

ANALYSIS OF LEAD MONITORING DATA IN DRINKING WATER

By

Tony P. Tsui

A thesis submitted in conformity with the requirements
for the degree of Masters of Applied Science
Graduate Department of Civil Engineering
University of Toronto

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Tony P. Tsui
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Graduate Department of Civil Engineering
University of Toronto

ABSTRACT

Historical lead in tap water data from the City of London and the City of Ottawa were examined for trends and correlations over time. Factors such as the sampling protocol, temperature, and pH were analyzed to determine their specific impacts on lead. Linear and logistic regression models were also developed to predict lead concentrations in tap water based on different water quality parameters. Finally, a physical mass transfer and flow model (zonal model) was validated with the lead data from the two municipalities. Results indicate the potential use of the regression and zonal models to predict a range of lead concentrations for a number of homes in a Canadian city based on the field data.

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NOMENCLATURE

#	Number
β	Regression coefficient
σ	Standard deviation of ratios of predicted lead concentration over average lead concentration
%	Percent
$^{\circ}\text{C}$	Degree(s) Celsius
Π	Pi
30MS	Thirty-minute stagnation time
30MS1	30-minute stagnation time litre 1
30MS2	30-minute stagnation time litre 2
6HS	6-hour stagnation
A	Internal surface area of pipe (m^2)
ANOVA	Analysis of Variance
AVGR	Average of ratios of predicted lead concentration over average lead concentration
AWWARF	American Water Works Association Research Foundation
C	Lead concentration ($\mu\text{g/L}$) in element (i,j)
CaCO_3	Calcium carbonate
CCP	Corrosion control plan
COMP	Composite proportional sampling protocol
D	Difference in ranks for Spearman's Rank Correlation
EPA	Environmental Protection Agency
E	Equilibrium concentration of lead ($\mu\text{g/L}$)
FF	Fully flushed
GVRD	Greater Vancouver Regional District
HNO_3	Nitric acid
HOCl	Hypochlorous acid
IARC	International Agency for Research on Cancer
J	Element number
LCCA	Lead Contamination Control Act
L	Litre
LR	Logistic regression equation
LSL	Lead service line
LSLR	Lead service line replacement
M	Mass transfer rate ($\mu\text{g}/\text{m}^2/\text{s}$)
m	meter(s)
m^2	Square meter(s)
m^3	Cubic meter(s)
mg/L	Milligram(s) per litre
mL	Millilitre(s)
mm	Millimetre(s)
μg	Microgram(s)
$\mu\text{g/L}$	Microgram(s) per litre
$\mu\text{g/dL}$	Microgram(s) per decilitre

$\mu\text{g}/\text{m}^2/\text{sec}$	Microgram per square meter(s) per minute
μm	Micrometer
m/s	Meter(s) per second
Min	Minute
MLR	Multiple linear regression
MOE	Ontario Ministry of the Environment
n	Sample size
NA	Not applicable
NaOH	Sodium hydroxide
OLCC	On-line corrosion cell
OCI^-	Hypochlorite
p	Probability of a binary response taking the value of 0 or 1
p	Statistical significance of correlation
Pb	Lead
Pb01	Categorical variable for lead
PbO_2	Tetravalent lead dioxide
PbCO_3	Cerussite
$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$	Hydrocerussite
pH	The negative log of the hydrogen ion concentration; $-\log\{\text{H}\}$
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
Q	Flow rate of water (m^3/s)
Q1	First quartile
Q3	Third quartile
r_o	Radius of pipe (m)
r_j	Radius of element in pipe (m)
R	Linear regression equation
R^2	Coefficient of determination
RDT	Random daytime sampling
R_s	Spearman's Rank Correlation
Sec	Seconds
SDWA	Safe Drinking Water Act
SPS	Seattle Public Schools
t	Time (seconds)
T	Stagnation time (seconds)
U	Velocity of water within the pipe (m/s)
U	Velocity of water (m/s)
U.S.	United States
V	Volume of pipe (m^3)
WHO	World Health Organization
ΔX	Axial length of element i (m)
Y	Dependent variable
Z	Parameter used to calculate the probability in logistic regression

1. INTRODUCTION AND RESEARCH OBJECTIVES

1.1 Importance of Monitoring Lead in Drinking Water Systems

The leaching of lead into drinking water through corrosion in distribution systems may result in potential adverse health effects. The effects associated with blood lead levels $< 100 \mu\text{g/L}$ in infants and young children include lower birth weight and a slowing down of normal physical and mental development (Lanphear et al., 2000). Inhibition in development might decrease a child's IQ levels, as well as a reduction in hearing, and attention span leading to poor classroom performance (Lanphear 2000; Canfield 2003).

Adults are also susceptible to negative health effects from lead. The effects include kidney damage, an increase in blood pressure, and damage to the reproductive system (U.S. EPA, 2003). Recent research links adverse cardiovascular effects in adults to blood lead levels above $100 \mu\text{g/L}$ (Menke et al., 2006). Lead is also classified as a probable human carcinogen (Group 2A) by the International Agency for Research on Cancer (IARC) (Rousseau, 2005).

Lead in drinking water comes from plumbing materials such as lead pipes, solders, fittings, fixtures and faucets (brass) as well as galvanized and cement pipes (U.S. EPA, 2003). Lead leaches into water through corrosion, which is the dissolving or wearing away of metal caused by a chemical reaction between water and the plumbing (U.S. EPA, 2005).

1.2 Current State of Corrosion Control in Canada

In Canada, the drinking water regulations fall under provincial/territorial jurisdiction. Health Canada develops guidelines for water quality. Provinces and territories adopt health-based guidelines into regulations. A Health Canada guideline on corrosion control has been implemented to establish strategies to reduce the leaching of lead and other contaminants into drinking water and to recommend the implementation of corrosion control programs when the guideline is exceeded (Health Canada, 2007). The drinking water guideline for lead, based on negative health effects in children, is $10 \mu\text{g/L}$ (MOE, 2007a).

The Health Canada guideline on corrosion control (Health Canada, 2007) impacts water utilities in Canada by imposing more stringent sampling requirements. Previously,

required monitoring of lead at the tap in Canada was minimal, requiring one sample per year and was not targeted at high risk sites (Lemieux, 2007). These sites include locations where: i) high concentrations of lead ($>10 \mu\text{g/L}$) have been observed, ii) materials containing lead are known to exist, as well as those serving high-risk populations including children under age six, pregnant women and nursing mothers (U.S. EPA, 2005).

The guideline applies to residential and non-residential sites. Residential sites include single-family homes, multiple-family dwellings and high-rise apartment buildings. Non-residential sites include buildings and schools. Residential monitoring includes the identification of lead sources in both the distribution system and residential plumbing whereas non-residential monitoring focuses mainly on the source of lead within the building (Health Canada, 2007).

In addition to the Health Canada guideline, the Government of Ontario implemented a regulation in June, 2007 (O.Reg. 243/07) to reduce children's exposure to lead in drinking water (MOE, 2007a). This regulation requires all schools and day nurseries built before 1990 to flush their plumbing daily, and those built after 1989 to flush weekly. All schools and day nurseries (built before 1990) are required to test for lead in water from taps on an annual basis (MOE, 2007a). More stringent regulation requirements include mandatory community-wide testing, as well as notification of results from this program, and the development and implementation of corrosion control measures for lead reduction.

Issues regarding elevated lead levels in Canada have already occurred in several cities with lead service lines such as Ste-Agathe and Montreal in Quebec as well as Ottawa and London in Ontario (Lemieux, 2007). However, there are issues of cost and infrastructure associated with the removal or replacement in these lead lines. For example, in Toronto, the estimated cost for the Lead Water Service Replacement Program is \$17.9 million per year for design and construction work associated with additional water service replacement and water main reconstruction in addition to \$1.3 million per year for additional staff resources (Toronto Water, 2007).

1.3 Research Objectives

- 1) Determine the effectiveness of different sampling protocols for lead in tap water

- 2) Determine the effect of temperature and pH on lead concentrations in tap water
- 3) Develop models to predict lead concentrations in tap water based on pH, temperature, and total chlorine concentration
- 4) Apply an adaptation of a zonal model to predict a range of lead concentrations in tap water for a number of homes based on the historical lead data from Ottawa and London

1.4 Description of Chapters

- *Chapter 2* provides background information through a literature review of key areas related to this research: sources of lead in drinking water; analysis of lead sampling in drinking water; and case studies.
- *Chapter 3* presents results and provides a discussion of the analysis of the historical lead in tap water data for the City of Ottawa and London as well as the impact of water quality parameters (pH and temperature) and sampling protocols on measured lead concentrations
- *Chapter 4* presents results and provides a discussion of the development of statistical linear and logistic regression models to predict lead concentrations in tap water
- *Chapter 5* presents results and provides a discussion of the application of the zonal model, which can be used to predict a range of lead concentrations for a number of homes to the lead in tap water data from Ottawa and London
- *Chapter 6* summarizes the significant findings of this research and provides recommendations for future work.

2. LITERATURE REVIEW

2.1 Background

2.1.1 History of the Use of Lead in Pipes and Solder

In Europe, the use of lead as a plumbing material in the construction of houses started being phased out during the 1950s and 60s (Scottish Government Publications, 2002). By the 1970s, water bylaws were introduced to ban the use of lead plumbing and lead solder in copper pipes. The use of lead solder in copper pipes was also banned at that time. The European directive governing the quality of water intended for human consumption, “The Drinking Water Directive”, determines over 40 water quality parameters, including lead concentration in tap water. It also prescribes patterns and minimum frequencies for sampling and analyses. The quality standards are based largely on the World Health Organization (WHO) recommendations of the time. Lead pipe replacement plans in older homes are currently underway (Scottish Government Publications, 2002).

The first major initiative in the U.S. to control lead in drinking water was the “Federal Lead Ban”, a set of amendments to the Safe Drinking Water Act, signed into law in December 1986 (AWWARF, 2000). The amendments banned the use of solders and flux containing more than 0.2% lead, previously, typical levels of lead in solders and flux were 40% to 50%. Furthermore, the allowable amount of lead in any brass or other material intended to be in contact with water was restricted to less than 8% (AWWARF, 2000). However, the use of lead in plumbing materials is still widespread. The estimated numbers of lead service connections and lead service lines in the U.S. is approximately 6.4 million and 3.3 million respectively (AWWARF, 2000). The majority of these lead service lines are found in the Midwest and parts of the North East (AWWARF, 2000).

In 1988, the U.S. Lead Contamination Control Act (LCCA) was put in place to protect the health of children (Maas et al., 2005). The purpose of the LCCA was to assist schools in implementing measures to test for and reduce lead contamination in drinking water from water coolers and other sources. This was accomplished by requiring the Environmental Protection Agency (EPA) to publish a guidance document and testing protocols. By 1990, there was increased awareness of the connection between lead in drinking water, and the childhood lead exposure problem (Maas et al., 2005). Pressure

was placed on the EPA and the public water supply industry by medical and public health organizations to further reduce lead in drinking water (Maas et al., 2005). In June 1991, the EPA issued the federal Lead and Copper Rule to reduce drinking water lead exposure by 50% by the end of the decade.

Similar to the U.S., Canada has also taken action to reduce the use of lead in pipes and plumbing, although there are still a number of homes with lead service lines (Health Canada, 2007). In addition, homes that were built prior to 1986 may have copper piping and lead solder (Health Canada, 2007). Homes also exist with leaded brass taps, water meters and other leaded-brass fittings. In Ontario, older homes built before the mid-1950s may have lead pipes and service lines (MOE, 2007a). If built between the mid-1950s and 1989, lead may be present in fixtures or solder used to connect the pipes (MOE, 2007b). Homes built after 1989 should not contain lead in pipes, service lines, solder or joints (MOE, 2007a).

In summary, there is currently a potential for lead to enter drinking water from many sources. These include: household plumbing materials such as pipes, lead solder and faucets with brass or bronze (AWWARF, 2005; Maas et al., 1993); lead in brass and bronze plumbing fittings; lead in goosenecks, valve parts, or gaskets used in water treatment plants or distribution mains (Health Canada, 2007); the connection of lead pipe to copper, which can increase lead leaching to water because of a higher corrosion rate and/or lower pH at the surface of the lead material (Triantafyllidou et al., 2007); and galvanized pipes, which contain sources of lead as an impurity (Leroy et al., 1996). Cement pipes do not contribute directly to elevated lead levels although degradation of cement based materials can be a source of calcium hydroxide (lime) in the distributed water (Leroy et al., 1996). Lime from cement can release calcium ions and hydroxyl ions into the drinking water resulting in an increase in pH, depending on the buffering capacity of the water (Leroy et al., 1996).

2.1.2 Factors Influencing Levels of Lead at the Tap

Lead concentration in water from lead solders and brass fittings decreases with age (Neuman, 1995) with the highest lead concentration in the first year after installation, and stabilization thereafter (Schock et al., 1996). However, lead piping can continue to

provide a source of lead after many years of service (Schock et al, 1996). At sites with lead-soldered joints, brass faucets contribute, on average, one third of the lead in a 1-L first-draw standing overnight sample (Kimbrough, 2001; Lee et al., 1989). In homes with plastic and galvanized plumbing, brass faucets have been reported to be responsible for all lead contribution (Lee et al., 1989).

Lead values rapidly increase upon stagnation, but approach a constant equilibrium value after overnight stagnation (Lytle and Schock, 2000). For example, water sampled in a one-year old household plumbing system consisting of copper pipe with tin-lead solders could exceed 0.05 mg lead/L after 4 to 20 hours of stagnation. Water in contact with lead pipes could exceed 0.05 mg lead/L in 10 to 100 minutes (Wong and Berrang, 1976). Lytle and Schock (2000) reported that lead levels increased most rapidly over the first 10 hours, reaching approximately 50 to 70% of the maximum observed value.

2.2 Lead Uptake Mechanisms

Before discussing sampling protocols for lead in tap water, it is important to understand the theory behind the uptake of lead from pipes and plumbing into water. Both dissolved and particulate forms of lead contribute to the total amount of lead in tap water. There is extensive literature on the mechanisms of lead corrosion that result in the uptake of dissolved lead in water (AWWARF, 2000). However, the uptake of particulate lead is less well known than dissolved lead. According to Triantafyllidou et al. (2007), particulate lead can constitute a “large” fraction of the total lead present in the water, depending on the type and age of the source material. In addition, Lytle et al. (1993) also states that particulate lead released from lead-based solders is “highly” variable.

Dissolved lead release rates are based on electrochemical and solubility theory, and can often yield a good indication of the tendency for lead uptake under various water quality conditions. However, electrochemical mechanisms for lead release from lead pipes are different from those of lead solders. In the case of a lead pipe with a pure lead surface, the theoretical mechanisms are the establishment of a corrosion concentration cell on the lead surface, similar to many other metals (Singley, 1994). The presence of oxidants that accept electrons drives the corrosion reaction, releasing lead ions to solution. In the case of lead solder joining a copper pipe, it has been proposed that the

mechanism for lead release is galvanic corrosion (Singley, 1994). This galvanic condition occurs when lead, in contact with copper, corrodes via electrochemical means and is released. A second galvanic condition occurs within the lead:tin solder itself where tin has a greater tendency to corrode in relation to lead, leaving exposed lead. Research by Reiber (1991) using electrochemical techniques indicates that galvanic stimulation is an important lead release mechanism for new lead solder, but the effect is rapidly lost as the surface ages and passivation occurs.

2.3 Monitoring of Lead in Drinking Water

Monitoring for lead levels in tap water at specific sites can provide baseline and post-treatment data on reductions in lead levels. The sites can be categorized by piping type, system hydraulics and distance from the point of treatment (AWWARF, 2000). Sites that require sampling include single-family dwellings, multiple-family dwellings and non-residential locations (schools, workplaces, restaurants, and community centers). Monitored sites should include i) locations with lead service lines (LSLs), ii) locations that contain copper pipes with lead solders or lead pipes and/or iii) locations with lead-containing brass fittings or in-line devices (MOE, 2007a). Furthermore, the sampling locations should cover a wide geographical area while still targeting those locations most likely to have lead in their tap water. A wider distribution of sampling points allows for better representation of lead in the entire system. Areas of the distribution system with LSLs that are also susceptible to reduction in pH should be monitored (Lemieux, 2007).

Several factors contribute to the potential variability measured in lead levels. These are shown in Table 2.1 and are based on statements by AWWARF (2004). Even though these factors can be controlled by selecting sites with similar characteristics, variability can still be observed in lead levels due to the chemical and physical factors that affect the corrosion of materials. For example, Maas et al. (1995) has shown that the temperature of the water as it stood in residential plumbing system or the strength of the galvanic field generated by a specific residential electricity cold-water ground system are difficult to quantify, and may have an effect on the observed concentration.

Table 2.1: Factors Impacting Variability in Lead Levels Measured at the Tap

Factor	Contribution to Variability
Age of Material	High
Form of Lead (Soluble vs. Particulate)	High
Stagnation Time	High
Distribution System Water Quality Variations such as pH and Alkalinity	High
Amount and Type of Lead Material	Medium
Water Usage	Medium
Quality of Workmanship	Medium
Analytical Variability	Low

Adapted from AWWARF (2004)

To minimize variability, the AWWARF (2004) study proposed an alternate monitoring protocol (Table 2.2), which suggests a reduced pool of sampling sites that are more stable, and available for continued, long-term monitoring. The monitoring schedule for this protocol provides sufficient data to evaluate tap lead levels in a system for a desired accuracy and confidence level as well as capturing fluctuations in lead levels due to water quality changes. Furthermore, the AWWARF project also developed a preliminary on-line corrosion cell (OLCC) predictive technology, which may provide a tool that eliminates the need for widespread in-home customer tap sampling, and would allow utilities to monitor and evaluate the corrosion potential of water several times a day. This technology also reduces field activities, costs, and analytical costs associated with conducting an in-home tap sampling program as well as variability issues associated with materials, workmanship, and customer sampling (AWWARF, 2004).

The following sections cover the requirements for monitoring and sampling locations, and provide a comparison of the sampling protocols used by Health Canada, the Ontario Ministry of the Environment (MOE), the U.S. Environmental Protection Agency (EPA), and AWWARF (2004). Although these methods have similar requirements, some differences may ultimately affect the lead concentrations observed in tap water.

Table 2.2: Alternate Lead Tap Monitoring Protocol Summary

Number of sites	12 to 43
Number of samples/site	One per sampling period
Evaluation period	Quarterly
Site selection criteria	Local sites in areas of the distribution system that exhibit consistent water quality
	Sites with similar physical conditions with respect to type and age of lead source
	Sites with consistent physical and age characteristics within each specific sample pool
For lead sites	Single family residences with lead solder installed prior to 1982 or lead service lines
Data collection and analysis criteria	1-liter total. Split sampling with initial 125 mL followed by 875 mL.
	Analyze total lead levels
	Minimum 6 hour stagnation time. All samples should have similar stagnation times.

Source: AWWARF (2004)

2.3.1 Monitoring Frequency and Seasonal Requirements

By monitoring lead concentrations and routinely testing tap water, communities can identify when action is required to reduce lead levels. In addition, this testing can provide evidence of changes in lead levels over time and help distinguish whether the lead originates from the drinking water system or from the corrosion of lead-containing plumbing materials. A comparison of the required monitoring frequency for residential and non-residential sites (schools and commercial buildings) is provided by Health Canada, MOE, U.S. EPA, and AWWARF (Table 2.3).

For residential sites, Health Canada only requires annual sampling between May and October since these are the summer months with the highest temperatures, and are most likely to result in the most amount of lead being leached from the pipes. Both the MOE and the U.S. EPA require two sampling periods (during the winter and summer months of each year), and this approach results in a more thorough analysis of the variations in lead concentrations throughout the year. In comparison, the AWWARF sampling protocol requires four sampling periods per year, which provide more timely

data to make comparisons and determine if lead levels have changed because of water quality fluctuations in the system.

Table 2.3: Monitoring Frequency and Period Requirements for Residential and Non-Residential Sites

Type	Reference	Frequency	Period
Non-Residential	(Health Canada, 2007)	Once per year	Between May and October
	(MOE, 2007b)	Once per year	Between June 15 and August 15 for public and private Schools. Between May 1 and October 31 for day nurseries.
	(U.S. EPA, 2005)	Twice per year (Schools under safe drinking water act (SDWA), non-residential buildings)	Every six months
		Voluntary (Schools not under the SDWA)	
Residential	(Health Canada, 2007)	Once per year	Between May and October
	(MOE, 2007c)	Twice per year	Once between December 15 and April 15. Once between June 15 and October 15
	(U.S. EPA, 2004)	Twice per year	Every six months
	(AWWARF, 2004)	Four times per year	Every three months

Health Canada (2007) suggest that annual sampling for lead needs to be continued even after corrosion control has been optimized, due to changes in water quality conditions (Health Canada, 2007). This sampling should take place during the same period every year since lead leaching, as well as the leaching of other materials within the distribution system increases with warmer temperatures (Douglas et al., 2004). For example, in a study conducted in Old Ottawa South, the average lead concentration at the

sampling sites increased from 1.6 µg/L in May, 2003 to 5.4 µg/L in August, 2003 (Douglas et al., 2004).

2.3.2 Site Number Requirements Based on Sampling Location

The requirements for the type of sampling location differ slightly depending on the jurisdiction (Health Canada, 2007; U.S. EPA, 2008; MOE, 2007f). The number of sampling locations required by Health Canada, the MOE, and the U.S. EPA for residential and non-residential sites are shown in Table 2.4. The U.S. EPA uses a tiered system (U.S. EPA, 2008). Tier 1 sampling sites consist of single family structures that contain copper pipes with lead solder installed after 1982 or contain lead pipes and/or a lead service line. Tier 2 sampling sites are used when a community water system has an insufficient number of Tier 1 sampling sites, and consists of buildings that include multiple-family residences with copper pipes and lead solder (installed after 1982) or contain lead pipes and/or a lead service line. Tier 3 sampling sites consist of single family structures that contain copper pipes with lead solder installed before 1983. Sites with commonly used plumbing materials are selected throughout the distribution system if the system does not contain a sufficient number of Tier 1, Tier 2, and Tier 3 sampling sites. The requirements for non-transient, and non-community water systems are similar to the ones for community water systems (U.S. EPA, 2008e). Finally, AWWARF (2004) recommends utilities sample from a number of sites that range from 12 to 43, with one sample per site in a zone. Each zone is defined in the site selection criteria and large water systems such as those of New York City or Los Angeles may have several zones.

For schools, the requirements are different depending on whether the school is supplied by municipal or private water sources, such as wells. The number of sampling locations, based on school population for U.S. Schools under the Safe Drinking Water Act (SDWA) is shown in Table 2.5. Schools supplied by municipal water fall under the SDWA. For U.S. schools not covered by the SDWA, the U.S. EPA requests that every drinking water fountain and cold-water outlet for drinking water purposes be monitored initially. Health Canada and the U.S. EPA share the same requirements. The MOE requires the operator of a school, private school, or day nursery to take two one-liter samples of cold water at least once per year from the same tap with the aerator left on.

The tap can be a kitchen tap or a tap used to provide water for consumption by children less than 18 years of age, and served by lead plumbing or plumbing that contains lead solder.

Table 2.4: Number of Tap Water Samples Sites Based on Population

System Size (# of people served)	# of Lead Sample sites (Initial Monitoring Once Per Year)		# of Lead Sample sites (Reduced Monitoring Once Per Year)		# of Non-Residential Lead Tap Sample Sites for the Ontario Ministry of Environment ^a	
	Health Canada/ U.S. EPA ^b	Ontario Ministry of Environment ^a	Health Canada/ U.S. EPA ^b	Ontario Ministry of Environment ^a	Initial Monitoring Once Per Year	Reduced Monitoring Once Per Year
>100,000	100	100	50	50	10	5
50,000-100,000	60	80	30	40	8	4
10,000-50,000	60	60	30	30	6	3
3,300-10,000	40	40	20	20	4	2
500-3,300	20	20	10	10	2	1
100-500	10	10	5	5	1	1
<100	5	5	5	3	1	0

^aMOE (2007a)

^bHealth Canada (2007)

Table 2.5: Number of Sampling Locations Based on School Population for U.S. Schools under the Safe Drinking Water Act

School or Child Care Facility Daily Population Served	Number of Lead and Copper Tap Sample Sites (Standard Monitoring)	Number of Lead and Copper Tap Sample Sites (Reduced Monitoring)
10,001-50,000	60	30
3,301-10,000	40	20
501-3,300	20	10
101-500	10	5
≤100	5	5

Source: U.S. EPA (2005)

A reduced monitoring program may be implemented if sampling locations, after a specified number of consecutive cycles of testing, show that 10% of the locations have

lead levels below 10 µg/L (U.S. EPA, 2008; Health Canada, 2007; MOE, 2007f). The MOE states that all the water systems can reduce the number of sampling locations by 50% after two years (four consecutive rounds) of tests showing 90% or fewer of the locations have lead levels below the lead standard of 10 µg/L (MOE, 2007b) (Table 2.6). In addition, systems serving fewer than 50,000 people can reduce the number of sampling locations by 50% after one year (two consecutive rounds) of testing if results show 90% or fewer locations with lead levels below 5 µg/L with no results exceeding 10 µg/L (MOE, 2007b). Details on the criteria that allow a system to have reduced monitoring under the U.S. EPA regulations are found in the Electronic Code of Federal Regulations, Section 141.86: Monitoring Requirements for Lead and Copper in Tap Water (U.S. EPA, 2008e).

2.3.3 Sampling Protocols

Sampling protocols for lead from tap water in residential and non-residential sites from Health Canada, MOE, and the U.S. EPA have been compared. The alternate tap sampling protocol by AWWARF (2004) for residential sites was also included in this comparison. Summary tables of these protocols for residential sites and non-residential sites are shown in Tables 2.6 and 2.7 respectively.

In Table 2.6, some similarities can be observed between the different sampling protocols. For example, the volume of the first-draw sample is 1 L with an initial stagnation time of six hours for Health Canada, the U.S. EPA, and the AWWARF protocols. However, there is no first-draw sample for the MOE due to stakeholder concerns around practicality (MOE, 2007b). It is more practical for consumers to ensure the tap and plumbing be unused for 30 minutes as opposed to six hours (MOE, 2007b). In addition, there does not appear to be a follow-up sample for the U.S. EPA sampling protocol, which differs from Health Canada and the MOE. One reason may be because the first-draw sample is the most conservative measure of lead at the tap since it indicates the concentration of lead that has leached into the water after a period of stagnation. Furthermore, a 1-liter sample was suggested for all the jurisdictions because that volume is sufficient to measure the lead contribution from the faucet as well as the interior plumbing of the home (U.S. EPA, 1992).

Table 2.6: Sampling Protocol for Residential Sites

Jurisdiction	Initial Stagnation Time	Draw Volume after Stagnation Time	Flushing Time	Subsequent Stagnation Time	Second draw volume
Federal (Health Canada, 2007)	6 hours	1 L	5 minutes	30 minutes	2 L
Ontario (Provincial) (MOE, 2007b)	None	None	5 minutes	30-35 minutes	Two 1-liter samples (multiple containers allowed)
American (U.S. EPA, 2008)	6 hours	1 L (One container only)	None	None	None
American Water Works Association Research Foundation (AWWARF, 2004)	6 hours	1 L (Split sampling with initial 125 mL followed by 875 mL)	None	None	None

The U.S. EPA only allows a single container to be used to collect the 1-liter sample, whereas the MOE allows multiple containers for the collection of samples. The U.S. EPA suggests that one container provides a more accurate representation of the actual concentration of lead in the water sample. In the AWWARF sampling protocol, the consecutive 125 mL and 875 mL first-draw tap water samples from cold-water kitchen or bathroom taps allows the faucet contribution to lead levels to be determined. However, variability stills exists due to the presence of particulate lead, and an analysis of both dissolved and total lead concentrations would isolate the contribution of particulate lead to total lead levels.

If the lead concentration is greater than 0.015 mg/L in more than 10% of the samples collected at high-risk sites, a second sample is taken under the Health Canada sampling protocol. A 2-liter sample is taken after a period of stagnation of 30 minutes after flushing the system for five minutes. This sample reflects the average amount of

lead ingested by residents because the flushing time purges the initial amounts of lead in the water that is stagnant (Health Canada, 2007).

Table 2.7: Sampling Protocol for Non-Residential Sites (Schools and Buildings)

Jurisdiction	Initial Stagnation Time	Draw volume after stagnation volume	Flushing Time	Subsequent Stagnation Time	Second draw volume
Federal (Health Canada, 2007)	8 hours	250 mL	1 minute	None	250 mL
Ontario (Provincial) (MOE, 2007b)	6 hours (Schools)	Two 1-liter samples	5 minutes	30-35 minutes	Two 1-liter samples
American (U.S. EPA, 2008)	8-18 hours (Schools)	250 mL	30 seconds (before school opens)	None	250 mL
Non-residential buildings follow the same protocol as residential sites for the MOE, and the U.S. EPA.					

According to the U.S. EPA, a smaller than 1-litre sample volume is more effective in identifying the sources of lead at an outlet because this sampling volume is more representative of lead in the plumbing as well as the average amount of water pre serving consumed by a child (U.S. EPA, 2006). In addition, a 250-mL sample from a faucet would not include portions of the plumbing before the faucet when compared to the 1-liter sample, which would include a longer line of plumbing with its valves, tees, elbows, and soldered joints (U.S. EPA, 2006). This will allow the school to detect whether the elevated lead levels are coming from the water in contact with the faucet, or the plumbing before the faucet.

