. In some of the cases as in location I and P, the lead concentrations start decreasing a month after the replacement and in location E the lead concentration increases until 3 months after the replacement and starts decreasing by the 6 month sampling period.

Table 5.3 Full and Partial replacements for various sites.

	Initial Lead	**Full/Partial**	**72 Hours**	**1 Months**	**3 Months**	**6 Months**
A	13.02	**Full**	3.38	0.95	-	
H	15.17	**Full**	3.13	1.19	1.82	
K	8.31	**Full**	1.46	1.23	-	
I	22.08	**Partial**	26.27	20.00	16.64	10.90
E	2.36	**Partial**	2.75	2.78	3.78	
P	19.83	**Partial**	55.34	35.78	-	

The sample collection was done on a volunteer basis, hence a couple of the locations had missing sampling periods because the customer did not collect the samples. Table 5.4 details the water main material and type of replacement conducted for all the locations in the LSLR program.

Table 5.4 Water main material, condition of water main and replacement type for all locations.

Location	Water Main	Cleaned & Lined	Partial/Full
A	Ductile Iron	NO	FULL
B	Cast Iron	NO	FULL
C	Cast Iron	NO	PARTIAL
D	Cast Iron	NO	PARTIAL
E	Cast Iron	NO	PARTIAL
F	Cast Iron	YES(Cleaned)	PARTIAL
G	Cast Iron	YES(Cleaned)	FULL
H	Cast Iron	NO	FULL
I	Cast Iron	NO	PARTIAL
J	Cast Iron	NO	FULL
K	Cast Iron	NO	FULL
L	Cast Iron	NO	PARTIAL
M	Ductile Iron	NO	PARTIAL
N	Ductile Iron	NO	PARTIAL
O	Cast Iron	YES(Cleaned)	FULL
P	Cast Iron	NO	PARTIAL
Q	Cast Iron	YES	FULL
R	Cast Iron	YES	PARTIAL
S	Cast Iron	NO	FULL
T	Cast Iron	YES	FULL
U	Cast Iron	NO	FULL
V	Cast Iron	NO	FULL
W	Ductile Iron	NO	PARTIAL
X	Ductile Iron	NO	FULL
Y	Cast Iron	YES	FULL
Z	Cast Iron	NO	FULL
AA	Cast Iron	YES	PARTIAL
BB	Cast Iron	YES(Cleaned)	PARTIAL

5.4.3 Lead and Water Main Interaction

Previous experience by Halifax Water determined that unlined cast iron water mains pigged without been lined will be tuberculated within five to 10 years (Yates 2012). The tuberculation of a recently pigged water main occurs due the exposure of the iron surface to the water and several other water quality parameters (pH, alkalinity, dissolved oxygen and microbial activity) that influence iron corrosion (McNeill & Edwards 2001). A pigged and lined condition means the water main has been mechanically cleaned and lined with either epoxy or cured in place liners, therefore, the water is not in contact with the wall of the pipe. Lastly, the not pigged or lined condition means there are no recorded issues with tuberculation for that water main. Furthermore, data analysis of the LSLR program samples demonstrated that samples that had iron levels below the detection limit (6µg/L) of the ICP-MS also had low lead levels; whereas higher iron levels were associated with high lead concentrations (Figure 5.6).

An interaction between the water main and lead release was observed in the service replacement program. In particular, service lines connected to tuberculated cast iron water mains are a source of iron minerals (e.g., magnetite and goethite). The iron-based corrosion scales detach from the walls of the water main and are then flowing within the customers' connection. Previous lead research demonstrated the adsorption of lead on $FeSO_4$ (McFadden et al, 2011) and hypothesized the adsorption of lead on iron particles (Cartier et al, 2011; Deshommes et al, 2011). The condition of the cast iron water main was obtained and compared to the results from the LSL replacement program. The "Pigged" condition refers to water mains that were mechanically cleaned with pigs in 1960's but were not lined following the pigging process. Previous experience by Halifax Water determined that unlined cast iron water mains pigged without being lined were tuberculated within five to 10 years (Yates 2012). The tuberculation of a recently pigged water main occurs due the exposure of the iron surface to the water and several other water quality parameters (pH, alkalinity, dissolved oxygen and microbial activity) that influence iron corrosion (McNeill & Edwards 2001). A "Pigged and Lined" condition means the water main has been mechanically cleaned and lined with either epoxy or cured in place liners. Thus, distributed water from the "Pigged and Lined" water main was not likely in contact with the wall of the cast iron pipe. Lastly, the "Not pigged or Lined" condition indicated that there were no recorded issues with tuberculation for that water main.

Figure 5.5 shows results from Full replacement of the service lines connected to the different cast iron mains. The lead concentrations are average lead concentrations for five1-L sequential volumes with one standard deviation indicated by the error bars. It was expected that lead concentrations would be below the MAC of 10µg/L, which was observed in all the full replacements connected to ductile iron or "Pigged and Lined" cast iron water mains. The presence of iron minerals in the pigged cast iron condition resulted in lead concentrations much higher than the other two cast iron pipe conditions. Although the concentrations decreased over time, the lead concentrations were still above the MAC.

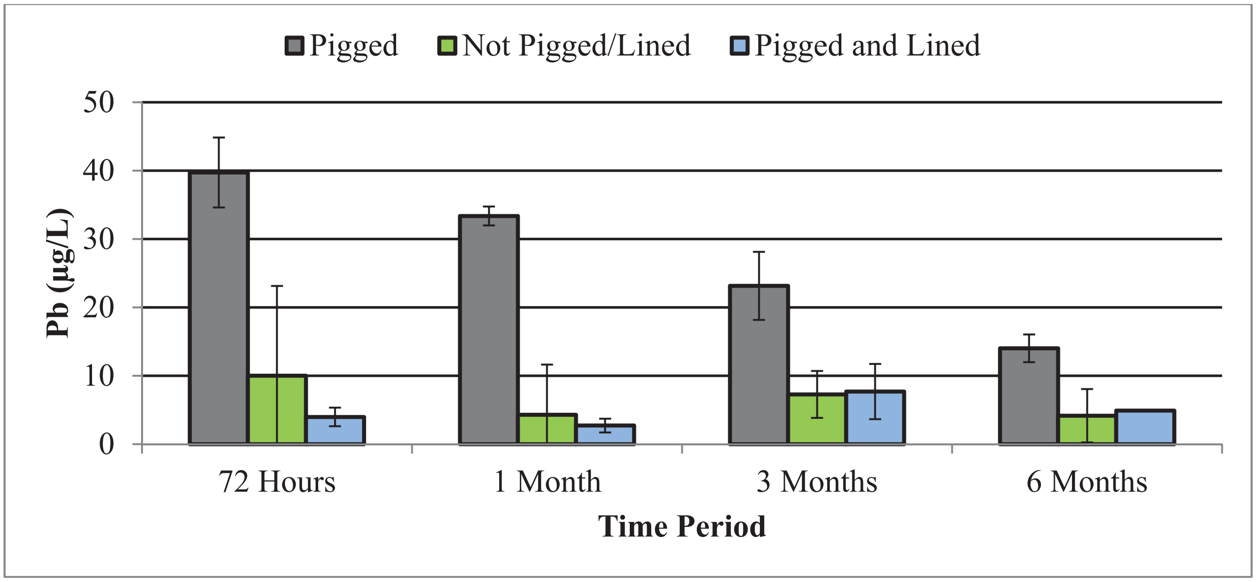
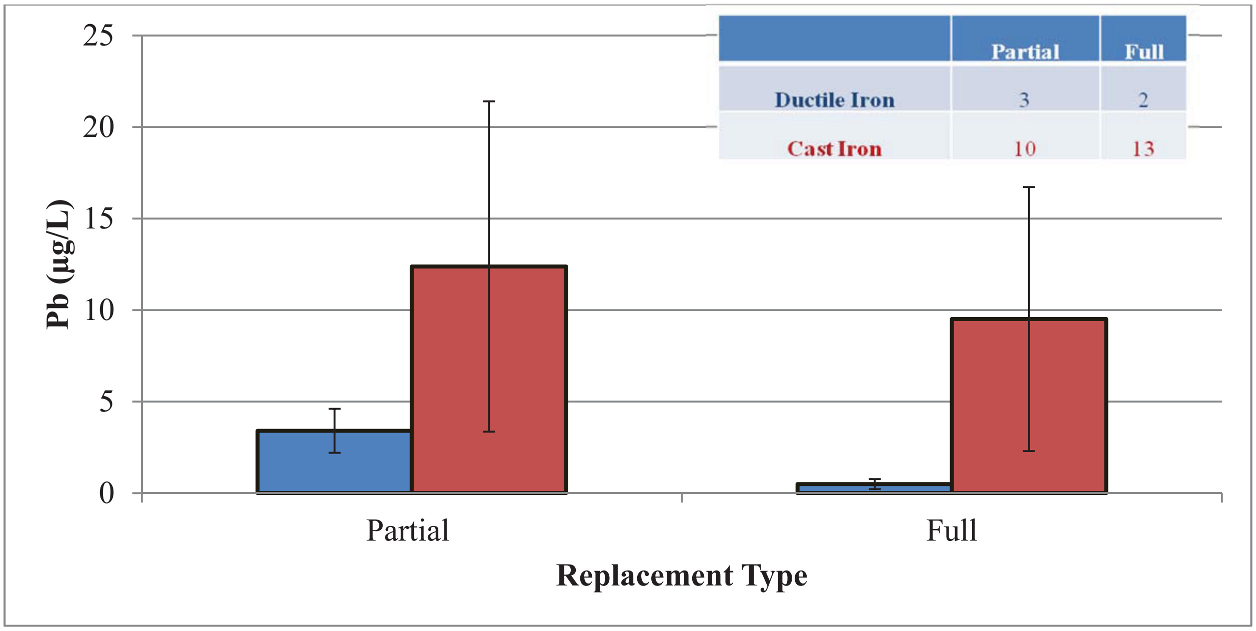


Figure 5.5 Comparison between different cast iron main conditions and lead release.

Service lines connected to ductile iron mains had lower lead release in both the partial and full replacement (3.5µg/L and 1µg/L respectively). As shown in Figure 5.6, the lead concentrations are averaged lead concentrations for the five 1-L sequential volumes and across the number of locations studied. The ductile iron mains used in Halifax are cement mortar lined with an asphaltic coating (Halifax Water 2012). Hence there were very little to no issues with tuberculation in the ductile iron water mains. Consistent with other studies (Cartier et al, 2012a; Cartier et al, 2012b) partial replacements had more lead release than full replacements regardless of the water main material.



	Partial	Full
Ductile Iron	3	2
Cast Iron	10	13

Figure 5.6 Comparison between different water main materials and replacement types (averaged results).

Figure 5.7 shows that for lead samples that have a concentration less than 10 µg/L, there is relatively little dependence on the iron concentration. Figure 5.7a represents water samples collected in the 1st and 2nd liter, which included the water found in the fixtures and plumbing of the home (Figure 5.7a). However, the dependence of the lead concentration on the iron concentration was more predominant in the 3rd and 4th liters (Figure 5.7b), which represents the water contained in the service lines and part of the premise plumbing. While these observations are limited to volunteer sampling and uncertainty volumes, they provide preliminary evidence between the roles of particulate iron on lead release in the customer’s tap.

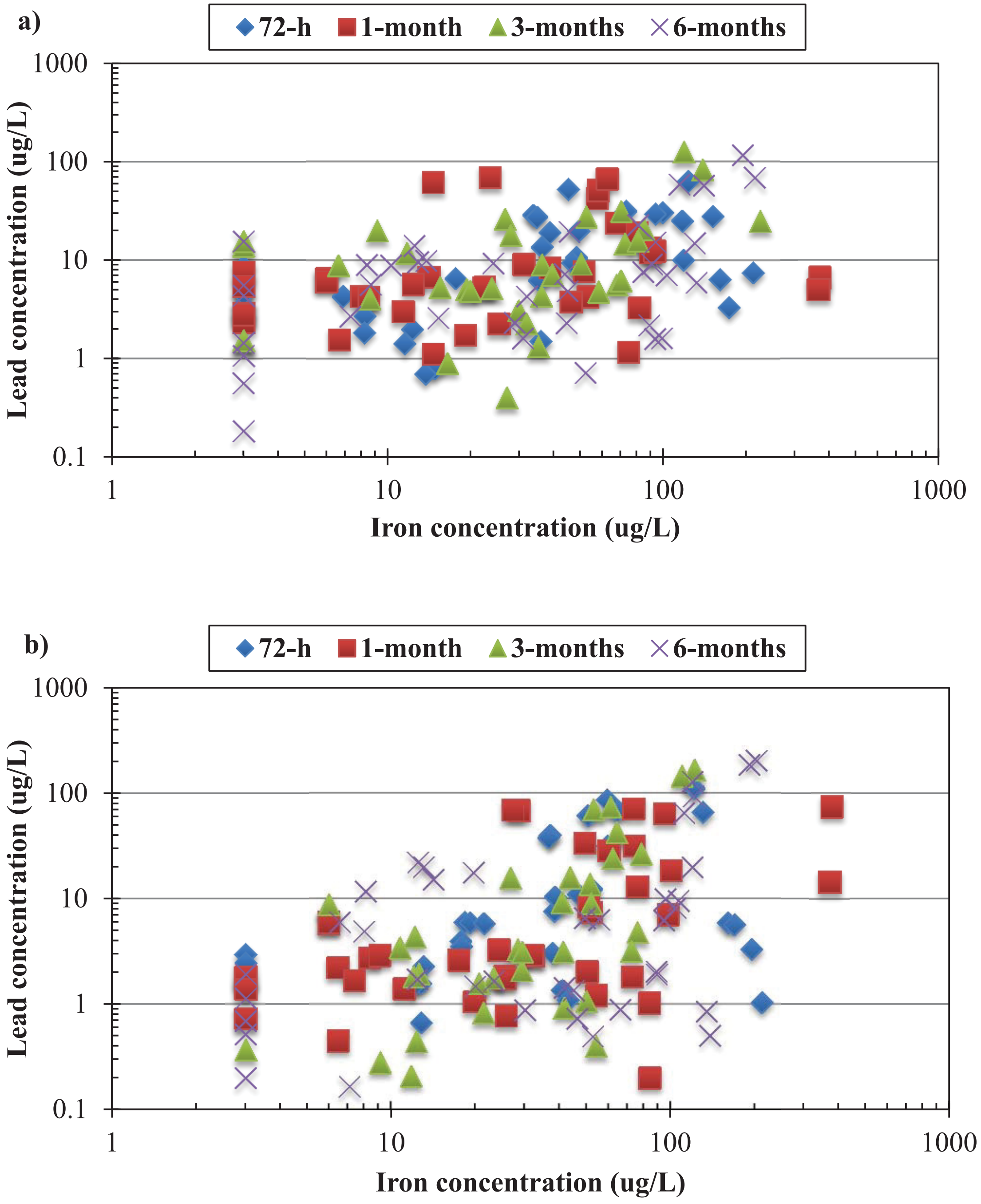


Figure 5.7 Lead concentration versus iron concentration for all measured samples that had lead service lines connected to a cast iron water main. (a) Liters 1 & 2, (b) Liters 3 & 4.

In the locations with a ductile iron water main, the dependence of the lead concentration on the iron concentration was also more predominant in the 3rd and 4th liters compared to the 2nd liter (Figure 5.8). As noted previously, the 2nd liter represents water from brass fixtures and plumbing of the home and the 3rd and 4th liter would likely correspond to the water in the lead service line and premise plumbing. Conceptually, iron does not necessarily indicate lead; however, if iron were present, it would have the potential to adsorb lead if there are lead sources in the premise plumbing. At this point, further controlled studies are required to understand the interaction between lead and iron, which will lead to improved corrosion control management strategies.

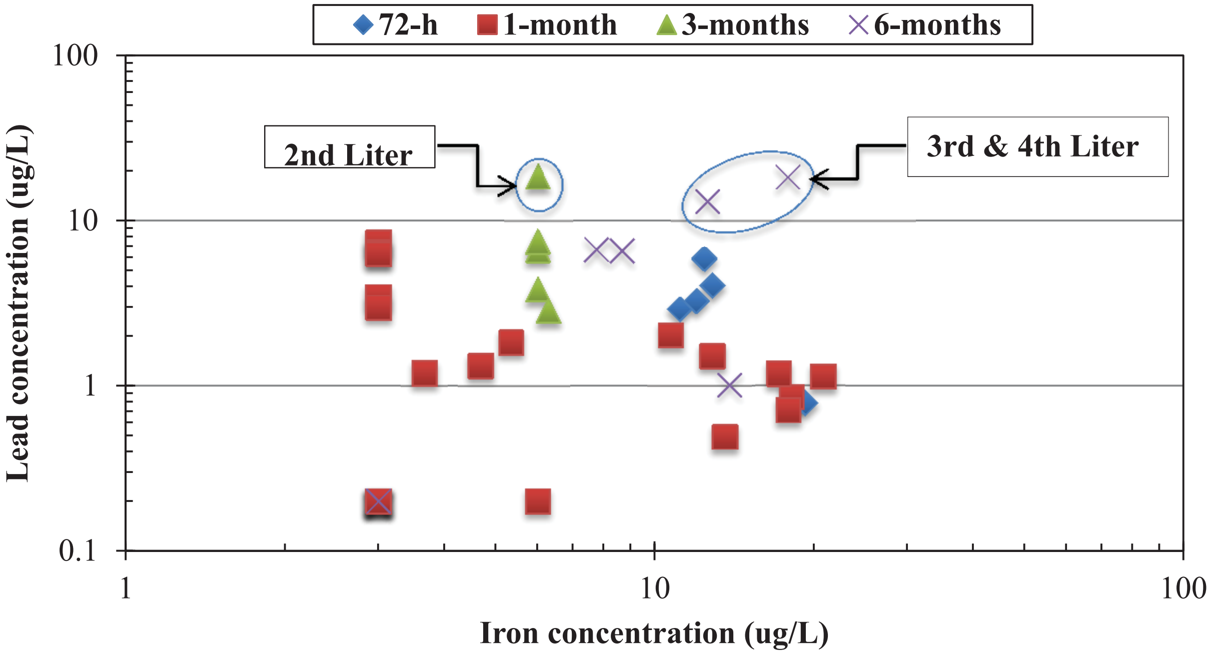


Figure 5.8 Lead concentration versus iron concentration for all measured samples that had lead service lines connected to a ductile iron water main.

5.5 CONCLUSIONS

This study set out to determine the relationship between lead adsorption to goethite and magnetite and overall lead release in a lead service line replacement program conducted in Halifax, Nova Scotia. Results show that full replacements consistently produced lower lead release than partial replacements in this study area. Furthermore, an interaction between cast iron pipe and lead release was found. Tuberculated cast iron water mains rich in goethite and magnetite exacerbate lead release, especially in homes still containing lead soldered joints or brass with high lead content.

Lead service lines connected to ductile iron mains also showed the lowest lead release because no iron was being leached into the water. Finally, there was a dependence of lead concentrations on iron concentration for lead sample concentrations greater than 10µg/L in the LSL replacement program as indicated by the results.

Although most of the sites in the LSLR program meet guidelines, sites with high lead release were identified and Halifax Water has advised the home owner to further reduce lead in their home.

CHAPTER 6 PILOT SCALE INVESTIGATION ON THE EFFECTS OF WATER MAIN MATERIAL ON LEAD RELEASE

6.1 ABSTRACT

The effects of water main material on lead release were investigated in a pipe loop and copper pipe rack experiment. The pipe loop simulated the distribution system and the copper pipe rack simulated premise plumbing. The copper pipe racks contained twenty four-50/50 lead/tin soldered joints, which were the source of lead for the study. The effect of two different pipe materials (cast iron and polyvinyl chloride (PVC)) in the distribution system on lead release in premise plumbing was examined. Cast iron water mains obtained from the Halifax Water distribution system and PVC pipe were used in the pipe loop. Results from the pipe loop and copper pipe rack study showed that the copper pipe racks connected to the pipe loops with the cast iron test section produced the most lead release compared to the copper pipe racks connected to the pipe loops with the PVC test section. A longer stagnation time (23 hours) resulted in lead concentrations 2.5 to 5 times greater than the lead concentration for the short stagnation time (30mins). A comparison of a high chlorine and low chlorine concentration showed that lead release decreased with an increase in chlorine concentration. Thus, this study showed that cast iron material used in water mains exacerbated lead release.

6.2 INTRODUCTION

The quality of treated water in distribution systems remains a serious concern for water utilities. High levels of lead in the distribution system is of particular concern because it is well known that lead in drinking water has adverse impacts on human health and on the cognitive development of children (Fewtrell *et al.,* 2004; Bellinger *et al.,* 1991; Triantafyllidou *et al.,* 2007).

6.2.1 Iron Scales and Lead Release

Corroded unlined cast iron pipes are present in many water distribution systems but are of particular concern in North America due to aging buried infrastructure (Cromwell *et al.* 2001). The corrosion scales present in iron pipes consists of various iron compounds. The two dominant species are goethite and magnetite (Sarin et. al 2001). Iron can be released from cast iron pipes through the dissolution of the corrosion scales or the dislodging of the scales due to pressure changes (Sarin et. al 2004). The adsorption of lead onto iron sulphate found in galvanized iron pipes in premise plumbing has been shown to be responsible for high lead levels (McFadden et. al 2011). However, the adsorption of lead onto iron minerals (e.g. goethite; magnetite) is poorly understood. This knowledge gap is particularly relevant for water utilities that have a significant amount of unlined cast iron pipes in their water distribution system.

McFadden et. al (2011) hypothesized that exposed iron scales on galvanized iron piping in homes adsorbs and releases particulate lead that were initially mobilized from the upstream lead service line. This led to a hypothesis that the iron corrosion scales released from unlined cast iron pipes can probably adsorb lead from the service line. The iron particle can plausibly release particulate lead in the piping of the home, as suggested by McFadden *et al.* (2011). Common lead sources include brass devices, which can contain up to 8% lead by weight and lead solder. While, lead solder use was discontinued in 1986 by the National Plumbing Code of Canada, older homes might still have lead solder joints connecting copper pipes.

6.2.2 Stagnation Time

Studies conducted by Lytle and Schock (2000) to evaluate the impact of stagnation on metal dissolution from plumbing materials (lead, copper, brass) showed that metal levels increase exponentially with time. In their study, Gagnon and Doubrough (2011) showed that lead concentrations were 2.5 times greater in a 23 hours stagnation compared to 30 minutes stagnation. Lasheen et al. (2008) also concluded that a longer stagnation resulted in a higher lead and iron release in their study. Therefore, an increase in lead release is expected with a longer stagnation time.

6.2.3 Disinfectant Residual

Recent research has shown that Pb (IV) oxides (PbO_2) play a significant geochemical role in drinking water distribution systems. However, most of the guidance for lead control in drinking water is based on the presumption that Pb (II) solids control the solubility of lead (Lytle and Schock 2005). The high redox potential necessary to achieve PbO_2 formation in water can only be met with the use of strong oxidants (e.g. free chlorine, chlorine dioxide) and the persistence of these strong oxidants into the distribution system (Lytle and Schock 2005, Davidson et al., 2004, Edwards and Dudi 2004). Formation of PbO_2 in chlorinated water requires time to overcome kinetic barriers and may require precursor Pb (II) mineral phases (Lytle and Schock 2005).

6.2.4 Phosphate Corrosion Inhibitors

Phosphate based inhibitors were discovered to be beneficial only at low alkalinity water sources (< 30mg/L as $CaCO_3$) at all pH values by Dodrill *et. al* (1995). At the James Douglas Kline Water Supply Plant (JDKWSP) a zinc/ortho polyphosphate blend is used as a corrosion inhibitor, which helps to decrease the lead release. However, further optimization of the phosphate based inhibitor is required.

A pilot scale pipe loop and copper pipe rack experiment at the JDKWSP in Halifax, Nova Scotia was used in order to investigate the effects of water main material, stagnation time, and chlorine concentration on lead release. The pipe loop simulated a distribution system; while the copper pipe rack simulated premise plumbing.

The objectives of this study were to determine the effects of a corroded cast iron distribution system on lead release at the pilot scale, and to examine the role of stagnation time as a factor in lead release when the service line is connected to a cast iron distribution system.

6.3 MATERIALS AND METHODS

6.3.1 Clearwell Water

The pilot set up was located at the JDKWSP. The JDKWSP is a direct filtration plant operated and maintained by Halifax Water (HW) that treats water from Pockwock Lake. The plant utilizes pre-screening, oxidation, pre-chlorination, coagulation, hydraulic flocculation, filtration and chlorination. Pre-screening of the raw water removes all large impurities in the water. Potassium permanganate ($KMnO_4$) is then added to oxidize any manganese and iron present. Next, carbon dioxide (CO_2) is added to adjust the pH to 5.5 – 6. Alum is then added as a coagulant at a concentration of 8mg/L. During the cold weather months (November to June) cationic polymers are then added to aid floc strengthening and to ensure the removal of natural organic matter. Pre-chlorination, which follows the addition of the coagulant, prevents the growth of bio film in the filters. Hydraulic flocculation, direct filtration, and chlorination of the filtered water follow in the respective sequence. Water is then held in the clearwell and then chlorinated. In the pilot study, the feed water for the pilot was piped from the clearwell (before chlorine addition) to the basement of the JDKWSP where the pilot experiment occurred. Table 6.1 shows the characteristics of the clear well water during the duration of the pilot study.

Table 6.1 Clear well characteristics from August 2011 to June 2012.

Parameter	Average ± Standard deviation
Turbidity (NTU)	0.094 ± 0.061
Total Cl_2 (mg/L)	0.054 ± 0.01

6.3.2 Pipe Loop Description

The Dalhousie Pipe Loop© is a recirculating pipe loop with variable flow rate and retention time designed by Rutledge (2003). The Dalhousie Pipe Loops© have been used by previous researchers for corrosion studies and water distribution modeling (Gagnon et al. 2008, Eisnor et. al. 2003, Eisnor et al. 2004). A detailed description of the Dalhousie Pipe Loops© can be found in Gagnon et al. (2008). Key features of the pipe loop include a test pipe section, a recirculation pump, return section, transition section, and aluminum support frame. (Figure 6.1). However, other components of relevance to the operation of the pipe loop are the feed pump,influent and effluent water ports, and the chemical feed jugs.

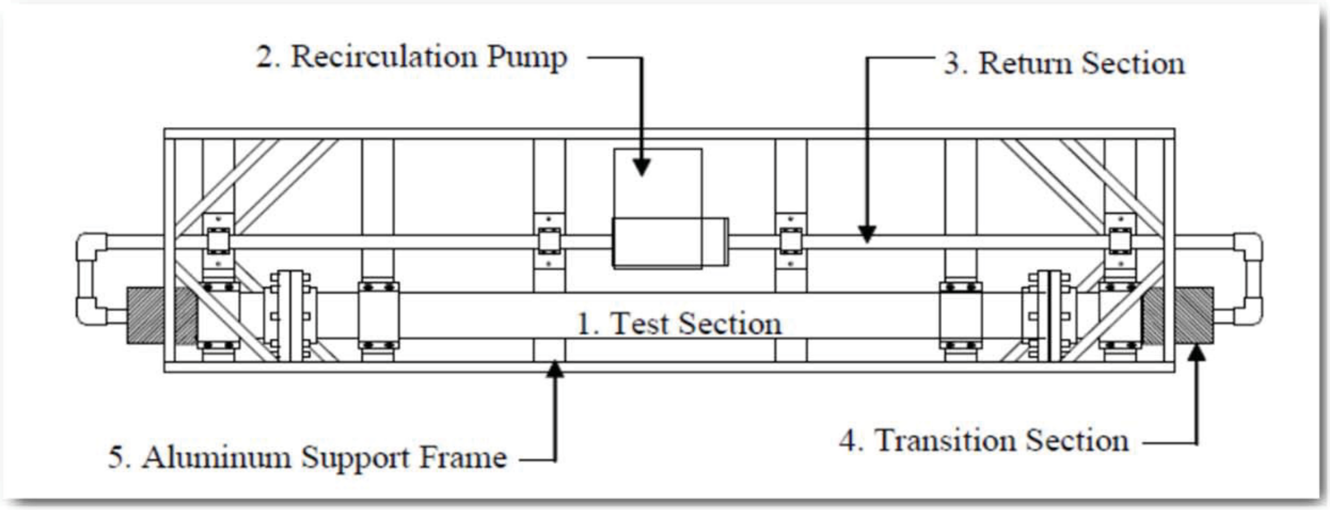


Figure 6.1 Top view of the Dalhousie Pipe Loop©.

In this study, the test pipe section consisted of polyvinyl chloride (PVC) and cast iron pipe sections. The cast iron pipe sections were harvested from the HW distribution system. The PVC test section was 1.8m (6’) in length and 100mm (4”) in diameter. The cast iron test was a 6” diameter pipe retrofitted with a 6” diameter to 4” diameter pipe reducer at Dalhousie University to fit on the pipe loop (Figure 6.2). Table 6.2 provides a description of the test section pipe material and condition.

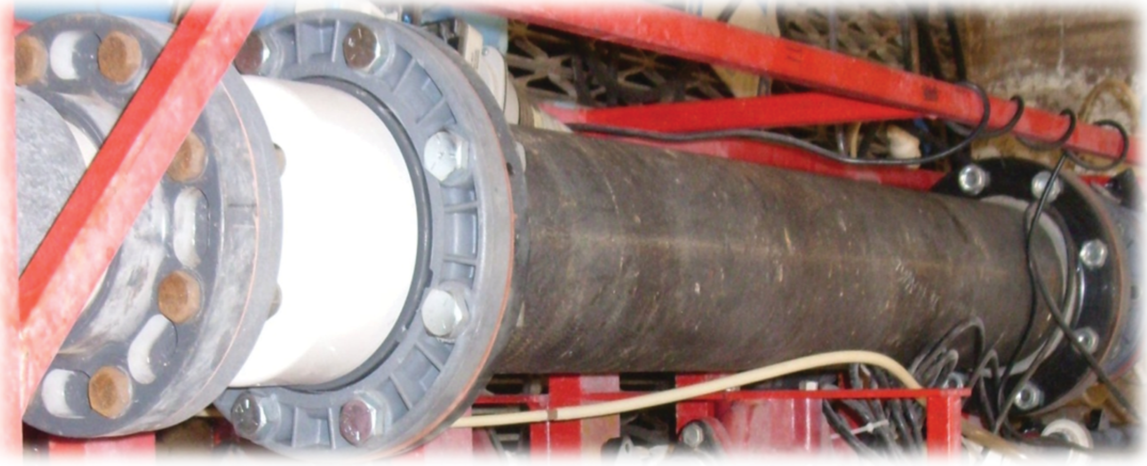


Figure 6.2 Retrofitted cast iron test section mounted on the Dalhousie Pipe Loop©.

Table 6.2 Test section pipe material and condition.

Pipe Section	Pipe Material	Description
Pipe Loop 1	Cast Iron	Heavily tuberculated, suspected to be older pipe.
Pipe Loop 2	Cast Iron	Less tuberculated
Pipe Loop 3	PVC	9 year old PVC pipe
Pipe Loop 4	PVC	9 year old PVC pipe

Water was recirculated through the pipe loops using a centrifugal pump rated at 146L/min (38.5 gpm (US)) at 2.1m (7.0') of head through 25mm (1") PVC pipe and pipe fittings. The velocity in the test section was 0.30m/s (1fps), which is representative of flow in a distribution system (Rutledge 2003). In this study, the pipe loops were used primarily to simulate water aging and in the case of the cast iron test section to seed the water with iron particles. The pipe loops had a hydraulic retention time of 12 hours.

Chemicals were added to the pipe loop by pumping the chemicals from 20L blue jugs (feed containers) by using a variable speed peristaltic pump (Masterflex, Vernon Hill, IL) with a 1 to 100rpm motor and L/S 14 PHAR-MED tubing with an inner diameter of 1.6mm. The flow rate used was 3ml/min to ensure enough chlorine residual in the pipe loop on the sampling days. Chlorine was added to maintain total chlorine residual, zinc/ortho polyphosphate was added for corrosion control. 1 M Sodium Hydroxide (NaOH) or 1 M Hydrochloric Acid (HCl) was added for pH adjustment. The volume of chlorine, the volume of phosphate and the volume of acid or base was adjusted on a trial and error basis to maintain the required testing conditions. Trial and error method was performed because of the variability of the feed water and the chemical concentration in the effluent of the pipe loops,

After the water had been aged in the pipe loop for 12 hours, the effluent of the pipe loops was collected in a reservoir bin and then pumped through the copper pipe racks.

6.3.3 Copper Pipe Rack Description

Each copper pipe rack consisted of seven, 12 feet lengths of ½" diameter Class M copper pipe. Twenty-four 50/50 lead/tin soldered joints connected the seven lengths of the copper pipes. At beginning of the copper pipe rack, there is a brass fitting that connects the tubing between the reservoir bin and the copper pipe rack. At the end of the copper pipe rack, the brass fitting connects the copper pipe rack to tubing for sample collection. The only source of lead from the copper pipe rack is the twenty-four 50/50 lead/tin solders. Water was pumped through the copper pipe racks using a Masterflex IP Peristaltic Pump that uses IP/73 tubing, which allows high water velocity.

The pump was set on a computer timed stagnation and flush cycle. Water was stagnant in the copper pipe racks for 23 hours and flushed for five minutes at 5.6L/min, followed by a 30 minute stagnation period and final five minutes of flushing. The flow through design for this study was based on previous works of Eisnor and Gagnon (2003) and Gagnon and Doubrough (2011). Samples were collected from the effluent of the copper pipe racks following both the long and short stagnation times. A schematic of the experimental setup is shown in Figure 6.3.

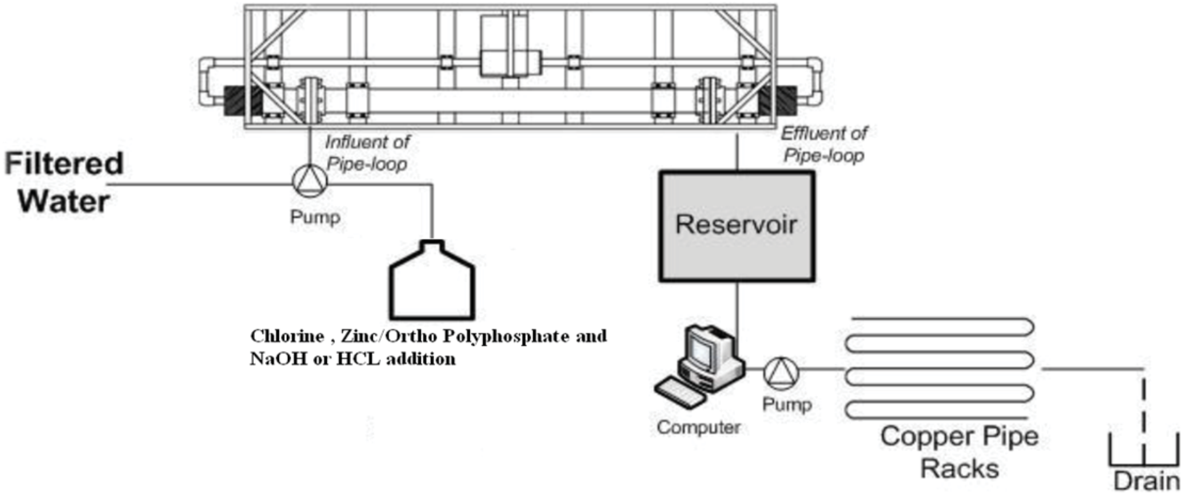


Figure 6.3 Schematic of the Dalhousie Pipe Loop and Copper pipe rack setup (Adapted from Woszcynski 2011).

6.3.4 Experimental Procedures

Data collection for the copper pipe racks and pipe loop studies spanned a 10 month period with the first four months used for the acclimation of the pipe loop and copper pipe rack system. However, previous research using the Dalhousie Pipe Loop© and copper pipe rack determined that an acclimation period of 30 days is reasonable (Gagnon and Doubrough 2011, Eisnor and Gagnon 2004, Rahman et al. 2007), hence, an acclimation period of four months was equally reasonable.

Sample collection and refill of the chemical feed containers were conducted every Monday and Thursday throughout the duration of the pilot study. On every sample collection day, the recirculation pump was checked to ensure that the pump did not overheat, which is an indication of a pump malfunction. The effluent of the pipe loops was measured for chlorine, phosphate and pH to determine if the chemical dose in the feed containers had to be adjusted. The test factors considered were a pH of 5.5, total chlorine concentration of 0.2mg/L and 2mg/L, and phosphate concentration of 0.5mg/L. However, the total chlorine concentrations and pH in the different pipe racks were variable (Table 6.2 and Table 6.3). The pipe loops with the PVC test section had a high and low chlorine concentration. Effluent samples from the pipe loop were analyzed for lead, copper, iron and aluminum. A high and low chlorine concentration for the pipe loops was however not possible with the cast iron test section since the cast iron pipe sections were harvested from different locations in the HW distribution system. Effluent samples from the copper pipe racks were analyzed for lead, copper, iron, aluminum and tin.

Table 6.3 Total Chlorine concentrations measured during pilot scale study.

	Total Cl_2 residual, mg/L X ± Std.
Pipe Rack 1	0.26 ± 0.26
Pipe Rack 2	1.86 ± 0.61
Pipe Rack 3	1.67 ± 0.68
Pipe Rack 4	1.64 ± 0.76

Table 6.4 pH measured during pilot scale study**.**

	pH X ± Std.
Pipe Rack 1	5.52 ± 0.22
Pipe Rack 2	5.68 ± 0.63
Pipe Rack 3	5.83 ± 0.51
Pipe Rack 4	5.82 ± 0.53

6.3.5 Analytical Procedures

Throughout the study, reverse osmosis (RO) water was used for all cleaning and rinsing of the glassware. The glassware was rinsed three times using RO water obtained from a Milli-Q® purification system. A combination pH/mV/Temperature/ DO and Conductivity meters (Accumet XL 25 and XL 60 models) with plastic bodied, gel-filled, combination pH electrodes (Accument Accu-Cap) were used for the pH measurement. A three - point calibration (pH 4, 7, 10) was conducted prior to any pH measurement on the Accumet. A HACH DR/4000 UV/VIS spectrophotometer (Hach Company, Loveland, CO) was used to measure chlorine and phosphate concentration in the pipe loop effluent.

Lead, iron, copper, aluminum and tin samples were prepared by lowering the pH of the solution to below 2 with concentrated nitric acid and then stored at 4ºC until analysis. Total and dissolved metals were measured using the inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific X-Series 2). The method detection limit (MDL) for the ICP-MS was: Aluminum – 2µg/L, Iron– 6µg/L, Copper – 0.7µg/L, Lead – 0.4µg/L, and Tin – 0.6µg/L. Before the water samples were acidified, the water sample was filtered through a 0.45µm polsulfone filter membrane (GE Water & Process Technologies) that had been pre rinsed with 500ml of RO water. The filtered sample was then acidified before the metal analysis on the ICP-MS to measure the dissolved metals. The ICP-MS has quality control checks built in to ensure the accuracy of the results. Duplicate samples were used when the quality control standards and blanks were inaccurate during the measurement.

6.3.6 Statistical Analysis

ANOVA, paired t-test and simple linear regression statistical analyses were applied on the data to determine whether the results were indeed similar or statistically different and also to find trends and correlation in the data.

6.4 RESULTS AND DISCUSSION

Figure 6.4 and Figure 6.5 show the total lead release from the pipe racks following 23 hours and 30 minutes respectively. The lead concentrations from the copper pipe racks connected to the pipe loops with the cast iron test section had a much higher lead concentration than the copper pipe racks connected to the pipe loops with a PVC test section.

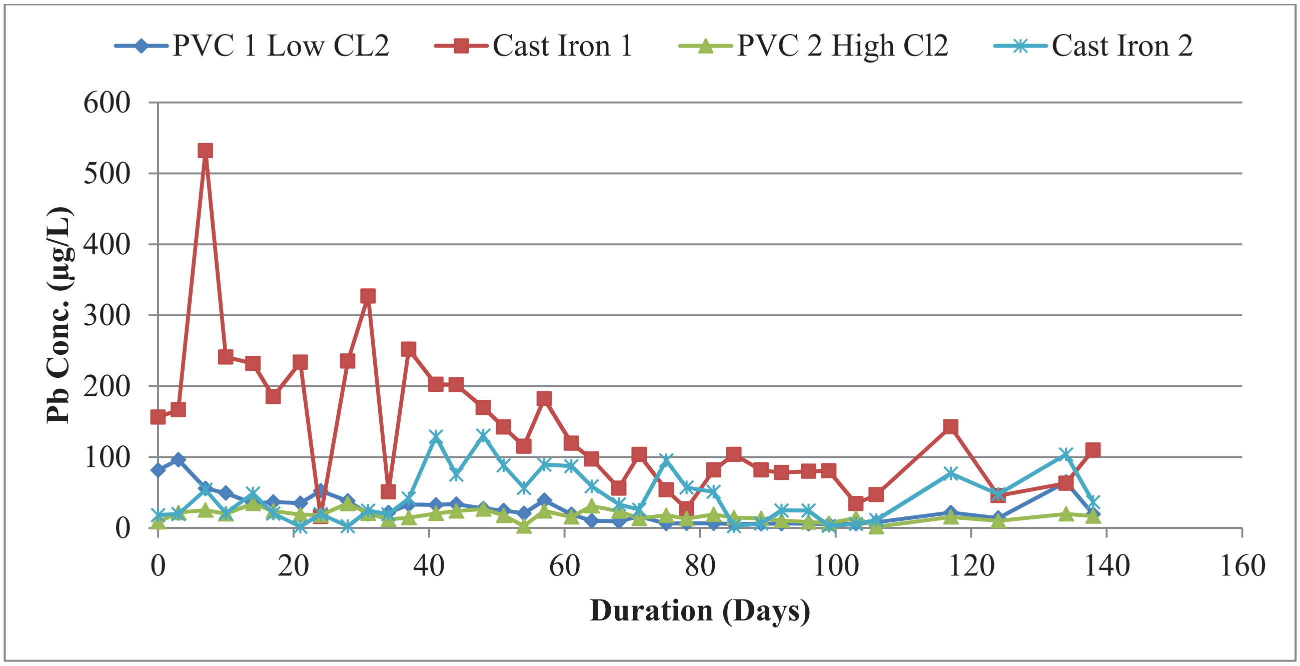


Figure 6.4 Total lead concentrations from the effluent of the copper pipe racks following 23 hour stagnation.

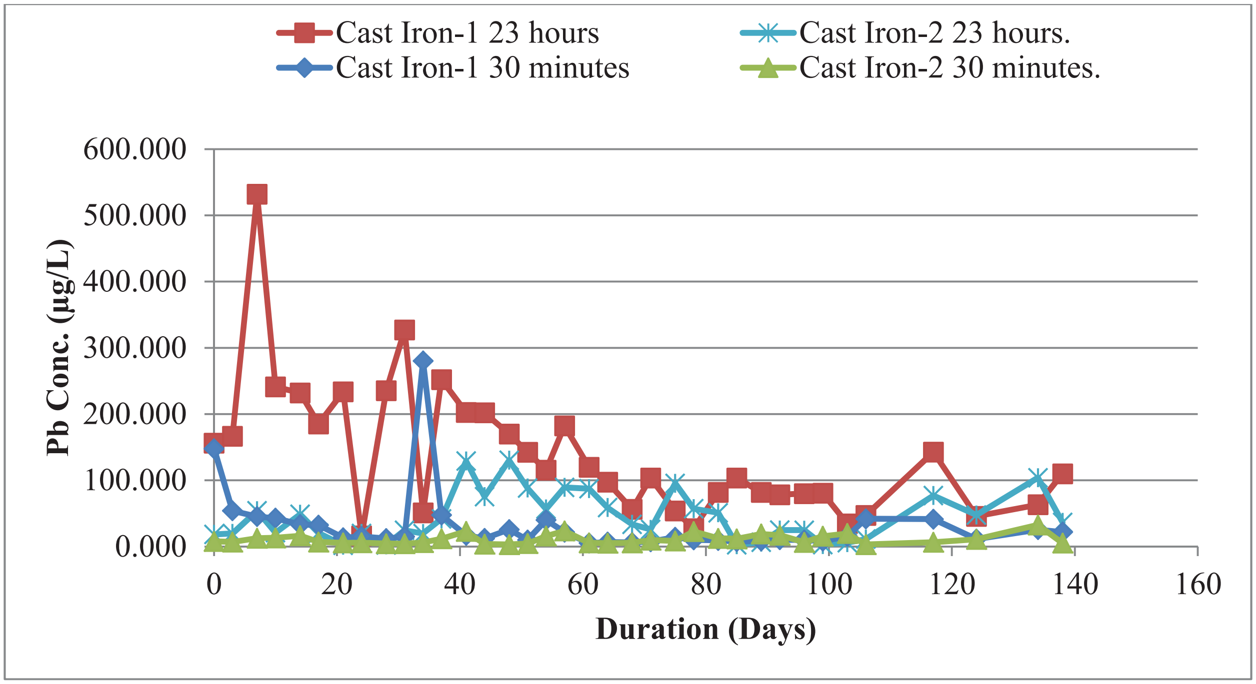


Figure 6.5 Total lead concentrations from the effluent of the copper pipe racks following 23 hours stagnation and 30 minutes stagnation for the copper pipe racks connected to the cast iron test section pipe loops.