Under both Health Canada and the U.S. EPA regulations, follow-up samples are taken only if the lead concentration in any of the original samples is greater than 20 µg/L. The follow-up flush samples are to be taken before a facility opens and before any water is used (U.S. EPA, 2006). The purpose of the follow-up sample is to analyze the lead content of the water in the plumbing behind the wall (U.S. EPA, 2006). Furthermore, the

presence of an aerator may also contribute particulate lead to the water samples. Hence, the water samples should be collected after cleaning the aerator or screen (U.S. EPA, 2006). A comparison of the initial and follow-up samples identifies whether the source of lead is from the faucet or from the plumbing behind the faucet. Finally, the U.S. EPA guidelines for the follow-up flush sample are only applicable to schools not under the Safe Drinking Water Act (SDWA). Schools in the U.S. under the SDWA, are required to have first-draw samples, but if 10% of the tap water samples exceeds 0.015 mg/L for lead, then water quality parameter monitoring, corrosion control treatment, source water monitoring/treatment, public education, and lead service line replacement may be necessary (U.S. EPA, 2006).

2.3.4 Action Levels

The U.S. EPA's Lead and Copper Rule requires each public water supply system to determine the extent of lead contamination in high-risk residences (U.S. EPA, 2008). Water samples are collected after a stagnation period of 6 hours. If more than 10% of the water samples have lead levels exceeding a concentration $\geq 15 \mu\text{g/L}$, the public water supplier is required to: i) provide warning notices to all customers and encourage them to test their water for lead; ii) determine experimentally (using "pipeloop tests" or studies conducted by similar water utilities), including pH or alkalinity adjustments; iii) implement corrosion-optimization methods and monitor at-the-tap lead levels to determine the effectiveness of the treatment modifications (Maas et al., 2005). If the water exceeds the lead action level after optimal corrosion control treatments, lead service lines must be replaced in the distribution system (Maas et al., 2005).

The Health Canada corrosion guidelines have two action levels (Health Canada, 2007). For residential areas, the first action level $\geq 15 \mu\text{g/L}$ in 10% of the 1-L samples (90th percentile) after a stagnation period of 6 hours. The second action level is a concentration $\geq 10 \mu\text{g/L}$ for a 2-L sample taken after a stagnation period of 30-minutes. Corrective actions include public education to flush plumbing, implementation and optimization of corrosion control (pH, alkalinity, corrosion inhibitors), and a pipe replacement program. For non-residential areas, the first action level is $20 \mu\text{g/L}$ for a 250 mL first-draw sample taken after a period of stagnation of eight hours. The second sample of 250 mL is taken after a 30-second flush. This is based on the EPA LCCA for

drinking water fountains and taps where the second sample narrows down the source of the problem. The second action level is 10 µg/L. A 250-mL sample is taken after flushing for one minute at drinking water fountains and cold drinking water outlets exceeding the first action level. If the lead concentration exceeds 10 µg/L, then corrective actions are taken to determine the sources of lead, implement a flushing program, educate the public, replace pipes, and apply chemicals.

The MOE has an action level of 10 µg/L (MOE, 2007e). Municipalities have to take corrosion control measures if samples exceed the 90th percentile. The action level applies only to large municipal residential system and only if in two of three most recent rounds of testing, more than one percent of test results in each round exceeded the 10 µg/L standard for lead. The municipalities must prepare and submit a corrosion control plan (CCP) to MOE within one year of the sampling period during which the test results triggered the CCP requirement. For non-residential sites such as buildings and schools, more details can be found in the “Information for Municipal and Non-Municipal Owners and Operating Authorities of Drinking Water Systems on the Community Lead Testing Program” document outlining steps to be taken by owners and operators to reduce any potential health risks (MOE, 2007e).

2.3.5 Ontario Community Lead Testing Program

The Community Lead Testing program is part of O.Reg.170/03 under the Safe Drinking Water Act, 2002 (MOE, 2009). In July 2007, the regulation was revised to address concerns of elevated lead concentrations in tap water, and requires Ontario owners of municipal and non-municipal residential drinking water systems to test for lead twice per year. The two annual sampling periods are from December 15th to April 15th and from June 15th to October 15th. The results of the testing assist in determining whether a pattern of lead levels exists in drinking water for a municipality that indicates a need for action.

The following is a summary of the MOE (2009) report on the results of the Community Lead Testing Program: Round 1 (December 2007 to April 2008). The MOE prescribes that samples be taken from both residential and non-residential plumbing locations as well as distribution system locations. The sampling protocol requires five minutes of flushing followed by a 30-minute stagnation period before collecting two 1-

litre samples for each plumbing location. The number of locations depends on the population. Residential plumbing samples are obtained from volunteers who wish to participate in the testing program. Priority is placed on obtaining samples from locations where lead is present or likely to be present such as older homes in neighborhoods, and areas with lead service connections or water mains. If municipal residential systems report greater than 10% plumbing exceedances ($>10\mu\text{g/L}$) in any two out of three sampling rounds and if at least two samples in each of those two rounds exceeded the Ontario Drinking Water Quality standard of $10\mu\text{g/L}$, these systems have to implement a corrosion control plan..

The overall results from approximately 600 municipal residential and 400 non-municipal year-round residential systems had lead concentrations below the Ontario Standard of $10\mu\text{g/L}$. 97.6% of all plumbing samples (from pipes inside homes or buildings) met the standard. 97.6% of municipal distribution samples from pipes leading to homes or buildings also met the provincial standard. The vast majority of non-municipal year-round residential plumbing systems plumbing and distribution samples also met the provincial standard. 99.1% of all plumbing samples met the provincial standard. 99.6% of non-municipal year-round residential distribution samples met the provincial standard. No apparent geographical trends were observed for systems with lead exceedances. The number of plumbing samples submitted by municipalities generally met the submission requirements. However, for non-municipal year-round residential systems, the number of samples submitted was well below submission requirements. As a result, the MOE will continue to work with the local drinking water system and the public to encourage more participants in the Community Lead Testing program. More details on the results are published on the MOE website (MOE, 2009).

2.4 Lead Sampling Results for Municipalities Required to Sample Under the “Ontario Tap Water Order”

Thirty-six municipalities participated in the MOE testing for lead in tap water and distribution systems (as sampled from hydrants) from May 23, 2007 to June 7, 2007 (MOE, 2007d). These municipalities were selected by the MOE to represent all areas of the province (MOE, 2007d). The sampling protocol (Table 2.8) used was mandated by the Ontario Chief Drinking Water Inspector, and is not the same as the one outlined in

O.Reg.170/03 (MOE, 2007d). A summary of the results is shown in Table 2.9. The highest concentration of lead observed by the municipalities was 23 µg/L in the City of St. Catharines. The results indicate that just over half (55%) of the tested water systems in Ontario contained less lead than the provincial standard of 10 µg/L. Sixteen of the municipalities (45%) had lead exceedances (>10 µg/L) in their tap water samples. Each municipality selected 20 single-family homes in an area with lead service pipes or likely to have lead service pipes. However, it was not stated how “likely to have lead service pipes” was defined. Municipal personnel collected two successive 500 mL samples of cold water from the kitchen sink tap after flushing water from the cold-water tap for five minutes. According to O.Reg.170/03 (Section 2.3.3), personnel would have taken two 1-liter samples from the tap after a 30-minute stagnation period (MOE, 2007b). The differences in volume and stagnation time could affect the measured lead concentrations in the samples.

Each municipality also collected an additional set of three 500-mL samples from five different locations in the distribution system (e.g. hydrants) within the selected area and in proximity to the 20 homes that were selected for sampling as required under the “Ontario Tap Water Order” in Table 2.8. The number of lead samples taken in the distribution system by each municipality ranged from 5 to 25 samples (Table 2.9). Of the 36 municipalities tested, only Timmins had four of the nine lead samples in the distribution system that exceeded 10 µg/L with no lead exceedances in tap water samples.

Lead exceedances in tap water samples for each municipality varied in number from one to eight as shown by the frequency distribution plot in Figure 2.1. Eleven of the sixteen municipalities with lead exceedances had only one or two samples that exceeded 10 µg/L. Municipalities on the other end of the scale with seven to eight exceedances such as Trenton, Renfrew, and Smiths Falls may require corrosion control measures.

Nine municipalities had at least 10% of their samples with lead exceedances while seven other municipalities had less than 10% of their samples with lead exceedances (Figure 2.2). Peterborough had the smallest number of tap-water samples with lead exceedances at approximately 3.3% whereas Smiths Falls had the largest percentages of samples with lead exceedances at approximately 40%. Furthermore, a larger number of samples did not necessarily result in a lower percentage of samples exceeding the lead

regulation. For example, Peterborough and Brantford both collected more than 20 samples and had only one to two samples that exceeded the lead regulation. In some cases, simply collecting the required 20 samples indicated lead exceedances. For example, in municipalities such as Quinte West and Renfrew, only 20 samples were collected and seven samples exceeded 10 µg/L with a range of 0.35 to 21.6 µg/L.

Table 2.8: Sampling Methods for Ontario Municipalities Required to Sample under the “Ontario Tap Water Order”

Sample Type	Sample Method	Sample Volume	Sample Purpose
Tap Water	2 successive samples taken after flushing for 5 minutes	500 mL	1st sample tested for temperature and 2nd sample tested for lead.
Distribution System	3 successive samples from each site	500 mL	1st sample tested for pH and temperature. 2nd sample tested for alkalinity. 3rd sample tested for lead.

Source: MOE (2007e)

Table 2.9: Sixteen Ontario Municipalities with Tap Water Samples Taken Between May 23, 2007 and June 7, 2007 Above the Provincial Lead Standard of 10 µg/L

Drinking Water System	Total Sample #	% exceeding 10 µg/L
Peterborough	30	3.33%
Windsor	21	5%
Kenora	21	4.76%
Brantford	41	4.88%
North Bay	20	5%
Sault Ste. Marie	20	5%
Hamilton	21	9.52%
Kawartha	20	10%
Toronto	20	10%
Welland	20	10%
Guelph	20	15%
St. Catharines	21	19%
Quinte West	20	35%
Renfrew	20	35%
Smiths Falls	20	40%
Thunder Bay	5	40%

Source: MOE, 2007e

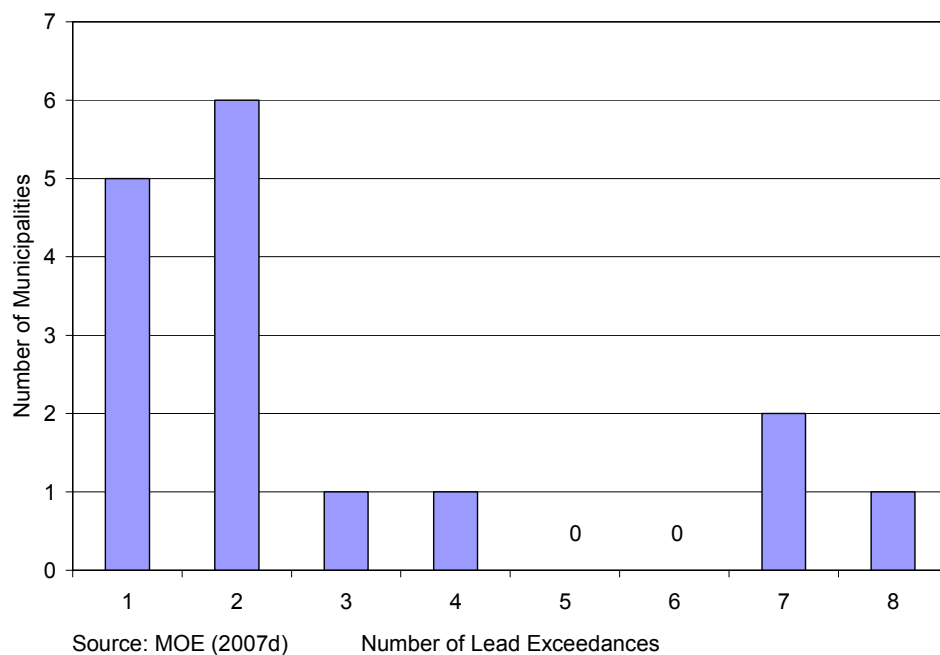


Figure 2.1: Frequency of Lead Exceedances for 36 Ontario Municipalities

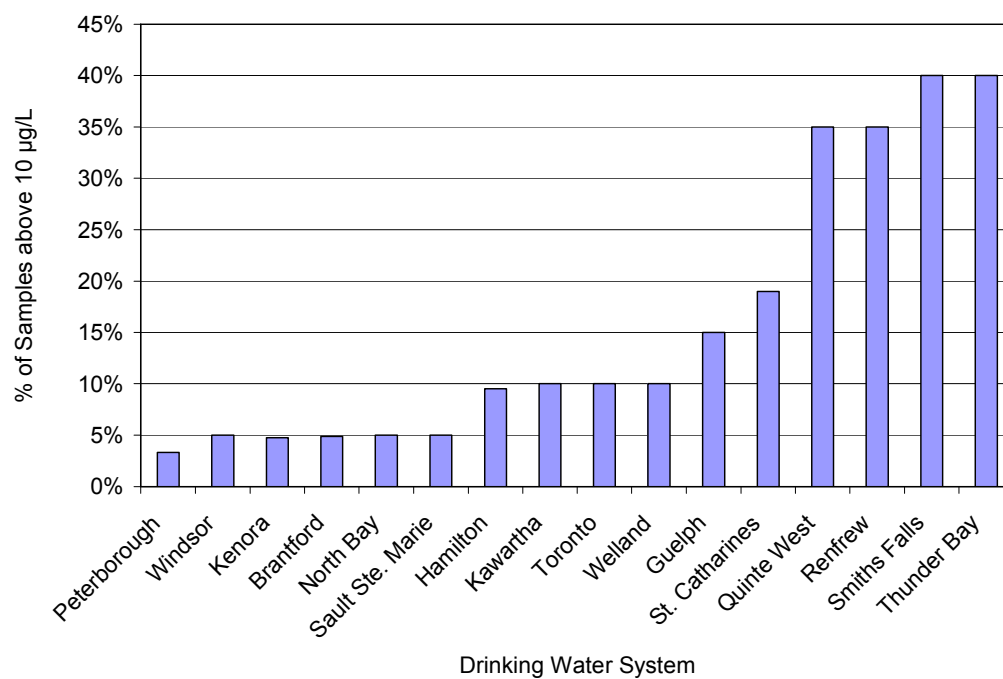


Figure 2.2: Ontario Municipalities with Lead in Tap Water Samples Above Provincial Standard of 10 µg/L

2.4.1 Smiths Falls Municipality Case Study

Smiths Falls had the highest number of lead exceedances with 8 of 20 lead measurements exceeding 10 µg/L. The raw data was analyzed to assess whether the lead exceedances at the tap occurred due to lead contributions from the distribution system. The actual lead contribution from the plumbing is calculated by taking the difference between the lead concentration in the distribution system (hydrant) and the final measured value at the tap (Table 2.10). The results show that in all cases, the lead exceedances would have occurred at the tap regardless of the contribution from the distribution system, which had lead levels as high as 1.06 µg/L (MOE, 2007d). However, despite the high number of exceedances, lead varied among homes significantly even though the water properties were identical. In other words, only certain areas in Smiths Falls exceeded the MOE regulation of 10 µg/L. In addition, not all measurements in any one site exceeded 10 µg/L. For example, four of the five measurements in Site 1 were below 10 µg/L with only one measurement at 10.39 µg/L. In some cases, the average lead measurements at a site were below 10 µg/L despite individual exceedances. The standard deviation for the lead measurements at each site ranged from 2.02 µg/L to 10.65 µg/L depending on the home, and this shows the range of variability within the same site (Figure 2.3).

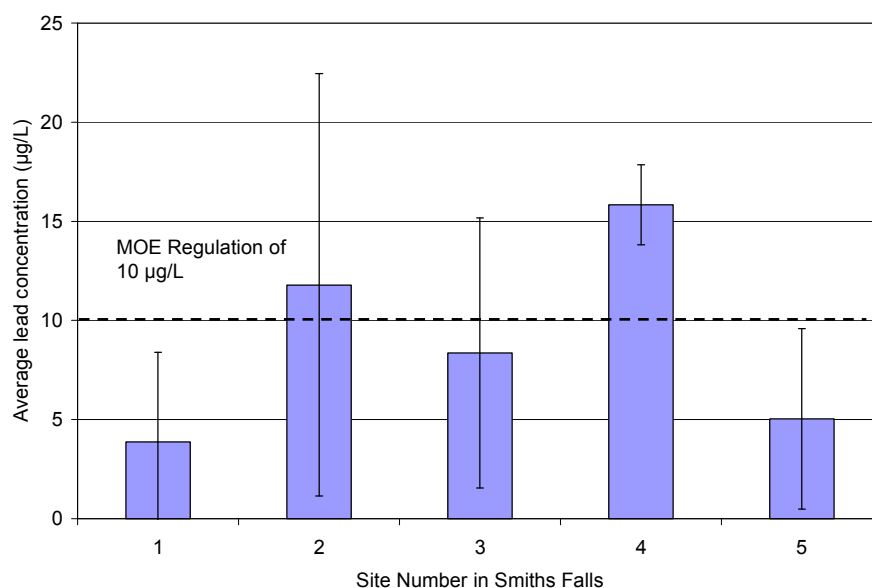


Figure 2.3: Average Lead Concentration (µg/L) at each Site in Smiths Falls (n = number of homes. Vertical bars represent standard deviation.) Source: MOE (2007d).

Table 2.10: Statistical Tap Water Data for Smiths Falls Drinking Water System

Site	Lead concentration (µg/L)		Difference (µg/L)	Average (µg/L)	Standard Deviation (µg/L)
1	Distribution	0.11	0		
	tap	7.89	7.78		
	tap	4.00	3.89		
	tap	10.5	10.4		
	tap	0.16	0.05		
	tap	0.61	0.5	3.88	4.52
2	Distribution	1.06	0		
	tap	19.0	18.0		
	tap	0.55	-0.51		
	tap	19.0	18.0	11.8	10.7
3	Distribution	0.25	0		
	tap	3.35	3.10		
	tap	16.3	16.1		
	tap	6.17	5.92	8.36	6.81
4	Distribution	0.10	0.00		
	tap	14.1	14.0		
	tap	15.6	15.5		
	tap	18.1	18.0	15.8	2.02
5	Distribution.	0.02	0.00		
	tap	5.03	5.01		
	tap	12.1	12.1		
	tap	8.78	8.76		
	tap	0.80	0.78		
	tap	1.08	1.06		
	tap	2.59	2.57	5.04	4.55

Bold = lead concentration above 10 µg/L

Source: MOE, 2007e

2.4.2 Water pH and Alkalinity

Three municipalities (Smiths Falls, Renfrew, and Quinte West) with the highest percentages of lead samples (Table 2.11) exceeding 10 µg/L (MOE, 2007d) were examined to assess any relationships between pH and alkalinity with respect to lead concentrations (Figure 2.4 and Figure 2.5). Many authors have stated that there is an inverse relationship between pH and alkalinity, and the tendency for lead to leach into water (Schock, 1989; Schock and Gardels, 1983; Britton and Richards, 1981). However, in this case, there does not appear to be a correlation between the pH values and sites with lead concentrations above or below 10 µg/L. This is shown by the low R^2 values

(0.0243 to 0.5372) in Figure 2.4. In addition, no correlation was observed between the alkalinity values and lead concentrations. Figure 2.5 shows that high alkalinity values (greater than 80 mg/L CaCO₃) were associated with lead exceedances while lower alkalinity values (less than 60 mg/L CaCO₃) often had lead concentrations below 10 µg/L. The pH and alkalinity data for the other municipalities yielded similar results (Figure 2.6 and Figure 2.7) as shown by the low R² values for pH (0.0928) and alkalinity (0.0043). In general across municipalities, locations with the same water properties had different results. The pH range (6.4 to 8.4) for the municipalities may contribute to these mixed results since studies have shown that the lowest lead concentrations occur in tap water that has a pH above 8 (Lee et al., 1989; Dodrill and Edwards, 1995; Douglas et al., 2004). In addition, insoluble tetravalent lead dioxide (PbO₂) solids were found in lead pipe deposits in several studies. This type of lead may not have an inverse relationship with pH (Schock et al., 1998; Schock et al., 2001).

Table 2.11: Water Properties (pH and alkalinity) for Smiths Falls, Renfrew, and Guelph

Smiths Falls	Site	pH	Alkalinity (mg/L CaCO₃)	# of samples with lead exceedances with corresponding lead (µg/L)			
	1	7.5	64	1	10.5		
	2	6.9	84	2	19	19	
	3	7.2	68	1	16.3		
	4	7.2	72	3	14.1	15.6	18.1
	5	7.1	72	1	12.1		
Renfrew	Site	pH	Alkalinity (mg/L CaCO₃)	# of samples with lead exceedances with corresponding lead (µg/L)			
	1	7.25	56	1	21.6		
	2	7.3	52	2	13.6	13	
	3	7.29	58	0			
	4	7.15	58	3	15	11.6	14
	5	7.24	48	1	11.8		
Guelph	Site	pH	Alkalinity (mg/L CaCO₃)	# of samples with lead exceedances with corresponding lead (µg/L)			
	1	7.6	293	2	21	11	
	2	7.7	313	0			
	3	7.8	281	0			
	4	8	283	1	14		
	5	7.7	296	0			

Source: MOE, 2007e

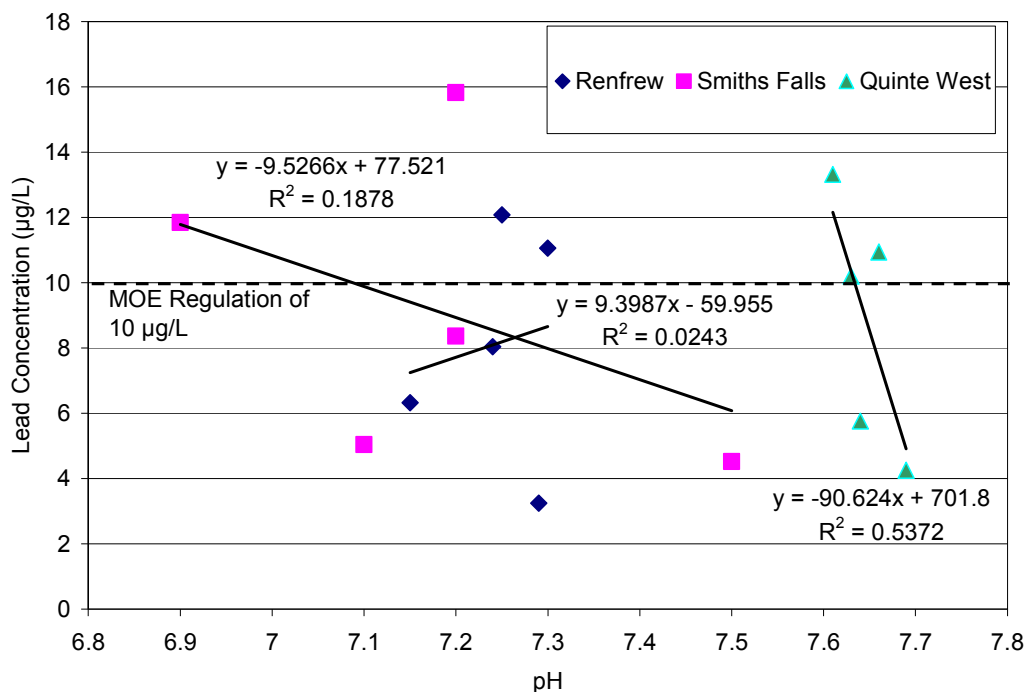


Figure 2.4: pH and lead concentrations for Renfrew, Smiths Falls, and Quinte West (Each data point indicates an average of the lead concentrations in tap water measured in different homes at each site with a total of five sites per municipality where sites with no lead detected are not shown) Source: MOE, 2007e

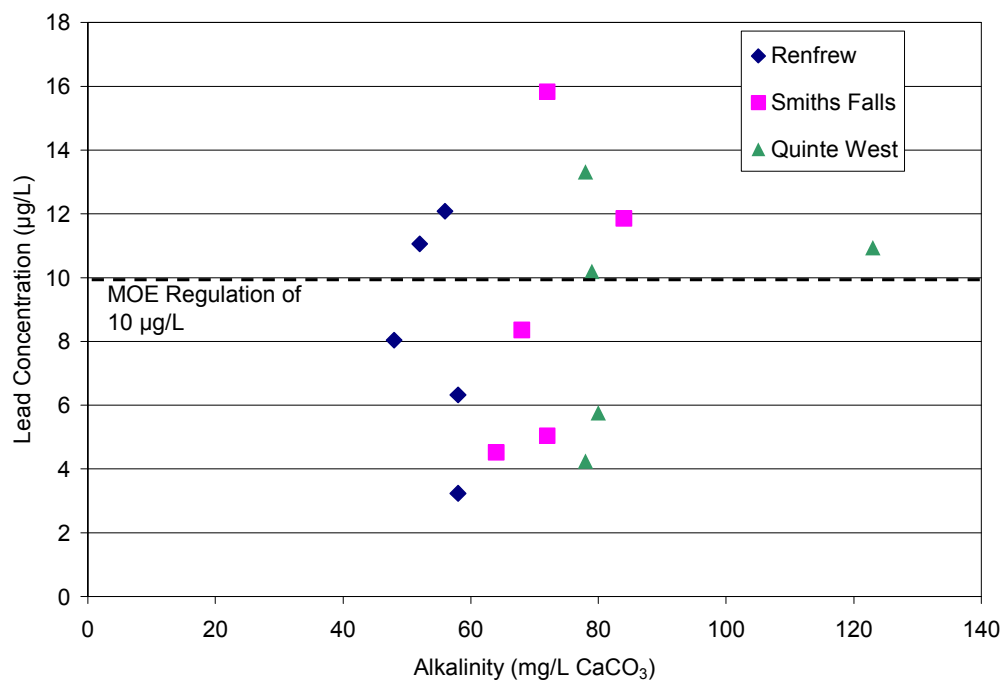


Figure 2.5: Alkalinity and lead concentrations for Renfrew, Smiths Falls, and Quinte West (Alkalinity values were measured in hydrants at each site with a total of five sites per municipality) Source: MOE, 2007e

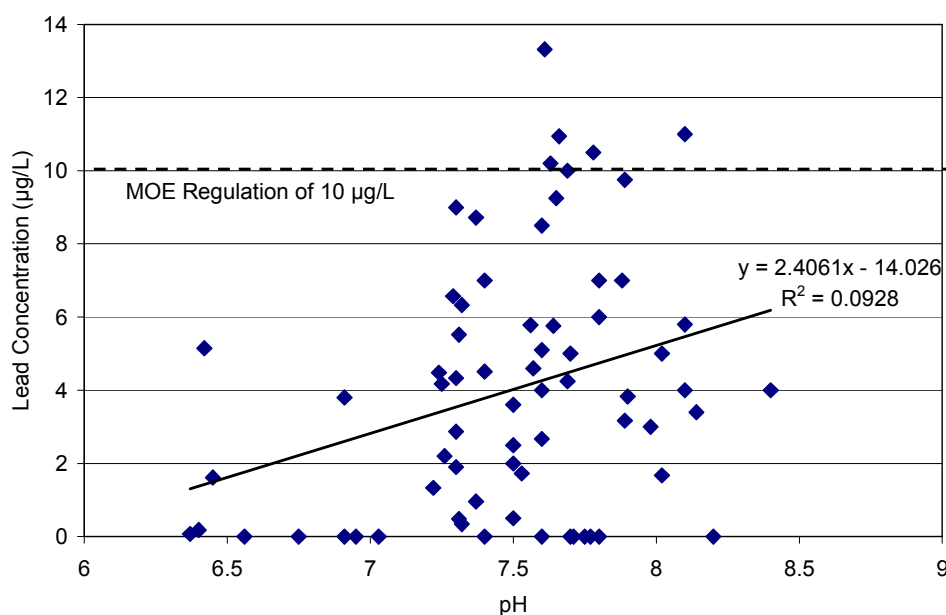


Figure 2.6: pH and lead concentrations for all municipalities except those with lead exceedances (Each data point indicates an average of the lead concentrations in tap water measured in different homes at each site with a total of five sites per municipality where sites with no lead detected are not shown) Source: MOE, 2007e

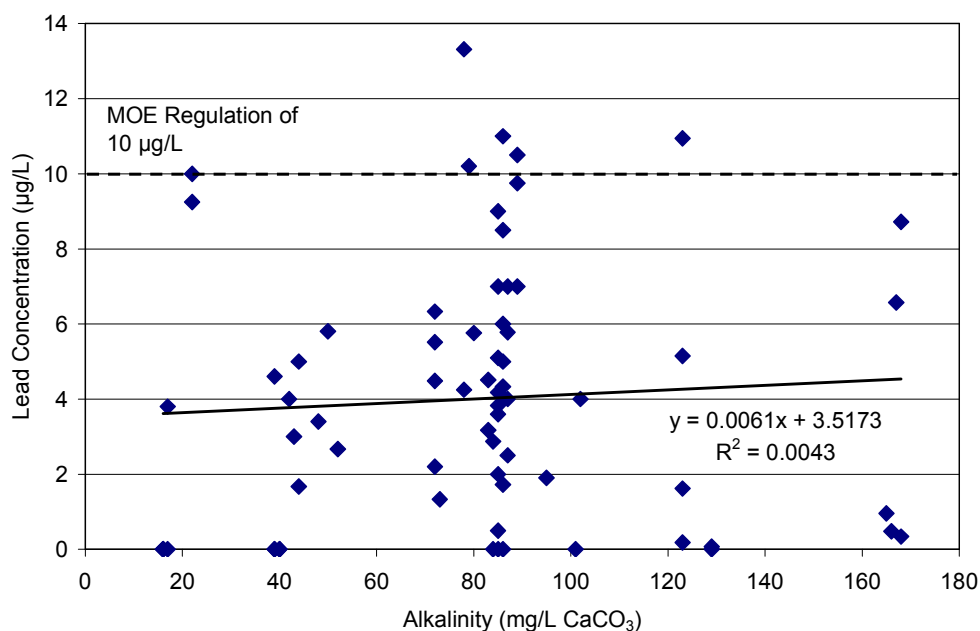


Figure 2.7: Alkalinity and lead concentrations for all municipalities except those with lead exceedances (Alkalinity values were measured in hydrants at each site with a total of five sites per municipality) Source: MOE, 2007e

2.5 Case Studies on Lead Sampling Protocols

2.5.1 Studies Conducted in Europe

In 1999, a European study tested and evaluated several sampling methods. The results are shown in Table 2.12 (Van Den Hoven, 2006). The test areas were selected on the basis of water composition (such as lead solubility, hardness, plumbing materials), and the willingness of water companies and consumers to cooperate. The six sampling procedures included: i) random daytime sampling (RDT), ii) fully flushed (FF), iii) first liter of the 30-minute stagnation sample (30MS1), iv) second liter of the 30-minute stagnation sample (30MS2), v) average of the values from the RDT and FF sampling methods, and vi) composite proportional (COMP). These methods were evaluated on the basis of representativeness, reproducibility, costs, practicality, and consumer acceptance. The first five methods were also evaluated against the composite proportional sample (COMP), which is the most accurate weekly representation. COMP covers all factors influencing average weekly lead intake of the consumer such as water quality, plumbing materials, network design, and consumer behavior. The study concluded that RDT is practical and acceptable to the consumer whereas 30MS is more reproducible and sufficient at assessing the average lead concentrations in a consumer's tap water.