Furthermore, it was also evident that the 23 hours stagnation time resulted in an increase in lead concentrations when compared to the 30 minute stagnation time. This observation was also noted in previous studies by Gagnon and Doubrough (2011) and Lytle and Schock (2000). The lead concentrations from the pipe racks with the long stagnation time had, on average, a lead concentration that was 2 – 5.5 times greater than the short stagnation period (Table 6.4). Control charts were used to determine the significance of each data point on the average lead concentration. Control charts are provided in Appendix C.

Table 6.5 Lead concentration of the copper pipe racks with different stagnation times.

	Long Stagnation	**Short Stagnation**
Test Section	**Mean (µg/L) ± Std**	**Mean (µg/L) ± Std**
PVC Low Cl_2	27.7 ± 7.55	4.70 ± 0.97
Cast Iron 1	138.1 ± 31.69	21.04 ± 14.38
PVC 2 High Cl_2	16.57 ± 2.60	5.97 ± 2.80
Cast Iron 2	48.64 ± 8.84	10.99 ± 1.88

The copper pipe racks connected to the pipe loops with the cast iron test section had the most lead release; however, cast iron 1 had a much higher lead release than cast iron 2. An ANOVA and paired t-test with a 95% confidence interval indicated that the results from the two pipe racks connected to the pipe loops with a cast iron test section were significantly different. A study by Sarin et al. (2001) demonstrated that the percentage of magnetite and goethite in a cast iron pipe can vary within a distribution system which was the case in this study (Appendix C). From the result shown in Table 6.4, the cast iron 1 test section had a higher lead release than the cast iron 2 test section, which is probably due to the higher amount of magnetite and goethite found in cast iron 1 compared to cast iron 2. The exact amount of magnetite and goethite in the cast iron test sections could not be determined without disassembling the pipe loop, which made it impractical.

A significant difference between the high and low chlorine concentration was observed in the copper pipe racks connected to the PVC test sections in pipe loop 1 and pipe loop 3. Previous research shows that a higher chlorine concentration results in lower lead release due to the oxidation of metallic lead to lead oxide. Lead oxide is insoluble in water thus it reduces lead in water (Davidson et al., 2004; Edwards and Dudi 2004; Lytle and Schock 2005; Xie and Giammar 2011).

ANOVA and paired t-test showed a significant difference on the lead release in the comparison between pipe rack 1 (low Cl_2) and pipe rack 3 (High Cl_2) (Appendix C).

High iron concentrations correlated to high lead release in the copper pipe racks (Figure 6.6 and Figure 6.7). There is a dependence of the lead concentrations on iron concentrations for all of the test sections. A strong correlation is observed in the copper pipe racks connected to Cast Iron 1 test section and the PVC test section with a low chlorine concentration. The dependence of the particulate lead concentrations on the particulate iron was less predominant in the copper pipe rack with the PVC test section and high chlorine concentration. However, the correlation of particulate lead with particulate iron was observed in all the copper pipe racks regardless of the test section used, for particulate lead concentrations greater than 10µg/L. The difference in iron correlations between the two PVC test sections is due to the accumulation of iron present in the water from the plant. The Dalhousie Pipe loops have been in operation for nine years. Hence, iron found in the clearwell water has accumulated in the test section and was been leached into the water

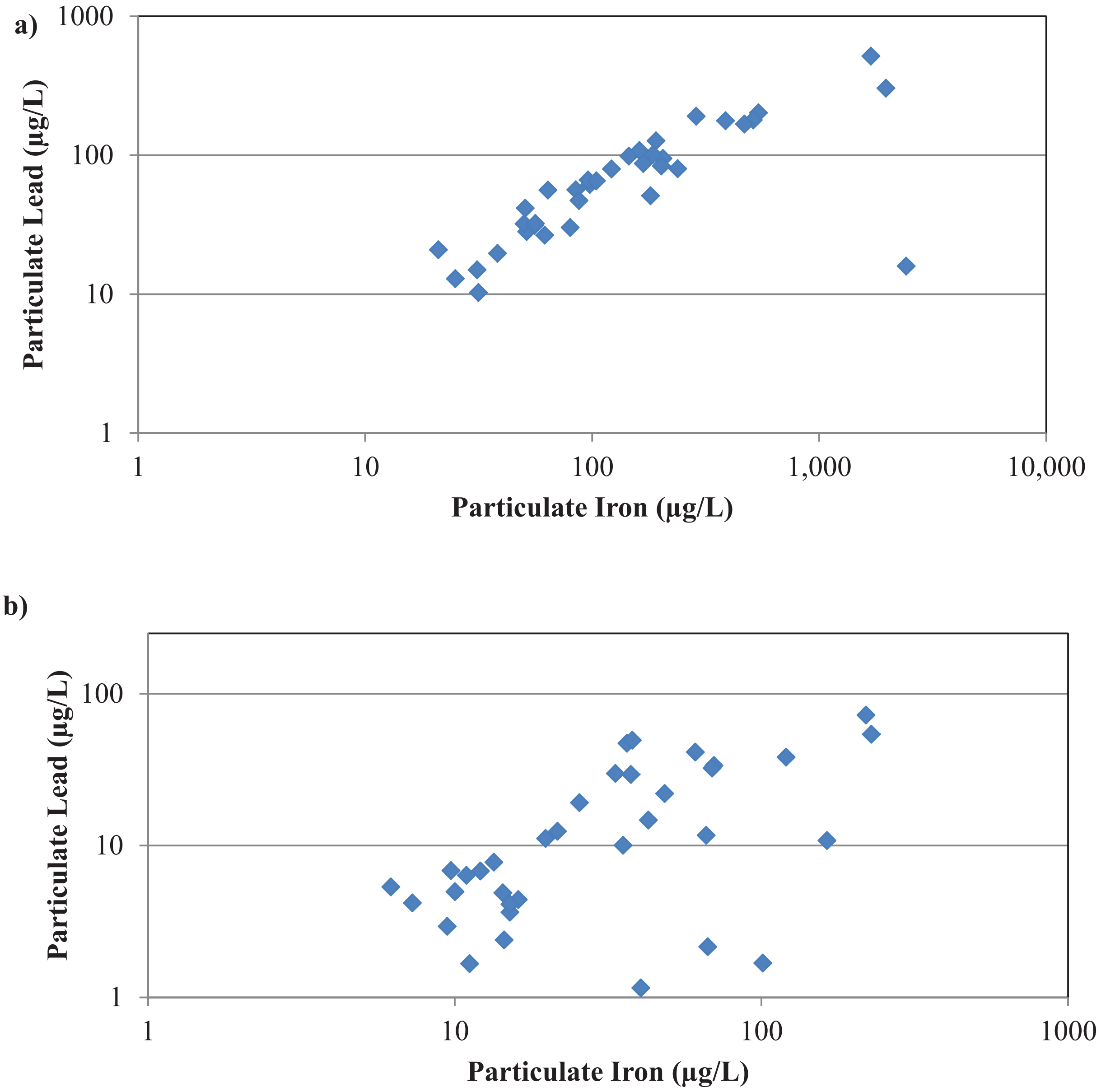


Figure 6.6 Particulate lead versus Particulate iron for the copper pipe rack connected to the pipe loop with the cast iron test sections (Long Stagnation). A) Cast Iron 1, B) Cast Iron 2.

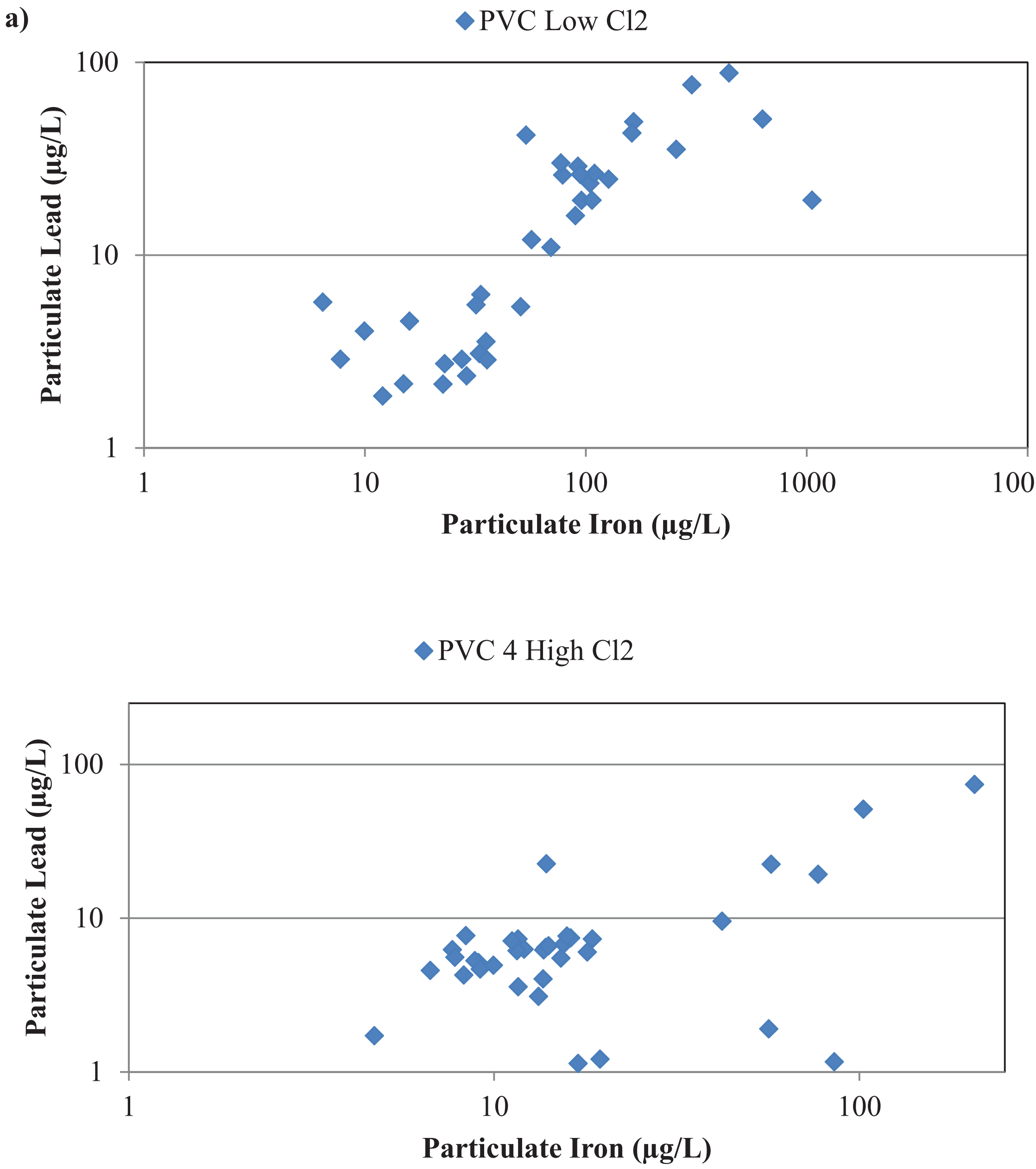


Figure 6.7 Particulate lead versus Particulate iron for the copper pipe rack connected to the pipe loop with the PVC test sections (Long Stagnation). A) PVC Low Cl_2, B) PVC High Cl_2.

6.5 CONCLUSIONS

Results from this study indicate that the presence of corroded cast iron increases lead release. Different cast iron water mains with varying goethite/magnetite ratios can explain the variation in lead release observed in this study. A correlation between particulate iron in the water main and particulate lead release was also shown. Higher chlorine concentration resulted in lower lead release as compared to the lead release in the low chlorine condition in this study. Utilities that have tuberculated cast iron water mains, which are a rich source of magnetite and goethite, can experience high lead release in homes with lead services connected to the tuberculated water main.

CHAPTER 7 RECOMMENDATIONS

Whilst conducting this research, a few issues were encountered and opportunites for future research work were identified. These potential research topics were beyond the scope of this research project, but will further help in increasing the knowlegde base on the relationship between iron particles and lead release. Suggestions on how to better avoid the problems encountered during this research and future research topics for each experiment chapter is presented below.

7.1 LSL REPLACEMENT PROGRAM

The LSLR program was conducted on a volunteer basis. Frequent problems encountered with the sampling program were:

- Improper sample collection.
- Lack of sufficient stagnation time.
- Lack of participation in the program, particularly with households whose lead levels have decreased below the MAC.
- Lack of a complete metal profile (Before, 72 hours, 1 month, 3 months & 6 months).

In order to prevent the issues listed above, a more detailed sample collection instruction sheet should be prepared. The instructions should be explained to the customer in person to ensure that they are properly followed.

The importance of the stagnation time on the metal analysis should also be explained and research showing the importance of stagnation time on metal concentrations should be shown to the customer. If the customer understands that the difference between two – hour stagnation and six – hour stagnation can mean the difference between a sample being below the MAC or exceeding the MAC, the customer will be more mindful of maintaining a minimum six hour stagnation.

Lack of participation in the program for households whose lead levels are below the MAC is a difficult issue to solve without proper incentive. The importance of obtaining a complete profile of the LSLR can be explained to customers. A more active initiative will be to call the customers a day before the scheduled sample collection and to remind them to collect the samples the next day rather than waiting for the customer to call for the sample pick up.

Finally, the best way to ensure proper participation and commitment to the program is to provide some type of incentive that will make it worthwhile for the customer to take part in the program.

7.2 POTENTIAL BENCH SCALE VERIFICATION

Pipe section experiments in the water quality laboratory can be used as bench-scale verification. The pipe sections are full copper, full lead, and lead/copper galvanically connected. The pipe sections have already been used by Knowles *et al.* (2010) using a dump and fill procedure. The effects of iron particles (magnetite/goethite) in the system can be investigated by using the same finish water conditions from the JDKWSP with the additional use of the iron particles to determine whether they exacerbate lead release.

7.3 INTERACTION BETWEEN DIFFERENT WATER MAIN MATERIALS.

To further improve the operation of the pipe loops, an automatic chemical adjustment system should be installed in the pipe loops. During the study, the trial and error method used made it very difficult to ensure the same test conditions. When the peristaltic pump was nonoperational the problem would not be discovered until the next sample collection day.

Furthermore, a potential research topic will be the investigation of various pipe materials (ductile iron, PVC, and cast iron) on lead release. However, this project will use lead service line pipe racks instead of copper pipe racks to compare the results obtained from the LSLR program. To make the best use of resources, and to simulate field conditions, pipe racks using lead and copper should be used to simulate a partially replaced service line. Hence, the effects of galvanic corrosion can also be determined in the study.

CHAPTER 8 CONCLUSIONS

8.1 SUMMARY

The main purpose of this research work was to determine the relationship between iron particles found in water mains and lead release in the Halifax distribution system. Magnetite and goethite were the main iron particles of focus in this thesis. In order to investigate the effects of iron particles on lead release, bench-scale, pilot-scale, and full-scale experiments were designed to satisfy the following research objectives:

- Investigate the adsorption of lead on different iron minerals (magnetite and goethite) using RO water and treated water, and evaluate the pH effect on the adsorption process.

- Determine the relationship between lead adsorption to goethite and magnetite and overall lead release in a lead service line replacement program conducted in Halifax, Nova Scotia and determine which type of service line replacement is beneficial for Halifax.

- Determine the effects of a corroded cast iron distribution system on lead release in a pilot study and examine the role of stagnation as a factor in lead release when the service line is connected to a cast iron distribution system.

8.1.1 Bench-Scale Adsorption Experiment

Several bench-scale adsorption experiments were conducted to investigate the adsorption of lead on magnetite and goethite. The first trial of the adsorption experiment investigated the adsorption of lead on these iron particles in a high and low pH solution that was determined from the water samples in the LSLR program. Initial lead concentration used for the adsorption study was a concentration of 100µg/L.

Subsequent adsorption experiments were conducted to create adsorption isotherms for magnetite and goethite at pH values of 5.5, 6.5, and 7.5. In the solutions of pH 6.5 and 7.5, the adsorption experiments were repeated with a higher initial lead concentration of 500µg/L because it was determined that there was a higher adsorptive capacity at high pH values.

Adsorption experiments using finished water from the JDKWSP (Cl_2 1.02mg/L, pH 7.28, and PO_4 0.5mg/L) were also conducted to determine the possibility of the adsorption of lead in finished water conditions. Adsorption experiments used an initial lead concentration of 100µg/L for the first trials but subsequent adsorption trials used initial lead concentrations of 500µg/L due to the higher adsorptive capacity of lead on magnetite and goethite at high pH values. All the bench scale trials were completed in eight months.

Results from the bench-scale adsorption experiments showed that the hypothesis that lead adsorbs on magnetite and goethite was accurate.

8.1.2 Lead Service Line Replacement Program

Profiles of the metal concentration were conducted following both full and partial replacements. Water samples were collected before the replacement of the service line, 72 hours, 1 month, 3 months, and 6 months following the replacement of the service line. Sample collection was done on a volunteer basis with the customer collecting the samples by following sample collection instructions provided by Halifax Water. The water samples were analyzed for lead, iron, copper, aluminum and tin. The condition of the water main was also determined through historical records maintained by Halifax Water.

The differences between full and partial replacement profiles were identified and correlation in the data collected was investigated. The results of the metal sample profiles were compared to the information for the water main to determine the effects of tuberculated water mains, which are a rich source of magnetite and goethite, have on the lead release observed.

8.1.3 Pilot-Scale Pipe Loop and Copper Pipe Rack Study

In order to investigate the effects of water main material, stagnation time, and chlorine concentration, the pipe loop and copper pipe rack pilot scale study at the JDKWSP was used. The pipe loop was designed and built by Rutledge (2003) to be a research standard that simulates a distribution system and the copper pipe racks were designed by Gagnon and Doubrough (2011) to simulate premise plumbing. The test section on the pipe loop setup was replaced on two of the pipe loops with cast iron test sections to simulate a cast iron distribution system. In this study, the pipe loops were used primarily to simulate water aging and in the case of the cast iron test section to age the water and seed the water with iron particles. The pipe loops had a hydraulic retention time of 12 hours. After the water had been aged in the pipe loop, the effluent of the pipe loops was collected in a reservoir bin and then pumped through the copper pipe racks.

The pump was set on a computer-timed stagnation and flush cycle. Water was stagnant in the copper pipe racks for 23 hours and flushed for five minutes followed by a 30 minutes stagnation period and another five minutes of flushing. Samples were collected from the effluent of the copper pipe racks following both the long and short stagnation times. Samples were analyzed for lead, copper, iron, and aluminum in the effluent of the pipe loop and in the effluent of the copper pipe racks tin was analyzed in addition to the other metals mentioned. The data collection for the copper pipe racks and pipe loop study spanned a 10 month period with the first four months used for the acclimation of the pipe loop and copper pipe rack system.

8.2 CONCLUSIONS

The results from the bench-scale, pilot-scale, and full-scale experiments show that there is indeed a relationship between the iron particles in the water main and lead release. Tuberculated water mains had a negative impact on lead release regardless of the type of LSLR. This information will benefit Halifax Water because it is now known that the water main material has an effect on lead release. Hence, this information will help with prioritization of LSLRs and water main renewals, which will reduce lead release.

8.2.1 Bench-Scale Adsorption Experiment

Magnetite and goethite were capable of adsorbing lead from both lead spiked RO water and lead spiked finished water. One of the key factors of lead adsorption on the iron particles was the pH of the water. A higher pH favored the adsorption of lead on magnetite more than the adsorption of lead on goethite. There is a higher adsorptive capacity of lead on magnetite and goethite at pH values above 6.5. Adsorption of lead in finished water shows that the adsorption of lead on magnetite and goethite that detach from the walls of the water mains is a possibility in the field.

The adsorption of lead on the iron particles that detach from the walls of the cast iron pipe can exacerbate lead release if not properly monitored.

8.2.2 Lead Service Line Replacement Program

Following the analysis of the LSLR program samples, it was concluded that a majority of the sites in the LSLR program meet regulatory guidelines. Additionally, full replacements continually produced lower lead release than partial replacements in this study area. Furthermore, we found an interaction between cast iron pipe and lead release. Tuberculated cast iron water mains rich in goethite and magnetite exacerbate lead release, especially in homes still containing lead soldered joints or brass devices with high lead content. Furthermore, service lines connected to ductile iron mains also showed the lowest lead release because no iron was being leached into the water. The results from the LSLR program show that the condition of the water main is important when considering a LSLR. Following the full replacement of the LSL in some of the sites with tuberculated water mains, high lead release was still observed. This observation shows that full replacements are more suitable for Halifax in order to reduce lead release. However, if the water main is a tuberculated water main, high lead release will still be observed. In situations where a tuberculated water main is present, the water main has to be replaced or pigged and lined before a service line replacement can be considered.

8.2.3 Pilot-Scale Pipe Loop and Copper Pipe Rack Study

Results from this study indicate that the presence of corroded cast iron increases lead release. Different cast iron water mains with varying goethite/magnetite ratios will affect the release of lead differently. Chlorine concentration had a significant impact on the concentration of lead released in this study. Higher chlorine concentration results in a lower lead release than a lower chlorine concentration. Previous research shows that higher chlorine concentration resulting in high ORP promotes the oxidation of metallic lead to lead oxide which is insoluble in water thus reducing lead in water (Davidson et al., 2004; Edwards and Dudi 2004; Lytle and Schock 2005; Xie and Giammar 2011).