Variations in lead concentrations are determined by water composition, plumbing systems, and consumer behavior. Water composition varies seasonally, and is influenced by traffic vibrations, which release lead from service pipes in short time periods. Water consumption patterns vary from day to day depending on household use. Furthermore, in two separate studies, results show that the average weekly concentration of lead in drinking water can vary considerably from week to week. (Haring, 1984; Tielemans et al., 1995; EUR19087, 1999 as cited by Van Den Hoven, 2006).

The European study in 1999 revealed a linear relationship between the sampling protocols and the composite proportional method (COMP) (EUR19087, 1999 as cited by Van Den Hoven, 2006). However, there was a poor correlation (R^2) between the various sampling protocols and COMP (Table 2.13). Reproducibility is expressed as the relative range of three samples taken at one property. The relative range is defined as the difference between the maximum value and minimum value divided by the mean value of the samples. The 30MS and FF sampling performed best in reproducibility since both

protocols reflected water composition and household variation without the variable behavior of the consumer, which influenced the results from the RDT sampling method. RDT tended to overestimate the average daily intake when compared to COMP since RDT has a stagnation time close to or higher than the actual average inter-use stagnation time. RDT is more representative of the actual water consumption pattern of the consumer. The European study concluded that each method led to different results in lead concentration, but the overall trend in lead levels was the same for all the methods.

Table 2.12: Comparison of Sampling Procedures of Lead in Drinking Water from the Tap in Europe

Procedure	Description	Time needed by sampler	Practicality	Consumer Acceptance
Composite proportional (COMP)	A device is attached to the drinking water tap, which splits off approximately 5% of every volume drawn during one week.	60-75 min	Poor	Poor
Fully flushed (FF)	A water sample is taken after flushing the tap for at least 3 plumbing volumes or several minutes.	5-10 min	Good	Good
Random daytime sampling (RDT)	Water samples are taken at a property at random times during office hours. A 1-liter sample is taken from a drinking water tap without flushing any water from the tap.	10-15 min	Good	Good
Fixed stagnation time (30MS)	Tap water is flushed for a period of time, and then water samples are taken after a stagnation period of approximately 30 minutes.	45-60 min	Moderate	Moderate

Source: Van Den Hoven et al. (2006)

The COMP procedure was found to be the most expensive in terms of time spent and equipment needed, followed by the 30MS, FF, and RDT sampling methods. The 30MS method was expensive due to the 30-minute stagnation period. Practicality was evaluated based on how easily the procedure was applied and whether specific tools were needed. Consumer acceptance refers to the willingness of a consumer to cooperate and accept disturbance. FF and RDT have high practicality and consumer acceptance (Table 2.12). However, there is a poor correlation between the FF and the COMP results. Hence, RDT may be regarded as the most practical and acceptable method to the consumer while 30MS is more reproducible.

Table 2.13: Comparison of Sampling Methods Relative to the Composite Proportional Sampling Method

Sampling Method	Slope	R ² (relative to Composite Proportional Sampling Method)
Composite proportional (COMP)	1	1
Random daytime sampling	Greater than 1	0.5-0.6
Fixed stagnation time (30 minutes)	Less than 1	0.5-0.6
Fully flushed	0.57	0.29

Source: Van Den Hoven et al. (2006)

2.5.2 Field Experiments

Field experiments were carried out in France to test and further develop three sampling protocols (RDT, FF, and 30MS) for lead in tap water (Baron, 2001). Five supply areas of France were selected based on geographical location, which is a city or a grouping within a city or of villages in a region supplied by a distribution system with the same water quality such as pH, hardness, and alkalinity. At least 60 addresses per study area were chosen at random. Three samples were taken at the kitchen cold-water taps using RDT, FF, and 30MS protocols with no COMP samples taken. The results supported the conclusions of the earlier European study. The authors concluded that RDT was more practical and acceptable to the consumer because the technician entered the home during

the day and collected the water samples with minimum disruption to the consumer whereas the collection of 30MS samples required the technician to remain in the property for a longer period of time due to the requirement for flushing and the 30-minute stagnation period. Baron (2001) stated that RDT tended to overestimate the lead levels detected by the 30MS method, but RDT was more practical and acceptable to the consumer whereas the lead levels from the 30MS method were more reproducible. Furthermore, FF sampling was not representative of the average lead concentration, but this protocol can detect the minimum lead concentration at the tap. These findings were supported by other studies in Germany (Fertmann et al., 2004; Zietz et al., 2001; Watt et al., 2000).

Haider et al. (2002) conducted a study in Vienna, Austria to compare lead levels with other locations in Europe. The researchers implemented the following sampling procedures: one sample without flushing and three further samples with flushing of 1 L, 3 L, and 10 L respectively. Using Newman-Keuls tests, Haider et al. (2002) found statistically significant decreases ($P < 0.05$) between flushing. Another study was conducted by Rajaratnam et al. (2007) on lead levels in drinking water from new housing estates in the Sydney area, Australia. Using pair-wise multiple comparison tests, findings showed statistically significant decreases ($P < 0.05$) from first-flush (first 125 mL in the morning) to post first-flush (next 1 L) to fully flushed water (125 mL taken after 2 minutes of flushing).

2.5.3 Studies in Canada and United States

Other studies have been conducted under different lead sampling programs to determine the efficiency of corrosion control measures. These studies focused on flushing the water and sampling it without a stagnation period. Two of these studies were conducted by Knox et al. (2005) and Singh et al. (1990) in the Greater Vancouver Regional District (GVRD), British Columbia. The other study was conducted by Cheng et al. (2005) in the Columbus municipality (Ohio, USA). Knox et al. (2005) found that the source water did not influence the amount of lead at the tap based on one-factor analysis of variance of the lead concentrations from four study areas each with different

source waters. In addition, seasonal temperature fluctuations (5 to 14°C) of distributed water did not affect the lead concentration in the water (Knox et al., 2005).

Based on the sampling programs in Table 2.14, both GVRD studies found that lead originates from the corrosion of the household plumbing system, as opposed to the distribution system. The conclusion was supported by the relatively higher lead concentrations in the first-draw samples (represent lead concentrations in faucet and interior plumbing system) ranging from 0 to 13 µg/L compared to the flushed samples (represent lead concentrations in distribution system) ranging from 0 to 3 µg/L collected from all four study areas in the study by Knox et al. (2005). Singh et al. (1990) had similar findings with the first-draw samples with lead concentrations ranging from 9 to 17 µg/L compared to the flushed samples with lead concentrations less than 5 µg/L. The study conducted in Columbus by Cheng et al. (2005) supported the results from the GVRD studies with the lead concentration in first-draw samples ranging from 0.20 to 20.9 µg/L, and flushed samples ranging from 0.26 to 2.10 µg/L. Knox et al. (2005) also stated that increasing the pH of the water from 6 to 7 or 8 did not affect the lead concentration. Other research by Schock (1989), and Dodrill and Edwards (1994) showed that the pH must be adjusted to above 8.4 before any significant reduction in the amount of lead in the water at the tap was observed.

2.5.4 Lead Release in School Plumbing

Boyd et al. (2008a) conducted field tests to determine the lead variability in the plumbing of Seattle public schools (SPS). The field-testing program at SPS implemented two sampling protocols, which included 384 first-draw and 384 flushed samples collected from 48 drinking water fountains over a two-month period. Samples collected from end-use plumbing configurations with brass materials (3-8% lead) had the highest average lead concentration (4.29 µg/L) and the greatest standard deviation (5.27 µg/L), whereas samples collected from low-lead bubblers and components had the lowest average lead concentration (1.38 µg/L) and the minimum standard deviation (0.71 µg/L). The lead released from new end-use plumbing components in SPS fountains was also studied by Boyd et al. (2008b). Results showed that the majority of lead contributions was from the first 50-mL drawn from the drinking water source. New end-use plumbing components

Table 2.14: Lead Sampling Program Used in Case Studies

Study	Sampling program	Reason for sampling
Greater Vancouver District (GVRD) 1 (Knox et al. 2005)	Overnight stagnation Sample 1: First water out of cold water tap (50 mL) Sample 2: Immediately following sample 1 (950 mL) Sample 3: After cold water had been running for 5 minutes (200 mL) Sample 4 (Session 1): After hot water had been running for 2 minutes Sample 4 (Session 2): First water out of hot water tap.	Sample 1: Lead in water as a result of faucet Sample 2: Lead in water as a result of building plumbing Sample 3: Lead in water as a result of water mains Sample 4: Lead in water as a result of the piping connecting the hot water tank and the faucet
Greater Vancouver District (GVRD) 2 (Singh et al., 1991)	Same sampling protocol as GVRD1 except Sample 2 is split into 2 separate samples (1 sample at 200 mL and another sample at 750 mL).	Same reasons as GVRD1.
Columbus (Cheng et al., 2005)	Overnight stagnation for 6 hours Sample 1: First water out of cold water tap (1 L) Sample 2: Flushed for a few minutes depending on pipe length and diameter of pipes and another sample taken (1 L)	First-draw sample represents the water from inside the house and the second-draw sample represents water from outside the house that had been in contact with lead service lines.

showed elevated lead concentrations ($>10 \mu\text{g/L}$) when first implemented. In addition, the researchers observed occasional spikes in lead likely due to the movement of valves and the release of metal particulates or dezincification of brass materials.

Bryant (2004) conducted another study on lead concentrations in drinking water in public schools in Philadelphia. The main finding was that 46.5% of the first-draw samples had greater than $20 \mu\text{g/L}$ of lead whereas only 13.8% of the flush samples had

greater than 20 µg/L of lead. These results suggest that lead was leaching from components of the plumbing system (brass faucets, soldering lead piping, and pipe fittings). If both first-draw and flush samples contain almost equal amounts of lead, the source of contamination is most likely behind the wall or outside of the building structure.

2.5.5 Lead Levels Before and After Lead Control Actions

A study was recently conducted by Kwan (2007) at HDR Engineering on the lead levels before and after the replacement of lead service lines in several cities in Canada and the United States. In Toronto, the total and dissolved lead concentrations were measured before and after lead service line replacement (LSLR). The lead concentration was relatively higher in the third and fourth 1-liter samples ranging from 0 to 30 µg/L than the first and second 1-liter samples ranging from 0 to 15 µg/L before LSLR, indicating that the majority of the lead contribution was from lead service lines. Recent data from the City of Ottawa also indicated that four liters would capture the LSL contribution (Douglas et al., 2007). Kwan (2007) stated that lead concentrations were relatively higher after full or partial replacement ranging from 0 to 45 µg/L due to the disruption of lead accumulations in household plumbing, but these spikes in lead concentrations would decrease and stabilize after two months to less than 10 µg/L. In Boston and Washington D.C., the situations were similar to Toronto with high (>10 µg/L) initial lead concentrations after LSLR, but with significant decreases (<10 µg/L) after one month and stabilization after two months.

Several conclusions were drawn from the field testing by Kwan (2007). Full LSL replacement does not necessarily reduce lead concentrations to zero since faucets and indoor plumbing are another source of lead in tap water. Partial replacement usually helps in reducing lead levels. Most cases show lead was in particulate form. Flushing after replacement helps scour the lead out. The method of cutting the pipes has no effect on lead release since different cutting methods had the same impact, and the release of lead was due to ground vibrations associated with excavation.

Other studies were also conducted in Canada in cities such as Winnipeg and Ottawa where the lead levels were monitored after corrosion control programs had been

implemented. In Winnipeg, a corrosion inhibitor, orthophosphate, was applied to their water. The five-minute flushing samples had lead concentrations ranging from 0 to 25 µg/L, which were relatively lower than the first-draw samples ranging from 0 to 35 µg/L (Kjartanson, 2007). In Old Ottawa South, the average lead concentrations from several sampling protocols were compared (Table 2.15). The total lead concentration at the tap is a combination of a variety of sources as outlined in Equation 1 (Douglas et al., 2007).

$$\text{Pb}[\text{total,tap}] = [\text{Pb}]\text{source} + [\text{Pb}]\text{trans,LSL} + [\text{Pb}]\text{stagnation,LSL} + [\text{Pb}]\text{trans,plumbing} + [\text{Pb}]\text{stagnation,plumbing} + [\text{Pb}]\text{particulate, scale} \quad [\text{Equation 1}]$$

Table 2.15: Average Lead Concentrations for Different Sampling Methods in Ottawa

Sampling Method	Average Lead concentrations (µg/L)
5 minute Flowing	2.7
30 minutes L1	2.6
30 minutes L2	3.0
6 hours L1	3.5

Source: Douglas et al., 2007

Douglas et al. (2007) also compared the effect of temperature on lead leaching into water. Cold-flowing water samples had the lowest lead concentration (<1 µg/L) relative to the 30-minute stagnation samples (2 to 4 µg/L) and the 6-hour stagnation samples (4 to 9 µg/L). Warm-flowing water samples also had the lowest lead concentration (<3 µg/L) relative to the 30-minute stagnation samples (3 to 8 µg/L) and the 6-hour stagnation samples (4 to 14 µg/L).

2.5.6 Particulate Lead in Potable Waters

In an U.S. study, there were cases where particles of lead such as Pb (IV) would pass through an aerator screen, and the standard U.S. EPA method of sampling under the Lead and Copper Rule could underestimate the actual amount of lead present in the water (Triantafyllidou et al., 2007). One reason is because water acidified with 0.15% HNO₃ (volume/volume) for 16 hours does not completely dissolve the lead. The researchers found that lead could be recovered at a level of 90-100% using a 2% HNO₃ (volume/volume) in-the-bottle digestion at 85-90°C after about one week (Triantafyllidou et al., 2007). Particulate lead usually comes from soldered lead-tin joints in pipe rigs

(Bisogni et al., 2000) and studies have shown that lead was present as particulates in first-draw tap water samples (McNeill and Edwards, 2004). The U.S. EPA protocol may miss a fraction of this lead. This may be a health concern because some lead particles such as Pb (IV) are bioavailable, and may be retained in the digestive tract for a long period of time Triantafyllidou et al. (2007).

Nour et al. (2007) conducted a study on particulate lead in Montreal. In this study, significant particulate lead concentrations ($>10 \mu\text{g/L}$) were observed in 4 out of 15 first-draw samples. The results showed that elevated particulate lead was mostly found in the first-draw samples of 250 mL taken with an aerator in place. However, no simple correlation was found between lead concentrations and flow rate. Flushing by one volume of interior plumbing was very efficient in reducing particulate lead. Flushing by a three-fold volume, which corresponds to approximately five minutes of flushing, was not sufficient to further reduce dissolved lead concentrations. Significant dissolved lead concentrations ($>10 \mu\text{g/L}$) were present after a short stagnation time of 30 minutes. During sampling, the release of particulate lead in Montreal water is viewed as a random event, leading to spikes in the lead concentration present in water samples. However, the frequency of these events depends on the specifics of the plumbing system and the flow hydraulics during sampling.

Another study was conducted in Montreal by Prevost et al. (2007). Extensive sampling was conducted in houses with LSLs, which included 51 wartime houses, 80 houses built before 1970, and detailed sampling in five of the above houses (impact of an aerator and impact of flow rate). The sampling protocols they implemented were flushing for five minutes, 30-minute stagnation, sampling with aerator with 1st liter (in-house premise plumbing), 2nd liter (mostly LSL), one minute of flushing (mostly main pipe), and five minutes of flushing (main feed pipe). For each sample, they measured dissolved lead (filtration on $0.45 \mu\text{m}$), total lead after acid digestion in sample bottle (>16 hours at 4°C), and total lead after aggressive digestion (48 hours at 85°C). They found that enhanced digestion required more effort, and did not reveal additional particulate lead.

2.6 Summary and Needs for Additional Research

From the above sections, several major observations can be made. First, the major lead sources appear to be from households and are primarily from solder joints. Results

from several research studies show higher lead concentrations in first-draw (first and second liter) samples relative to the subsequent samples (third and fourth liter) indicating that the majority of lead is leached from faucets and internal plumbing (Cheng et al., 2005; Knox et al., 2005; Singh et al., 1990). However, these studies did not compare overnight stagnation with the 30-minute stagnation period as suggested in the MOE protocol (O.Reg 170/03) (MOE, 2007e). The stagnation period is important since different households will have different stagnation periods. For example, some households may start using tap water earlier in the morning than other households since their work schedules may vary.

Second, particulate lead may be missed by the Canadian and U.S. sampling protocols. For example, the U.S. EPA LCR protocol gives a good representation of the amount of dissolved lead in the tap water, but not always the amount of particulate lead in the water (Triantafyllidou et al., 2007). The reason is not due to sampling methods, but rather in the preservation method as explained in Section 2.5.1. In the study conducted by Triantafyllidou et al. (2007), the researchers concluded that a higher concentration of HNO_3 (> 2% volume by volume) and a longer period of contact time (> 1 week) between the acid and the water in the plastic bottle are necessary to recover most of the lead in the water sample. The presence of particulate lead in tap water needs to be explored more carefully using the MOE and Health Canada lead sampling protocols.

Third, the presence of aerators raises an interesting concern. Particulate lead may get trapped in aerators depending on the size of the particles. The flow rate affects whether the lead particles trapped in the aerator can be flushed. Both the current MOE protocol (O.Reg 170/03) and the U.S EPA Lead and Copper Rule state that the aerators should be left on when sampling lead in tap water (U.S. EPA, 2008; MOEd, 2007). Health Canada does not mention aerators in their document on Corrosion Control in Drinking Water Distribution Systems. Hence, the influence of flow rate and aerators on the release of particulate lead into water should be further investigated.

Fourth, one of the major challenges of the proposed Health Canada guideline is the lack of experience sampling at the tap. Stagnation samples cannot be taken by the homeowner, and certified technicians are required. In addition, stagnation sampling is considered onerous and expensive by utilities. There is also a lack of customer

cooperation. Therefore, there is a need to come up with an accurate sampling protocol that is acceptable to both the consumers and the utilities.

Finally, a 30-minute stagnation period may underestimate the measured lead levels in tap water (Lemieux, 2007). A study conducted by Kuch and Wagner (1983) showed that maximum lead concentrations are reached after several hours of stagnation. However, the current MOE protocol uses a stagnation period of 30 minutes. Lead levels approach a maximum at more than 300-400 minutes (5-6.7 hours) depending on the size of the pipe (1/2"(12.7mm) and 3/4"(19.1mm) respectively). The LSL in Canada is generally 5/8"(15.9mm) and 3/4"(19.1mm) (Lemieux, 2007). Changing the sample volume can increase or decrease the lead value, depending on the lengths of leaded and unleaded supply pipe (Cardew, 2000). There is also a question about the representativeness of lead concentrations after a 30-minute stagnation period. First-draw stagnation times may be more appropriate since people may not flush the water out by showering early in the morning and consume the water instead (Palleja et al., 2001).

3. STATISTICAL ANALYSIS OF FACTORS AFFECTING LEAD CONCENTRATIONS IN TAP WATER FOR TWO CITIES IN ONTARIO, CANADA

3.1 Introduction

As a result of the introduction of the Ontario Ministry of the Environment regulations on lead sampling in municipalities (MOE, 2007a), there is a growing interest in reducing lead in tap water. Even though municipalities have sampled for lead in the past, these new regulations have created a greater need to analyze historical data in order to identify temporal trends and correlations in lead concentrations and examine the impact of corrosion control strategies. This study compares such data across and within the Cities of London and Ottawa, Ontario using statistical analysis.

Statistical analysis has been used by other researchers to analyze lead data in both pipe loop and field studies. However, Wysock et al. (1995) demonstrated that past laboratory and field corrosion studies by the US Environmental Protection Agency (U.S. EPA) evaluated using parametric statistical tests could be inadequate when the data were highly variable and non-normally distributed, which is typically the case. It is important to apply appropriate statistical procedures for data evaluation of corrosion studies in order to interpret the results correctly. A non-parametric statistical approach has been adapted by various researchers to evaluate pipe-loop studies (AWWARF, 1994; Cantor et al., 2003; Eisner and Gagnon, 2003; Boyd et al, 2004). Other researchers have also applied non-parametric statistics to analyze the effect of lead in tap water on blood lead in children (Meyer et al., 1998; Meyer et al, 2003), and factors affecting lead in house dust in Germany (Meyer et al., 1999a; Meyer et al., 1999b). However, little research has been published on the use of non-parametric statistics to analyze historical lead in tap water data.

To determine if parametric and non-parametric tests should be used, a test of normality using the 1-sample Kolmogorov-Smirnov test was suggested by Wysock et al. (1995). In addition, Wysock et al. (1995) also recommended the use of the Mann-Whitney U-test for statistical difference since lead data is usually non-parametric. These tests make no assumptions of the data and therefore no evaluation of normal (Gaussian)

distribution of data is necessary (Sharaf et al., 1986). The Mann-Whitney U-test has been applied by Cardew (2000) and Van Der Leer et al. (2005) to quantify the effects of corrosion inhibitors.

The City of Ottawa collected extensive data for homes sampled across the city from 1997 to 2008. The City of London sampled nine homes repeatedly from 2007 and 2009 and collected additional data for 110 homes from 2007 to 2009 as part of the requirements of O.Reg. 170/03 for the Community Lead Testing Program.

3.2 Research Objectives

The objective of this study was to analyze lead data from both London and Ottawa to identify trends in order to better design sampling protocols and corrosion control strategies.

3.3 Methods

3.3.1 Data Collection

Field data were obtained from the City of Ottawa for 1997 to 2008 and the City of London for 2007 to 2009 using a range of sampling protocols. For both cities, water quality parameters measured for each home where a fully-flushed sample was collected included lead, pH, and temperature. However, London measured free chlorine whereas Ottawa measured total chlorine (chloramine residual). Average lead concentrations from this protocol and the number of homes sampled each year are shown in Table 3.1 for the City of Ottawa. Maps showing the homes in Ottawa sampled for 1997 to 2008 are presented in Figures 3.1a, 3.1b, and 3.1c and London sampled for 2007 to 2009 are shown in Figure 3.1d. In 2002, tap water samples obtained from old homes in Ottawa (built before 1953) indicated elevated lead levels ($>10 \mu\text{g/L}$). The City of Ottawa changed its corrosion control strategy by increasing the pH of the treated water from 8.5 to 9.2 on August 31, 2002. Ottawa data collected between 2006 and 2008 included lead measurements from extended 30-minute and 6-hour stagnation sampling protocols for some homes (Campbell and Douglas, 2008). These sampling protocols consisted of eight 1.0 litre samples collected immediately following a 30-minute stagnation (30MS) period followed by a 6-hour stagnation (6HS) period and the collection of an additional eight 1.0

litre samples. The purpose of these sampling protocols was to help define the source of peak lead concentrations (1st and 2nd litres are assumed to be from the faucets and fittings; 3rd, 4th, and 5th litres from the homeowner's piping; 6th, 7th, and 8th litres from the watermain).

The London data gathered from 2007 to 2009 included nine sentinel homes where samples were collected 11 times (Huggins, 2008). These homes were chosen based on a range of low initial lead levels (4.62µg/L) to high initial lead levels (64.1µg/L) Two of the homes also had the watermain replaced, but the homeowner's portion retained a lead service line. In addition, three rounds of lead testing (December 2007 to April 2008, June 2008 to October 2008, December 2008 to April 2008) as part of the Community Lead Testing Program (MOE, 2007a), was included in the dataset.

Table 3.1: 1997 to 2008 Ottawa dataset.