Additionally, utilities that have tuberculated water mains, which are a rich source of magnetite and goethite, can experience high lead release in their lead sampling programs if a service line is connected to the water main and has lead sources in the plumbing of the building. Furthermore, the stagnation time used for any sampling will affect the concentration of the metals. An increase of the lead concentration from a factor of 2 to 5.5 times was observed between the 23 hour stagnation and 30 minutes stagnation. The effects of stagnation time on metal release was also documented by Gagnon and Doubrough (2011) and Lytle and Schock (2000).

The observations and results obtained from this study show that flushing the system for a minimum five minutes after a long stagnation time, which is typical of an overnight stagnation, is an appropriate method to minimize exposure to lead caused by stagnation of water in the pipes.

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APPENDIX A CHAPTER 4 RAW AND SUPPLEMENTAL DATA

Table A.1 Raw data showing the first trial of the dose response for magnetite and goethite.

Run 1					
Sample ID	**Conc. (mg/L)**	**Std**	**Average**	**Sample ID**	**Average Conc. (mg/L)**
	19.07			**0.1g/L Magnetite**	19.8
0.1g/L Magnetite	21.28	**1.29**		**0.5g/L Magnetite**	132.9
	19.02		**19.8**	**1.0g/L Magnetite**	209.3
				2.5g/L Magnetite	488
	558.2			**5.0g/L Magnetite**	693
0.5g/L Magnetite	468.2	**224.13**		**0.1g/L Goethite**	598.6
	132.9		**386.4**	**0.5g/L Goethite**	887
				1.0g/L Goethite	1449
	209.3			**2.5g/L Goethite**	1721
1.0g/L Magnetite	134.9	**173.26**		**5.0g/L Goethite**	2257
	465.2		**269.8**		
	248.1				
2.5g/L Magnetite	392.4	**121.00**			
	488.5		**376.3**		
	693.9			**Magnetite (g/L)**	**Fe (mg/L)**
5.0g/L Magnetite	388.8	**778.72**		0.1	19.8
	1864		**982.2**	0.5	132.9
				1.0	209.3
	902.8			2.5	488
0.1g/L Geothite	1100	**252.60**		5.0	693
	598.6		**867.1**		
				Geothite (g/L)	**Fe (mg/L)**
	1541			0.1	598.6
0.5g/L Geothite	887	**340.76**		0.5	887
	1048		**1158.7**	1.0	1449
				2.5	1721
	1832			5.0	2257
1.0g/L Geothite	1449	**216.92**			
	1464		**1581.7**		
	2208				
2.5g/L Geothite	1721	**454.40**			
	1300		**1743.0**		
	2257				
5.0g/L Geothite	1631	**322.42**			
	1810		**1899.3**		

Table A.2 Raw data showing the second trial of the dose response for magnetite and goethite.

Run 2					
Sample ID	**Conc. (mg/L)**	**Std**	**Average**	**Sample ID**	**Average Conc. (mg/L)**
	3.77			**0.1g/L Magnetite**	3.77
0.1g/L Magnetite	1.452	**1.27**		**0.5g/L Magnetite**	132.9
	1.705		**2.3**	**1.0g/L Magnetite**	209.3
				2.5g/L Magnetite	488
	558.2			**5.0g/L Magnetite**	693
0.5g/L Magnetite	468.2	**224.13**		**0.1g/L Goethite**	598.6
	132.9		**386.4**	**0.5g/L Goethite**	887
				1.0g/L Goethite	1449
	209.3			**2.5g/L Goethite**	1721
1.0g/L Magnetite	134.9	**173.26**		**5.0g/L Goethite**	2257
	465.2		**269.8**		
	248.1				
2.5g/L Magnetite	392.4	**121.00**			
	488.5		**376.3**		
	693.9				
5.0g/L Magnetite	388.8	**778.72**			
	1864		**982.2**		
	902.8				
0.1g/L Geothite	1100	**252.60**			
	598.6		**867.1**		
	1541				
0.5g/L Geothite	887	**340.76**			
	1048		**1158.7**		
	1832				
1.0g/L Geothite	1449	**216.92**			
	1464		**1581.7**		
	2208				
2.5g/L Geothite	1721	**454.40**			
	1300		**1743.0**		
	2257				
5.0g/L Geothite	1631	**322.42**			
	1810		**1899.3**		

Table A.3 Raw data from the initial adsorption experiment.

Factors				Control 1	Control 2	
pH	5.5	8.5		**(pH 5.5)**	**(pH 8.5)**	
Magnetite	2.25mg	4.5mg		**(µg/L)**	**(µg/L)**	
Goethite	1.5mg	15mg		73.85	66.01	
			(Centrifuge)		(Filtered)	
	Before Adsorption		**After adsorption**		**After adsorption**	
		Magnetite	**Fe**	**Pb**	**Fe**	**Pb**
	pH	(mg/L)	**(µg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**
M-1	5.5	15	18.68	53.57	2.104	43.64
M-2	8.5	15	14.96	60.37	2.109	53.08
M-3	5.5	30	10.35	34.84	2.379	31.22
M-4	8.5	30	5.663	56	5.647	51.06
G-1	5.5	10	14.54	59.51	21.13	50.5
G-2	8.5	10	28.32	71.36	6.2	52.33
G-3	5.5	100	23.46	33	5.509	27.59
G-4	8.5	100	160.6	64.04	6.471	49.88

Table A.4 Raw data for the adsorption experiments with the different mass of magnetite with initial lead concentration of 100µg/L.

	Factors			**Control 1**	**Control 2**	**Control Mag**					
pH	5.5	6.5		**(pH 5.5)**	**(pH 6.5)**	**(pH 7.5)**					
				(µg/L)	**(µg/L)**	**(µg/L)**					
Magnetite	15mg/L	100mg/L		74.56	28.85	23.69					
	30mg/L	200mg/L									
	50mg/L										
			(Centrifuge)		**(Filtered)**						
	Before Adsorption		**After adsorption**		**After adsorption**						
		Magnetite	**Fe**	**Pb**	**Fe**	**Pb**					
	pH	**(mg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	Volume (L)	q_e (µg/g)	log q_e	Log Ce	Ce/q
M-1	5.5	15	16.52	43.17	9.187	36.6	0.15	2530.7	3.40	1.56	0.014
M-2	5.5	30	59.82	20.1	7.955	10.77	0.15	2126.3	3.33	1.03	0.005
M-3	5.5	50	13.26	12.87	7.486	1.395	0.15	1463.3	3.17	0.14	0.001
M-4	5.5	100	88.82	17.39	10.29	0.985	0.15	735.8	2.87	-0.01	0.001
M-5	5.5	200	64.33	9.059	6.482	0.17	0.15	372.0	2.57	-0.77	0.000
M-6	6.5	15	15.52	13.09	5.56	1.943	0.15	1793.8	3.25	0.29	0.001
M-7	6.5	30	13.72	7.91	6.616	2.626	0.15	874.1	2.94	0.42	0.003
M-8	6.5	50	23.17	10.41	7.937	0.639	0.15	564.2	2.75	-0.19	0.001
M-9	6.5	100	11.46	4.838	9.667	0.607	0.15	282.4	2.45	-0.22	0.002
M-10	6.5	200	23.36	6.358	7.218	0.51	0.15	141.7	2.15	-0.29	0.004
M-11	7.5	15	6.388	5.993	5.383	2.998	0.15	1379.5	3.14	0.48	0.002
M-12	7.5	30	6.078	2.341	4.798	0.993	0.15	756.6	2.88	0.00	0.001
M-13	7.5	50	14.18	3.605	5.745	0.402	0.15	465.8	2.67	-0.40	0.001
M-14	7.5	100	98.98	9.749	6.88	0.111	0.15	235.8	2.37	-0.95	0.000
M-15	7.5	200	46.97	4.502	5.406	0.189	0.15	117.5	2.07	-0.72	0.002

Table A.5 Raw data for the adsorption experiments with the different mass of goethite with initial lead concentration of 100µg/L.

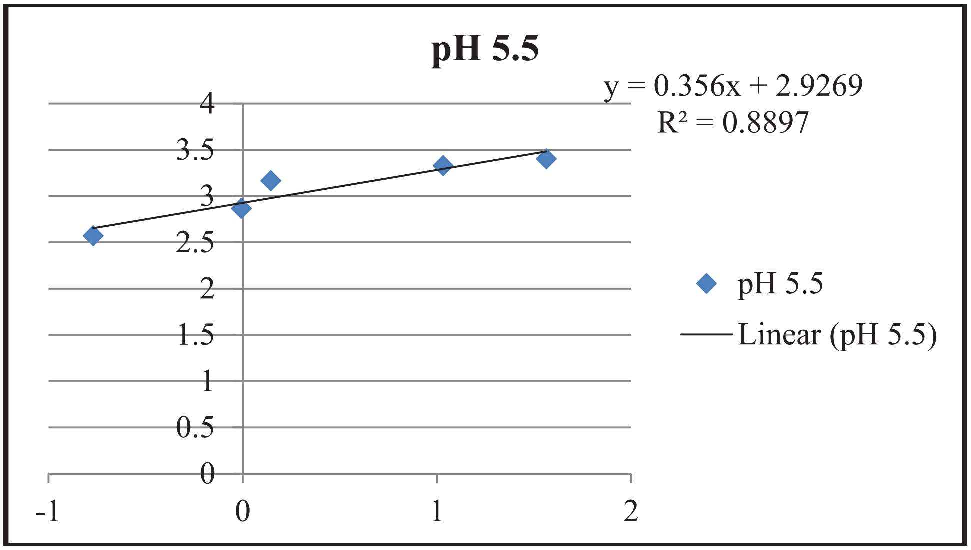
	Factors			Control 1	Control 2	Control Geo					
pH	5.5	6.5		**(pH 5.5)**	**(pH 6.5)**	**(pH 7.5)**					
				(µg/L)	**(µg/L)**	**(µg/L)**					
Goethite	15mg/L	100mg/L		92.14	57.61	45.13					
	30mg/L	200mg/L									
	50mg/L										
			(Centrifuge)		**(Filtered)**						
	Before Adsorption		**After adsorption**		**After adsorption**						
		Goethite	**Fe**	**Pb**	**Fe**	**Pb**					
	pH	**(mg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	Volume (L)	q_e (µg/g)	log q_e	Log Ce	Ce/q
G-1	5.5	15	70.68	75.71	2.504	54.9	0.15	2482.7	3.394918	1.739572	0.022113
G-2	5.5	30	111.3	70.44	3.63	50.71	0.15	1381.0	3.140194	1.705094	0.03672
G-3	5.5	50	92.08	55.41	ND	35.02	0.15	1142.4	3.057818	1.544316	0.030655
G-4	5.5	100	66.36	16.71	ND	9.931	0.15	822.1	2.914919	0.996993	0.01208
G-5	5.5	200	125.5	10.75	1.169	4.525	0.15	438.1	2.641548	0.655619	0.010329
G-6	6.5	15	12.96	15.36	ND	7.776	0.15	3322.3	86.50234	0.890756	0.002341
G-7	6.5	30	33.67	9.633	ND	3.191	0.15	1814.0	94.46103	0.503927	0.001759
G-8	6.5	50	67.22	9.98	ND	3.537	0.15	1081.5	93.86044	0.548635	0.003271
G-9	6.5	100	67.22	11.27	ND	4.168	0.15	534.4	92.76514	0.619928	0.007799
G-10	6.5	200	70.5	7.444	ND	1.686	0.15	279.6	97.07342	0.226858	0.00603
G-11	7.5	15	13.11	10.75	6.247	3.207	0.15	2794.9	92.89386	0.506099	0.001147
G-12	7.5	30	18.68	14.64	6.305	3.238	0.15	1396.4	92.82517	0.510277	0.002319
G-13	7.5	50	5.01	4.619	11.61	1.646	0.15	869.7	96.35276	0.21643	0.001893
G-14	7.5	100	116.3	5.74	4.369	0.51	0.15	446.2	98.86993	-0.29243	0.001143
G-15	7.5	200	150.4	6.399	4.031	0.323	0.15	224.0	99.28429	-0.4908	0.001442

Table A.6 Raw data for the adsorption experiments with the Finished water using magnetite & goethite with initial lead concentration of 100µg/L.

	Factors			**Control 1**	**Control 2**							
pH	5.5	6.5										
				(µg/L)	**(µg/L)**							
Mag/Goe	15mg/L	100mg/L		56.99	39.28							
	30mg/L	200mg/L										
	50mg/L											
			(Centrifuge)		**(Filtered)**							
	Before Adsorption		**After adsorption**		**After adsorption**							
		Magnetite	**Fe**	**Pb**	**Fe**	**Pb**						
	pH	**(mg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	Volume (L)	q_e (µg/g)	log q_e	Log Ce	qA	Ce/q
FM-1	7.2	15	140.6	28.11	12.3	18.31	0.15	2578.7	3.411395	1.262688	1855.887	0.007101
FM-2	7.2	30	38.09	10.75	16.13	7.604	0.15	1646.2	3.216483	0.881042	1263.851	0.004619
FM-3	7.2	50	161.2	10.16	3	2.334	0.15	1093.1	3.038668	0.368101	754.1155	0.002135
FM-4	7.2	100	704.7	15.57	34.8	7.426	0.15	495.6	2.695166	0.870755	1250.83	0.014983
FM-5	7.2	200	126.5	4.731	3	0.272	0.15	283.6	2.452691	-0.56543	294.6441	0.000959
FG-1	7.2	15	26.8	11.57	3	4.813	0.15	3478.5	3.541388	0.682416	663.0467	0.001384
FG-2	7.2	30	68.55	17.69	3	7.53	0.15	1648.7	3.217133	0.876795	1248.522	0.004567
FG-3	7.2	50	42.09	17.02	65.25	7.042	0.15	999.0	2.999548	0.847696	1135.665	0.007049
FG-4	7.2	100	55.92	12.62	3	3.374	0.15	536.2	2.729294	0.528145	401.2409	0.006293
FG-5	7.2	200	134	10.06	45.42	2.574	0.15	272.1	2.434697	0.410609	273.6583	0.00946

Table A. 7 Raw data for the adsorption experiments with the different mass of magnetite with initial lead concentration of 500µg/L and Langmuir and Freundlich model plots.

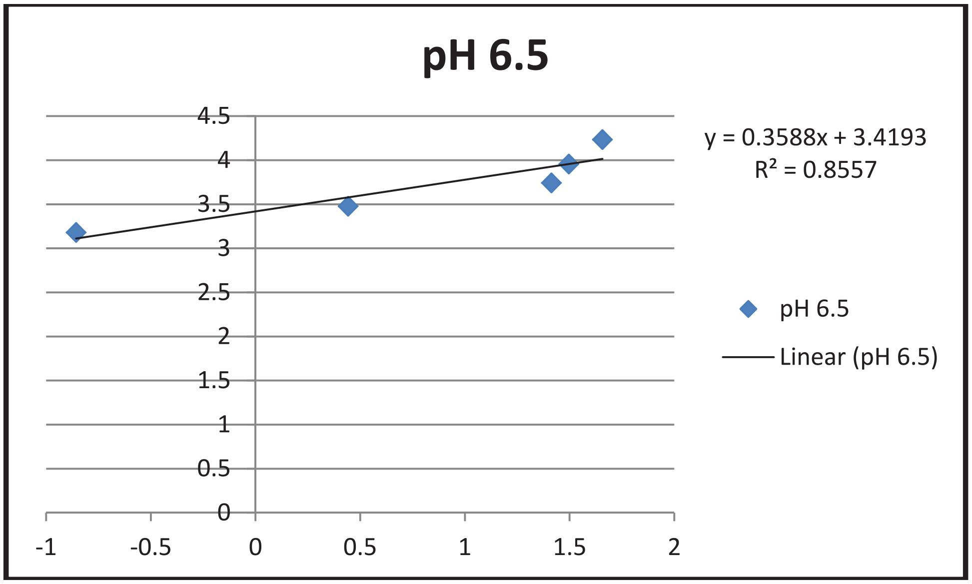
	Factors			**Control 1**	**Control 2**	**Control 3**						
pH	5.5	6.5		**(pH 5.5)**	**(pH 6.5)**	**(pH 7.5)**						
				(µg/L)	**(µg/L)**	**(µg/L)**						
Magnetite	15mg/L	100mg/L		74.56	302.1	314.3						
	30mg/L	200mg/L										
	50mg/L											
			(Centrifuge)		**(Filtered)**							
	Before Adsorption		**After adsorption**		**After adsorption**							
		Magnetite	**Fe**	**Pb**	**Fe**	**Pb**						
	pH	**(mg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	Volume (L)	q_e (µg/g)	log q_e	Log Ce	qA	Ce/q
M-1	5.5	15	16.52	43.17	9.187	36.6	0.15	2530.7	3.403235	1.563481	3044.44	0.014463
M-2	5.5	30	59.82	20.1	7.955	10.77	0.15	2126.3	3.327631	1.032216	1969.595	0.005065
M-3	5.5	50	13.26	12.87	7.486	1.395	0.15	1463.3	3.165333	0.144574	951.4293	0.000953
M-4	5.5	100	88.82	17.39	10.29	0.985	0.15	735.8	2.86673	-0.00656	840.5652	0.001339
M-5	5.5	200	64.33	9.059	6.482	0.17	0.15	372.0	2.570485	-0.76955	449.7259	0.000457
M-6	6.5	15	10.98	59.96	27.03	45.41	0.15	17112.7	4.233318	1.657152	10324.78	0.002654
M-7	6.5	30	56.48	46.28	1.471	31.34	0.15	9025.3	3.955463	1.496099	9038.472	0.003472
M-8	6.5	50	147.8	60.38	1.223	25.9	0.15	5524.0	3.742254	1.4133	8440.86	0.004689
M-9	6.5	100	582.9	50.58	1.405	2.768	0.15	2993.3	3.476153	0.442166	3783.937	0.000925
M-10	6.5	200	470.2	11.51	1.285	0.139	0.15	1509.8	3.178921	-0.85699	1293.625	9.21E-05
M-11	7.5	15	7.31	141.6	72.29	43.7	0.15	18040.0	4.256237	1.640481	11672.75	0.002422
M-12	7.5	30	1.476	66.14	1.17	31.93	0.15	9412.3	3.973697	1.504199	10167.06	0.003392
M-13	7.5	50	17.53	74.02	1.52	20.16	0.15	5882.8	3.769584	1.304491	8304.309	0.003427
M-14	7.5	100	60.02	45.61	6.88	3.109	0.15	3111.9	3.493027	0.492621	3647.536	0.000999
M-15	7.5	200	55.82	6.221	4.006	0.329	0.15	1569.9	3.19586	-0.4828	1357.423	0.00021