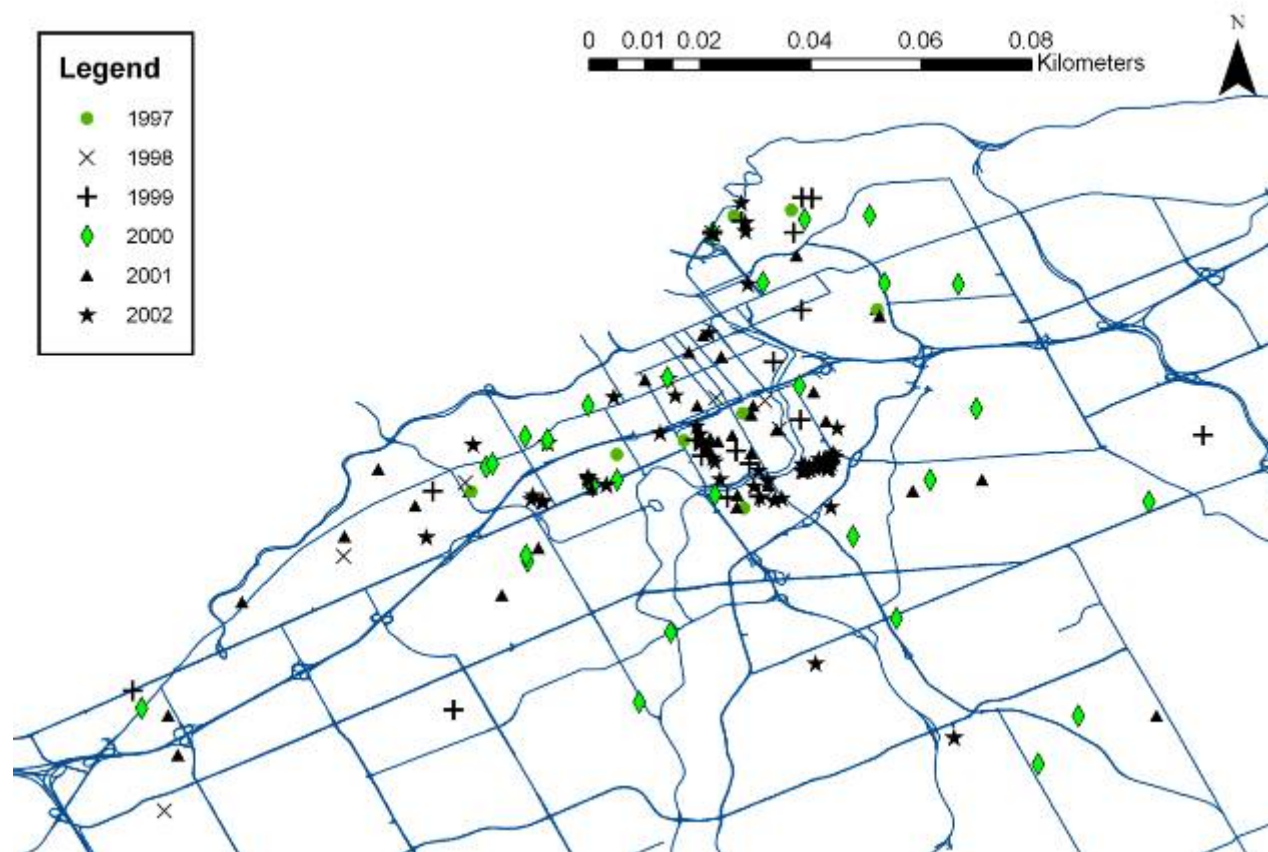
Year	Number of Homes Sampled	Average Lead Concentration (µg/L)
1997	17	2.7
1998	15	1.4
1999	30	1.5
2000	56	1.7
2001	75	1.6
January to August 2002 (pH 8.5)	114	6.8
September to December (pH 9.2)	390	4.9
2003	228	3.8
2004	81	1.4
2005	62	1.4
2006	125	1.4
2007	1258	1.3
January to August 14, 2008 (pH 9.2)	301	1.4
August 15 to August 27, 2008 (pH 9.5)	14	3.3
August 28 to September 18, 2008 (pH 9.2)	16	3.1

3.3.2 Statistical Methods

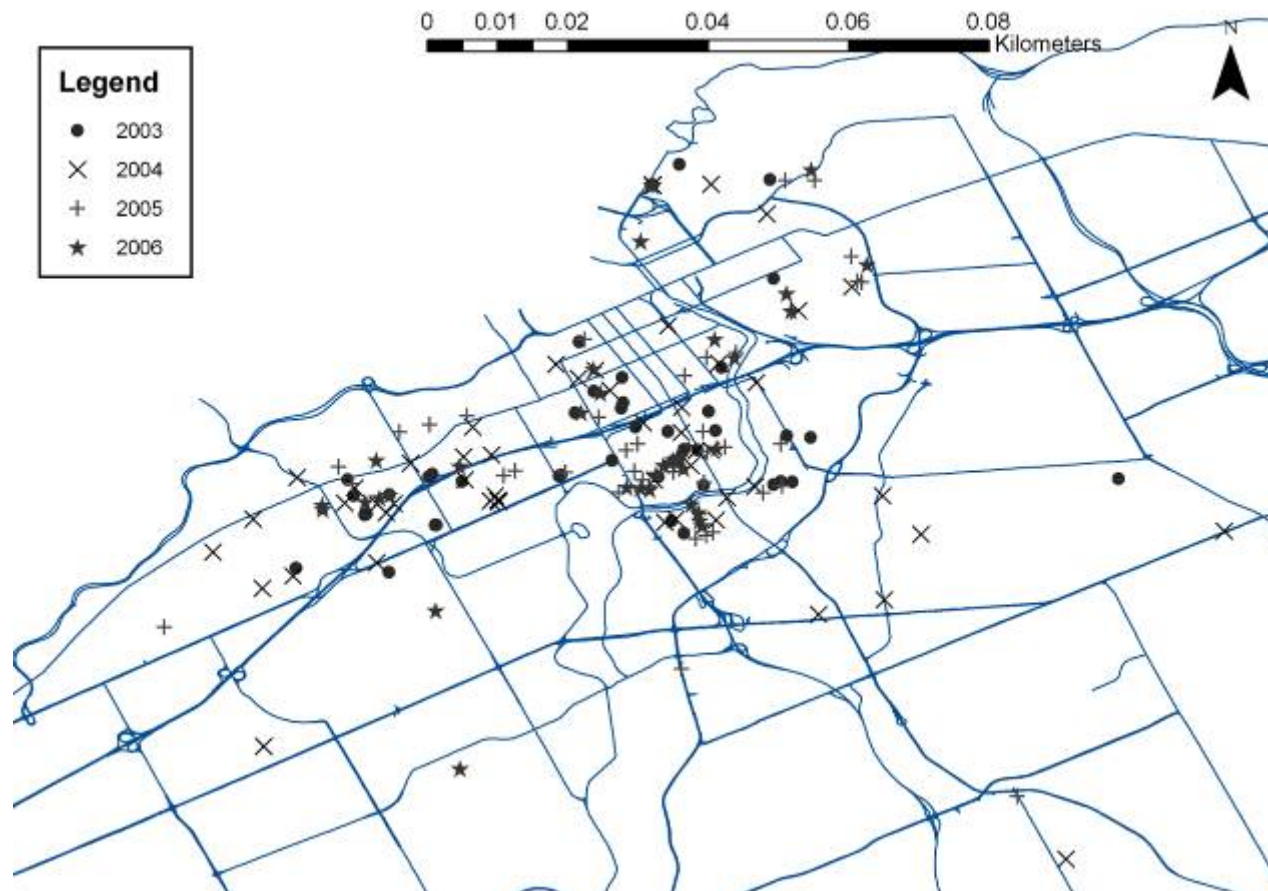
3.3.2.1 Test of Normality

Prior to any statistical analyses, a test of normality was performed on individual water quality parameters (lead concentration, total chlorine, free chlorine, pH, and temperature) to determine whether parametric or non-parametric tests should be

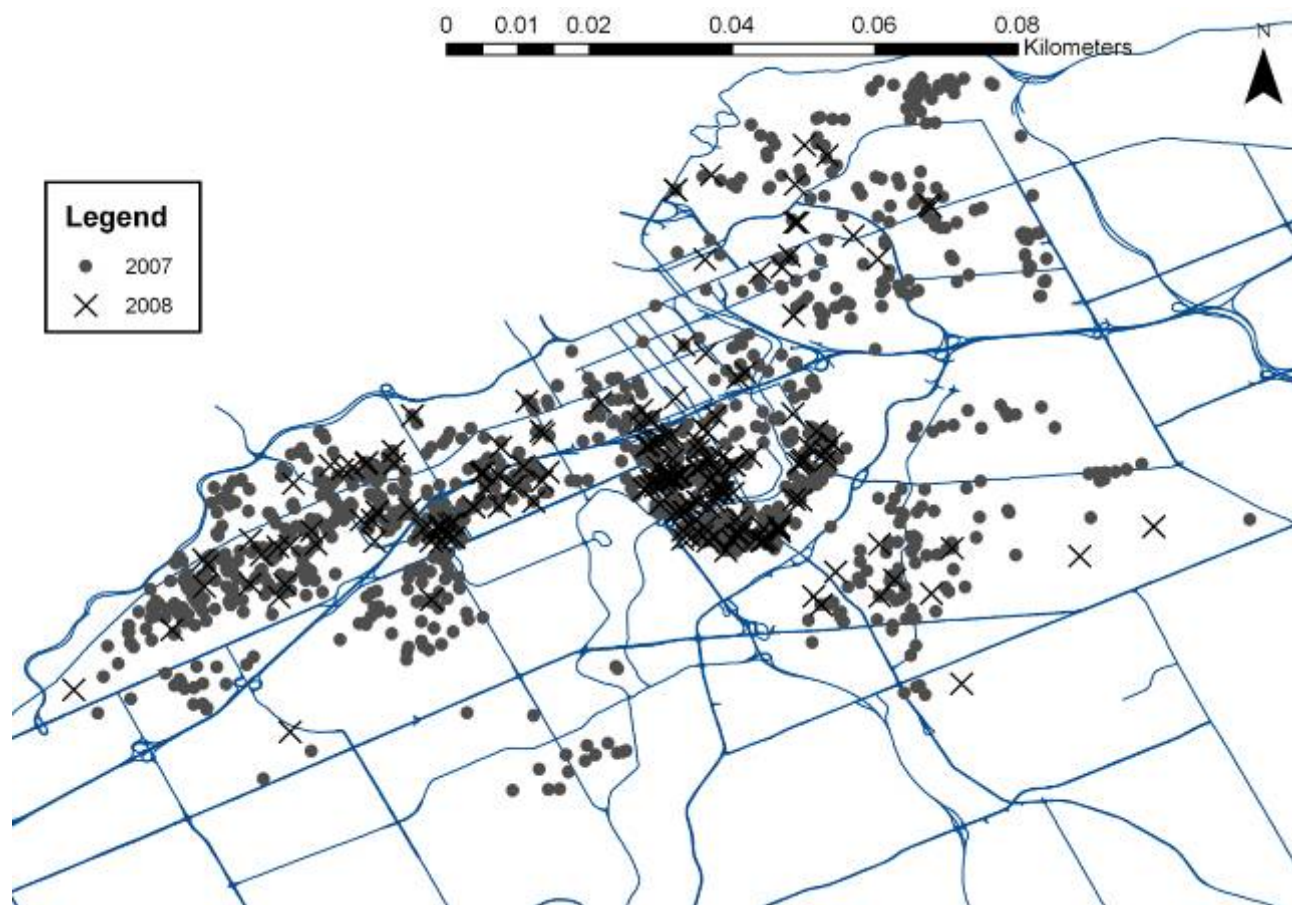
(a)



(b)



(c)



(d)

44

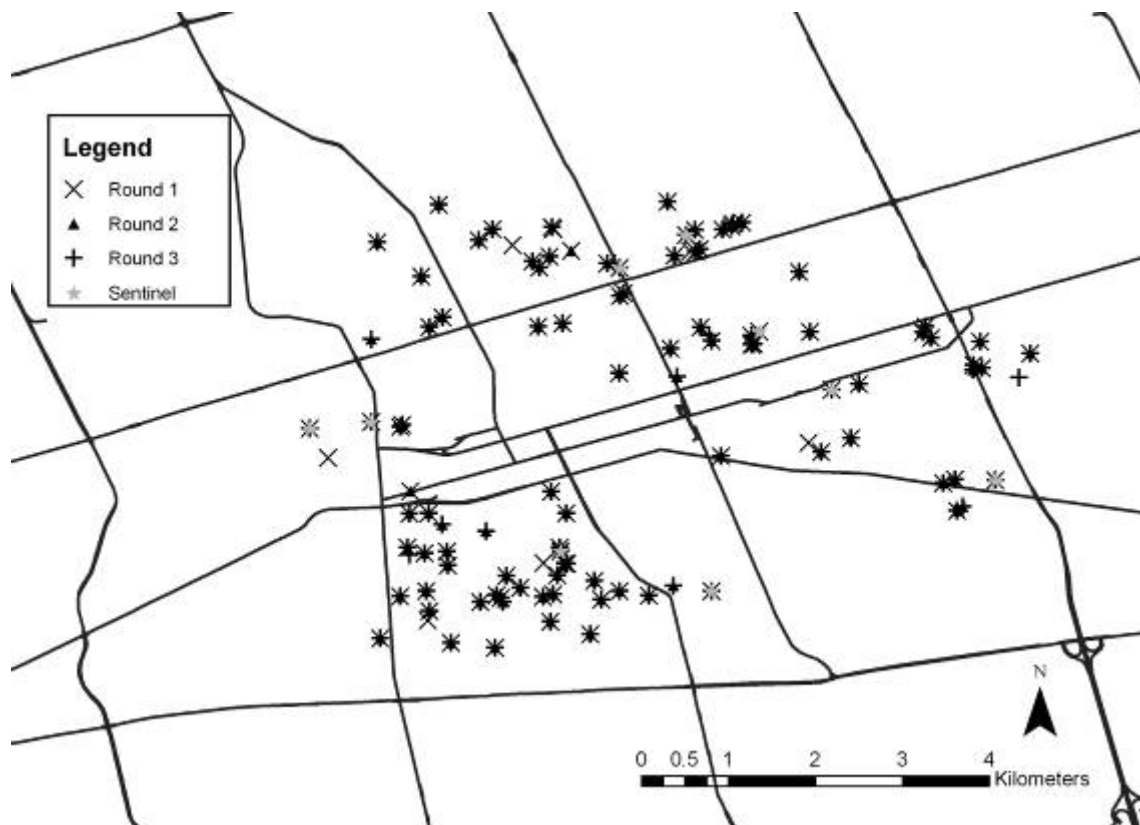


Figure 3.1: Homes sampled in City of Ottawa for lead in tap water (Generated using ArcGIS 9.3) (a) 1997 to 2002 (b) 2003 to 2006 (c) 2007 to 2008 (d) City of London: Round 1 - December 2007 to April 2008. Round 2 - June 2008 to October 2008. Round 3 - December 2008 to April 2009. Sentinel homes were sampled repeatedly from 2007 to 2009.

conducted when making comparisons between two groups of data. To determine whether parametric tests could be used, the 1-Sample Kolmogorov-Smirnov procedure was used to test the null hypothesis that a sample comes from a normal distribution. Non-parametric tests do not make any assumptions about the parameters such as the mean and variance of a distribution (Ho, 2006).

Using SPSS 16 for Windows (SPSS Inc., Chicago, IL), a test of normality (1-Sample Kolmogorov-Smirnov) was performed on each parameter. Results showed that only the total chlorine (chloramine residual) had a P-value < 0.05 suggesting that this variable followed a normal distribution. The remaining parameters did not follow a normal distribution with P-values > 0.05 .

3.3.2.2 Test for Statistical Differences

The non-parametric Mann-Whitney U-test was used to test different subsets of the Ottawa data from 1997 to 2008 for statistical significance at the 95% confidence level to determine if two sets of data are different. This statistical test is used for unpaired samples, and does not require any assumptions to be made about the population's distribution. The main assumption of the Mann-Whitney test is that the two samples are randomly and independently drawn (Lowry, 2008). Since this test can be carried out on unpaired data, it is possible to compare a set of n_1 values (corresponding to samples before a change in water quality (e.g. pH increase) with a set of n_2 values (corresponding to samples after the change in water quality) where n_1 does not have to be the same as n_2 . Since the house address and the time of day varied for each sample collection, the data points are treated as unpaired samples.

3.4 Results and Discussion

Lead data from the City of Ottawa and the City of London were examined through statistical analysis for trends and correlations. First, the historical lead concentrations were analyzed to determine if there were any changes in the observed lead concentrations from year to year. Second, the effect of temperature on lead concentration was examined by dividing the dataset into three temperature ranges from 0 to 5°C, 5 to 15°C, and $>15^\circ\text{C}$ to represent the effects of summer and winter seasons. Third, the effect of a pH change on lead concentrations in August 2002 from 8.5 to 9.2 was examined for

the City of Ottawa. Fourth, the effect of monitoring intensity was examined. Fifth, the lead concentrations associated with three different sampling protocols were compared. Sixth, the effect of partial lead service line replacement on reducing lead concentrations was examined. One difficulty in analyzing the dataset is that different homes that were monitored from year to year.

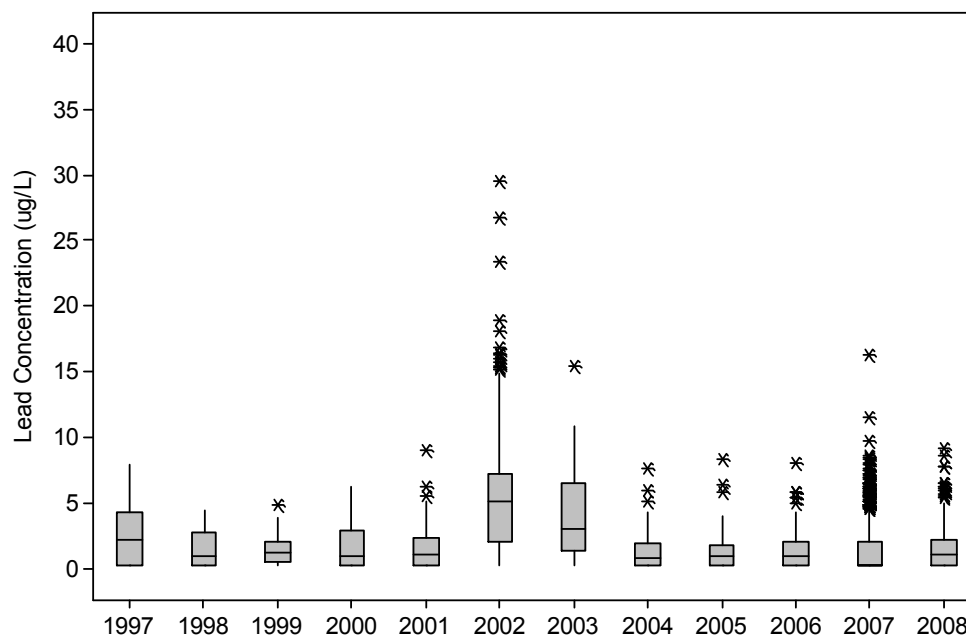
3.4.1 Historical Changes in Lead Concentration

Lead concentrations in Ottawa from two consecutive years were compared using the Mann-Whitney U-test to observe if there were any changes from year to year prior to the pH increase in August 2002 for corrosion control (Table 3.2). Lead concentrations from 1997 to 2002 prior to the pH change were not found to be statistically significant at the 95% confidence level. This level of significance was subsequently applied unless otherwise noted. Years following 2002 revealed significant differences in lead concentrations, most likely due to the selection of homes sampled since older homes built before the mid-1950s are more likely to have lead pipes (MOE, 2007a). Box plots (also called box-and-whisker plot) of lead concentrations for Ottawa from 1997 to 2008 and for London from 2007 to 2009 are shown in Figures 3.2a and 3.2b respectively. Box plots provide a visual impression of the location and shape of the underlying distributions (Montgomery and Runger, 2003). The line across the box represents the median, whereas the bottom and top of the box show the locations of the first and third quartiles (Q_1 and Q_3). The whiskers are the lines that extend from the bottom and top of the box to the lowest and highest observations inside the region defined by $Q_1 - 1.5(Q_3 - Q_1)$ and $Q_3 + 1.5(Q_3 - Q_1)$. Asterisks indicate points with values outside these limits (outliers). For example, box plots with long whiskers at the top of the box such as the years 2002 and 2007 (Figure 3.2a) indicate that the underlying distribution is skewed towards higher lead concentrations. By inspecting these plots, it is also possible to compare differences in lead concentrations among the years. For example, there is a greater spread in lead concentrations in the years 1997, 2002, and 2003 as shown by the larger size of these boxes relative to the years 1998 to 2001 and 2004 to 2008 (Figure 3.2a). These box plots also indicate homes with lead concentrations above 10 µg/L as outliers (asterisk).

Table 3.2: Comparison of statistical significance of lead data from 1997 to 2008 using a five-minute fully flushed protocol.

Dataset Number	Year 1 (Homes Sampled)	Year 2 (Homes Sampled)	Statistically Significant ($P < 0.05$)
One	1997 (17)	1998 (15)	No
	1998 (15)	1999 (30)	No
	1999 (30)	2000 (56)	No
	2000 (56)	2001 (75)	No
	2001 (75)	2002 before pH change (114)	Yes
Two	2002 before pH change (114)	2002 after pH change (390)	No
	2002 after pH change (390)	2003 (228)	Yes
Three	2003 (228)	2004 (81)	Yes
Four	2004 (81)	2005 (62)	No
	2005 (62)	2006 (125)	No
	2006 (125)	2007 (1258)	No
	2007 (1258)	2008 (331)	Yes

(a)



(b)

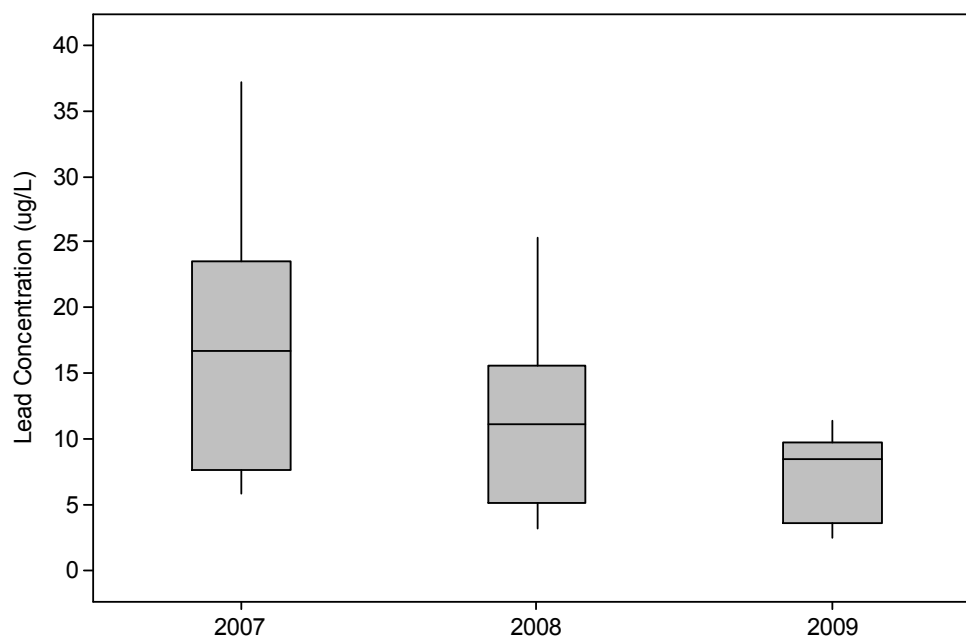


Figure 3.2 Box plot of historical lead concentrations (a) 1997 to 2008 (Ottawa) and (b) 2007 to 2009 (London).

3.4.2 Effect of Temperature Change

Temperature influenced the observed lead concentrations for both Ottawa and London. The entire Ottawa dataset (1997 to 2008) was separated into three temperature ranges (0 to 5°C, 5 to 15°C, and >15°C) to assist in isolating any effect of summer and winter temperatures on lead concentrations. Box plots of lead concentrations indicated a larger spread as temperature increased as noted by the higher number of outliers at temperatures (>15°C) (Figure 3.3a). Furthermore, a Mann-Whitney U-test showed a statistically significant difference when comparing lead concentrations at the temperature range (>15°C) to those at both (5-15°C) and (0-5°C). A significant difference in lead concentration was not observed between (0-5°C) and (5-15°C). Similarly, Knox (2003) also reported that there was no significant difference in lead concentrations for water samples collected during the summer (12-14°C) when compared to those collected during the winter (5-6°C) in Vancouver, Canada. These results suggest that higher lead concentrations occur at temperatures > 15°C.

Results from the 2007 to 2009 London lead data support the trends observed for

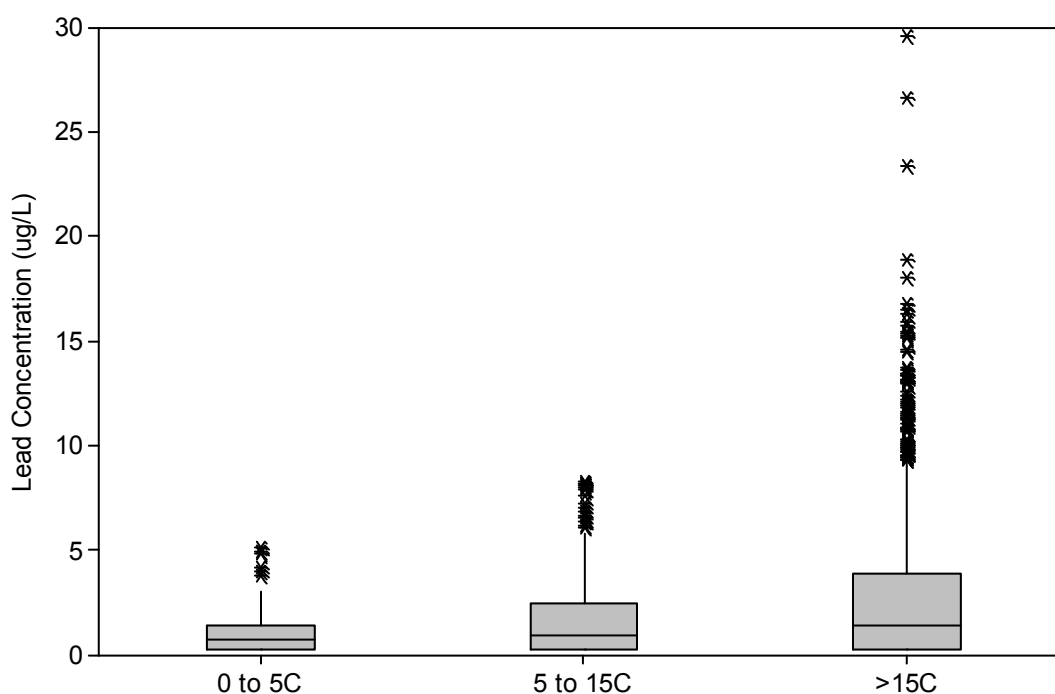
in Ottawa at the same temperature ranges (0 to 5°C, 5 to 15°C, and >15°C) (Figure 3.3b). Higher temperatures resulted in higher lead concentrations with a significant spike at temperatures > 15°C.

For the same temperature ranges, the Ottawa data was further divided into subsets representing periods before and after a pH increase to examine whether this influenced lead concentrations. The Mann-Whitney U-test showed that the change in lead concentration was significantly lower for temperatures > 15°C after the pH increase from 8.5 to 9.2 in August, 2002 (Table 3.3). Furthermore, at both pH values of 8.5 and 9.2, increases in water temperature resulted in significantly higher lead concentrations.

Table 3.3: Effect of temperature range before and after pH increase from 8.5 to 9.2 (0.3 µg/L data removed)

Water Temperature Range (°C)	Average [Pb] at pH 8.5 (µg/L)	Average [Pb] at pH 9.2 (µg/L)	Statistically Significant (p<0.05)
0 to 5	1.2	1.01	No
5 to 15	1.58	1.7	No
>15	5.1	2.4	Yes

(a)



(b)

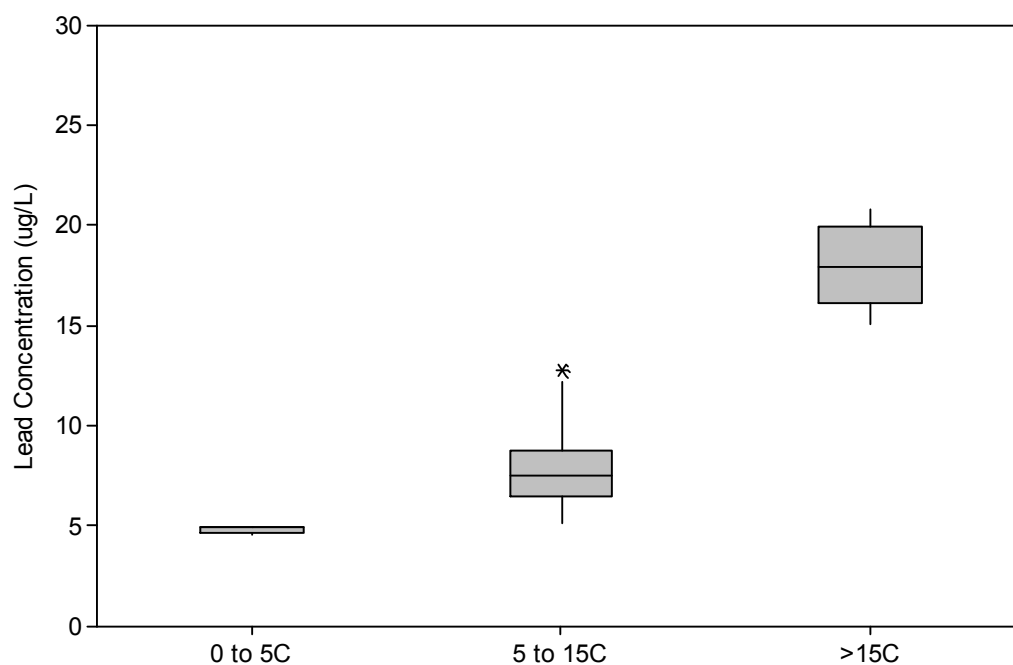


Figure 3.3 Box plot of lead concentrations at different temperatures (a) Ottawa and (b) London.

3.4.3 Effect of pH Change

The Ottawa dataset from 1997 to 2008 was divided into subsets to examine the effect of pH on lead concentration for different periods, prior to and after the increase from 8.5 to 9.2 in August 2002 (Figure 3.4). Box plots of lead concentrations at a pH of 8.5 and 9.2, suggests a decrease in lead concentration at higher pH (Figure 3.5). To confirm this observation, a Mann-Whitney U-test was used to compare the lead data before the pH change (1997 to August 2002) and after the pH change (September 2002 to 2008). Results showed a statistically significant decrease in the average lead concentration of 2.63 $\mu\text{g/L}$ (pH 8.5) to 1.70 $\mu\text{g/L}$ (pH 9.2) suggesting that increasing the pH was an effective means to reduce lead concentrations.

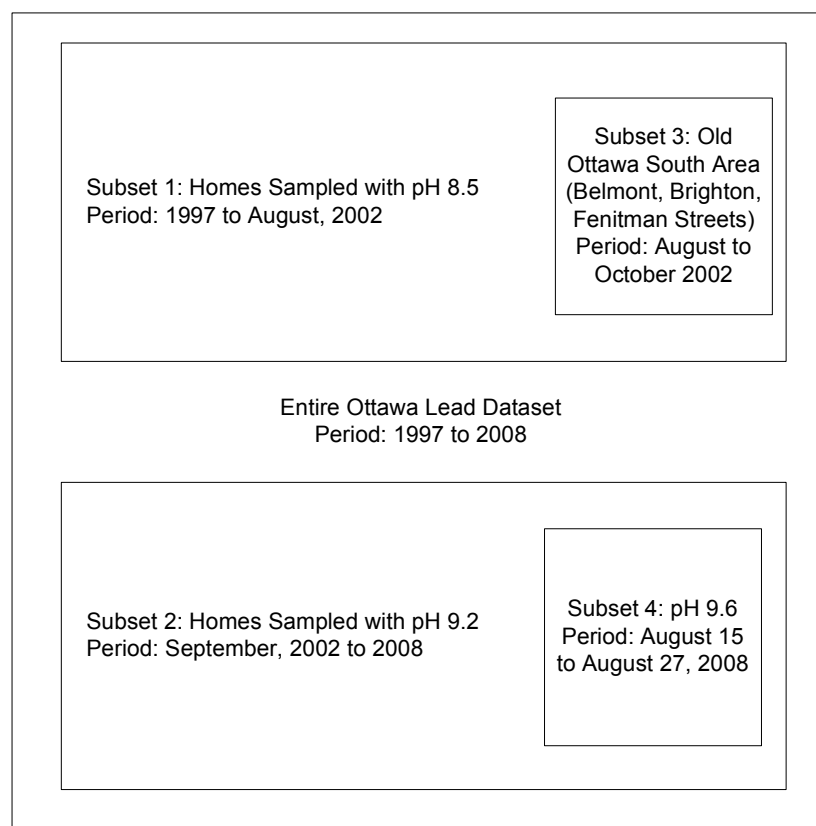


Figure 3.4: 1997 to 2008 Ottawa dataset division into subsets.

The previous comparison of lead concentrations before and after the pH change included an area known as Old Ottawa South (Homes on Belmont, Brighton and Fenitman Streets). This area consists of older homes built in the 1950s with lead pipes, and higher lead concentrations ($>10 \mu\text{g/L}$) were historically measured here when compared to other areas in the City of Ottawa. By removing these homes from the analysis, a statistically significant decrease in lead concentrations from $1.8 \mu\text{g/L}$ (pH 8.5) to $1.4 \mu\text{g/L}$ (pH 9.2) was still observed (Figure 3.5). However, only 8% of the same homes were sampled both before and after the pH increase, which means that 92% of the homes were different and as such the results may not be directly comparable.

There also exists a possible confounding effect between temperature and pH. For example, the reduction in lead concentration in 2002 may have been due to the pH increase in August 2002 or due to a decrease in temperature. To reduce the potential effect of temperature on observed lead concentrations, the standardized residuals were obtained from a scatter plot of Temperature vs. Lead Concentration through a regression

trend line (Figure 3.6). These standardized residuals were then compared using a Mann-Whitney U-test for before and after the pH change in August 2002, and was found to be statistically significant suggesting that the pH change was effective in reducing lead concentrations.

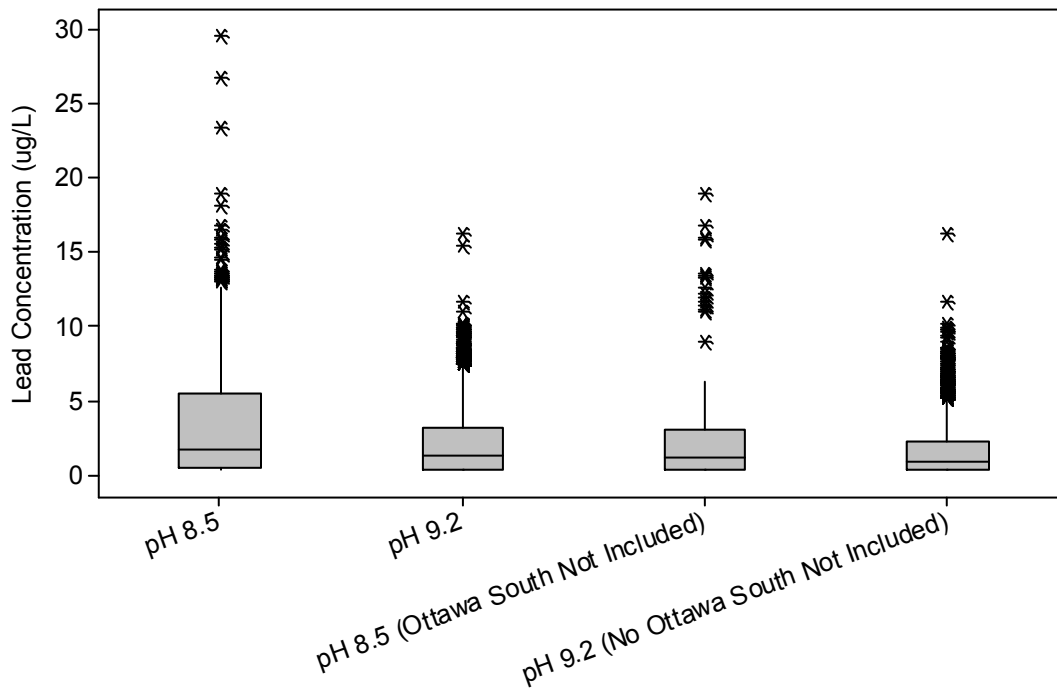


Figure 3.5: Box plot of lead concentrations at pH values of 8.5 and 9.2 with and without Old Ottawa South dataset.

In particular, Old Ottawa South was isolated from the rest of the homes in the Ottawa dataset to examine the effect of pH change on lead concentrations for this specific area (Subset 3). First, a comparison of lead concentrations was made for the two-week period before and after the pH increase. The average decrease in lead concentration from 8.4 $\mu\text{g/L}$ to 5.3 $\mu\text{g/L}$ was statistically significant (Figure 3.7), indicating that the pH increase exerted a positive impact. Second, in the weeks following the pH change in August 2002, there was no significant difference between the lead concentrations in September and October associated with continued maintenance of pH 9.2.

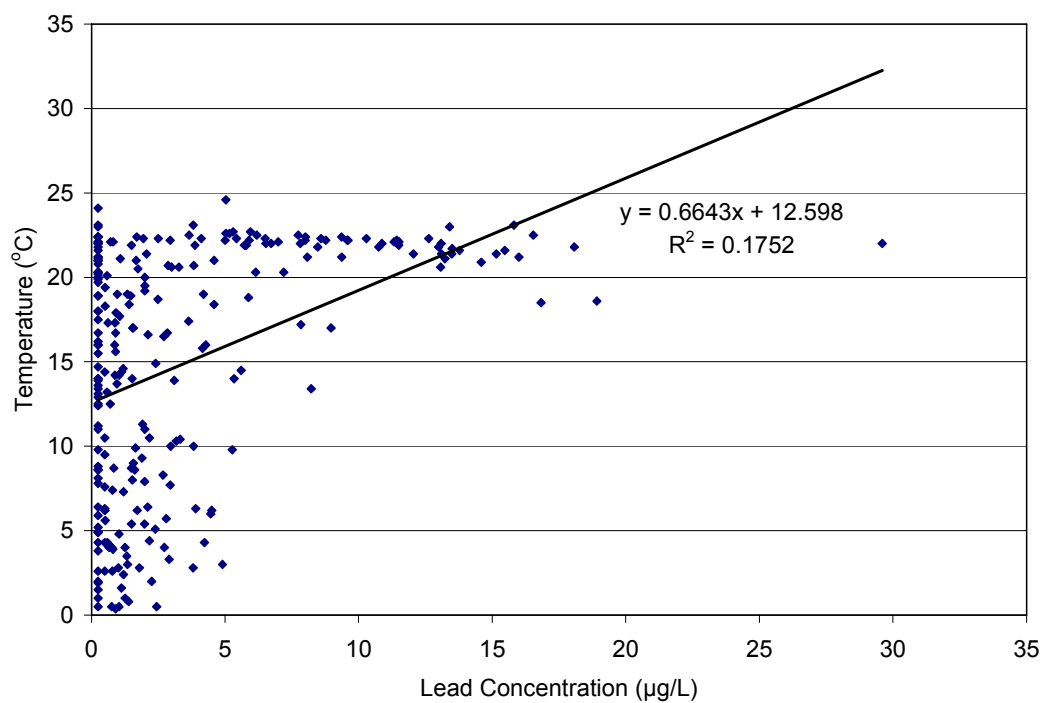


Figure 3.6: Scatter plot of lead concentrations vs. temperature.

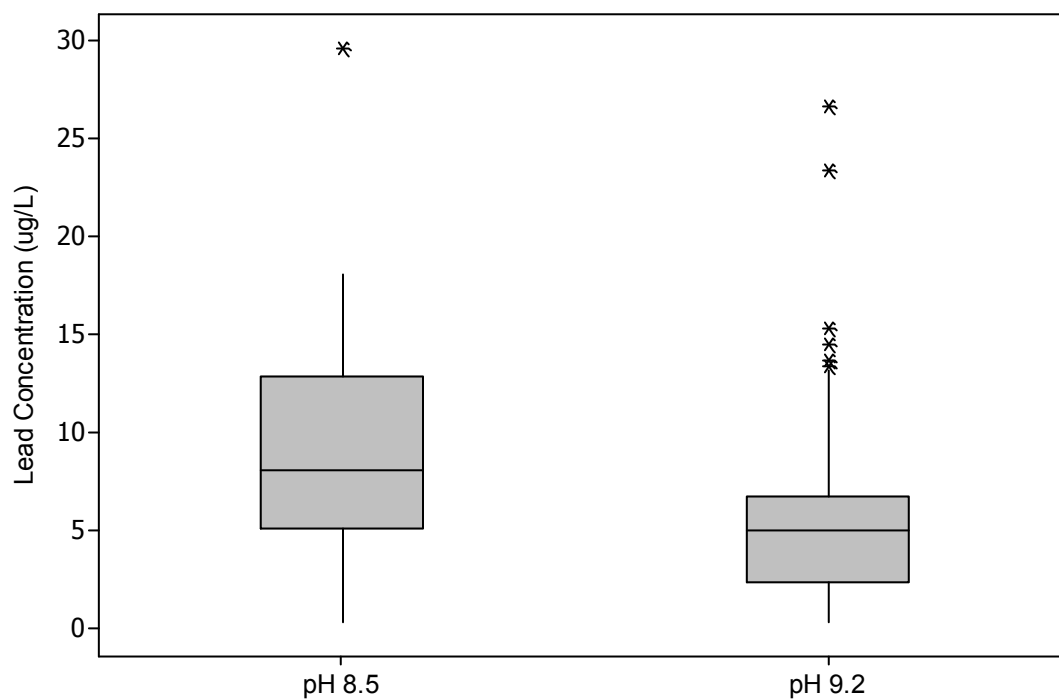


Figure 3.7: Box plot of lead concentrations at pH values of 8.5 and 9.2 in Old Ottawa South.

Another comparison of lead concentrations was made for homes sampled at a pH of 9.2 in 2008 versus homes sampled at a pH of 9.6 during the summer of 2008 from August 15 to August 27 to assess the significance of this for the pH increase on lead reduction (Subset 4). August was chosen since lead solubility tends to increase at higher temperatures (Colling et al., 1992; Schock, 1990). The average lead concentrations for homes sampled in 2008 prior to the increase (3.2 $\mu\text{g/L}$) and following (3.8 $\mu\text{g/L}$) did not show a statistically significant difference (Figure 3.8). Although the literature suggests that lead concentrations should decrease with increasing pH, there may be a plateau in the effect of pH on lead once the pH is above 8.4 since the greatest impacts are observed at that pH (Dodrill and Edwards, 1995; Reiber 1991; Lee et al., 1989; Schock 1989). Douglas et al. (2004) reported that the purpose of the pH change from 8.5 to 9.2 was to prevent nitrification from lowering the pH to below 8. However, it could be speculated that an increase from 9.2 to 9.6 may not have a significant effect since nitrification during the summer would not decrease either a pH of 9.2 or 9.6 to below 8.4.

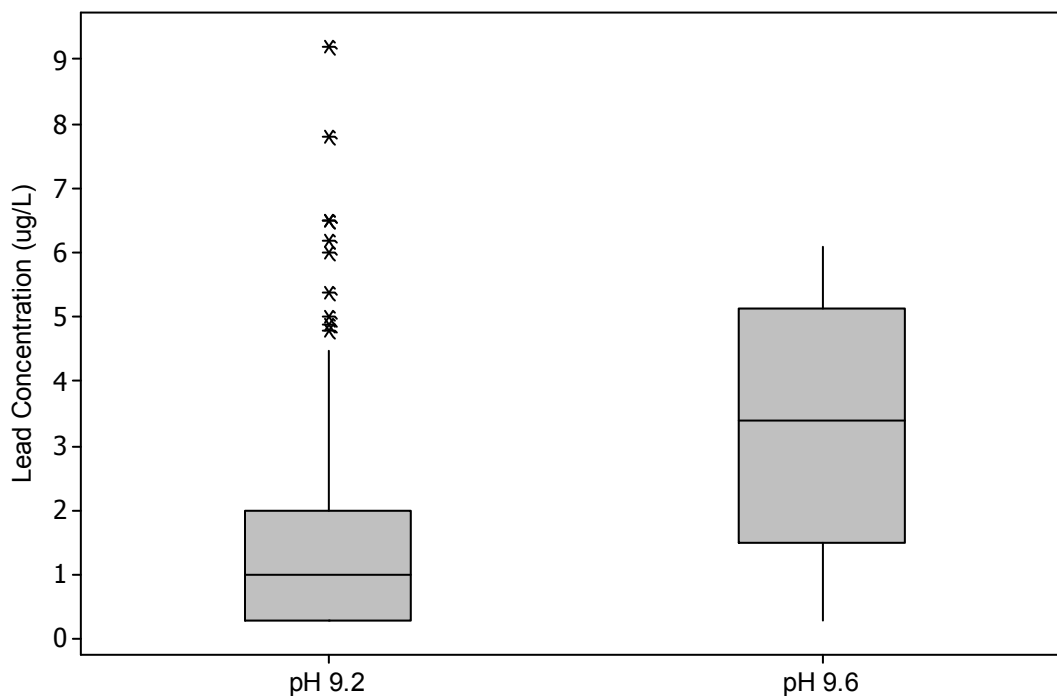


Figure 3.8: Box plot of lead concentrations at pH values of 9.2 and 9.6 in 2008.

For the City of London, only June 2007 to February 2009 data were available, and the pH was raised from 7.1 to 8.2 at the water treatment plant starting in January, 2008. The data shown in Figure 3.9 represents the pH of the water samples collected from each home. As a result, the data was analyzed in a different manner from Ottawa. The pH measured from tap water samples taken were analyzed to see if there is an association between lower pH values and higher lead concentrations. Results shown for London supported the findings in Ottawa with higher lead concentrations observed at a water treatment plant pH of 7.1.

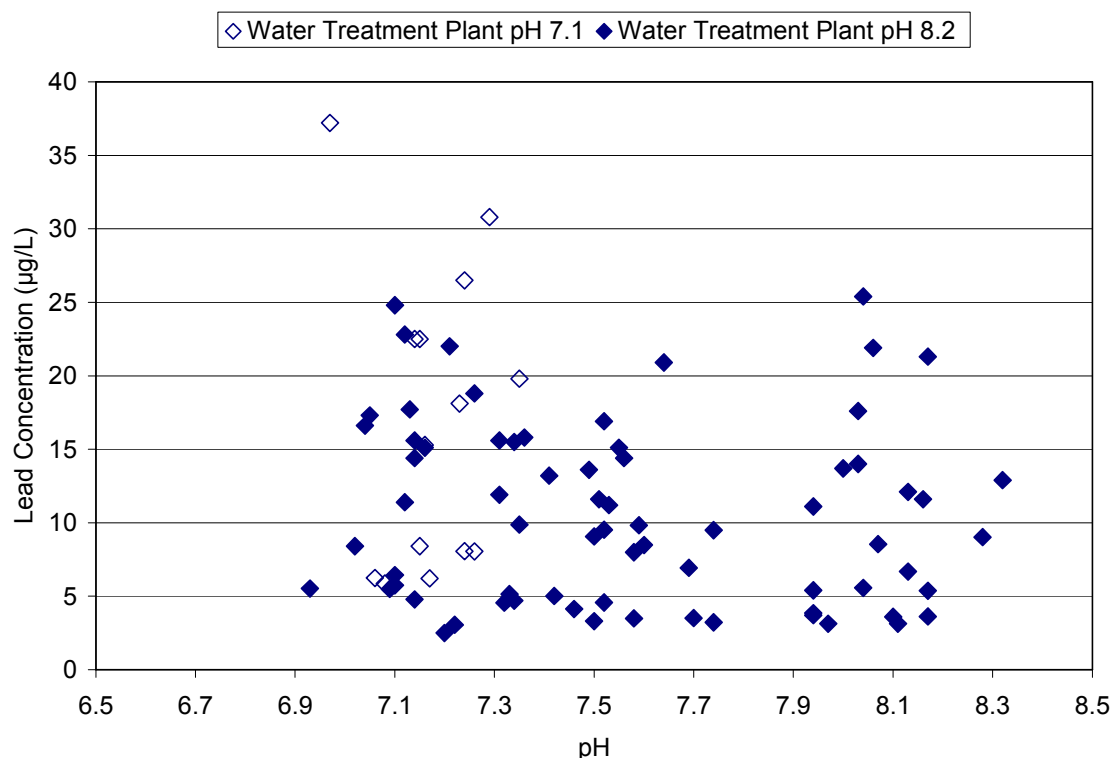


Figure 3.9: Changes in lead concentration as a function of pH for London.

3.4.4 Effect of Monitoring Intensity (City of Ottawa)

Periods of intensive sampling resulted in peaks in the distribution of lead concentrations from 1997 to 2008 (Figure 3.10). During these periods, homes built before 1953 were targeted since lead pipes were banned in Ontario in the mid-1950s (MOE, 2007a). As a result, these homes were more likely to contain lead service lines and result in higher lead concentrations. In 2002, Old Ottawa South (Homes on Belmont, Brighton,

and Fenitman Streets) indicated lead levels $>10 \mu\text{g/L}$ where the tap was flushed for five minutes prior to the sample being collected. The apparent higher number of $>10 \mu\text{g/L}$ values in the summer of 2002 was associated with an increase in the number of homes sampled that year as well as in subsequent years. In 2006 and 2007, a study was conducted by the City of Ottawa to evaluate typical lead exposure due to piping and plumbing materials and to assess the impact of lead service line replacement. In 2008, the Ontario Ministry to the Environment implemented a new regulation, which required the City of Ottawa to sample 100 homes believed to have lead service lines since they were built in the 1950s. The number of homes sampled is based on the population served by the drinking water system of 100,000 or more people (MOE, 2007f). The higher frequency of sampling points also resulted in a greater probability of observing higher lead concentrations in homes.

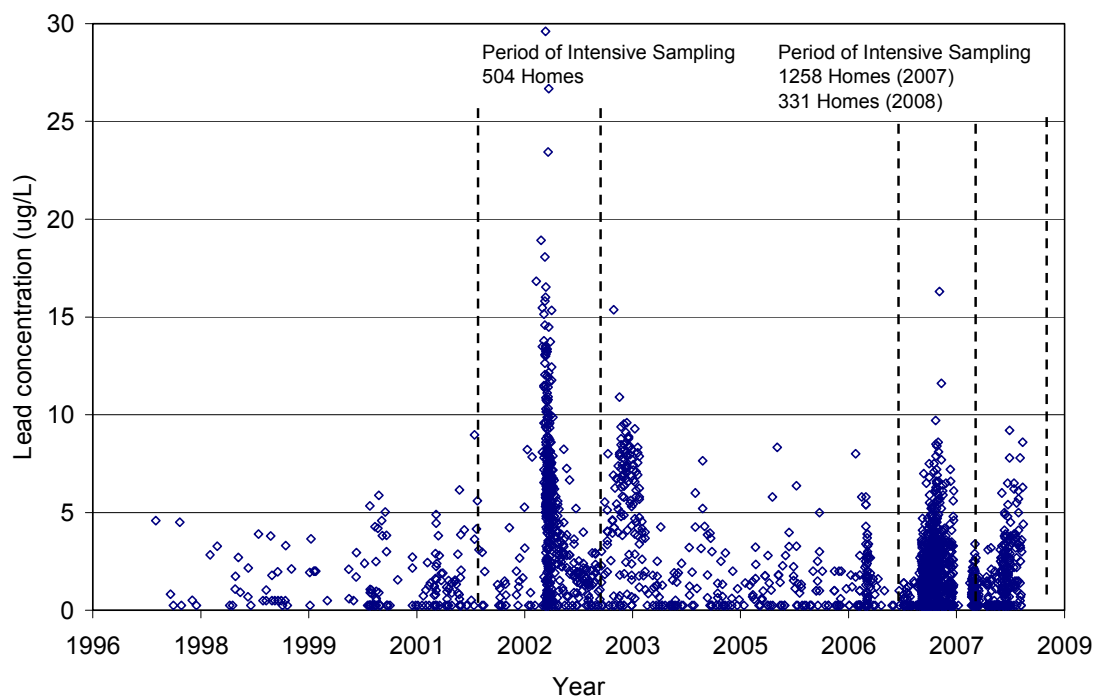


Figure 3.10: Ottawa lead concentrations from 1997 to 2008 (All homes reported).

3.4.5 Effect of Different Sampling Protocols for Lead in Tap Water

Table 3.4 shows the different sampling protocols used by the City of Ottawa and the City of London. The 30-minute (30MS) and 6-hour (6HS) stagnation protocols

consistently showed two to six times the average lead concentrations when compared to the fully flushed (FF) protocol at temperatures both $> 15^{\circ}\text{C}$ and $< 5^{\circ}\text{C}$ (Table 3.5). This finding illustrates the use of stagnation protocols to obtain a potential “worst-case” representation of lead concentrations in tap water.

Table 3.4: Lead sampling protocols used by London and Ottawa.

Sampling Protocol	City	Description
Fully Flushed (FF)	London and Ottawa	Flush tap for 5 minutes before collecting 1-litre water sample
30-Minute Stagnation	London and Ottawa	Flush tap for 5 minutes, wait for 30 minutes, collect 1-litre water sample.
6-Hour Stagnation	Ottawa	Flush tap for 5 minutes, wait for 6 hours, collect 1-litre water sample

Table 3.5: Average lead concentrations when using different sampling protocols for London and Ottawa.

City (Year)	Temperature Range($^{\circ}\text{C}$)	Average FF ($\mu\text{g/L}$)	Average of all litres 30MS ($\mu\text{g/L}$)	Average of all litres 6HS ($\mu\text{g/L}$)
Ottawa (2006 to 2008)	0-5	2.2	3.2	6.3
Ottawa (2006 to 2008)	>15	2.1	7.2	12.7
London (2007 to 2009)	>15	13.7	22.6	n/a

FF = Fully-Flushed

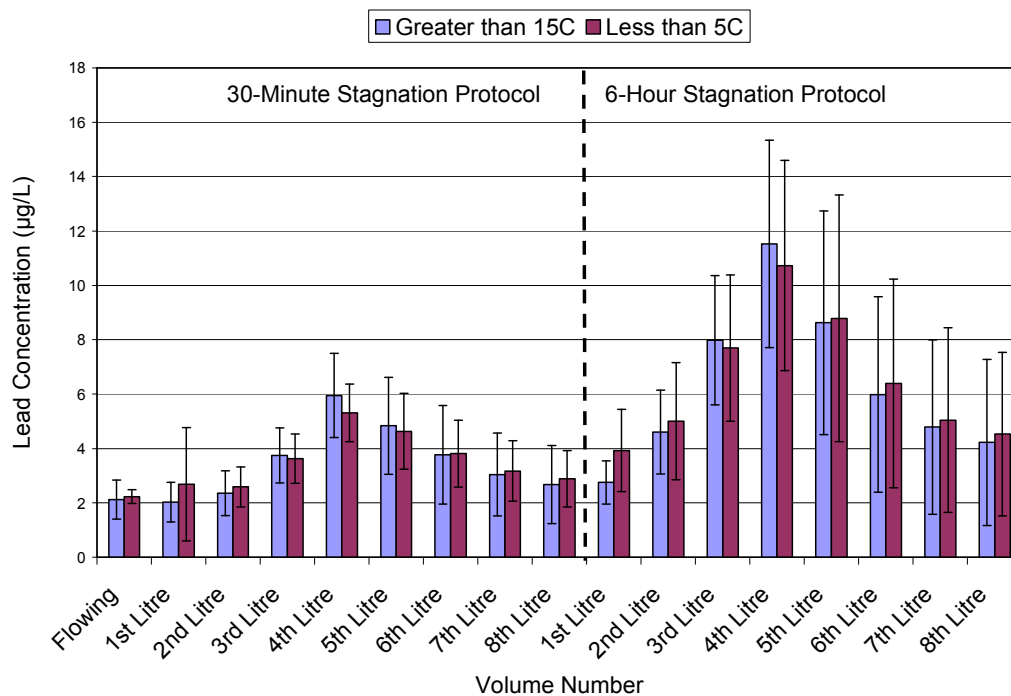
30MS = 30-Minute Stagnation

6HS = 6-Hour Stagnation

Figure 3.11a compares the average Ottawa lead concentrations from Litre “X” for 30MS and 6HS where $X = 1, 2, 3, 4, 5, 6, 7$, and 8 at temperatures $> 15^{\circ}\text{C}$ and $< 5^{\circ}\text{C}$, respectively. Peak lead concentrations were observed in the 4th litre and 5th litre samples (water in contact with a lead service line), with the 6th litre sample (water in contact with the watermain) showing the lead concentration beginning to decline. The 6HS protocol was consistently associated with approximately twice the lead concentrations when compared to the 30MS protocol, with the highest lead concentrations occurring in the 3rd, 4th, and 5th litres.

London lead concentrations were lower in filtered tap water (0.20 μm filter) when compared to unfiltered tap water. Filters were used to determine whether the lead was particulate or dissolved (Braam, 2008). Figure 3.11b illustrates the lead concentrations from the different sampling protocols for filtered and unfiltered tap water. Lead concentrations decrease significantly with the use of a filter with the peak lead concentrations occurring in the third, fourth, and fifth litres, which support the earlier findings for the City of Ottawa. In addition, even though filters were used, the third, fourth, and fifth litres indicated lead concentrations greater than 10 $\mu\text{g/L}$. In addition, the unfiltered 5-minute flush lead concentrations were lower than the 30-minute stagnation sampling protocols, but higher than the filtered lead concentrations in the 30-minute sampling protocol. These results suggest the effectiveness of using a filter to reduce lead concentrations in tap water.

(a)



(b)

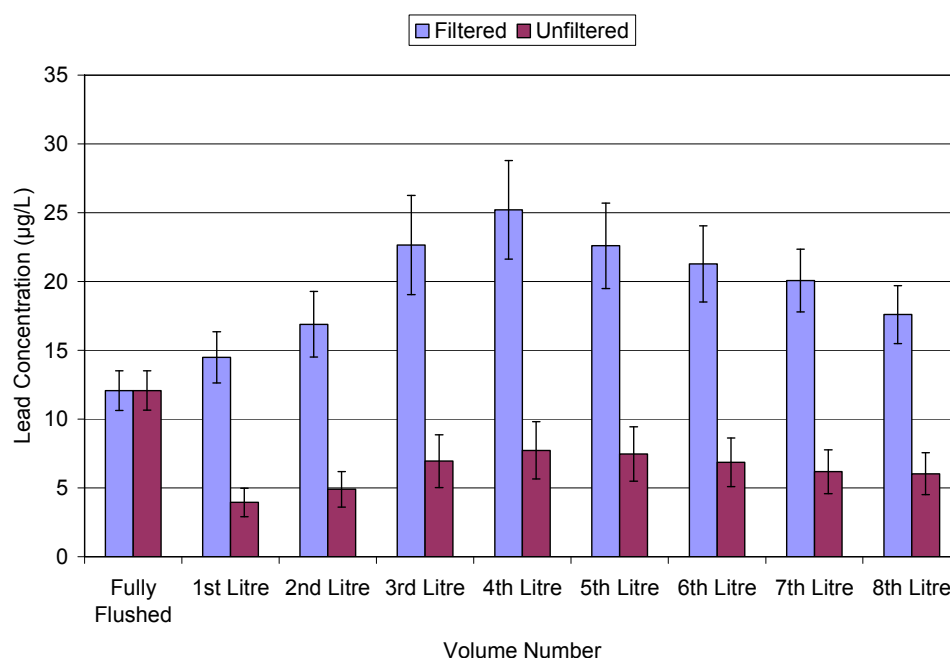


Figure 3.11: Comparison of fully flushed protocol to stagnation protocols (a) 30-minute and 6-hour stagnation protocols at $> 15^{\circ}\text{C}$ and $< 5^{\circ}\text{C}$ for Ottawa and (b) filtered vs. unfiltered 30-minute stagnation protocols. (Error bars indicate 95% confidence intervals).

3.4.6 Effects of Partial Lead Service Line Replacement in the City of Ottawa

Lead concentrations in 13 homes were examined using extended sampling protocols for both before and after partial replacement of the service line. First, the lead concentrations from the fully flushed protocol before ($2.2\mu\text{g/L}$) and after replacement ($1.8\mu\text{g/L}$) did not show a statistically significant difference. Second, lead concentrations from the 30-minute stagnation protocol and the fully-flushed protocol were compared, and results showed a significant difference in lead concentrations for the 3rd, 4th, and 5th litres. The average lead concentrations for before and after partial lead service line replacement are shown in Figure 3.12, and suggest a reduction in lead concentrations following lead service line replacement.

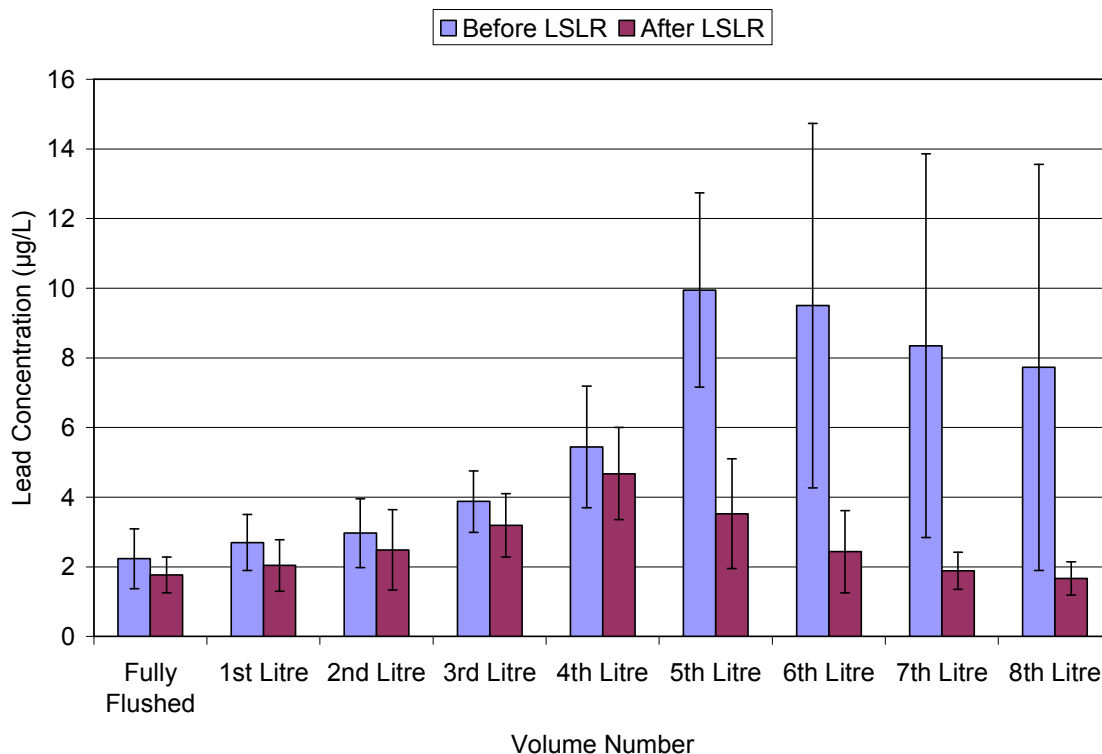


Figure 3.12: Average Ottawa lead concentrations before lead service line replacement and after lead service line replacement (Error bars indicate 95% confidence intervals).