1/n	slope	0.356
log K	intercept	2.9269

$q_A = K_A\, C_A^{1/n}$

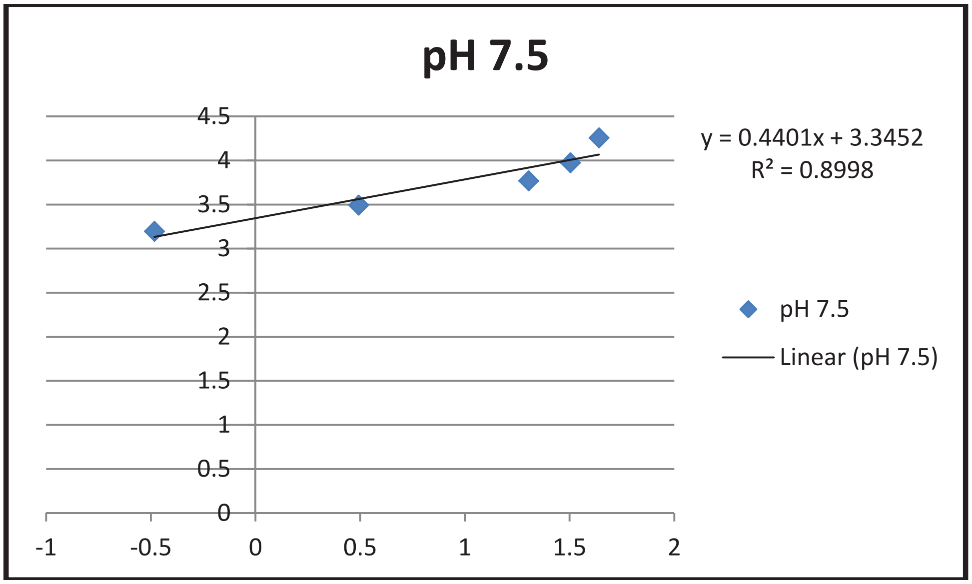
$q_A = 845.1\, C_A^{0.356}$



1/n	slope	0.3588
log K	intercept	3.4193

$q_A = K_A\, C_A^{1/n}$

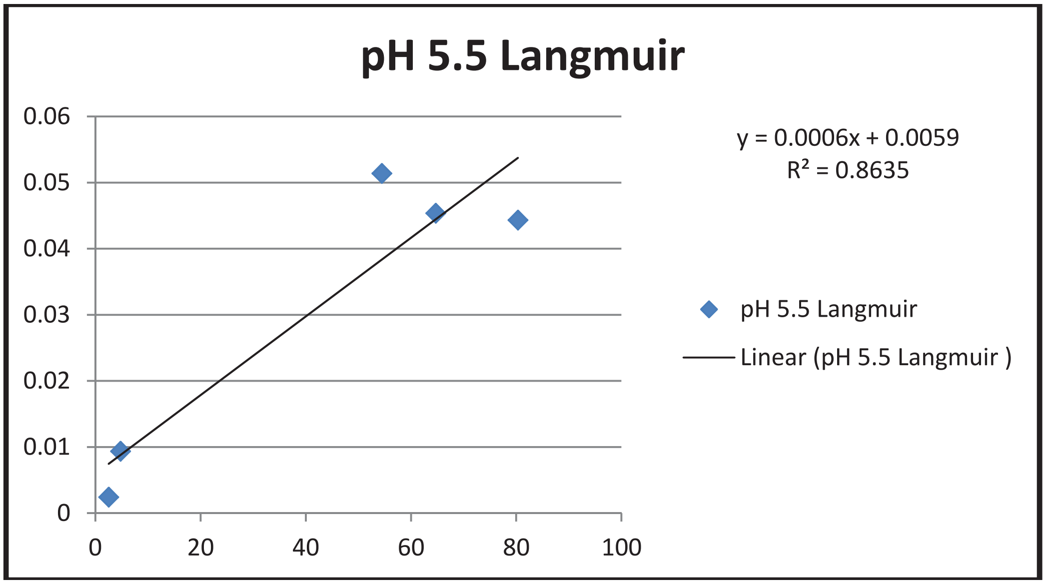
$q_A = 2626\, C_A^{0.3588}$



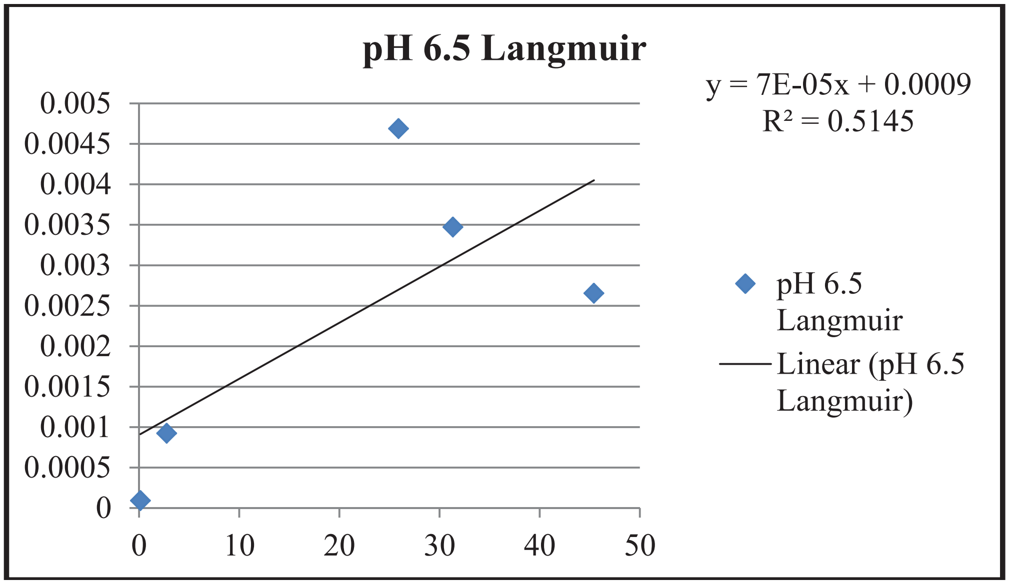
1/n	slope	0.4401
log K	intercept	3.3452

$$q_A = K_A\ C_A{}^{1/n}$$

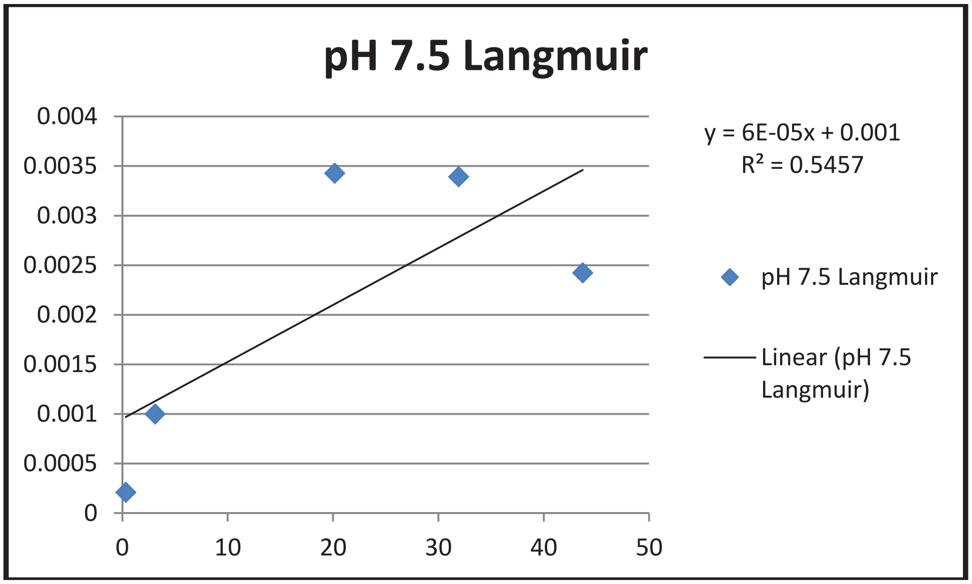
$$q_A = 2214.1\ C_A{}^{0.4401}$$



slope	0.0006	Qmax	1666.666667
intercept	0.0059	K	0.101694915



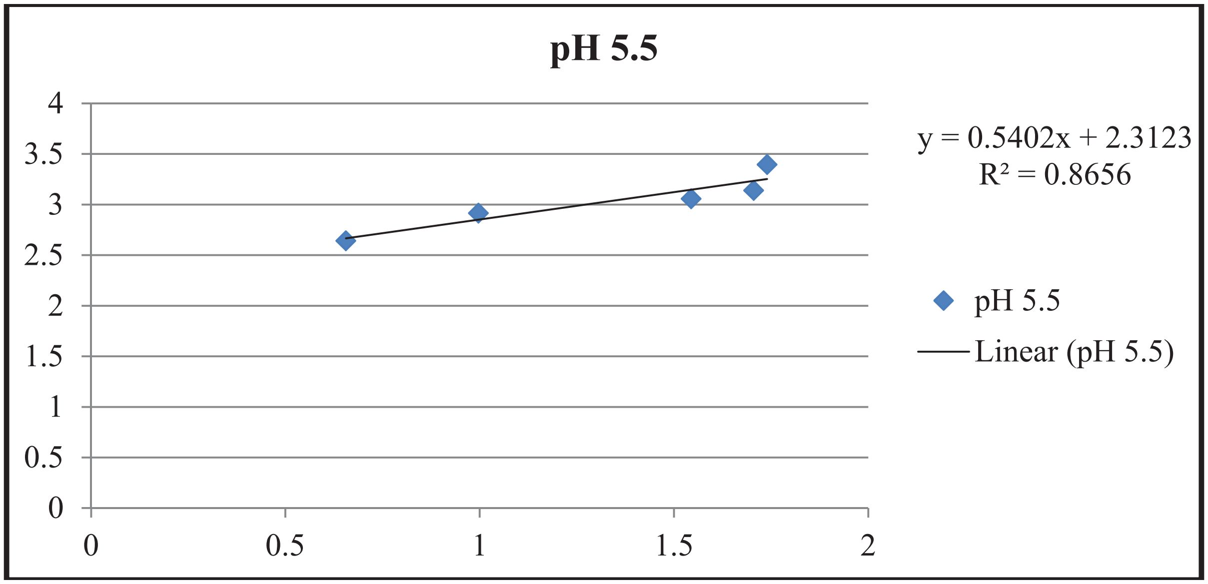
slope	7.00E-05	Qmax	14285.71
intercept	0.0009	K	0.077778



slope	6.0E-05	Qmax	16666.67
intercept	0.001	K	0.06

Table A. 8 Raw data for the adsorption experiments with the different mass of goethite with initial lead concentration of 500µg/L and Langmuir and Freundlich model plots.

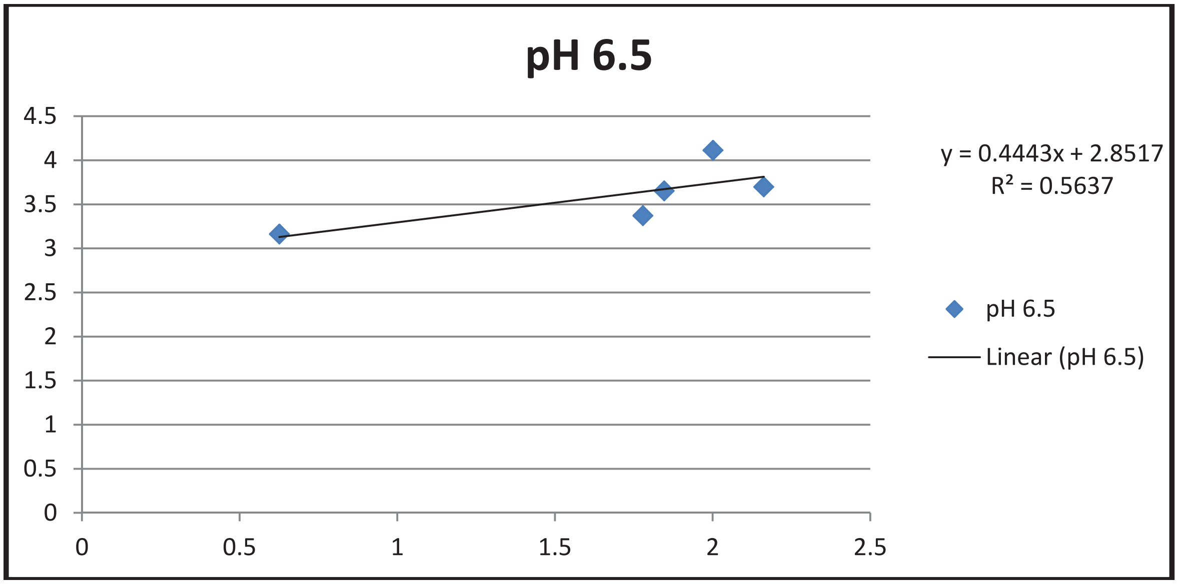
	Factors			**Control 1**	**Control 2**	**Control 3**						
pH	5.5	6.5		**(pH 5.5)**	**(pH 6.5)**	**(pH 7.5)**						
				(µg/L)	**(µg/L)**	**(µg/L)**						
Goethite	15mg/L	100mg/L		92.14	295	314.3						
	30mg/L	200mg/L										
	50mg/L											
			(Centrifuge)		**(Filtered)**							
	Before Adsorption		**After adsorption**		**After adsorption**							
		Goethite	**Fe**	**Pb**	**Fe**	**Pb**						
	pH	**(mg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	Volume (L)	q_e (µg/g)	log q_e	Log Ce	qA	Ce/q
G-1	5.5	15	70.68	75.71	2.504	54.9	0.15	2482.7	3.394918	1.739572	1786.923	0.022113
G-2	5.5	30	111.3	70.44	3.63	50.71	0.15	1381.0	3.140194	1.705094	1711.908	0.03672
G-3	5.5	50	92.08	55.41	ND	35.02	0.15	1142.4	3.057818	1.544316	1401.614	0.030655
G-4	5.5	100	66.36	16.71	ND	9.931	0.15	822.1	2.914919	0.996993	709.5199	0.01208
G-5	5.5	200	125.5	10.75	1.169	4.525	0.15	438.1	2.641548	0.655619	464.0386	0.010329
G-6	6.5	15	12.96	6.029	6	100.3	0.15	12980.0	4.113275	2.001301	5506.356	0.007727
G-7	6.5	30	33.67	9.633	1.673	145.3	0.15	4990.0	3.698101	2.162266	6492.036	0.029118
G-8	6.5	50	67.22	9.98	1.422	70.24	0.15	4495.2	3.652749	1.846585	4700.281	0.015626
G-9	6.5	100	67.22	11.27	1.404	60.12	0.15	2348.8	3.370846	1.779019	4386.362	0.025596
G-10	6.5	200	70.5	7.444	1.806	4.228	0.15	1453.9	3.162523	0.626135	1348.584	0.002908
G-11	7.5	15	17.46	25.17	9.195	27.11	0.15	19146.0	4.282078	1.43313	14359.19	0.001416
G-12	7.5	30	145.9	128.6	0.875	25.31	0.15	9633.0	3.983762	1.403292	13583.89	0.002627
G-13	7.5	50	91.05	28.71	29.42	8.626	0.15	6113.5	3.786288	0.935809	5693.05	0.001411
G-14	7.5	100	113.1	17.49	4.708	3.96	0.15	3103.4	3.491838	0.597695	3035.166	0.001276
G-15	7.5	200	2.822	5.438	1.401	1.823	0.15	1562.4	3.193788	0.260787	1621.788	0.001167



1/n	slope	0.5402
log K	intercept	2.3123

$q_A = K_A C_A^{1/n}$

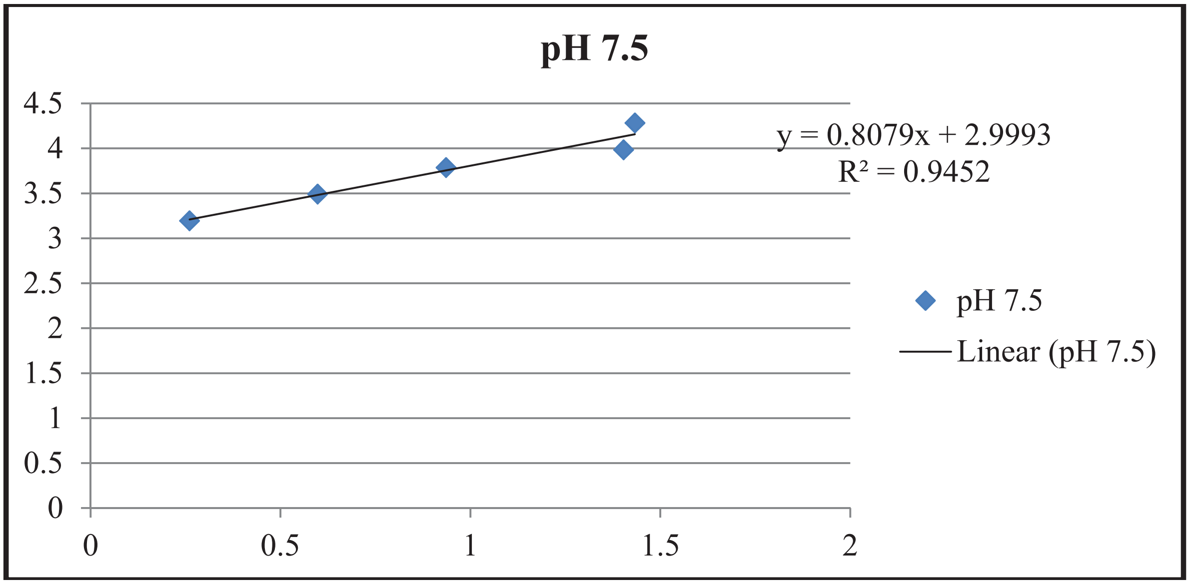
$q_A = 205.3\ C_A^{0.5402}$



1/n	slope	0.4443
log K	intercept	2.8517

$q_A = K_A C_A^{1/n}$

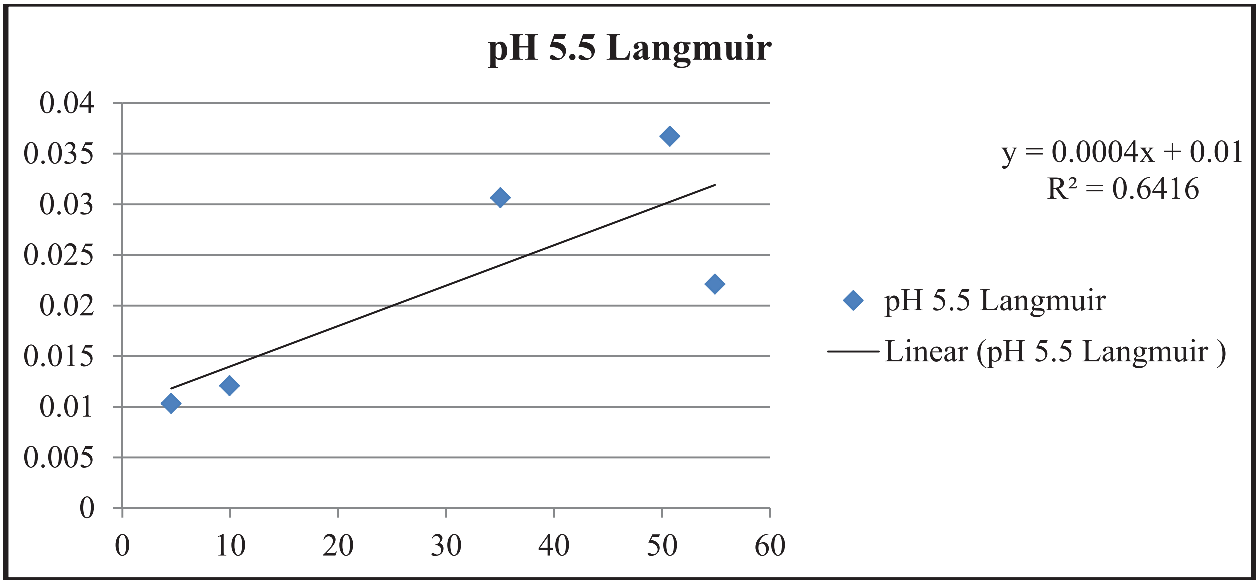
$q_A = 710.7\ C_A^{0.4443}$



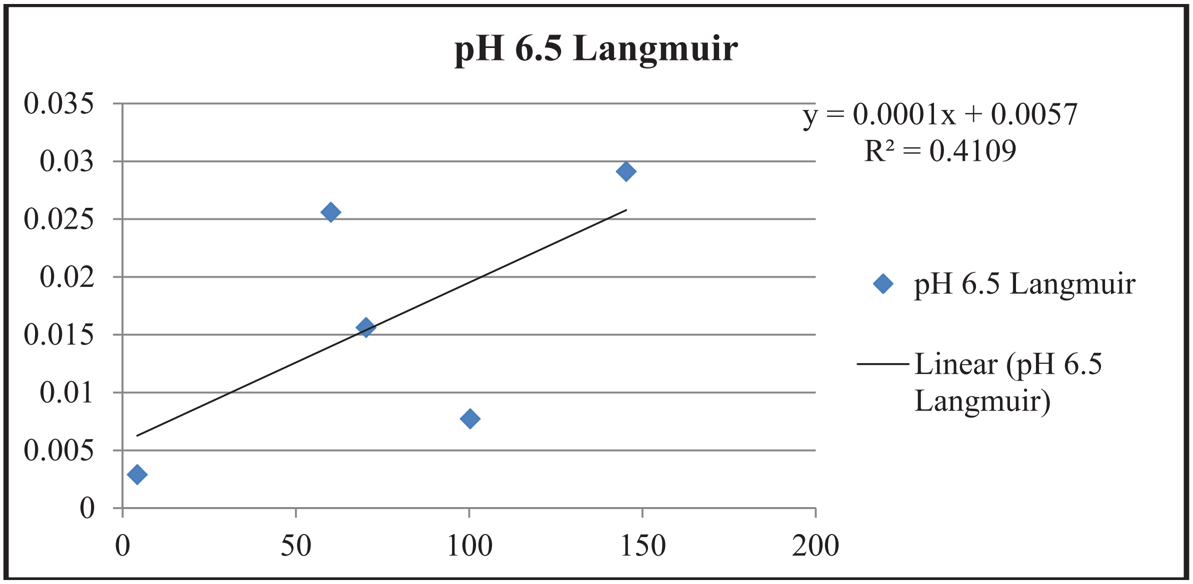
1/n	slope	0.8079
log K	intercept	2.9993

$q_A = K_A \, C_A^{1/n}$

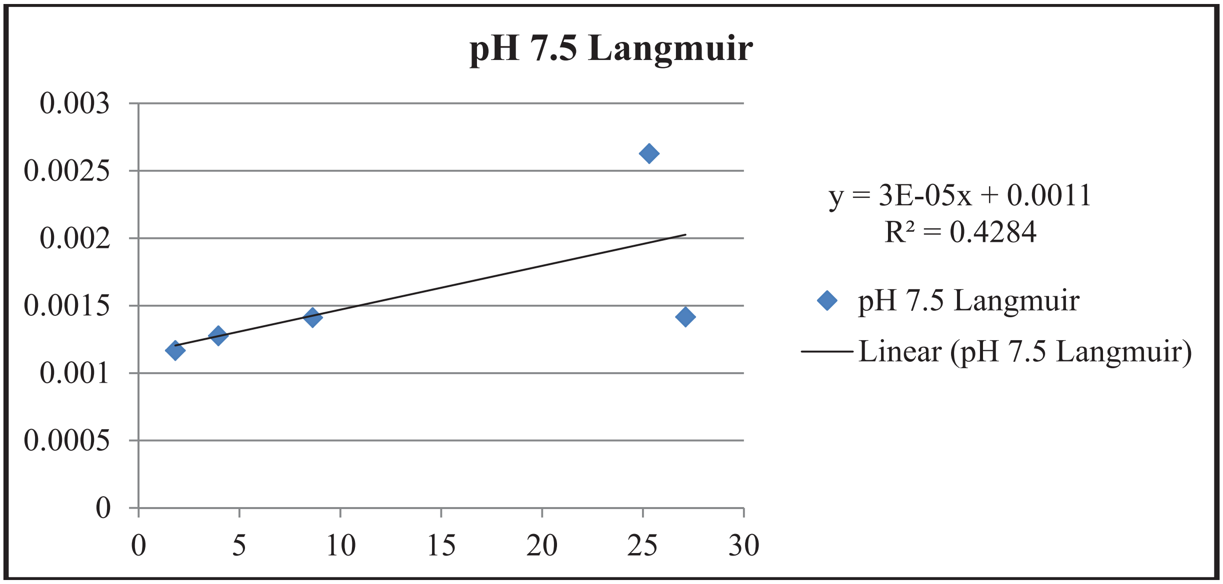
$q_A = 998.4 \, C_A^{0.8079}$



slope	0.0004	Qmax	2500
intercept	0.01	K	0.04



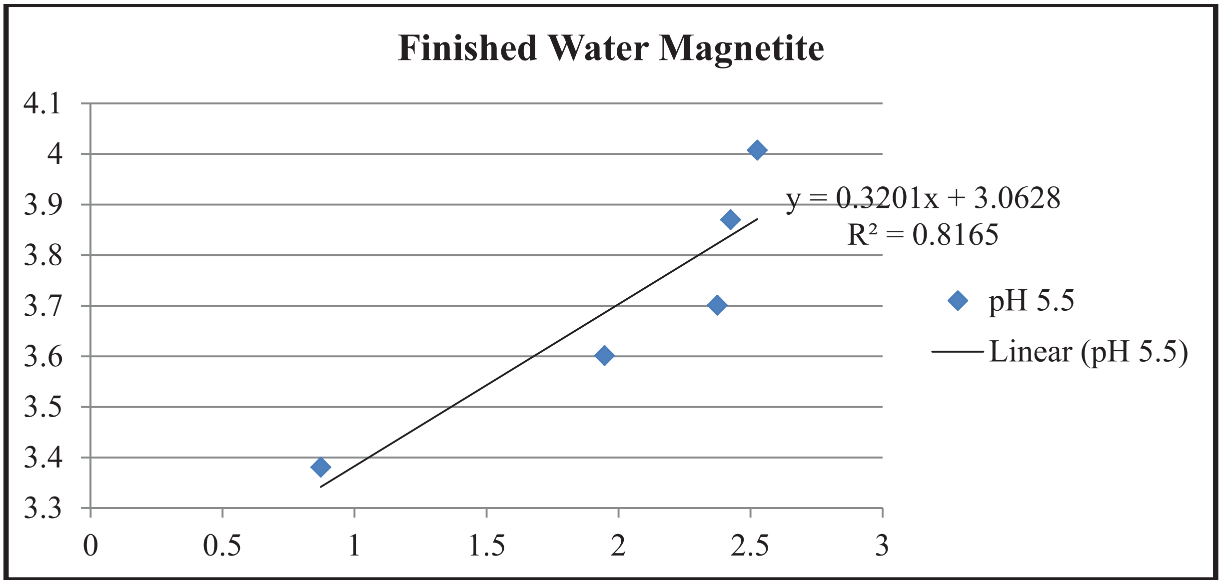
slope	1.0E-04	Qmax	10000
intercept	0.0057	K	0.017544



slope	3.0E-05	Qmax	3.33E+04
intercept	0.0011	K	0.027273

Table A.9 Raw data for the adsorption experiments with finished water with an initial lead concentration of 500µg/L and Freundlich and Langmuir plots.