3.4.7 Results from the Community Lead Testing Program (London)

The community lead testing program is part of O.Reg.170/03 under the Safe Drinking Water Act, 2002 (MOE, 2009). In July 2007, the regulation was revised to address concerns of elevated lead concentrations in tap water, and requires Ontario owners of municipal or non-municipal residential drinking water systems to test for lead twice per year. The two annual sampling periods are from December 15th to April 15th and from June 15th to October 15th. Results of this type of testing help determine whether there is a pattern of lead levels in drinking water for a municipality that indicates a need for action.

City of London data obtained from three rounds of testing is shown in Figure 3.13 illustrating that the average lead concentrations were below 10 µg/L. However, the 90th percentile lead concentrations exceeded 10 µg/L for all 3 rounds. The differences in lead concentrations between Litre 1 and Litre 2 from the 30-minute stagnation protocol were not statistically significant at the 95% confidence level for any of the sampling events.

The results show that the lead concentrations remain fairly constant between different rounds of sampling, and suggest that the 30-minute sampling protocol used is adequate.

Hydrant samples were also taken in the distribution system for each round of lead testing. Lead concentrations usually ranged from 0 to 1 µg/L with only 2 incidences above 3 µg/L; 3.03 µg/L (December 2008 to April 2009) and 4.12 µg/L (December 2007 to April 2008). Therefore, it may be assumed that the contribution of lead from the distribution system is negligible.

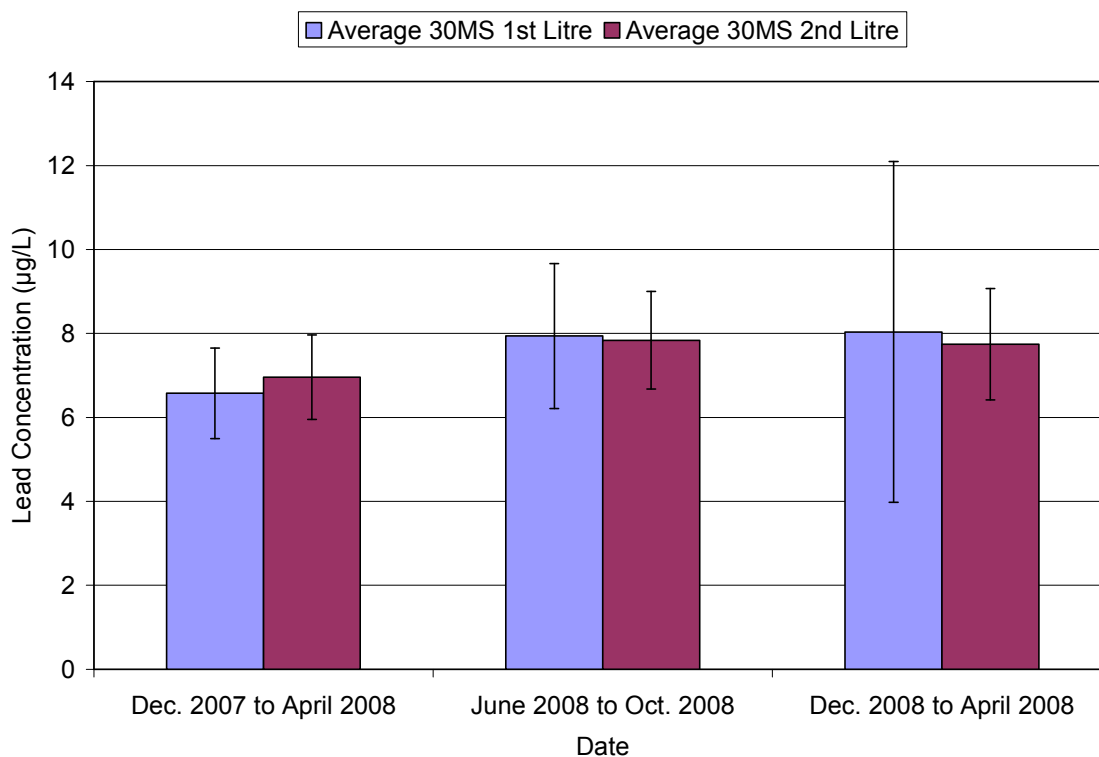


Figure 3.13: Average London lead concentrations from the Community Lead Testing Program (Error bars indicate 95% confidence intervals).

3.5 Summary

In this study, lead concentration data obtained for homes in Ottawa from 1997 to 2008 and London from 2007 to 2009 were analyzed for statistically significant trends. Both datasets consisted of additional water quality parameters, including pH and temperature. Ottawa measured total chlorine whereas London measured free chlorine. First, lead concentrations in tap water were compared with different sampling protocols used by Ottawa and London. Results showed that the average Ottawa lead concentrations

from the fully-flushed protocol were significantly lower at the 95% confidence level ($p < 0.05$) when compared to the 30-minute and 6-hour stagnation protocols at temperature ranges $> 15^{\circ}\text{C}$ and $< 5^{\circ}\text{C}$. Using the Ottawa dataset from 2006 to 2008, the fully-flushed lead samples were found to be consistently lower than the stagnation samples associated with the 6-hour stagnation protocol. A similar result was observed for the London data where the lead concentrations from the 5-minute were statistically significantly lower ($p < 0.05$) when compared to the 30-minute stagnation protocol. For both municipalities, as temperature increased, the average lead concentrations also increased.

A second analysis was conducted for the London dataset from 2007 to 2009 and the Ottawa dataset from 1997 to 2008 over a range of temperatures to represent seasonal effects: ($0-5^{\circ}\text{C}$), ($5-15^{\circ}\text{C}$), and ($> 15^{\circ}\text{C}$). For Ottawa, the application of the Mann-Whitney U-test showed a statistically significant difference ($p < 0.05$) when comparing lead concentrations for the temperature range ($> 15^{\circ}\text{C}$) to lead concentrations at ($5-15^{\circ}\text{C}$) and ($0-5^{\circ}\text{C}$). A significant difference was not observed when comparing lead concentrations at ($0-5^{\circ}\text{C}$) and ($5-15^{\circ}\text{C}$). For London, no significant differences were observed between the different temperature ranges.

Third, the impact of a pH increase in 2002 from 8.5 to 9.2 by the City of Ottawa was found to be statistically significant with respect to reducing lead levels at the 95% confidence level ($p < 0.05$) for temperatures $> 15^{\circ}\text{C}$. However, the pH change from 9.2 to 9.6 during the brief period of August 15 to August 27, 2008 was not statistically significant at the 95% confidence level ($p < 0.05$).

Fourth, when comparing different sampling protocols, the 30MS and 6HS protocols consistently resulted in higher lead concentrations when compared to the fully flushed protocol, especially for homes with or suspected to have lead service lines. In addition, homes with lead service lines were found to have lead concentrations measured below the detection limit ($0.3 \mu\text{g/L}$) using the fully flushed protocol. This shows the potential importance of using the extended stagnation sampling protocols in order to obtain greater information. From the sampling results, it appears that it is often the 3rd, 4th, and 5th litres that have the highest lead concentrations for homes with lead service lines.

4. DEVELOPMENT OF STATISTICAL MODELS FOR PREDICTING LEAD CONCENTRATIONS IN TAP WATER BASED ON TWO CITIES IN ONTARIO, CANADA

4.1 Introduction

Lead in drinking water originates from plumbing materials such as lead pipes, solders, fittings, fixtures and faucets (brass) as well as galvanized and cement pipes (U.S. EPA, 2003). Lead leaches into water through corrosion, which is the dissolving or wearing away of metal caused by a chemical reaction between water and plumbing fixtures (U.S. EPA, 2005).

In Canada, the drinking water regulations fall under provincial/territorial jurisdiction. Health Canada develops guidelines for water quality. Provinces and territories adopt health-based guidelines into regulations. A Health Canada guideline on corrosion control has been implemented to establish strategies to reduce the leaching of lead and other contaminants into drinking water and to recommend the implementation of corrosion control programs when the guideline is exceeded (Health Canada, 2007). The drinking water guideline for lead, based on negative health effects in children, is 10 µg/L (MOE, 2007a).

The new Health Canada guideline on corrosion control (Health Canada, 2007) will impact water utilities in Canada by imposing more stringent sampling requirements. In the past, required monitoring of lead at the tap in Canada was minimal, requiring one sample per year and was not targeted at high risk sites (Lemieux, 2007). These sites include locations where high concentrations of lead (>10 µg/L) have been found in the past, sites where materials containing lead are known to exist, as well as sites serving high-risk populations such as children under age six and pregnant women and nursing mothers (U.S. EPA, 2005). The guideline applies to residential and non-residential sites. Residential sites include single-family homes, multiple-family dwellings and high-rise apartment buildings. Non-residential sites include buildings and schools. Residential monitoring includes the identification of lead sources in both the distribution system and residential plumbing whereas non-residential monitoring focuses mainly on the source of lead within the building (Health Canada, 2007).

In addition to the Health Canada guideline, the Government of Ontario implemented a new regulation in June, 2007 (O.Reg. 243/07) to reduce children's exposure to lead in drinking water (MOE, 2007a). This new regulation requires all schools and day nurseries built before 1990 to flush their plumbing daily, and those built after 1989 to flush weekly. All schools and day nurseries (built before 1990) are required to test for lead in water from taps on an annual basis (MOE, 2007a). More stringent regulation requirements include mandatory community-wide testing, as well as notification of results from this program, and the development and implementation of corrosion control measures for lead reduction.

Issues regarding elevated lead levels in Canada have already occurred in several cities with lead service lines such as Ste-Agathe and Montreal in Quebec as well as Ottawa and London in Ontario (Lemieux, 2007). However, there are issues of cost and infrastructure associated with the removal or replacement in these lead lines. For example, in Toronto, the estimated cost for the Lead Water Service Replacement Program is \$17.9 million per year for design and construction work associated with additional water service replacement and water main reconstruction in addition to \$1.3 million per year for additional staff resources to oversee the design and construction work (Toronto Water, 2007).

The objective of this study was to develop statistical models to predict lead concentrations in tap water based on water quality parameters including pH, total chlorine, free chlorine, and temperature. The purpose of these models is to assist municipalities in determining the potential impact of corrosion control strategies such as increasing pH. To develop these models, field data were obtained from the City of Ottawa for 1997 to 2008 and for the City of London from 2007 to 2009, which incorporated a fully-flushed protocol (five minutes of flushing prior to collecting the water sample). Water quality parameters measured included lead, pH, and temperature for both cities. London uses chlorine as a secondary disinfectant and measures free chlorine whereas Ottawa practices chloramination and measures the total chlorine concentration.

There have been several studies reported in the literature that have applied statistics in terms of predicting lead levels in tap water (Tang et al., 2006; Sung, 2003;

Maas et al., 2000). The coefficient of determination (R^2) values achieved for these studies have varied depending on study location and measured water quality parameters.

However, the models used in these studies could not be applied to the Ottawa and London field data due to limited water quality parameters. For example, Sung (2003) had UV-254 in the model and Tang et al. (2006) had sulphate in the model, which were not measured in the Ottawa and London datasets.

4.2 Methods

4.2.1 Test of Normality

A 1-sample Kolmogorov-Smirnov procedure was used to test for normality in the distribution of water quality parameters (lead, total chlorine, free chlorine, pH, and temperature) to assess whether parametric or non-parametric tests should be used for correlation analysis. Non-parametric tests are used to assess the statistical significance of data, and do not depend on a distribution unlike parametric tests, which require the data to fit an underlying distribution (Ho, 2006). A test of normality showed that the parameters did not follow a normal distribution ($p < 0.05$) and that non-parametric tests should be used.

4.2.2 Correlation Analysis

Correlation analysis was used to determine if any association existed among the variables. A Spearman's Rank Correlation was selected because it may be used to test the direction and strength of the relationship between two non-parametric variables. First, the null hypothesis is that there is no relationship between the two sets of data. Next, both sets of data (one for each variable) are ranked from the highest to the lowest (Lowry, 2008). The two sets of ranks are subtracted to obtain the difference (D). These D values are then squared and added to get $\sum D^2$. The Spearman's rank correlation coefficient R_s is computed using the following Equation:

$$R_s = 1 - \frac{6 \sum D^2}{N(N^2 - 1)} \quad [4.1]$$

Where N= number of D values

If R_s is ± 1 , there a perfect positive or negative correlation. If it falls between ± 1 and ± 0.5 , there is a strong positive or negative correlation. If it falls between ± 0.5 and 0, there is a weak positive or negative correlation. If it is 0, there is no correlation.

4.2.3 Regression Analysis

4.2.3.1 Multiple Linear Regression

Prediction models for lead in tap water were developed using multiple linear regression, a method of analysis used to predict a dependent variable (Y) with observed values, $y_1, y_2, \dots, y_n$ (where n is the sample size) and q explanatory variables, $x_1, x_2, \dots, x_q$ with observed values, $x_{1i}, x_{2i}, \dots, x_{qi}$ for $i=1, \dots, n$ as shown in Equation 4.2 (Landau and Everitt, 2004):

$$y_i = \beta_0 + \beta_1 x_{1i} + \beta_2 x_{2i} + \dots + \beta_q x_{qi} + \varepsilon_i \quad [4.2]$$

The regression coefficients, $\beta_0, \beta_1, \dots, \beta_q$, are generally estimated by least squares. The term ε_i is the residual or error for each individual case and represents the deviation of the observed value of the response for each individual case from that expected by the model. These error terms are assumed to have a normal distribution with variance σ^2 . Analysis of variance (ANOVA) provides an F-test of the null hypothesis that each of $\beta_0, \beta_1, \dots, \beta_q$, is equal to zero.

Stepwise regression was selected whereby each water quality parameter (independent variable) was entered in sequence and its value was assessed for statistical significance at the 95% confidence level. If adding the variable contributed significantly to the model then the variable was retained, but all other variables in the model were then re-tested to assess their contributions. Therefore, only statistically significant (P-value < 0.05) variables remained in the final models. It is anticipated that this method would end up with the smallest possible set of predictor variables.

The coefficient of determination (R^2) is used as a measure of linear correlation. It is a fraction ranging from 0 (no correlation) to 1 (positive or negative perfect correlation). When R^2 is equal to 0, the best-fit curve fits the data no better than a horizontal line through the mean of all Y values (GraphPad, 2007).

A Box-Cox power transformation on the dependent variable was used to minimize heteroscedasticity, which is when the variance of the dependent variable varies

across the data, and violates the assumption of equal variance in multiple linear regression (Box and Cox, 1964). In this case, the dependent variable Y is positive, and the following transformation can be used as shown in Equation 4.3:

$$y_i^\lambda = \frac{y_i^\lambda - 1}{\lambda} \text{ when } \lambda \neq 0 \quad [4.3]$$

$$y_i^\lambda = \log(y_i) \text{ when } \lambda = 0$$

Given $y = y_1, y_2, \dots, y_n$, λ is chosen to maximize the logarithm of the likelihood function

$$F(y, \lambda) = -\frac{n}{2} \ln \left[\sum_{i=1}^n \frac{(y_i(\lambda) - \bar{y}(\lambda))^2}{n} \right] + (\lambda - 1) \sum_{i=1}^n \ln(y_i)$$

Where $\bar{y}(\lambda) = \frac{1}{n} \sum_{i=1}^n y_i(\lambda)$ is the arithmetic mean of the transformed data.

4.2.3.2 Ratio between Predicted Lead Concentrations from Regression Model and Actual Lead Concentrations

The ratio between the lead concentrations predicted by the regression model and the actual lead concentrations is another way to express the representativeness of the regression equation (Van Den Hoven, 2006). Ideally, the ratio between the predicted lead concentrations obtained by the model and the actual lead concentrations should be unity. To determine the variation in the ratio between the predicted lead concentrations and the actual lead concentrations, the average ratio is calculated. The 95% prediction range of the average ratio is shown in Equation 4.4:

$$95\% \text{ Prediction Range} = AVGR \pm 1.96 \frac{\sigma}{\sqrt{n}} \quad [4.4]$$

where σ = standard deviation of ratios of predicted lead concentration over average lead concentration, n = number of samples, and $AVGR$ = average of ratios of predicted lead concentration over average lead concentration. A narrow prediction range indicates that the ratio is fairly constant over the range of lead concentrations involved.

4.2.3.3 Logistic Regression

Prediction models for lead in tap water were also developed using logistic regression. Binomial logistic regression is a technique used to predict a dichotomous

dependent variable when the independent variables are continuous and/or discrete (Landau and Everitt, 2004). Logistic regression does not require assumptions of normality for the variables in the model (Landau and Everitt, 2004), which is suitable for non-parametric variables. In logistic regression, the expected value is the probability p of a binary response taking the value of 0 or 1. Instead of modeling p directly as a linear function of the explanatory variables and estimating the regression coefficients by least squares since the observed values do not follow a normal distribution with mean p , a more suitable approach is to model p indirectly via the logit transformation of p i.e.

$\ln \frac{p}{1-p}$. The logistic regression model can be written as Equation 4.5.

$$z = \ln \frac{p}{1-p} = \beta_0 + \beta_1 x_1 + \dots + \beta_q x_q \quad [4.5]$$

The parameters ($\beta_0, \beta_1, \dots, \beta_q$) in the logistic regression model can be estimated by maximum likelihood (Collett, 2003). The z value from Equation 4.6 is then input into Equation 4.6:

$$\text{probability of 0 or 1} = \frac{1}{1 + \exp(-z)} \quad [4.6]$$

4.3 Results and Discussion

4.3.1 Dataset Preparation for Regression

Prior to performing multiple linear regression (MLR), a Spearman's correlation was used to assess the association between lead concentrations (Pb) and other water quality parameters including (i) total chlorine, pH, and temperature for data obtained from the City of Ottawa and (ii) free chlorine, pH, and temperature for data obtained from the City of London (Table 4.1). The purpose of this task was to assess multicollinearity, which exists when two or more predictor variables in a multiple regression model are highly correlated (>0.6). The estimate of one variable's impact on the response variable while controlling for other variables tends to be more precise if the predictors are not correlated with one another (Lowry, 2008). Results showed that total chlorine is moderately correlated with temperature (0.531) and pH (0.439). Free chlorine illustrated a similar correlation with temperature (0.406) and pH (0.428). The results also

showed a weak correlation (<0.5) between Pb and the other parameters (pH, total chlorine, free chlorine, temperature). However, the correlations between these variables (<0.3) was not large enough for multicollinearity to be an issue (Falenchuck, 2008). Finally, Pb had the strongest correlation (0.134) with temperature.

Table 4.1: Spearman's correlation of water quality parameters (Ottawa: N=1176 homes and London: N=85 homes)

Ottawa	Total Chlorine (mg/L)	pH	Temp (°C)	Lead (µg/L)
Total Chlorine (mg/L)	1.000	0.439	0.531	-0.120
pH	0.439	1.000	0.369	-0.089
Temp (°C)	0.531	0.369	1.000	0.300
Lead (µg/L)	-0.120	-0.089	0.300	1.000
London	Free Chlorine (mg/L)	pH	Temp (°C)	Lead (µg/L)
Free Chlorine (mg/L)	1.000	0.428	0.406	-0.266
pH	0.428	1.000	0.307	-0.205
Temp (°C)	0.406	0.307	1.000	0.188
Lead (µg/L)	-0.266	-0.205	0.188	1.000

4.3.2 Predicting Lead Levels in Tap Water

4.3.2.1 Multiple Linear Regression Analysis

First, regression models were developed to predict lead based on the 1997 to 2008 dataset obtained from the City of Ottawa. The dataset was revised by removing all homes with missing water quality parameters. The resulting model derived for this dataset using stepwise-MLR is shown in Equation R-1 (Table 4.2). A plot of standardized residuals vs. the standardized predicted values for Equation R-1 illustrated a slight curvature (Figure A.1), which implied that the model could be improved by applying a Box-Cox transformation, which normalized the Pb variable, and minimized the standardized

residuals to below three standard deviations. Using SPSS 16, the Box-Cox transformation results showed a lambda value of 0, which means that the Pb variable should be logarithmically transformed. Step-wise regression was again applied with log Pb as a function of the independent variables. The Box-Cox transformation was successful as shown by examining the standardized residuals vs. the standardized predicted values since a random pattern of residuals exists, which means that the model is correct (Figure A.2). This model is shown as Equation R-2 (Table 4.2).

Next, lead regression models were developed for use with homes with lead service lines. The same procedures were applied to the entire dataset from 1997 to 2008 except that homes with $< 1.0 \mu\text{g/L}$ were removed. According to Campbell (2009), the method detection limit for lead is $0.5 \mu\text{g/L}$, and homes that indicated lead $< 1.0 \mu\text{g/L}$ can be assumed to not have lead service lines (LSLs) or have LSLs less than 1 foot (0.305m) (Campbell, 2009). The resulting model is shown in Equation R-3, and the model with a logarithmic transformation on Pb is shown in Equation R-4. After applying a Box-Cox transformation to this dataset, a lambda value of -0.10 was obtained, suggesting that the dependent variable should be raised to the exponent of -0.10. The resulting model is shown in Equation R-5 (Table 4.2).

To evaluate the accuracy of the regression models, the 95% prediction range (as described earlier) was calculated using Equation 4.4 for the regression models (Equation R-3, Equation R-4, and R-5) with the three highest R^2 values (Table 4.2). Ideally, the ratios would be close to 1 and the 95% prediction ranges be narrow (Van Den Hoven, 2006). Equations R-4 and R-5 proved to be close to each other and both are better than Equation R-3. Equation R-4 ($R^2 = 0.34$) is better since the coefficient of determination is slightly higher than Equation R-5 ($R^2 = 0.334$). The measured lead vs. the predicted lead concentration for Equation R-4 is shown in Figure 4.1. The 45° line indicates that the model tends to underestimate the measured lead concentrations above $8 \mu\text{g/L}$.

In addition, the regression model with the highest R^2 (Equation R-4) was used to predict the lead concentrations by incorporating available water quality parameters to provide a visual representation of the results arising from the model in comparison to the 1997 to 2008 lead data (Figure 4.2).

Regression models (Equations R-6 and R-7) were also derived for London to predict lead concentrations based on temperature, free chlorine, and pH (Table 4.3). The predicted vs. measured lead concentration is shown in Figure 4.3 for Equation R-7. In addition, the predicted lead concentrations were superimposed on top of the actual lead concentrations (Figure 4.4). Qualitatively, the predicted lead concentrations appear to represent the measured lead concentrations less than $15\mu\text{g/L}$ quite well.

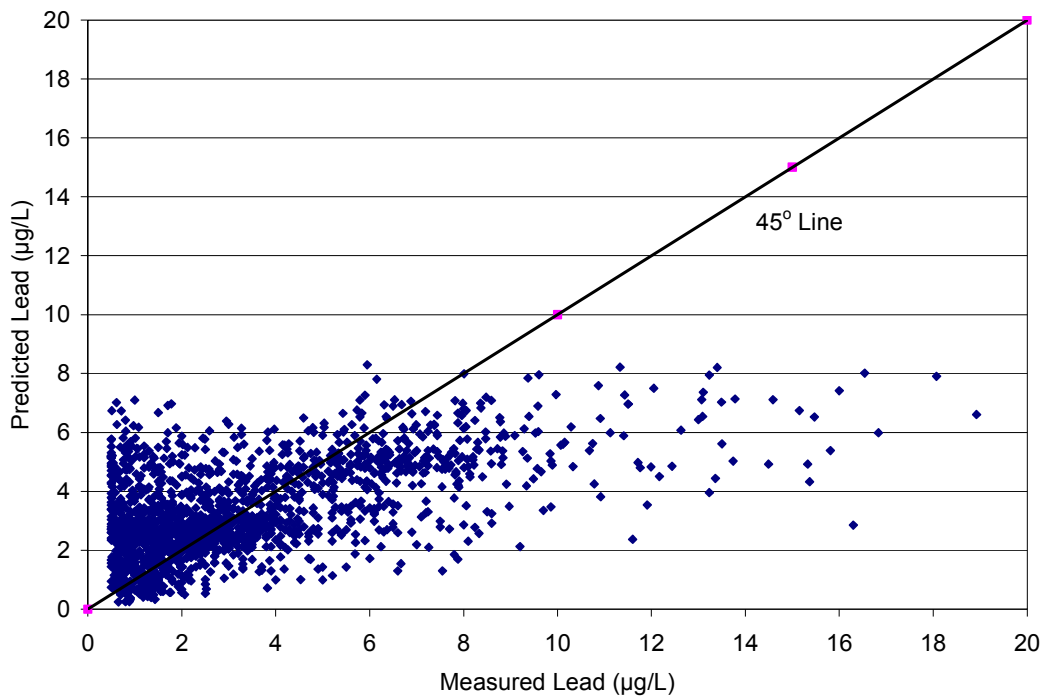


Figure 4.1: Predicted lead vs. measured lead for the 1997 to 2008 Ottawa dataset (homes $< 0.3\mu\text{g/L}$ removed) using Equation R-4.

The magnitude of the coefficients in the equations preceding the variables may be misleading. For example, in Table 3, the maximum and minimum values for each variable were obtained from the complete Ottawa 1997 to 2008 dataset and London 2007 to 2009 dataset. Although the coefficients in the equation may be small, the magnitude of variables such as temperature (0.37 to 29.60°C) is far greater than total chlorine (0.05 to 2.70 mg/L) for Ottawa.

Table 4.2: Regression models for Ottawa and 95% prediction ranges for average ratios

Regression (R) Equation # and Description	Regression Equation	R ²	95% Prediction Ranges
Ottawa			
R-1 – Stepwise MLR, all homes	$Pb = 9.070 + 0.189 \times \text{temp } (^{\circ}\text{C}) - 2.372 \times \text{total chlorine (mg/L)} - 0.675 \times \text{pH}$	0.264	n/a
R-2 – Box-Cox transformation applied to Equation R-1	$\text{Log Pb} = 0.773 + 0.029 \times \text{temp } (^{\circ}\text{C}) - 0.394 \times \text{total chlorine (mg/L)} - 0.064 \times \text{pH}$	0.161	n/a
R-3 – Stepwise MLR, excludes homes with lead <1.0 µg/L ^a	$Pb = 12.323 + 0.224 \times \text{temp } (^{\circ}\text{C}) - 2.317 \times \text{total chlorine (mg/L)} - 0.975 \times \text{pH}$	0.338	1.35 ± 0.046
R-4 – Stepwise MLR, Logarithmic Transformation, excludes homes with lead <1.0 µg/L ^a	$\text{Log Pb} = 1.179 + 0.025 \times \text{temp } (^{\circ}\text{C}) - 0.233 \times \text{total chlorine (mg/L)} - 0.085 \times \text{pH}$	0.340	1.18 ± 0.038
R-5 - Box-Cox transformation applied to Equation R-3	$Pb^{-0.1} = 0.760 - 0.005 \times \text{temp } (^{\circ}\text{C}) + 0.047 \times \text{total chlorine (mg/L)} + 0.017 \times \text{pH}$	0.334	1.125 ± 0.036
London			
R-6 – Stepwise MLR	$Pb = -15.493 \times \text{free chlorine (mg/L)} + 0.531 \times \text{temp } (^{\circ}\text{C}) - 10.157 \times \text{pH} + 91.769$	0.256	1.36 ± 0.18
R-7 – Box-Cox transformation applied to Equation R-6	$Pb^{-0.1} = 0.205 \times \text{free chlorine (mg/L)} - 0.005 \times \text{temp } (^{\circ}\text{C}) + 0.109 \times \text{pH} - 2.150$	0.230	1.22 ± 0.16

a = Assumes no LSL present since lead concentration < 1.0 µg/L

n/a = Not Applicable

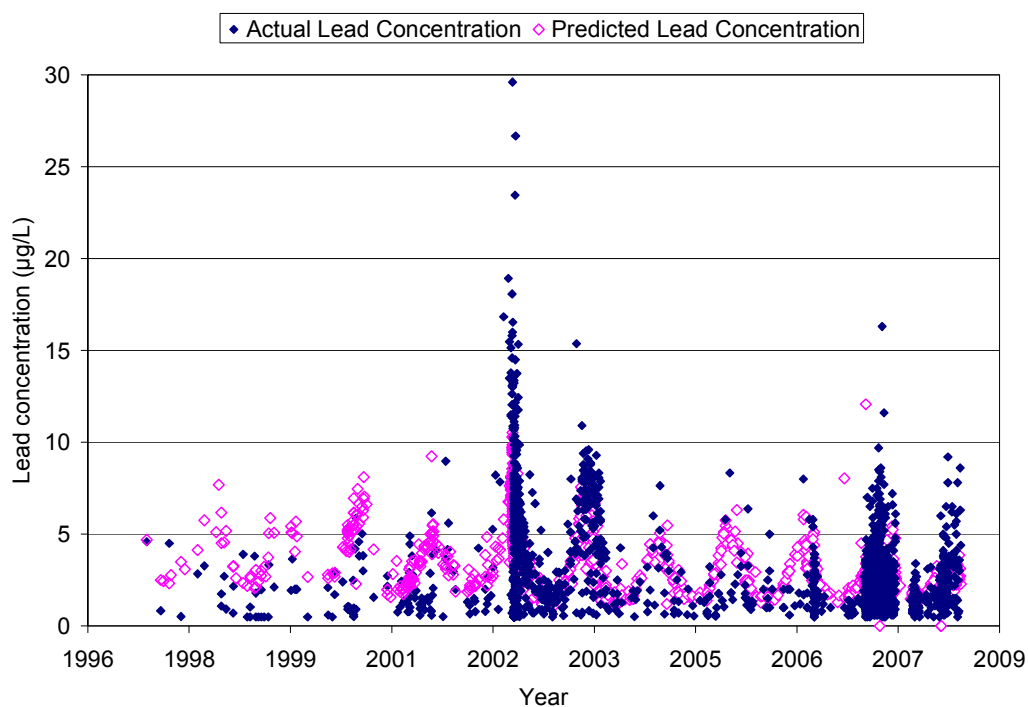


Figure 4.2: Predicted and measured lead concentrations for the 1997 to 2008 Ottawa dataset (homes $< 0.3 \mu\text{g/L}$ removed) using Equation R-4.