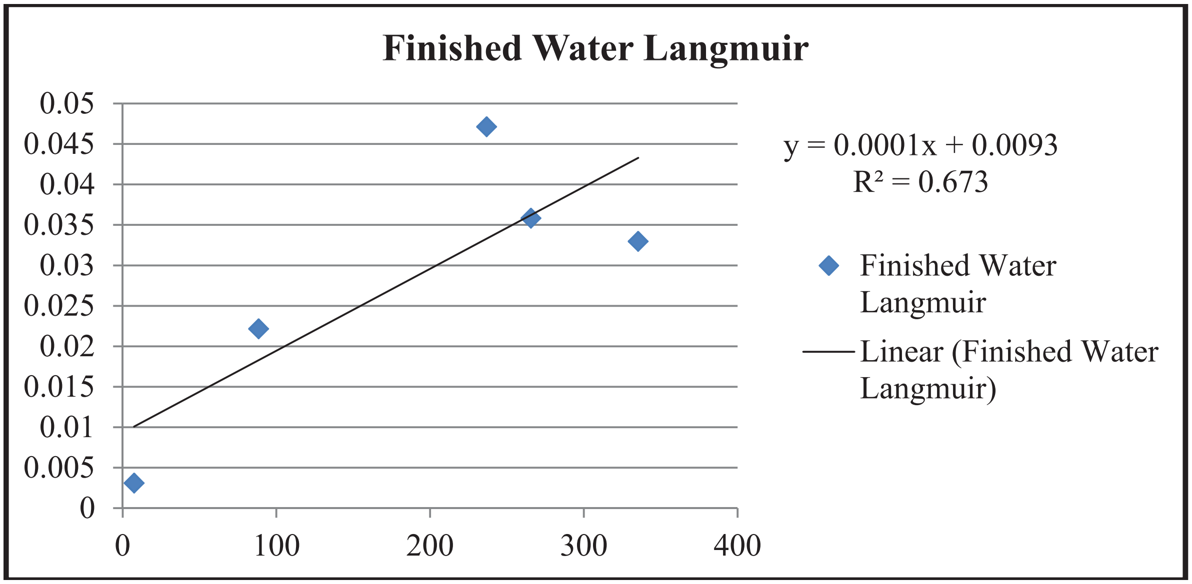
	Factors			**Control 1**	**Control 2**							
pH	5.5	6.5										
				(µg/L)	**(µg/L)**							
Magnetite	15mg/L	100mg/L		488	465.1							
	30mg/L	200mg/L										
	50mg/L											
			(Centrifuge)		**(Filtered)**							
	Before Adsorption		**After adsorption**		**After adsorption**							
		Magnetite	**Fe**	**Pb**	**Fe**	**Pb**						
	pH	**(mg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	Volume (L)	q_e (µg/g)	log q_e	Log Ce	qA	Ce/q
FM-1	7.2	15	61.49	403.2	73.65	335.4	0.15	10173.3	4.007463	2.525563	7436.876	0.032969
FM-2	7.2	30	17.18	308.1	13.64	265.6	0.15	7413.3	3.870014	2.424228	6901.655	0.035827
FM-3	7.2	50	20.22	282.9	15.63	236.8	0.15	5024.0	3.70105	2.374382	6652.692	0.047134
FM-4	7.2	100	40.31	102.4	31.62	88.51	0.15	3994.9	3.601506	1.946992	4855.009	0.022156
FM-5	7.2	200	49.63	10.9	20.51	7.449	0.15	2402.8	3.380709	0.872098	2198.449	0.0031
FG-1	7.2	15	439.8	409.9	89.05	345.6	0.15	9493.3	3.977419	2.538574	7608.134	0.036404
FG-2	7.2	30	148.1	307.8	23.19	259.5	0.15	7616.7	3.881765	2.414137	6704.085	0.03407
FG-3	7.2	50	144.8	223.7	21.97	186.2	0.15	6036.0	3.780749	2.26998	5790.204	0.030848
FG-4	7.2	100	111.5	118.3	9.786	84.57	0.15	4034.3	3.605768	1.927216	4086.617	0.020963
FG-5	7.2	200	72.26	29.32	11.64	19.51	0.15	2342.5	3.36967	1.290257	2138.683	0.008329



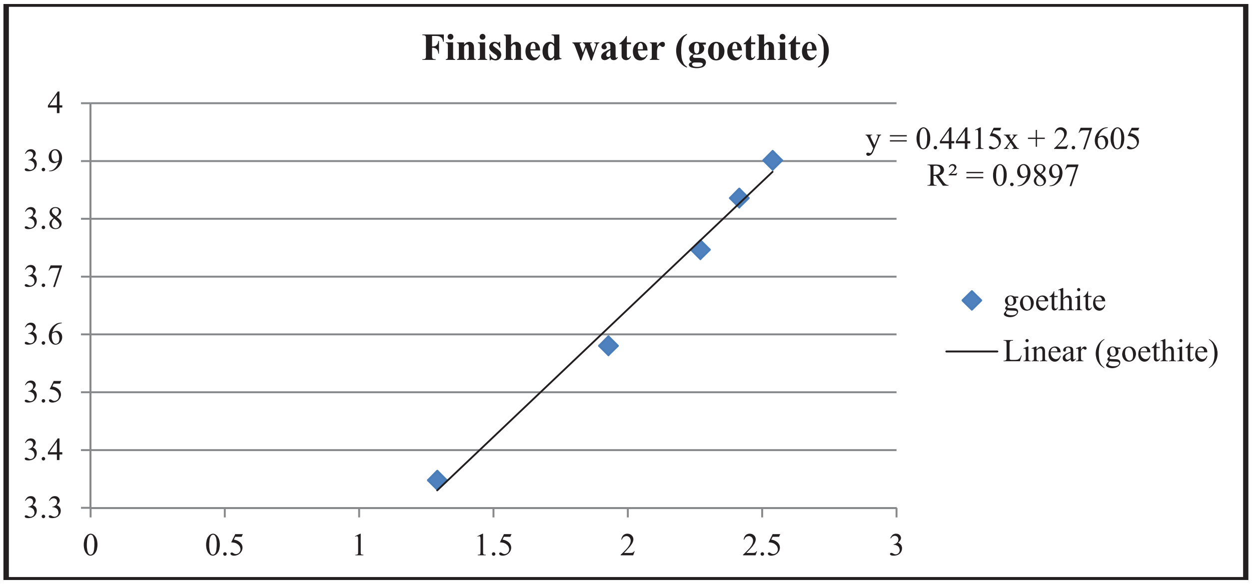
1/n	slope	0.3201
log K	intercept	3.0628

$$q_A = K_A\, C_A^{1/n}$$

$$q_A = 1156\, C_A^{0.3201}$$



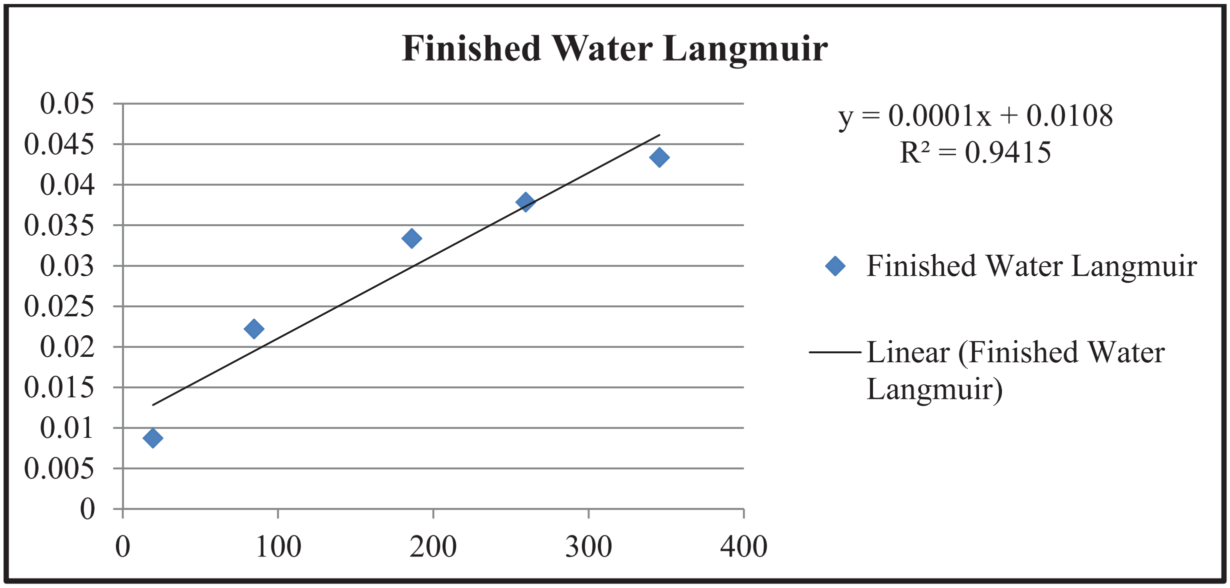
slope	0.0001	Qmax	10000
intercept	0.0093	K	0.01



1/n	slope	0.4415
log K	intercept	2.7605

$q_A = K_A C_A^{1/n}$

$q_A = 576.1\ C_{A0.4415}$



slope	0.0001	Qmax	10000
intercept	0.0108	K	0.01

Table A.10 Raw data showing the results of the Langmuir isotherm model for all the adsorption trials of lead on magnetite.

	Iron Mineral												
	Mag	**Mag**	**Mag**	**Mag**	**Mag**	**Mag**	**Mag**	**Mag**	**Mag**	**Mag**	**Mag**	**Mag**	**Mag**
Initial pH	5.5	5.5	6.5	6.5	6.5	6.5	7.5	7.2	7.2	7.2	7.5	7.5	7.5
Initial C (µg/L lead)	74.56	107.5	28.85	107.9	302.1	338.2	23.69	56.99	41.03	488	32.39	314.3	275.1
Q_{max} (µg Lead/g solid)	2500	1666.7	200000	1000	14285.7	10000	2500	3333.3	1000	10000	1250	16666.7	10000
K	0.57	0.1	0	0.102	0.08	0.03	0.44	0.09	1.43	0.01	0.89	0.06	0.08
Langmuir R^2	0.99	0.86	2.0E-05	0.3	0.51	0.74	0.61	0.19	0.89	0.67	0.39	0.55	0.85

Table A.11 Raw data showing the results of the Langmuir isotherm model for all the adsorption trials of lead on goethite.

	Iron Mineral												
	Goe	**Goe**	**Goe**	**Goe**	**Goe**	**Goe**	**Goe**	**Goe**	**Goe**	**Goe**	**Goe**	**Goe**	**Goe**
Initial pH	5.5	5.5	6.5	6.5	6.5	6.5	7.5	7.5	7.5	7.5	7.2	7.2	7.2
Initial C (µg/L lead)	92.14	101.5	57.61	96.99	295	430.6	45.13	43.01	314.3	272.4	39.28	32.02	465.1
Q_{max} (µg Lead/g solid)	2500	1111.1	2500	33333.3	10000	12500	10000	526.3	33333.3	16667	1666.7	1666.7	10000
K	0.04	0.007	0.07	0.0006	0.018	0.018	0.08	0.09	0.027	0.001	0.05	0.13	0.01
Langmuir R^2	0.64	0.81	0.13	0.0008	0.41	0.17	0.17	0.39	0.43	0.8	0.1	0.17	0.94

APPENDIX B CHAPTER 5 RAW AND SUPPLEMENTAL DATA

Table B.1 Sample raw data showing finished water for the duration of the LSLR program.

Date	pH	Turbidity	Alkalinity	Total Cl2	Free Cl2	PO4	Iron	Aluminum
4/1/2011	7.4	0.076	13.5	1.05	0.94	0.488	0	0.069
4/2/2011	7.2	0.213	9.5	1.08	0.93	0.414	0	0.164
4/3/2011	7.3	0.125	12.5	1.09	0.95	0.463	0.51	0.074
4/4/2011	7.25	0.124	14.5	1.03	0.87	0.445	0	0.076
4/5/2011	7.34	0.124	14.5	1.05	0.83	0.469	0	0.076
4/6/2011	7.56	0.093	14.5	0.99	0.91	0.532	0	0.095
4/7/2011	7.31	0.093	14.5	1.08	0.89	0.362	0	0.095
4/8/2011	7.6	0.093	14.5	1	0.85	0.393	0	0.095
4/9/2011	7.44	0.099	11.5	1.08	0.94	0.442	0.036	0.061
4/10/2011	7.77	0.099	11.5	1.07	0.98	0.44	0.036	0.061
4/11/2011	7.41	0.099	11.5	1.07	0.97	0.61	0.036	0.061
4/12/2011	7.43	0.086	13	1.04	0.93	0.594	0	0.072
4/13/2011	7.18	0.077	13.5	1.05	0.92	0.527	0	0.077
4/14/2011	7.36	0.077	13.5	1.06	0.97	0.596	0	0.077
4/15/2011	7.43			1.04	0.89	0.703		
4/16/2011	7.44	0.102	12.5	1.06	0.95	0.561	0	0.066
4/17/2011	7.57	0.08	14.5	1.07	0.95	0.588	0	0.062
4/18/2011	7.27	0.08	14.5	1.05	0.93	0.556	0	0.062
4/19/2011	7.45	0.08	14.5	1.08	0.95	0.528	0	0.062
4/20/2011	7.34	0.077	15.8	1.06	0.97	0.539	0	0.057
4/21/2011	7.27	0.077	15.8	1.09	0.97	0.578	0	0.057
4/22/2011	7.36	0.086	16	1.03	0.93	0.619	0.009	0.049
4/23/2011	7.51	0.076	16	1.14	0.96	0.577	0.012	0.067
4/24/2011	7.55	0.074	16	1.21	1.05	0.693	0	0.064
4/25/2011	7.63	0.081	16	1.151	0.92	0.635	0	0.061
4/26/2011	7.45	0.085	15.3	1.16	1.01	0.472	0	0.06
4/27/2011	7.36	0.084	15.1	1.16	1.01	0.6	0	0.097
4/28/2011	7.45	0.085	16	1.15	1.03	0.568	0.014	0.035
4/29/2011	7.38	0	16.5	1.18	1.09	0.53	0.002	0.047
4/30/2011	7.35	0.073	14.9	1.16	1.02	0.541	0	0.082
5/1/2011	7.4	0.08	15.1	1.16	1.03	0.543	0	0.084
5/2/2011	7.32	0.083	15.2	1.2	1.09	0.523	0	0.081
5/3/2011	7.43	0.083	15.2	1.08	0.9	0.587	0	0.081
5/4/2011	7.47	0.084	15.2	1.23	0.97	0.605	0	0.046

Table B.2 Water main information obtained from ArcGIS maintained by Halifax Water.

Sample I.D	Water Main Material	Water Main Information	Cleaned and Lined
A	Ductile Iron	200mm CL-54, March 1981	No
B	Cast Iron	150mm, March 1940	No
C	Cast Iron	200mm, March 1947	No
D	Cast Iron	200mm, March 1947	No
E	Cast Iron	200mm, March 1947	No
F	Cast Iron	150mm, March 1943	Cleaned in 1977
G	Cast Iron	150mm, March 1943	Cleaned in 1977
H	Cast Iron	150mm, April 1989	No
I	Cast Iron	150mm, January 1926	No
J	Cast Iron	200mm, March 1945	No
K	Cast Iron	100mm	No
L	Cast Iron	150mm, March 1946	No
M	Ductile Iron	300mm CL-54, March 1982	No
N	Ductile Iron	250mm CL-54, March 1987	No
O	Cast Iron	150mm, March 1943	Cleaned in 1977
P	Cast Iron	150mm, March 1944	No
Q	Cast Iron	150mm, March 1906	Cleaned and Lined in 2004
R	Cast Iron	150mm, March 1935	Cleaned and Lined in 1995
S	Cast Iron	250mm, March 1934	No
T	Cast Iron	150mm, March 1933	Cleaned and Lined in 2006
U	Cast Iron	150mm, March 1934	No
V	Cast Iron	200mm, March 1947	No
W	Ductile Iron	200mm CL-52, July 2011	No
X	Ductile Iron	200mm CL-52, July 2011	No
Y	Cast Iron	150mm, March 1941	Cleaned in 1983 (Bayers Rd Cleaned and Lined in 2002)

Z	Cast Iron	200mm, March 1946	No
AA	Cast Iron	375mm, March 1914	Cleaned and Lined in 1998
BB	Cast Iron	150mm, March 1929	Cleaned in 1979

Table B.3 Plumbing information provided in the sample collection instruction sheet.

Location	Public Service	Private Service line	Plumbing Present in the home
A	Lead	Lead replaced with copper a year ago	Plastic
B	Copper(Just replaced)	No	Copper
C	Lead	No Information given	No Information given
D	Lead	Not lead.	Copper?
E	Lead	Not known	Plastic
F	Copper(Just replaced)	Not known	Plastic, Copper
G	Copper(Just replaced)	Copper	Copper
H	Lead	Lead	Mostly copper inside, PEX at new bathroom
I	Lead	Lead	
J	Copper(Just replaced)	Copper (just replaced 2-3 weeks ago)	Plastic
K	Lead	Copper (replaced this spring)	Copper
L			
M	Lead	Lead	Copper
N	Lead	Lead	Copper and Brass
O	Copper(Just replaced)	Copper	plastic/copper
P	Lead	Lead	Plastic, Copper
Q	Lead	Copper	Copper
R	Copper(Just replaced)	Lead?	Plastic
S	Copper	Copper	Copper with Brass fittings
T	Lead	Lead?	Plastic

U	Lead	Copper	Copper
V	Lead	Lead?	
W	Copper	Copper	Copper,Plastic
X	Copper	Lead	copper
Y			
Z	Copper	Lead	Copper, plastic
AA	Copper	Lead	Copper, plastic
BB	Copper	Lead	Copper, plastic,brass

Table B.4 Raw data from the LSLR program for all the locations for (Pb,Fe and Cu).

	Before			72 Hours			1 month			3 months			6 months		
		Total			Total			Total			Total			Total	
	Pb	Fe	Cu	Pb	Fe	Cu	Pb	Fe	Cu	Pb	Fe	Cu	Pb	Fe	Cu
Location	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
A	13.02	12.21	59.13	3.38	13.52	117.69	0.95	15.92	109.50	-	-	-	-	-	-
B	-	-	-	12.50	29.00	251.69	4.61	30.30	178.03	9.88	22.54	135.05	12.69	51.87	311.71
C	3.50	7.17	28.12	1.01	13.34	18.83	2.98	6.22	175.76	-	-	-	-	-	-
D	7.83	5.76	16.63	2.40	1.92	166.01	1.48	5.45	239.87	0.78	6.64	184.87	0.94	<6	111.72
E	2.36	10.73	51.20	2.75	9.89	81.25	2.78	12.63	101.18	3.78	10.41	125.40	3.11	14.15	74.26
F	-	-	-	45.44	62.83	36.20	8.93	58.79	6.35	20.36	63.00	27.56	34.32	124.44	38.47
G	-	-	-	39.73	79.26	62.25	33.37	67.90	48.49	23.16	71.72	39.03	14.02	90.10	50.95
H	-	-	-	-	-	-	33.27	59.96	45.81	39.82	63.42	36.83	46.14	54.66	49.10
I	15.17	109.25	17.41	3.13	194.46	47.22	1.19	85.41	30.62	1.82	56.28	59.49	2.24	139.26	48.51
J	22.08	26.49	5.50	26.27	50.97	10.23	20.00	72.75	7.98	16.64	38.78	44.24	10.90	21.06	16.89
K	-	-	-	10.01	50.92	134.92	4.30	23.34	150.83	7.28	70.41	95.90	4.15	36.52	151.83
L	8.31	11.76	80.69	1.46	14.88	99.64	1.23	23.19	82.45	-	-	-	-	-	-
M	5.70	197.40	12.00	-	-	-	21.08	374.28	41.81	4.06	70.73	88.83	-	-	-
N	6.02	7.92	61.45	-	-	-	1.50	9.04	99.16	-	-	-	9.14	12.14	123.44
O	3.50	6.73	21.92	-	-	-	-	-	-	-	-	-	-	-	-
P	19.83	45.96	70.42	55.34	125.32	69.47	35.78	82.26	56.79	-	-	-	8.85	103.05	57.00
Q	9.76	9.01	49.60	-	-	-	-	-	-	-	-	-	-	-	-
R	-	-	-	-	-	-	-	-	-	3.46	26.74	6.29	18.01	12.97	23.48
S	-	-	-	6.94	43.64	129.70	2.13	27.13	117.36				5.96	47.45	167.51
T	-	-	-	3.98	15.85	77.00	2.72	9.26	100.66	7.70	12.58	107.89	4.90	11.41	131.08
U	-	-	-	9.86	47.32	71.06	10.17	96.22	110.01	7.03	42.11	164.48	5.07	47.33	117.79
V	-	-	-	1.21	29.64	86.37	2.33	40.41	240.76	0.57	16.03	59.16	0.23	9.20	37.15

W	-	-	-	5.98	161.32	150.45	-	-	-	-	-	-	1.58	96.12	75.91
X	-	-	-	-	-	-	5.31	1.34	43.98	7.86	5.80	59.57	-	-	-
Y	-	-	-	-	-	-	0.04	1.13	9.73	-	-	-	< 0.4	< 6.0	8.59
Z	-	-	-	-	-	-	-	-	-	-	-	-	1.58	3.99	48.34
AA	7.43	103.35	71.66	-	-	-	2.49	50.71	123.74	1.76	30.04	146.69	0.93	50.78	55.05
BB	-	-	-	-	-	-	6.04	4.80	58.11	11.19	4.14	75.57	7.66	7.39	53.29
CC	-	-	-	-	-	-	3.47	14.50	58.89	6.94	13.33	93.94	3.39	20.72	41.32

Table B.5 Raw data from the LSLR program for all the locations for (Al).