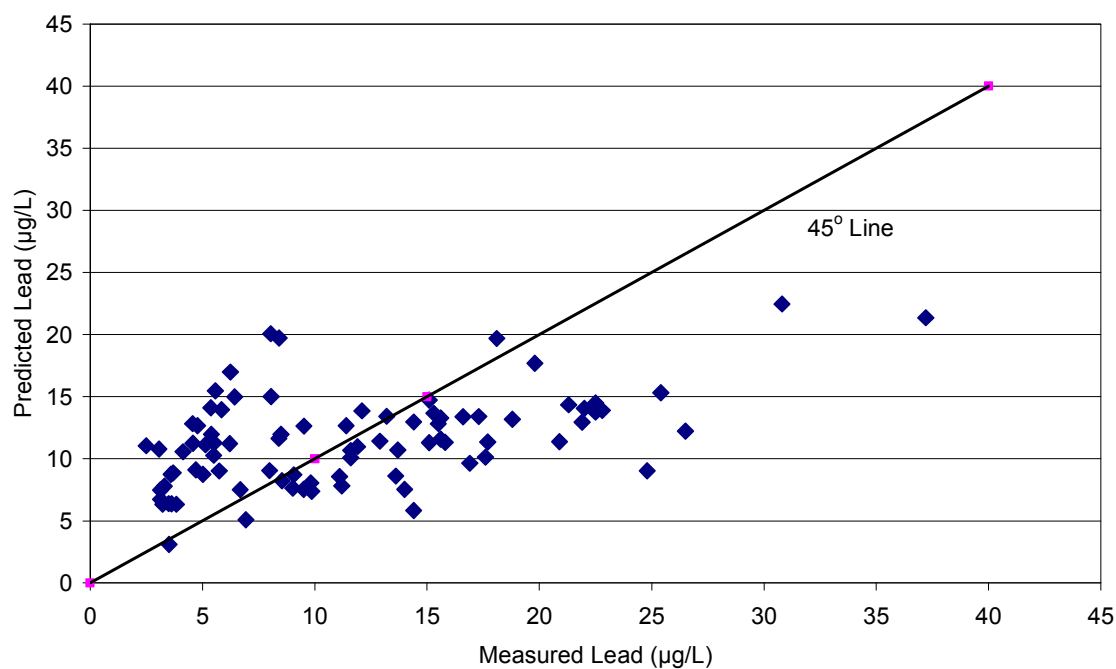


Figure 4.3: Predicted lead vs. measured lead for the 2007 to 2009 London dataset using Equation R-7.

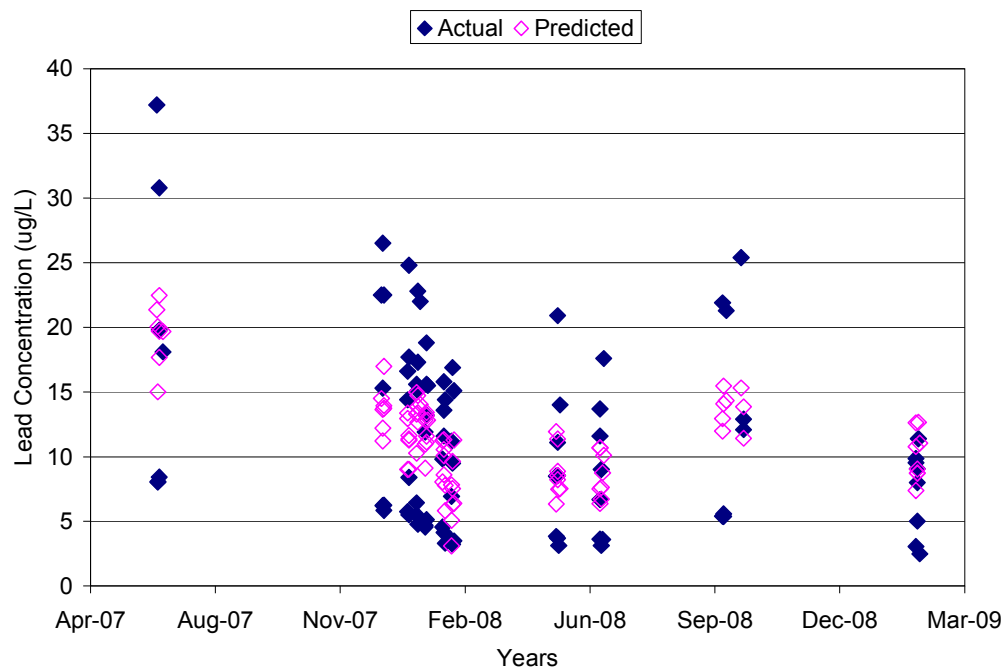


Figure 4.4: Predicted and measured lead concentrations for the 2007 to 2009 London dataset using Equation R-7.

Table 4.3: Maximum and minimum values for measured water quality parameters in Ottawa (1997 to 2008 dataset) and London (2007 to 2009 dataset)

	Total Chlorine (mg/L)	pH	Temp (°C)	Lead^a (µg/L)
Ottawa				
Sample Size	2706	2707	2657	2779
Max	2.70	9.87	29.60	29.60
Min	0.05	0.58	0.37	0.25
Average	1.58	9.09	16.60	2.33
	Free Chlorine (mg/L)	pH	Temp (°C)	Lead^a (µg/L)
London				
Sample Size	85	85	85	85
Max	0.95	8.32	20.8	37.2
Min	0.27	6.93	4.6	2.49
Average	0.62	7.51	10.51	11.6

a = Lead concentrations based on the 5-minute flush protocol

4.3.2.2 Logistic Regression Analysis

Logistic regression represents an alternate approach to predicting lead concentrations by changing the dependent variable (Pb) into a categorical one. First, homes with missing water quality parameters were removed from the 1997 to 2008 Ottawa dataset. A categorical variable, Pb01, was created where homes with lead concentrations less than or equal to 10 µg/L were assigned a value of 0 and homes with lead concentrations > 10 µg/L were assigned a value of 1. The resulting model based on total chlorine, pH, and temperature is shown in Equation LR-1 (Table 4.5). The value z was then input into Equation 4.6 as previously discussed where the probability is computed to yield a value close to 0 (i.e. lead concentration is < 10 µg/L) or a value close to 1 (i.e. lead concentration is ≥ 10 µg/L). A sample model validation is shown in Table 4.4 where the value of each water quality parameter was input into Equation LR-1 and the resulting N value was then input into Equation 4.6.

A second logistic regression equation was derived for the Ottawa lead dataset from 1997 to 2008 with homes having lead concentrations < 1.0 µg/L removed from the dataset and a threshold of 10 µg/L by assuming that these homes did not have lead service lines (LSLs) or have LSLs less than 1 foot (0.305m), which is an adequate assumption according to Campbell (2009). The resulting model is shown in Equation LR-2 (Table 4.5). The predicted vs. actual lead concentrations is shown in Figure 4.5a.

In the next two models, a lower threshold of 5 µg/L was set instead of 10 µg/L since having a lower threshold resulted in a greater number of data points in the second category of 1, which would show whether logistic regression can still provide similarly accurate results that were observed at a threshold of 10 µg/L. The resulting model is shown in Equation LR-3 (Table 4.5) for the 1997 to 2008 Ottawa dataset. Finally, homes with < 1.0 µg/L were removed from the dataset resulting in Equation LR-4 (Table 4.5). By setting a lower threshold of 5 µg/L, the accuracy of the models, LR-3 and LR-4, decreased by more than 10%.

A logistic regression model was also derived for the London data as shown by Equation LR-5 (Table 4.5). The predicted vs. actual lead concentrations are shown in Figure 4.5b. In contrast to the high (>90%) accuracy achieved for Ottawa, the accuracy for London was only 68% due to the smaller dataset (85 homes) compared to the Ottawa

dataset (2629 homes). These results suggest the potential use of logistic regression as a tool to predict whether the lead concentration will be $> 10 \mu\text{g/L}$ based on a fully-flushed protocol (5 minutes of flushing).

Table 4.4: Sample model validation for Equation LR-1

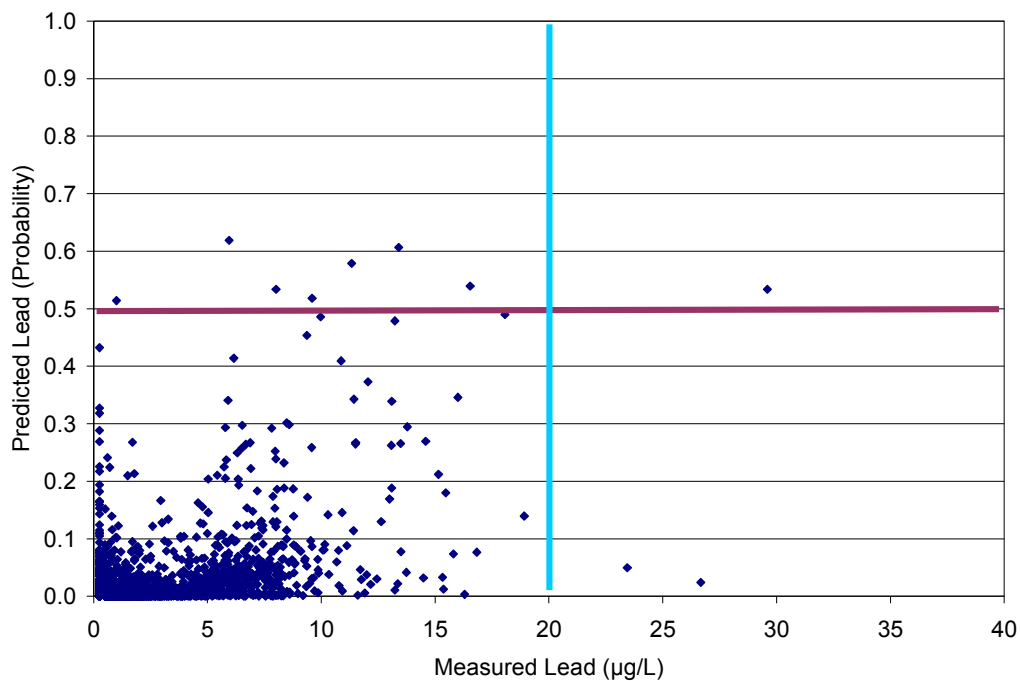
Home #	Total Chlorine (mg/L)	pH	Temp ($^{\circ}\text{C}$)	Lead ($\mu\text{g/L}$)	Output
1	1.12	8.00	15.6	0.9	0
2	1.20	8.36	17.2	7.8	0
3	0.74	8.30	18.5	16.8	1

Table 4.5: Classification tables for logistic regression models

Logistic Regression (LR) Equation # and Description	Logistic Regression Equation	Overall Percentage Correct (%)
Models based on Entire Ottawa 1997 to 2008 Dataset		
LR-1 – Threshold of $10\mu\text{g/L}$, entire dataset	$Z = -2.308 \times \text{total chlorine (mg/L)} - 0.780 \times \text{pH} + 0.354 \times \text{Temperature (}^{\circ}\text{C)} - 0.854$	97.9
LR-2 – Threshold of $10\mu\text{g/L}$, excludes homes with lead $< 1.0\mu\text{g/L}^a$	$Z = -1.752 \times \text{total chlorine (mg/L)} - 1.227 \times \text{pH} + 0.263 \times \text{Temperature (}^{\circ}\text{C)} + 4.640$	96.3
LR-3 – Threshold of $5\mu\text{g/L}$, entire dataset	$Z = -2.279 \times \text{total chlorine (mg/L)} - 0.407 \times \text{pH} + 0.277 \times \text{Temperature (}^{\circ}\text{C)} - 0.176$	86.2
LR-4 – Threshold of $5\mu\text{g/L}$, excludes homes with lead $< 1.0\mu\text{g/L}^a$	$Z = -2.166 \times \text{total chlorine (mg/L)} - 0.772 \times \text{pH} + 0.286 \times \text{Temperature (}^{\circ}\text{C)} + 4.214$	82.3
Models based on Entire London 2007 to 2009 Dataset		
LR-5 – Threshold of $10\mu\text{g/L}$	$Z = -5.486 \times \text{total chlorine (mg/L)} - 1.747 \times \text{pH} + 0.041 \times \text{Temperature (}^{\circ}\text{C)} + 16.023$	68.2

^aAssumes no LSL present since lead concentration $< 1.0 \mu\text{g/L}$

a)



b)

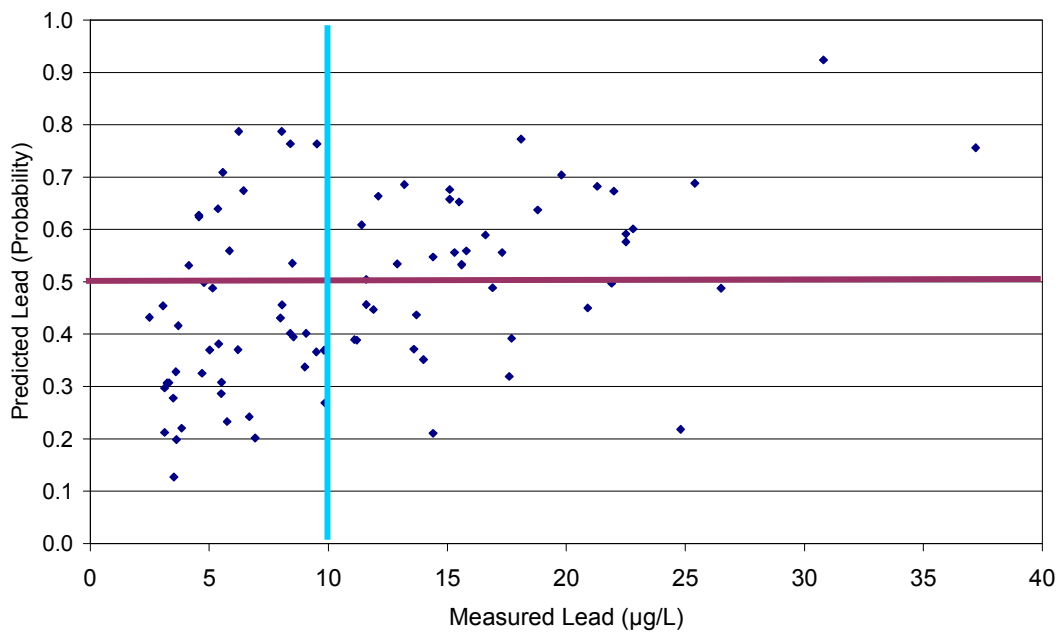


Figure 4.5: Predicted lead vs. measured lead for logistic regression (a) Equation LR-2 for the 1997 to 2008 Ottawa dataset (b) Equation LR-5 for the 2007 to 2009 London dataset. Points below the horizontal line are considered 0 ($<10 \mu\text{g/L}$). Points above the line are considered 1 ($\geq 10 \mu\text{g/L}$). The values in the top left and bottom right corners were predicted incorrectly.

4.3.3 Correlation Between Water Quality and Lead Concentrations in Tap Water

Lead concentrations are dependent on the water quality. As demonstrated by the signs of the coefficients for the regression equations (R-1 to R-7 and LR-1 to LR-5), lead concentration was shown to have an inverse relationship with pH and free chlorine, and a direct relationship with the concentration of the total chlorine (chloramine residual) and temperature.

4.3.3.1 Effect of pH

Lead concentrations were found to vary inversely with pH in this study as illustrated by the regression equations (R-1 to R-7 and LR-1 to LR-5). Water pH is an important parameter affecting lead leaching into tap water since this parameter controls the solubility of lead corrosion scales such as hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and cerussite (PbCO_3) (Tang, 2003). The results in this study support the general finding that lead solubility in distribution systems decreases with increasing pH (Singley, 1994; Schock, 1989; Schock and Gardels, 1983).

4.3.3.2 Effect of Total Chlorine and Free Chlorine Concentration.

Chlorine was found to have an inverse relationship with lead concentrations in tap water as shown by the models derived in this study (R-6 to R-7 and LR-5) based on the free chlorine data collected by London. One reason may be due to the side effect of using sodium hypochlorite for chlorination, which increases the pH and electrical activity of the water. As a result, the passivation barrier is improved and decreases lead solubility (Muylywyk and Gagnon, 2008).

Total chlorine (chloramine residual) was found to have an inverse relationship with lead release based on the total chlorine (chloramines residual) data from Ottawa. However, the literature has shown that the use of chloramines as a secondary disinfectant may result in an increase in lead concentrations. Edwards and Dudi (2004) demonstrated that chloramines do not form a low-solubility lead species when compared to chlorine species such as HOCl/OCl^- , which is a stronger oxidant and oxidizes Pb to Pb(IV) as an insoluble PbO_2 conversion coating. X-ray diffraction analyses have shown that the NH_2Cl oxidizes Pb to Pb(II) species such as $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ and PbCO_3 , which is more soluble than Pb(IV) species formed by chlorine (Switzer et al., 2006; Rajasekharan et al., 2007).

As such, the use of chloramines may result in a greater probability of higher lead concentrations. In this study, a direct relationship between chloramine residual and lead release was not observed in the regression models (R-1 to R-5). Instead, there was an inverse relationship between NH_2Cl and lead release. There have been some reports in the literature where this finding is applicable. In a study by Tang (2003) on the impact of blending different source waters on lead release, X-ray photoelectron spectroscopy surface characterization of lead coupons showed PbCO_3 negatively and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ positively correlated with total lead release in the presence of chloramines. The effect of chloramines on lead corrosion has also been studied using Potomac River water (Lin et al., 1997), which serves as the source water for Washington D.C. In contrast to free chlorine, chloramines actually reduced lead leaching in tests conducted using pure lead materials in a one-month experiment at a pH of 8.2 to 8.5. The spikes in lead concentrations in Washington D.C. may have occurred in older lead pipe samples where preexisting PbO_2 solids were present (Renner, 2004). PbO_2 solids were also reported on pipes by other researchers (Schock et al., 2001; Schock et al., 1996). However, these PbO_2 solids may not be present on the new pipes used in the studies by Lin et al. (1997). Therefore, the inverse relationship between chloramines and lead concentrations for the Ottawa models may be due to the lack of PbO_2 in the pipes.

4.3.3.3 Effect of Temperature

Lead concentrations were found to vary with seasonal variations in temperature, consistent with the models derived in this study (R-1 to R-7 and LR-1 to LR-5). These findings support previous studies where higher temperatures often resulted in higher lead concentrations (Colling et al., 1992; Schock, 1990; Colling et al., 1987; Karalekas et al., 1983). According to a study done in Boston by Karalekas et al. (1983), a close parallel between water temperature and lead was observed in the summer and winter months with a 14°C seasonal change in water temperature from 1976 to 1982. These results were supported by Colling et al. (1987), who reported that the Boston distribution system showed higher lead concentrations in summer than in winter in both untreated and phosphate-dosed waters. Colling et al. (1992) later confirmed this with water dosed at 1.0 mg/L of orthophosphate at 0°C , 5°C , 10°C , 15°C , 20°C and 25°C . Schock (1990) stated that past studies have shown that the effect of temperature for the waters studied was a 2

to 3-fold increase in lead solubility as the temperature was increased from 5 to 25°C, but this increase depends on the pH of the water and the carbonate content due to the effects of temperature on the dissociation, solubility and complexation reactions.

4.4 Summary and Conclusions

Regression models were developed to predict lead concentrations in tap water based on water quality parameters including pH, temperature, free chlorine, and total chlorine. Multiple linear regression proved to generate models with only limited accuracy for predicting lead concentrations. In contrast, a proposed logistic regression model may serve as a useful tool to indicate if water quality parameters may or may not be used to predict whether an elevated lead concentration ($>10 \mu\text{g/L}$) may exist.

5. APPLICATION OF ZONAL MODELS TO LEAD IN TAP WATER DATA FROM THE CITY OF LONDON AND THE CITY OF OTTAWA

5.1 Introduction

The previous chapter highlighted a statistical regression approach to predicting lead concentrations in tap water. This chapter discusses an alternate approach using physical mass transfer and flow models known as computer zonal modeling to predict lead and can be used to assess the effectiveness of lead mitigation strategies (Hayes et al., 2006; Cardew, 2000; Van Der Leer et al., 2002 and 2005). The single pipe model combines hydrodynamics and mass transfer within a pipe, and simulates the transfer of lead from a pipe into water (Van Der Leer, 2002). The zonal model can indicate the potential impacts of corrosion control changes by integrating the single pipe model into a Monte Carlo sampling model that enables the variations in lead service line lengths and lead solubility in the distribution system to be included (Van Der Leer, 2005).

The zonal model may be applied by municipalities such as the City of Ottawa to predict the impact of potential corrosion control strategies on lead concentrations. This model does not take into account particulate lead, and lead that can be leached into the water through household plumbing. Nonetheless, Hayes et al. (2006) have validated the zonal model with data from three English water companies and have stated that this model can be used with confidence for predictive purposes. To run the model, the number of homes and the percentage of those with lead pipes are specified for a particular zone. A zone, according to Van Der Leer (2003), consists of a set of independent houses, which do not affect lead emissions at any of the other houses in the zone, connected to the water main. The main output from the zonal model is a summary of the percentage of houses in the zone that exceed 10 µg/L lead.

Based on the Monte Carlo method, a simulated zone is created through the random ascription of variables such as lead pipe length and pipe diameter (Hayes et al., 2006). Random ascription is used to mimic the wide variation that occurs across real water supply zones. The following assumptions are made:

- 1) The lengths of lead service connections are log-normally distributed.

- 2) The plumbosolvency conditions of the water are based on the initial lead mass transfer rate and equilibrium concentration following a 6-hour stagnation period.

According to Van Der Leer et al. (2002), the plumbosolvency (solubility of lead) condition can be applied as a constant. The lead service connections are separated into a series of elements with each being treated as a stirred tank. According to Hayes et al. (2006), flow is simulated by passing the contents of one stirred tank to the next at a 1-second time interval. In addition, the rate of lead dissolution is determined by reference to an exponential curve that relates the lead concentration to stagnation time. This curve is determined through laboratory plumbosolvency testing or by stagnation sampling at appropriate “reference” houses assumed to have lead service lines. The variable "M" is the initial mass transfer rate that is obtained from the "initial slope" of the dissolution curve, and "E" is the equilibrium concentration after a stagnation period of 6 hours (Figure 5.1). As the value of these variables decrease, the water is less plumbosolvent (less lead dissolves). Van Der Leer (2002) has shown that the plug-flow and the exponential curve assumptions are valid when compared to an exact diffusion model and the three-dimensional simulation of turbulent flow. Water can be characterized by “high” plumbosolvency ($M = 0.2 \mu\text{g}/\text{m}^2/\text{s}$ and $E = 300 \mu\text{g}/\text{L}$), “moderate” plumbosolvency ($M = 0.1 \mu\text{g}/\text{m}^2/\text{s}$ and $E = 150 \mu\text{g}/\text{L}$), and “low” plumbosolvency ($M = 0.02 \mu\text{g}/\text{m}^2/\text{s}$ and $E = 30 \mu\text{g}/\text{L}$).

5.1.1 Calibration and Validation of Zonal Models

The most critical factors that need to be calibrated are the plumbosolvency of the water (M and E) and the percentage of houses that have a lead service line. Calibration means finding M and E for the exponential model of lead diffusion using existing lead data as well as lead service line length and diameter for a given water pH. The calibration varies depending on the availability of data; generic assumptions can be used for M and E as described by Van Der Leer (2002).

Hayes et al. (2006) derived M and E from the results of laboratory plumbosolvency testing (Colling et al. 1987), which involved pumping water through new lead piping (12mm internal diameter) at a constant flowrate of 0.5mL/min that had a retention time of 30 minutes, which equated to a 30-minute stagnation period (30MS), at a constant temperature of 25°C. At the end of the test period, flow was stopped for 16

hours before the lead concentration was determined, providing a measure of the equilibrium concentration (E).

Although M and E values were provided for “low”, “medium”, and “high” plumbosolvency conditions for a pipe with a diameter of 12mm in a study by Van Der Leer et al. (2002), it was also necessary to calculate these values for the lead data from the City of Ottawa to determine the accuracy of the model. Figure 5.1 compares the stagnation curve for low lead solubility from a study by Van Der Leer (2002) with the curve calculated for Ottawa using 2007 data. For this year, the average lead concentration from the first litre after a 30-minute stagnation period was 2.66 µg/L based on data collected from 74 homes, which is used to calculate M. An average lead service line diameter of 0.0127 meters (0.5 inches) and a length of 15 meters from the home to the watermain were assumed for the City of Ottawa (Campbell, 2009). The derivation of M is shown by Equation 5.1. The average lead concentration after a stagnation period of 6 hours is 3.25 µg/L, which is the E value.

$$M = \frac{[Pb] \times \text{Pipe Volume}}{\text{Internal Surface Area} \times 30 \text{ min}} \quad (\text{Equation 5.1})$$

$$M = 2.66 \frac{\mu\text{g}}{\text{L}} \times \frac{1000 \text{ L}}{\text{m}^3} \times \frac{0.0019 \text{ m}^3}{0.5982 \text{ m}^2} \times \frac{1}{30 \text{ min}} \times \frac{\text{min}}{60 \text{ sec}} = 0.0047 \frac{\mu\text{g}}{\text{m}^2 \text{ sec}}$$

Where:

[Pb] = lead concentration after 30-minute stagnation period

$$\text{Volume of pipe} = \text{Length of Pipe} \times \pi \times (\text{Radius of Pipe})^2 = (15\text{m}) \times 3.14 \times (0.0127\text{m}^2 \times 0.5)^2 = 0.0019 \text{ m}^3$$

$$\text{Internal Surface Area} = \text{Length of Pipe} \times 2 \times \pi \times \text{Radius of Pipe} = (15\text{m}) \times 2 \times 3.14 \times (0.0127\text{m}^2 \times 0.5) = 0.5982 \text{ m}^2$$

The lengths of a lead service line are assumed to be a log-normal distribution for the City of Ottawa (Figure 5.3). The purpose of the random ascription of pipe lengths to each pipe model is to take into account the variation in pipe lengths across the City of Ottawa.