	Before	72 Hours	1 month	3 months	6 months
	Total	Total	Total		Total
	Al	Al	Al	Al	Al
Location	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
A	37.94	53.68	35.29	-	-
B	-	32.86	34.84	25.16	186.88
C	32.94	23.57	118.50	-	-
D	29.69	24.21	68.37	157.12	24.59
E	31.29	28.97	126.36	239.24	129.82
F	-	31.73	41.69	20.83	183.12
G	-	33.34	31.16	26.41	180.90
H	-	-	41.12	26.99	97.14
I	91.87	88.31	70.87	39.61	34.24
J	69.71	61.90	55.30	73.68	20.70
K	-	30.96	23.16	22.52	184.40
L	48.36	57.46	47.42	-	-
M	40.40	-	61.76	150.00	-
N	48.82	-	34.96	-	127.89
O	39.00	-	-	-	-
P	40.03	41.45	26.56	-	202.34
Q	40.56	-	-	-	-
R	-	-	-	52.15	122.24
S	-	35.25	22.39	-	202.20
T	-	26.28	29.07	156.94	139.76
U	-	29.49	55.67	184.28	112.08
V	-	29.59	83.72	248.04	136.78

W	-	32.51	-	-	109.08
X	-	-	31.65	159.24	-
Y	-	-	32.54	-	171.40
Z	-	-		-	180.02
AA	39.94	-	117.42	193.40	109.53
BB	-	-	80.73	222.66	121.90

APPENDIX C CHAPTER 6 RAW AND SUPPLEMENTAL DATA

Table C.1 Sample raw data of the metal release from the copper pipe racks for the long stagnation time.

	Day			**0**	**3**	**7**	**10**	**14**	**17**
	Date (dd/mm/yy)	**Mean**	**Standard Deviation**	9/1/2012	12/1/2012	16/01/2012	19/01/2012	23/01/2012	26/01/2012
Parameter	**Sample Location**								
Total Iron, µg/L									
	Pipe Rack 1	137.011	202.006	301.900	453.800	171.50	167.600	83.120	78.400
	Pipe Rack 2	315.657	546.955	166.600	206.600	1692.00	544.800	388.600	199.300
	Pipe Rack 3	28.567	29.375	53.390	16.830	13.70	74.720	12.760	14.840
	Pipe Rack 4	51.525	55.801	6.189	17.530	62.30	20.820	14.860	165.400
Dissolved Iron, µg/L									
	Pipe Rack 1	10.362	9.119	0.000	9.195	6.83	5.900	4.572	1.368
	Pipe Rack 2	5.975	7.244	5.347	1.705	2.74	4.974	2.262	8.207
	Pipe Rack 3	6.998	10.515	44.450	3.631	1.59	15.650	3.130	5.000
	Pipe Rack 4	3.667	4.746	0.000	3.040	1.43	4.713	1.449	1.914
Total Lead, µg/L									
	Pipe Rack 1	27.092	22.181	81.780	96.360	55.88	49.500	34.780	36.830
	Pipe Rack 2	140.309	101.476	156.300	166.700	532.10	241.100	232.100	185.100
	Pipe Rack 3	17.754	7.739	8.663	21.920	25.43	20.150	34.650	24.100

	Pipe Rack 4	44.892	36.056	18.340	19.790	54.05	21.040	48.830	20.530
Dissolved Lead, µg/L									
	Pipe Rack 1	6.925	4.579	5.322	8.202	6.69	6.513	8.734	6.754
	Pipe Rack 2	48.088	24.542	48.090	71.850	14.58	39.000	54.950	58.010
	Pipe Rack 3	13.176	7.745	8.618	20.890	17.32	12.800	29.040	24.200
	Pipe Rack 4	27.913	21.835	13.000	17.400	12.75	16.640	41.070	9.735
Total Copper, µg/L									
	Pipe Rack 1	1225.836	433.880	421.300	1552.000	936.90	1252.000	1370	1344.000
	Pipe Rack 2	1909.764	519.107	1009.000	2003.000	3047.00	2372.000	2327	2120.000
	Pipe Rack 3	4042.430	1554.539	750.300	3643.000	3940.00	3119.000	4455.000	3955.000
	Pipe Rack 4	4857.021	2762.905	7008.000	5236.000	3275.00	5693.000	5556.000	4955.000
Dissolved Copper, µg/L									
	Pipe Rack 1	1057.709	443.515	309.5	1114.000	676.40	971.300	1159.000	1117.000
	Pipe Rack 2	1599.791	431.212	708.2	1595.000	1306.00	1514.000	1800.000	1737.000
	Pipe Rack 3	3850.476	1490.498	759.3	3777.000	3547.00	3163.000	4486.000	4023.000
	Pipe Rack 4	4568.621	2443.429	6632	5127.000	2918.00	5323.000	5369.000	4299.000
Total Aluminum, µg/L									
	Pipe Rack 1	85.886	104.375	317.000	324.300	146.10	148.800	115.600	138.800
	Pipe Rack 2	102.858	148.142	93.260	135.000	778.10	377.300	245.700	169.600
	Pipe Rack 3	86.679	41.634	206.900	67.290	62.65	127.600	79.780	85.600

	Pipe Rack 4	83.210	80.230	61.050	56.450	62.15	62.730	67.960	154.300
Dissolved Aluminum, µg/L									
	Pipe Rack 1	9.853	6.063	16.880	8.470	10.30	4.673	12.000	4.721
	Pipe Rack 2	7.299	4.522	10.430	3.551	6.39	8.434	12.170	20.910
	Pipe Rack 3	20.184	28.083	175.700	13.680	11.42	26.120	13.830	13.200
	Pipe Rack 4	12.639	14.370	6.511	10.2	12.35	8.936	8.447	10.25
Total Tin, µg/L									
	Pipe Rack 1	306.525	1779.057	17.79	6.616	4.77			0.94
	Pipe Rack 2	13.698	15.589	20.54	34.59	75.70			47.8
	Pipe Rack 3	0.263	0.300	0.356	0.703	1.71			0.4
	Pipe Rack 4	7.036	14.971	0.291	0.022	11.14			0.799
Dissolved Tin, µg/L									
	Pipe Rack 1	0.149	0.092	0.449	0.044	0.07			ND
	Pipe Rack 2	0.884	0.666	0.537	0.17	0.37			0.44
	Pipe Rack 3	0.099	0.064	0.309	0	0.07			ND
	Pipe Rack 4	0.174	0.186	0.309	0	0.09			ND

Table C.2 Sample raw data of the metal release from the copper pipe racks for the short stagnation time.

	Day			0	3	7	10	14	17
	Date (dd/mm/yy)	**Mean**	**Standard Deviation**	9/1/2012	12/1/2012	16/01/2012	19/01/2012	23/01/2012	26/01/2012
Parameter	**Sample Location**								
Total Iron, µg/L									
	Pipe Rack 1	120.856	100.270	113.500	347.200	123.900	92.480	66.520	57.560
	Pipe Rack 2	269.614	399.973	557.100	417.100	425.500	132.800	26.150	26.570
	Pipe Rack 3	55.747	62.369	53.620	21.830	19.380	254.400	18.690	22.470
	Pipe Loop 4	65.639	123.709	7.865	21.440	21.070	25.000	25.530	20.730
Dissolved Iron, µg/L									
	Pipe Rack 1	17.483	17.073	0.000	5.732	5.436	3.344	1.780	3.324
	Pipe Rack 2	9.490	10.760	18.060	2.938	1.354	3.561	9.799	2.348
	Pipe Rack 3	6.735	6.940	2.070	5.679	5.126	31.390	3.400	3.581
	Pipe Loop 4	13.117	26.680	0.480	4.913	4.150	6.910	2.142	158.100
Total Lead, µg/L									
	Pipe Rack 1	4.781	3.353	12.760	8.219	4.734	4.344	4.045	3.933
	Pipe Rack 2	31.351	49.638	147.800	54.020	45.370	42.930	33.320	32.360
	Pipe Rack 3	8.756	12.811	15.280	12.240	9.193	76.880	29.360	15.380

	Pipe Loop 4	10.972	7.153	7.865	6.951	12.660	13.140	16.380	6.941
Dissolved Lead, µg/L									
	Pipe Rack 1	1.926	1.672	3.735	1.679	0.686	1.320	1.662	2.449
	Pipe Rack 2	5.495	4.853	7.612	1.449	4.686	14.040	20.670	15.660
	Pipe Rack 3	4.662	3.734	13.040	10.530	8.383	2.330	6.931	12.250
	Pipe Loop 4	6.538	4.874	6.741	6.413	11.020	11.630	12.860	6.837
Total Copper, µg/L									
	Pipe Rack 1	531.624	203.226	952.900	580.700	348.500	546.000	570.100	593.500
	Pipe Rack 2	835.509	405.080	582.700	956.400	935.900	1275.000	1172.000	1748.000
	Pipe Rack 3	746.264	284.210	1107.000	770.800	699.500	1053.000	797.100	766.400
	Pipe Loop 4	1333.033	460.630	1326.000	1322.000	1154.000	1201.000	2177.000	1381.000
Dissolved Copper, µg/L									
	Pipe Rack 1	487.997	195.243	854.3	561.300	312.400	534.900	547.800	551.100
	Pipe Rack 2	741.112	356.381	241.3	526.200	819.900	1178.000	1127.000	1594.000
	Pipe Rack 3	691.979	257.678	1049	760.000	701.200	649.000	799.400	691.900
	Pipe Loop 4	1220.358	465.470	1292	1301.000	1133.000	1174.000	2107.000	1332.000
Total Aluminum, µg/L									
	Pipe Rack 1	78.059	57.440	165.400	196.500	140.100	135.600	125.700	160.900
	Pipe Rack 2	103.494	89.335	293.600	259.200	376.500	181.600	152.300	217.100

	Pipe Rack 3	149.083	67.220	158.100	130.000	118.700	376.700	119.300	184.100
	Pipe Loop 4	145.509	281.232	135.000	121.200	116.700	117.100	92.350	159.400
Dissolved Aluminum, µg/L									
	Pipe Rack 1	12.649	4.966	9.682	11.060	10.780	8.082	12.730	16.180
	Pipe Rack 2	12.954	9.204	17.210	2.267	13.970	21.800	44.980	37.800
	Pipe Rack 3	39.863	14.889	59.700	52.220	45.260	37.740	32.830	45.840
	Pipe Loop 4	30.357	15.524	34.66	43.08	40.63	45.1	20.05	52.79
Total Tin, µg/L									
	Pipe Rack 1	0.249	0.358	1.951	0.641	0.289			ND
	Pipe Rack 2	2.879	5.624	12.34	5.489	26.11			0.94
	Pipe Rack 3	0.255	0.422	0.923	2.309	0.186			0.783
	Pipe Loop 4	0.525	0.939	0.317	0.016	0.217			ND
Dissolved Tin, µg/L									
	Pipe Rack 1	0.089	0.077	0.329	0	0.053			ND
	Pipe Rack 2	0.162	0.087	0.483	0.05	0.085			ND
	Pipe Rack 3	0.076	0.049	0.286	0	0.101			ND
	Pipe Loop 4	0.089	0.048	0.237	0	0.09			ND

Table C.3 Sample raw data of the metal release from the pipe loop effluent.

	Day			**0**	**3**	**7**	**10**	**14**	**17**
	Date (dd/mm/yy)	**Mean**	**Standard Deviation**	9/1/2012	12/1/2012	16/01/2012	19/01/2012	23/01/2012	26/01/2012
Parameter	**Sample Location**								
pH									
	Pipe Loop 1	5.52	0.22	5.56	5.40	5.74	5.56	5.23	5.41
	Pipe Loop 2	5.68	0.63	7.27	5.90	5.62	5.36	9.08	5.32
	Pipe Loop 3	5.83	0.51	5.42	5.36	5.40	6.74	5.43	5.50
	Pipe Loop 4	5.82	0.53	5.45	5.29	5.28	5.29	5.41	5.38
Total Cl_2 residual, mg/L									
	Pipe Loop 1	0.26	0.26	0.16	0.46	0.74	0.34	0.35	0.28
	Pipe Loop 2	1.86	0.61	0.08	2.20	2.20	2.20	2.20	2.20
	Pipe Loop 3	1.67	0.68	0.21	0.47	0.72	2.20	1.19	1.07
	Pipe Loop 4	1.64	0.76	0.14	0.28	0.55	0.67	0.96	1.21
Total Iron, µg/L									
	Pipe Loop 1	616.141	1589.617	359.60	489.70	293.50	199.70	107.70	253.90
	Pipe Loop 2	2285.913	7986.514	674.50	960.40	39940.00	3328.00	244.10	30700.00
	Pipe Loop 3	104.989	97.479	35.35	56.97	123.20	213.40	52.78	51.59
	Pipe Loop 4	184.752	367.882	47.16	56.94	69.04	93.57	58.19	224.30

Dissolved Iron, µg/L									
	Pipe Loop 1	21.150	26.985	4.16	4.25	4.90	3.51	4.53	4.89
	Pipe Loop 2	18.626	29.936	144.90	2.05	3.18	1.12	1.23	8.38
	Pipe Loop 3	9.173	8.409	3.83	7.68	9.97	24.60	3.11	5.15
	Pipe Loop 4	13.266	12.567	6.69	9.26	9.36	7.56	5.85	5.24
Total Lead, µg/L									
	Pipe Loop 1	1.338	2.263	7.60	3.22	1.45	1.64	0.69	1.18
	Pipe Loop 2	1.903	6.151	1.73	2.33	37.39	3.20	0.40	10.19
	Pipe Loop 3	1.487	3.978	25.00	5.27	3.43	1.20	1.82	1.43
	Pipe Loop 4	0.502	0.474	2.40	0.95	0.71	0.51	0.37	0.69
Dissolved Lead, µg/L									
	Pipe Loop 1	0.214	0.178	0.99	0.26	0.13	0.21	0.29	0.22
	Pipe Loop 2	0.220	0.294	0.37	0.11	0.18	0.19	0.04	0.36
	Pipe Loop 3	0.983	3.143	19.61	3.61	2.48	0.25	1.17	0.75
	Pipe Loop 4	0.261	0.336	1.80	0.70	0.61	0.41	0.64	0.34
Total Copper, µg/L									
	Pipe Loop 1	50.489	36.005	125.50	47.70	22.64	18.66	13.81	16.37
	Pipe Loop 2	41.538	36.640	33.81	78.20	233.80	39.37	11.00	88.35
	Pipe Loop 3	13.804	35.907	229.20	35.31	24.43	12.94	13.37	13.20
	Pipe Loop 4	9.118	7.103	35.58	12.41	8.32	9.23	6.09	8.05

Dissolved Copper, µg/L									
	Pipe Loop 1	42.242	21.340	102.90	38.01	16.33	16.46	19.19	13.84
	Pipe Loop 2	32.294	13.939	10.43	42.69	25.28	24.45	6.11	28.94
	Pipe Loop 3	16.908	32.156	208.40	35.46	20.82	11.56	19.24	10.52
	Pipe Loop 4	12.105	6.453	33.12	15.93	11.43	11.81	15.12	7.15
Total Aluminum, µg/L									
	Pipe Loop 1	289.064	315.622	489.80	727.30	370.10	334.60	235.10	569.00
	Pipe Loop 2	281.172	777.443	355.10	566.10	4673.00	344.40	234.20	1592.00
	Pipe Loop 3	279.000	134.700	192.80	221.40	407.40	424.80	143.30	293.20
	Pipe Loop 4	283.996	266.588	225.30	255.50	211.20	301.70	236.70	798.70
Dissolved Aluminum, µg/L									
	Pipe Loop 1	17.917	6.209	23.92	18.62	14.16	22.49	28.80	30.12
	Pipe Loop 2	25.382	41.208	206.40	5.47	8.63	13.98	183.30	18.75
	Pipe Loop 3	53.462	25.312	87.95	80.51	85.77	36.76	56.51	76.93
	Pipe Loop 4	50.056	30.617	110.50	105.10	93.85	82.71	75.64	67.34

Table C.4 ANOVA analysis of the cast iron test sections

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Cast Iron 1	36	975.317	27.092	492.011		
Cast Iron 2	36	1616.1	44.892	1300		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5702.89	1	5702.89	6.36479	0.01392	3.97778
Within Groups	62720.4	70	896.006			
Total	68423.3	71				

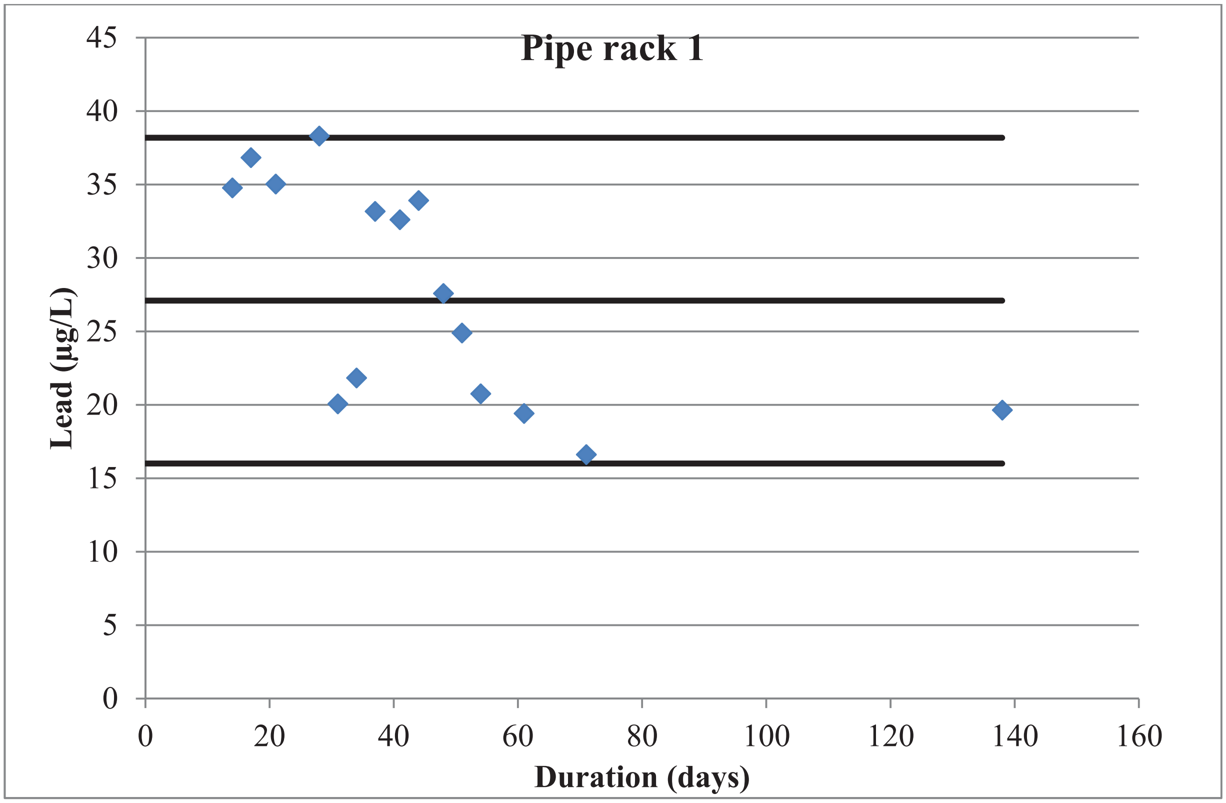
Table C.5 Paired t-test analysis of cast iron test sections.

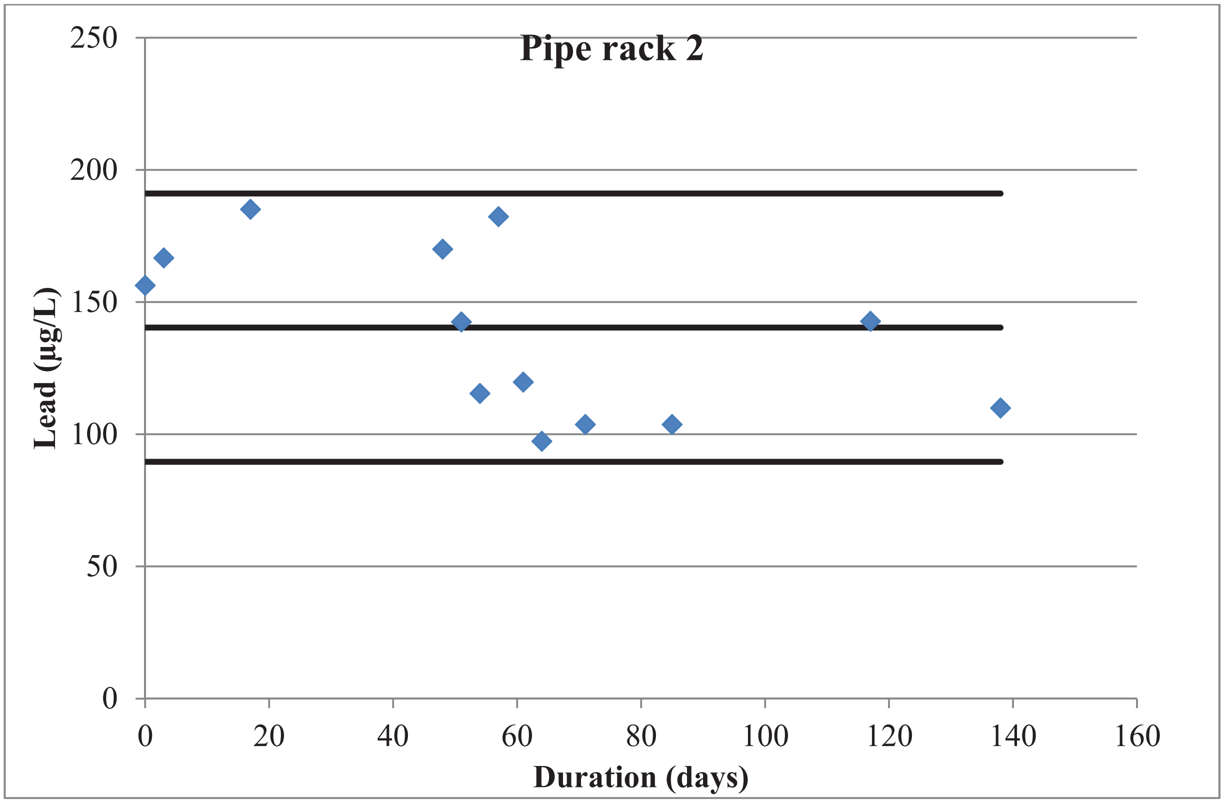
t-Test: Paired Two Sample for Means		
	Cast Iron 1	**Cast Iron 2**
Mean	140.309	44.892
Variance	10297.445	1300.0013
Observations	36	36
Pearson Correlation	0.0738	
Hypothesized Mean Difference	0	
df	35	
t Stat	5.444	
P(T<=t) one-tail	2.087E-06	
t Critical one-tail	1.690	
P(T<=t) two-tail	4.173E-06	
t Critical two-tail	2.030	

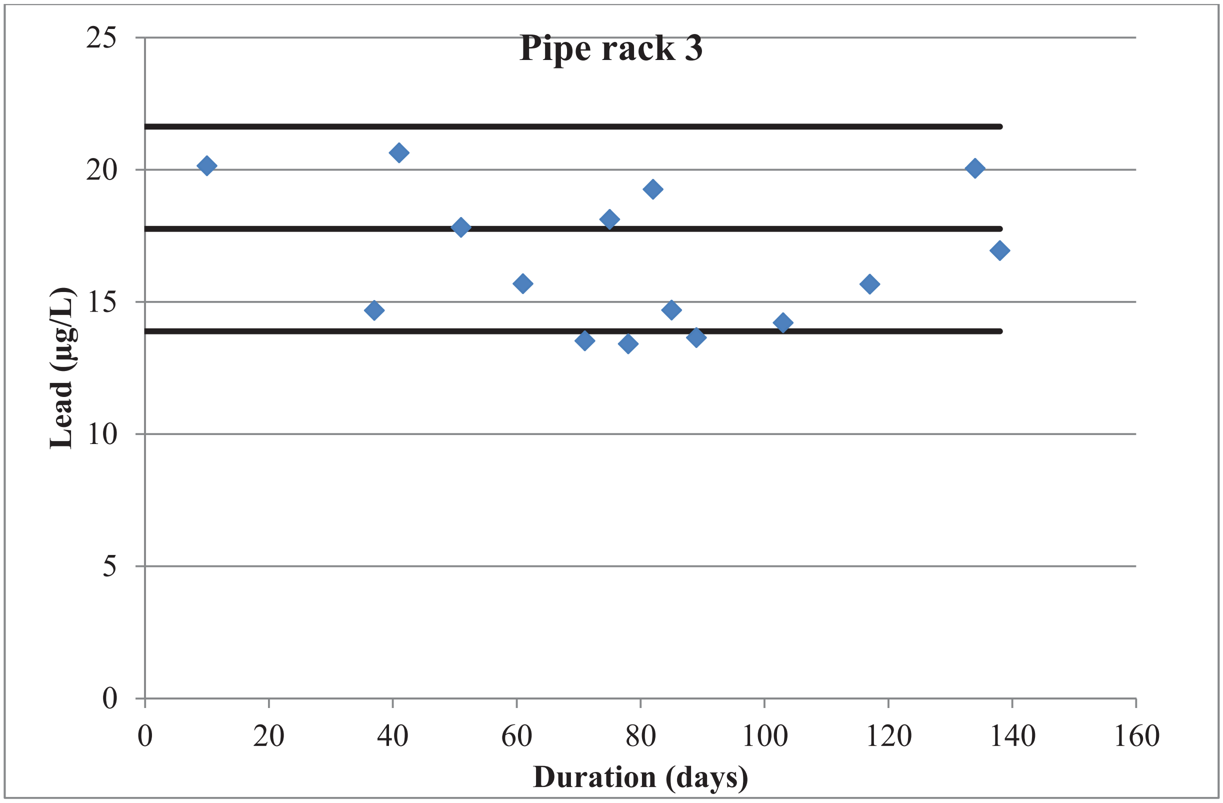
Table C.6 Paired t-test analysis of the high and low chlorine concentrations.

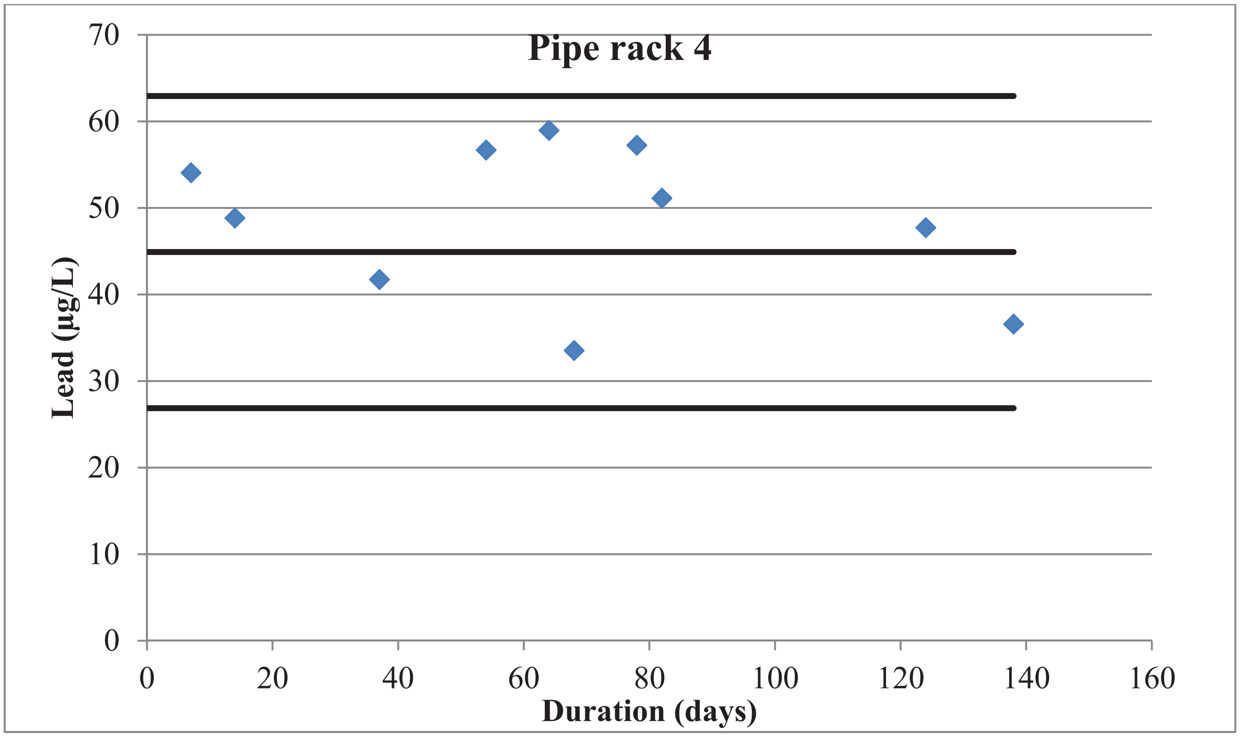
	Low Cl2	High Cl2
Mean	27.092	17.754
Variance	492.011	59.898
Observations	36	36
Pearson Correlation	0.296	
Hypothesized Mean Difference	0	
df	35	
t Stat	2.640	
P(T<=t) one-tail	0.00615	
t Critical one-tail	1.690	
P(T<=t) two-tail	0.0123	
t Critical two-tail	2.030	

Figures C.1 Control charts for pipe racks 1 to 4 (long Stagnation)

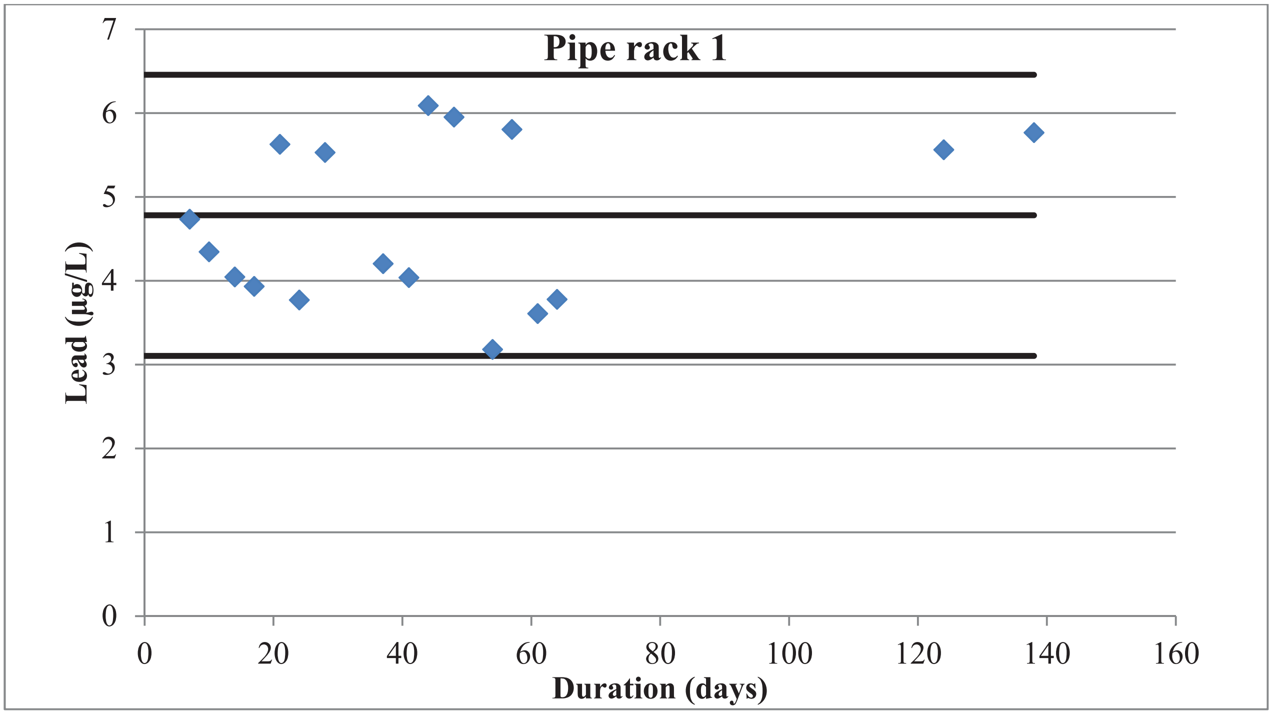


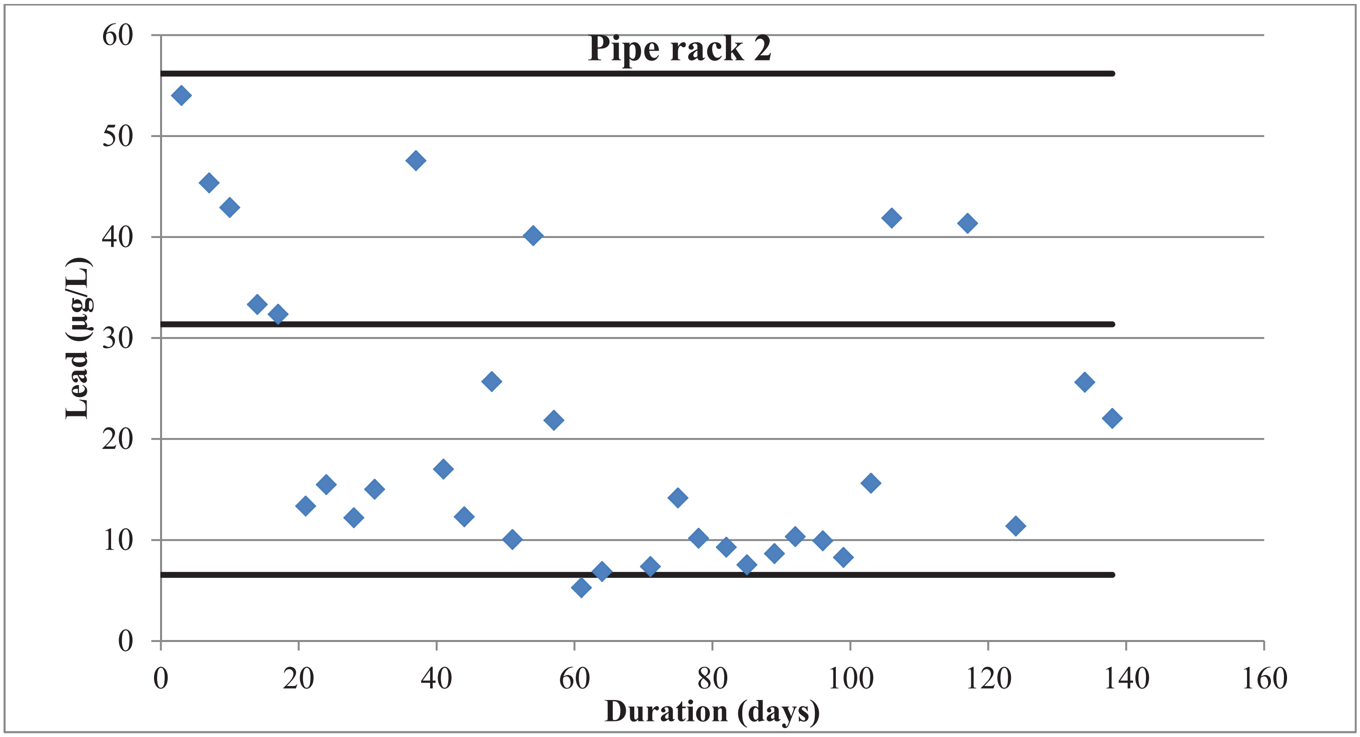

Pipe rack 2
Lead (µg/L)
250
200
150
100
50
0
0
20
40
60
80
100
120
140
160
Duration (days)

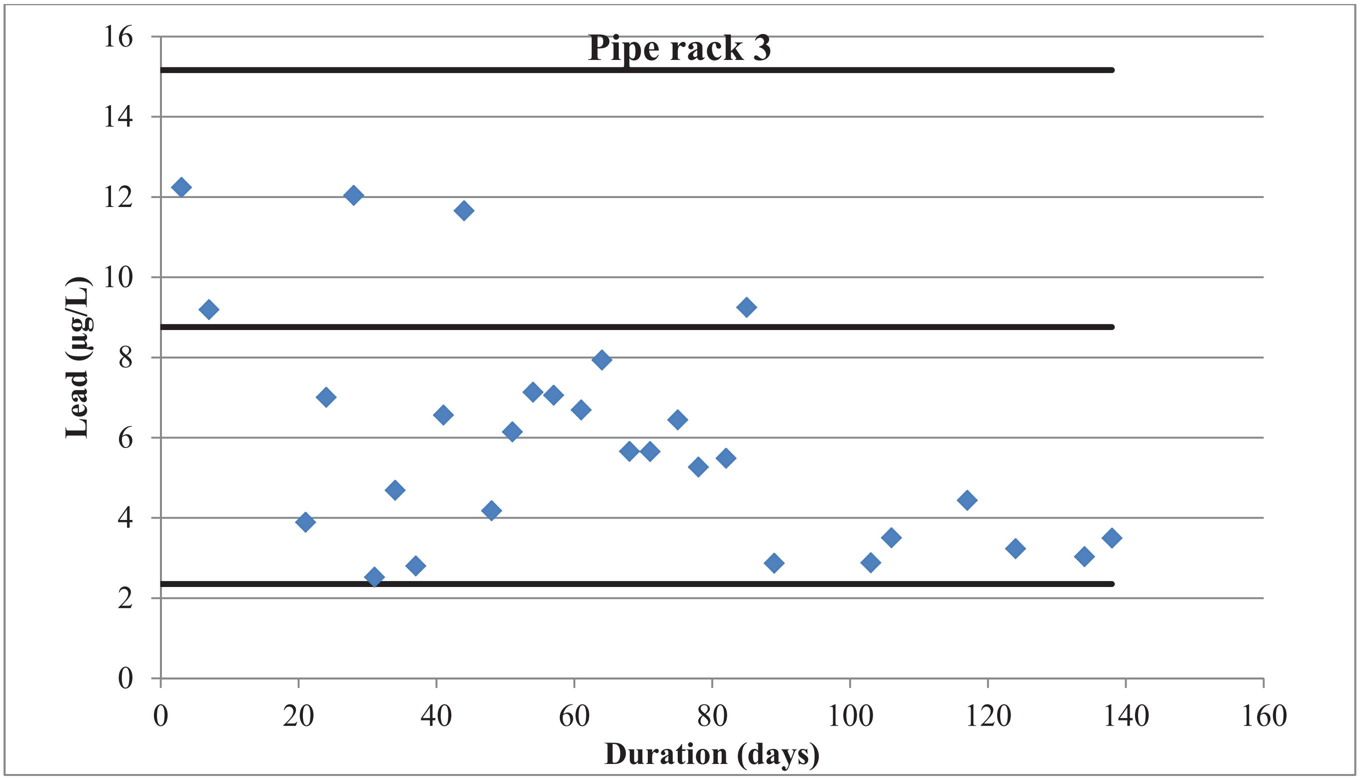

Pipe rack 3
Lead (µg/L)
25
20
15
10
5
0
0
20
40
60
80
100
120
140
160
Duration (days)

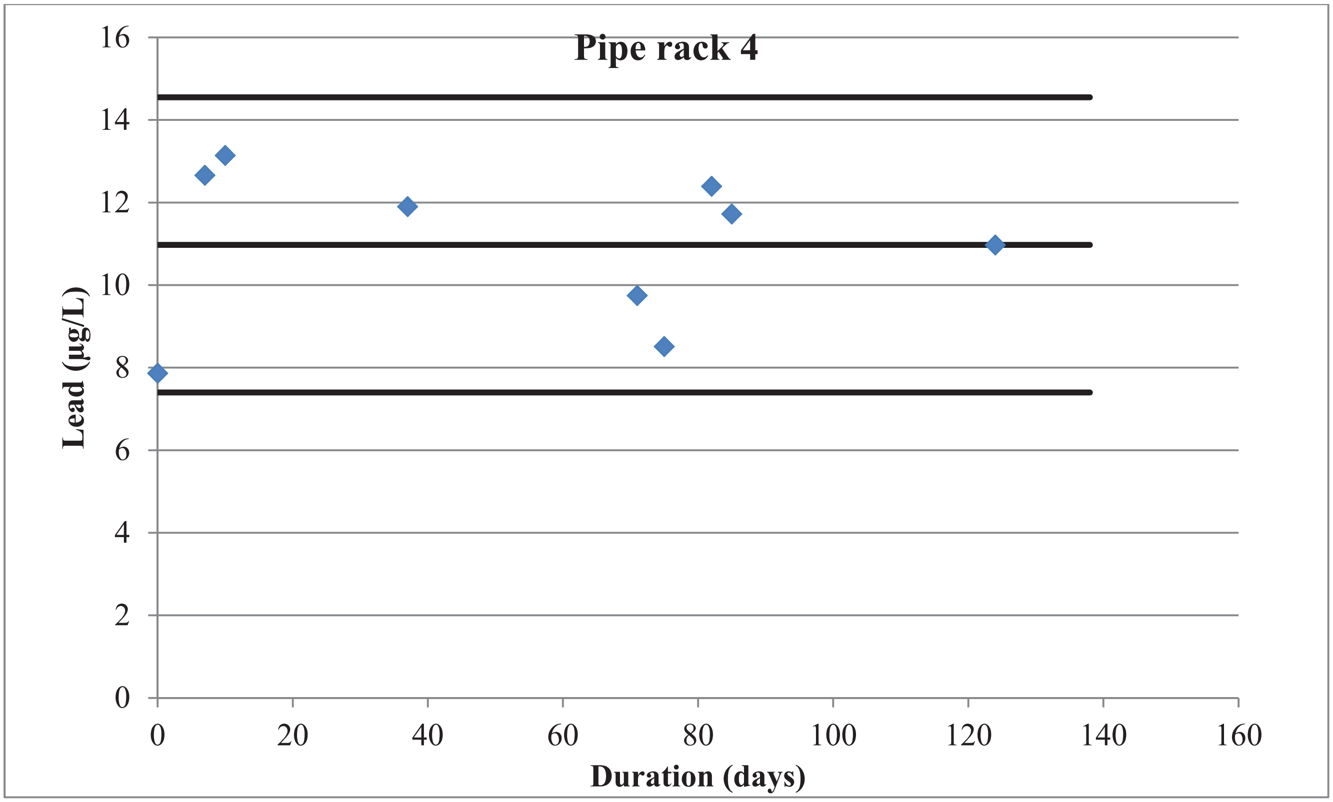


Figures C.2 Control charts for pipe racks 1 to 4 (Short Stagnation)




Pipe rack 2
Lead (µg/L)
Duration (days)
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160


Pipe rack 3
Lead (µg/L)
Duration (days)
16
14
12
10
8
6
4
2
0
0
20
40
60
80
100
120
140
160


Pipe rack 4
Lead (µg/L)
16
14
12
10
8
6
4
2
0
0
20
40
60
80
100
120
140
160
Duration (days)