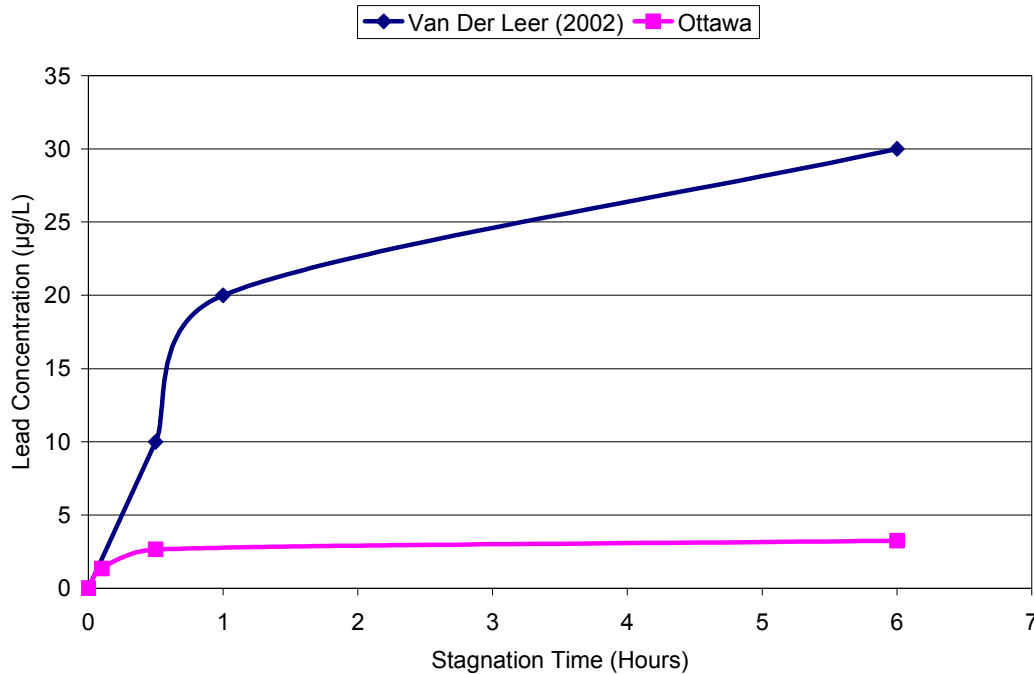


Figure 5.1: Stagnation Curves for M and E - Exponential Lead Diffusion Model based on Van Der Leer (2002) and Ottawa's 2007 Field Data

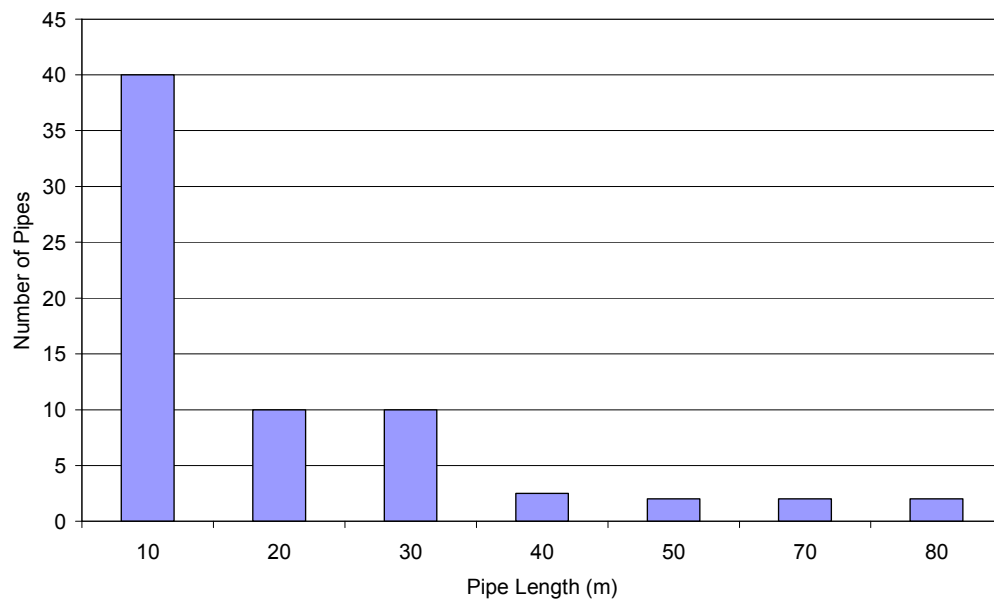


Figure 5.2: Log-Normal Distribution of Lead Service Line Lengths for Zonal Model for Ottawa

5.2 Single Pipe Model

The single pipe model developed by Van Der Leer et al. (2002) can assess the impact of corrosion control changes, such as a pH change, on lead concentrations. The

single pipe model combines hydrodynamics and mass transfer within a pipe, and simulates the transfer of lead from a pipe into water for a single home. Van Der Leer (2002) assumed an exponential diffusion model for lead, which is used to simulate the transfer of lead into water during flow through a pipe (Equation 5.2). Additional details are provided in Appendix B regarding the developing of this model.

$$C = E - (E - c_o) \exp\left(-\frac{AMT}{VE}\right) \quad (5.2)$$

Where

M = Mass transfer rate ($\mu\text{g}/\text{m}^2/\text{s}$)

E = Equilibrium concentration of lead ($\mu\text{g}/\text{L}$)

C = Lead concentration ($\mu\text{g}/\text{L}$)

A = Internal surface area of pipe (m^2)

V = Volume of pipe (m^3)

T = Stagnation Time (seconds)

Although the model is able to accept different flow regimes, the plug-flow assumption was made due to the heavy computational time that is required by the laminar and turbulent flow regimes. The plug-flow assumption was also used in the studies by Van Der Leer et al. (2002) and (2005). Hayes (2006) has also shown that the plug-flow assumption is valid when compared to turbulent flow. The velocity of water (u_j) is constant for plug flow.

5.3 Results from a Single Pipe Model

Figure 5.2 shows the changes in lead concentration at the tap for a house in Ottawa based on the literature M and E values for the exponential model by Van Der Leer et al. (2002) and from the Ottawa data for an average pipe length of 15m and an average pipe diameter of 12.7mm for a high plumbosolvency scenario. However, the model results are different from the actual field data where the peak lead concentrations occurred in Ottawa after 60 seconds, which corresponds to the 4th litre at a flow rate of 4L/minute. In addition, the model tends to underestimate the lead concentrations until 120 seconds where the model predicts the actual data well. This indicates that the single pipe model may have limited use.

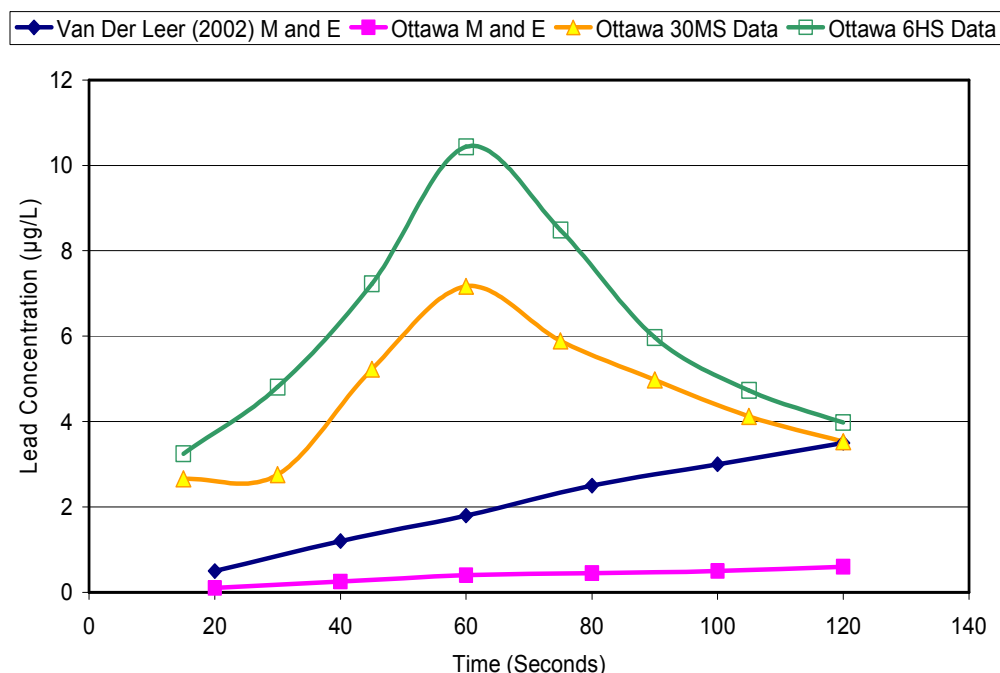


Figure 5.3: Changes in Lead Concentration at the Tap Assuming Plug Flow (Van Der Leer (2002): $M=0.03\mu\text{g}/\text{m}^2/\text{sec}$, $E=30\mu\text{g}/\text{L}$; Ottawa: $M=0.0047\mu\text{g}/\text{m}^2/\text{sec}$, $E=3.25\mu\text{g}/\text{L}$)

5.4 Results from Zonal Model Application

5.4.1 Application of Zonal Model to Ottawa's Lead Data

A comparison was made between the zonal model using the M and E values obtained from the literature and the Ottawa field data collected in 2007 (pH=9.2), which represents a low lead plumbosolvency scenario (Figure 5.4). The year 2007 was chosen since it had the most number of homes (74) sampled using the 30-minute stagnation (30MS) protocol compared to 2006 and 2008. In addition, new M and E values for the exponential model were derived based on the data from Ottawa by assuming an average pipe length of 15m and an average pipe diameter of 12.7mm (Table 5.1). M and E values could be derived for the year 2007 since data were collected using both 30-minute and 6-hour stagnation protocols. The model slightly overestimated the number of homes with lead concentrations $> 10 \mu\text{g}/\text{L}$.

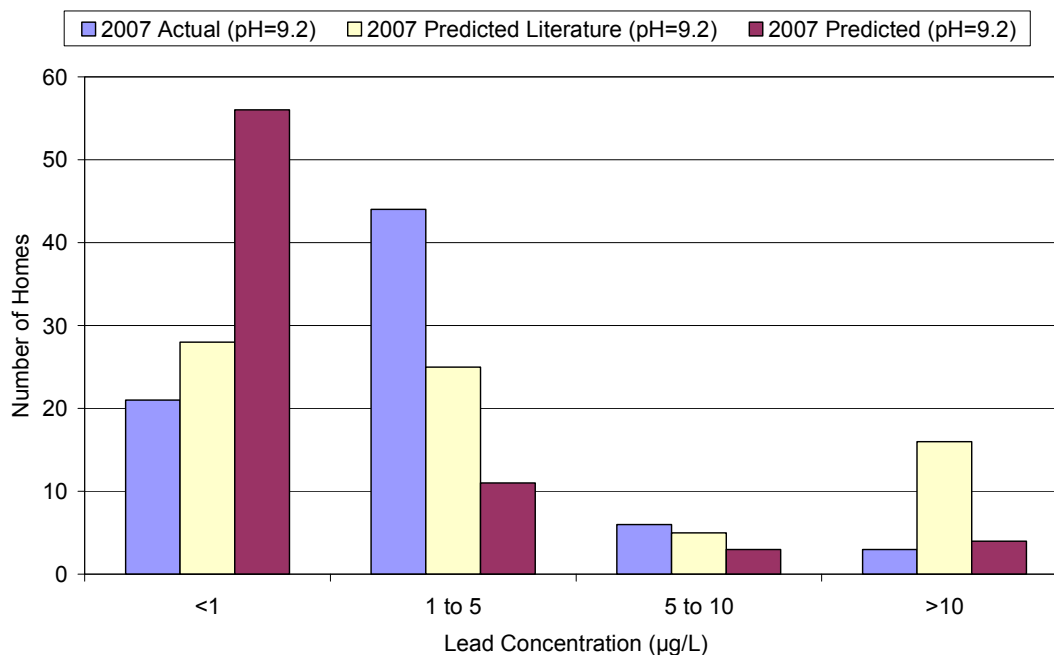


Figure 5.4: Actual vs. Predicted Lead Concentrations for 2007 (pH = 9.5, M = $0.0043 \mu\text{g}/\text{m}^2/\text{sec}$, E = $3.25 \mu\text{g}/\text{L}$; Literature: M = $0.03 \mu\text{g}/\text{m}^2/\text{sec}$, E = $31 \mu\text{g}/\text{L}$)

Table 5.1: High and Low Lead Solubility Scenarios for the City of Ottawa

Lead Solubility	M ($\mu\text{g}/\text{m}^2/\text{sec}$)	E ($\mu\text{g}/\text{L}$)	% houses > 10 $\mu\text{g}/\text{L}$	Actual % houses > 10 $\mu\text{g}/\text{L}$
Low (2007)	0.03 (Van Der Leer et al., 2002)	31	22% (16 out of 74 homes)	4% (3 out of 74 houses)
High (2007)	0.0043 (Based on Ottawa Pipe Length and Diameter)	3.25	6% (4 out of 74 homes)	4% (3 out of 74 houses)

Figure 5.5 illustrates the predicted vs. actual lead concentrations for the years 2002 and 2007. The zonal model tends to overestimate the actual lead concentrations at a pH of 8.5 and underestimate the actual lead concentration at a pH of 9.2.

5.4.2 Application of Zonal Model to London

The zonal model was also applied to the lead data gathered from homes in London from 2007 to 2009. Using data obtained from a pipe-loop study conducted in London, the M and E values necessary for the zonal model were found to be $0.212 \mu\text{g}/\text{m}^2/\text{sec}$ and $165 \mu\text{g}/\text{L}$ respectively. Details of the pipe loop study are provided in

Appendix B. The predicted and actual lead concentrations from the Ontario Ministry of Environment's Community Lead Testing rounds are illustrated in Figure 5.6. This program required the City of London to sample homes believed to have lead service lines from December 2007 to April 2008, June 2008 to October 2008, and December 2008 to April 2009 (MOE, 2009). The model overestimated the number of homes with lead concentrations $> 10\mu\text{g/L}$.

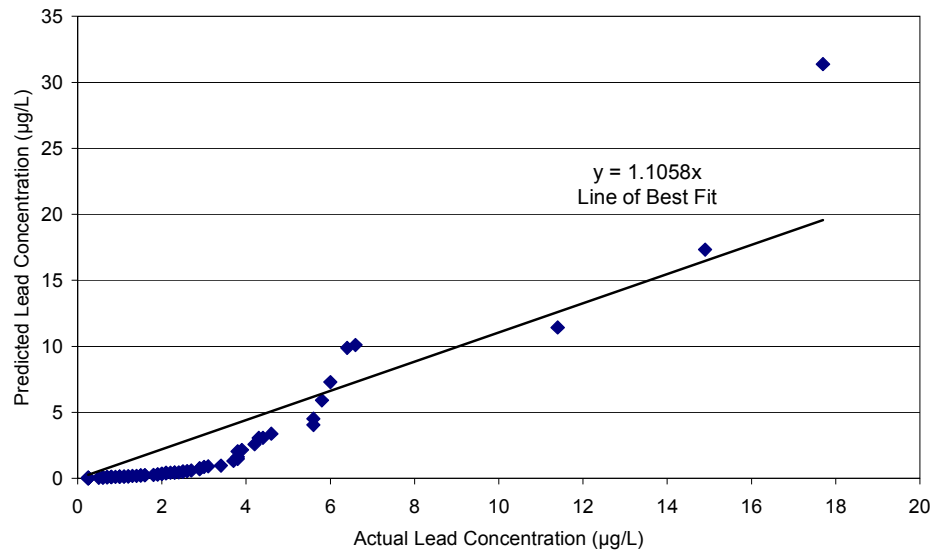


Figure 5.5: Predicted Lead vs. Actual Lead for 2007 Dataset (pH = 9.2) using zonal model ($M = 0.0043\mu\text{g/m}^2/\text{sec}$, $E = 3.25\mu\text{g/L}$)

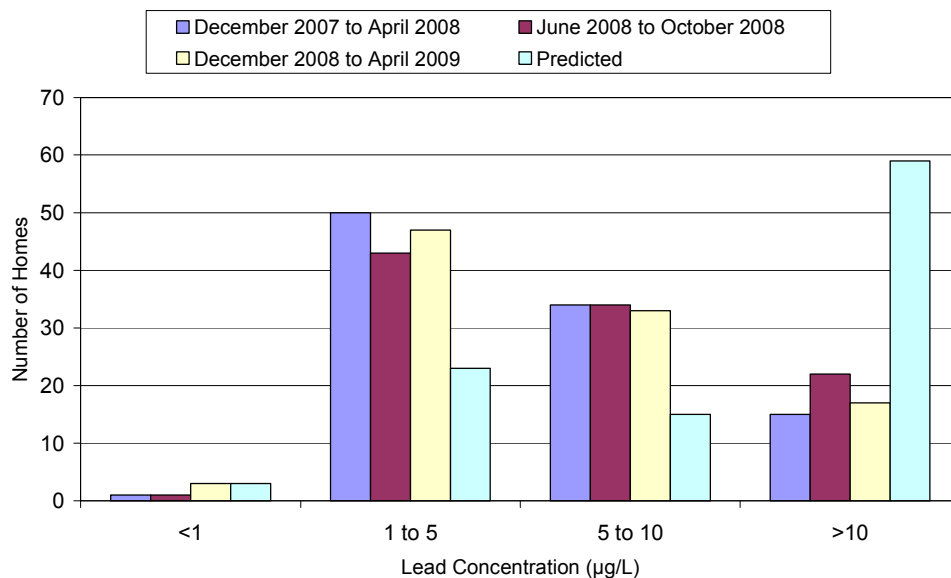


Figure 5.6: Actual vs. Predicted Lead Concentrations for London's Lead Data from the Community Lead Testing Program (pH = 8.1, $M = 0.212\mu\text{g/m}^2/\text{sec}$, $E = 165\mu\text{g/L}$)

5.5 Summary

This study applied the zonal model developed by Van Der Leer et al. (2002) to the City of Ottawa. The zonal model used to simulate the lead concentration at the tap used is based on the assumptions of an exponential model to simulate the transfer of lead into the water within a pipe during a stagnation period, and a plug flow model to simulate the flow of water through a pipe. A Monte Carlo framework was also used to randomly ascribe various pipe lengths to the single pipe model, and repeating this procedure many times (up to 100,000) to represent different homes in the city. The number of lead exceedances is then reported by the zonal model. In the case of Ottawa, the model overestimated the number of homes with lead concentrations $> 10\mu\text{g/L}$ for both the high and low lead solubility scenarios. One limitation of this zonal model is that it models the mechanism of lead leaching from a service line, and does not take into account particulate lead and lead leaching from the home's plumbing system such as the faucets and fittings. Nonetheless, this model may allow cities to obtain an estimate of the impact of corrosion strategies without apriori having to sample for lead in tap water from individual homes.

6. Summary and Recommendations

6.1 Summary

Historical lead in tap water data from two Canadian cities (Ottawa and London) were examined for trends and correlations over time as well as the impacts of temperature and a pH increase. Linear and logistic regression models were developed to predict lead concentrations in tap water based on temperature, pH, free chlorine, and total chlorine in the historical datasets. In addition, an adaptation of the zonal models used in studies by Van Der Leer et al. (2002) were applied to Ottawa and London to determine the accuracy of the model in predicting a range of lead concentrations for these Canadian cities.

The primary objective of this research was to determine the effectiveness of different sampling protocols for lead in tap water. Three sampling protocols were used to collect the lead data in Ottawa. The first was the 5-minute flush protocol where water is flushed for 5 minutes before collecting the water samples. The next two protocols require 30-minutes and 6-hours of stagnation after 5 minutes of flushing before samples are collected. Ottawa also collected eight 1-litre samples using the 30-minute and 6-hour stagnation protocols. In contrast, London used the 5-minute flush protocol to collect a 1-litre water sample and the 30-minute stagnation protocol to collect the first and second 1-litre samples.

Results indicated a difference in lead concentrations depending on the protocol and the volume of the samples collected. For example, the 5-minute flush protocol was consistently associated with lower lead concentrations when compared to the stagnation protocols for both cities. In addition, the 6-hour stagnation protocol indicated higher lead concentrations when compared to the 30-minute stagnation protocol. Furthermore, different litres collected using the stagnation protocol revealed differences in lead concentrations since they represent different sections of the plumbing. Often, the peak lead concentrations occurred in the fourth, fifth, and sixth litres, which indicated that most of the lead was leaching from the home's piping as opposed to the faucets and the fittings.

The second objective of this research was to determine the effect of temperature and pH on lead concentrations in tap water. Results indicated that higher water

temperatures resulted in an increase in lead concentrations in tap water. In Ottawa, when the pH of the effluent water leaving the water treatment plant was raised from 8.5 to 9.2, a statistically significant decrease was observed in lead concentrations at the 95% confidence level for water temperatures $>15^{\circ}\text{C}$. Similar results were observed in the London dataset where higher temperatures resulted in higher lead concentrations.

The third objective of this research was to develop models to predict lead concentrations in tap water based on the historical datasets from London and Ottawa. First, statistical regression models were created to predict lead concentrations in tap water based on pH, temperature, and total chlorine concentration. The models were derived using the datasets from each city based on the 5-minute flush protocol. Linear regression models proved to have limited accuracy when predicting lead concentrations. However, a simplified regression method known as logistic regression proved to be an accurate method for determining whether lead in tap water samples were greater than $10\text{ }\mu\text{g/L}$, which is the Ontario lead standard.

The fourth objective of this research was to apply the concept of a zonal model to predict a range of lead concentrations in tap water for a number of homes in a Canadian City. An adaptation of the zonal model created by Van Der Leer et al. (2002) was calibrated using the historical data from London and Ottawa. The models were then used to predict lead concentrations based on varying lead service line lengths. Results demonstrated that the model may be used with caution as the model tended to be accurate only when predicting lead concentrations greater than $5\text{ }\mu\text{g/L}$.

6.2 Conclusions

- Stagnation protocols consistently illustrate higher lead concentrations in tap water when compared to the 5-minute flush protocol.
- Lead concentrations vary depending on the volume collected by the sampling protocol, which represent different sections of the plumbing system.
- Increases in temperature result in higher lead concentrations.
- Increases in pH may be effective in lowering lead concentrations, but the exact pH value varies depending on the specific location and water quality.

6.3 Recommendations

- Pipe-loop studies should be conducted to assist when calibrating the zonal model for predicting lead concentrations in tap water.
- Alternative modeling tools should be investigated to predict lead concentrations in tap water such as artificial neural networks.
- Collection of important water quality parameters such as alkalinity, hardness and sulphate concentrations should be included in future studies for all homes sampled since these parameters may be used in statistical regression models for better prediction of lead concentrations.

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APPENDIX A: Statistical Analysis Residual Plots for Ottawa

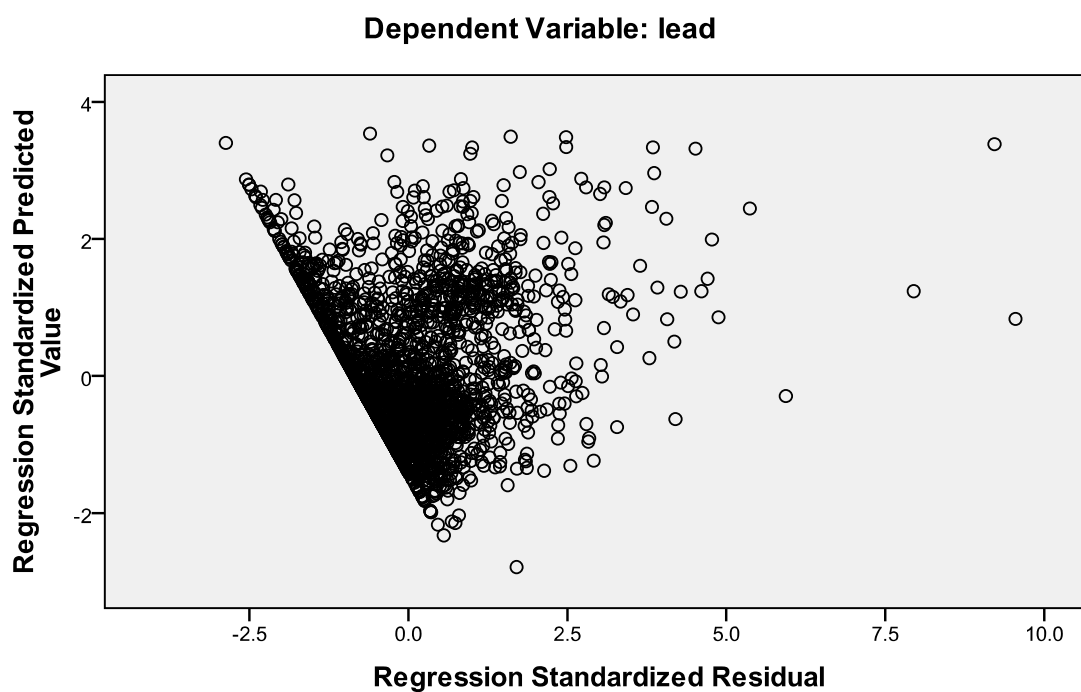


Figure A.1: Standardized Residuals vs. Standardized Predicted Value before Box-Cox Transformation

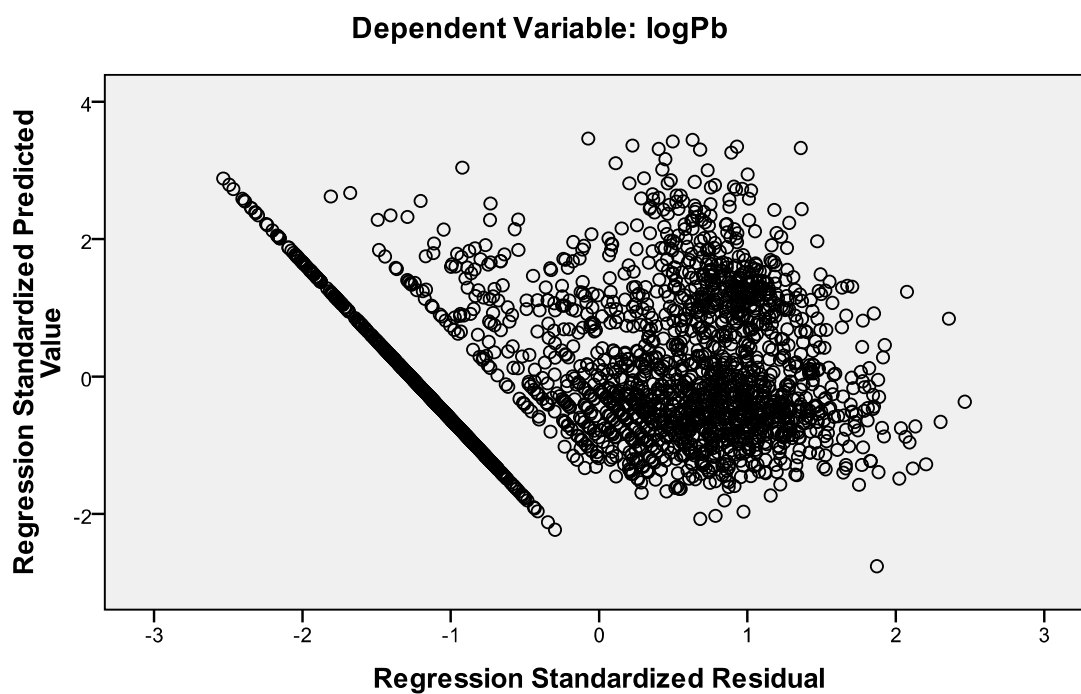


Figure A.2: Standardized Residuals vs. Standardized Predicted Value after Box-Cox Transformation

APPENDIX B: Details of the Zonal Model

B.1 Mass Transfer Model

The single pipe model developed by Van Der Leer et al. (2002) can assess the impact of corrosion control changes, such as a pH change, on lead concentrations without having to sample for lead in people's homes. The single pipe model combines hydrodynamics and mass transfer within a pipe, and simulates the transfer of lead from a lead pipe into water.

Van Der Leer (2002) assumed an exponential diffusion model for lead (Equation A.1). The exponential model is used to simulate lead transfer during flow (Equation A.2). To solve Equation A.1, a finite difference procedure is used where the pipe is treated as a cylinder which is discretised along the axis ($i, i = 1, N$) and in the radial direction ($j, j = 1, J$). Equation A.2, which is equivalent to the conservation of mass of lead within an element (i, j) leads to Equation A.3.

$$C = E - (E - c_o) \exp\left(-\frac{AMT}{VE}\right) \quad (\text{B.1})$$

Where

M = Mass transfer rate ($\mu\text{g}/\text{m}^2/\text{s}$)

E = Equilibrium concentration of lead ($\mu\text{g}/\text{L}$)

C = Lead concentration ($\mu\text{g}/\text{L}$)

A = Internal surface area of pipe (m^2)

V = Volume of pipe (m^3)

T = Stagnation Time (seconds)

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = \text{Source of lead} \quad (\text{B.2})$$

$$\frac{dC_{i,j}}{dt} = \frac{u_{i,j}}{\Delta X_i} (C_{i-1,j} - C_{i,j}) + A_i \left(\frac{M}{\sum_j V_{i,j}} \right) \left(\frac{E - C_{i,j}}{E} \right) \quad (\text{B.3})$$

M = Mass transfer rate ($\mu\text{g}/\text{m}^2/\text{s}$)

E = Equilibrium concentration of lead ($\mu\text{g}/\text{L}$)

C = Lead concentration ($\mu\text{g}/\text{L}$) in element (i, j)

U = velocity of water (m/s)

$A_i = 2\pi r \Delta x_i$ = Internal surface area of element I at the wall of the pipe (m^2)

$V = \pi r^2 l$ = Volume of pipe (m^3)

ΔX = axial length of element i (m)

t = time (seconds)

Using equation B.4, we can find the lead concentration over space and time.

Equations B.4 to B.5 were used to simplify Equation B.3, and were entered into MATLAB (MATLAB Code in Appendix B.3).

$$\frac{dC_{i,j}}{dt} = \frac{u_j}{\Delta X_i} (C_{i-1,j} - C_{i,j}) + d \left(\frac{E - C_{i,j}}{E} \right) \quad (B.4)$$

$$\frac{dC_{i,j}}{dt} = \frac{u_j}{\Delta X_i} (C_{i-1,j}) - \left(\frac{u_j}{\Delta x} + \frac{d}{E} \right) * C_{i,j} + d \quad (B.5)$$

B.2 Flow in Pipe

There are three different flow regimes that can be assumed. The velocity of water (u_j) is constant for plug flow. The velocity of the water is represented by Equation A.6 for laminar flow and Equation B.7 for turbulent flow. Equation A.8 relates r_j to r_o .

$$u_j = \frac{2Q}{\pi r_o^4} (r_o^2 - r_j^2) \quad (B.6)$$

$$u_j = \frac{Q}{0.817 \pi r_o^2} \left(\frac{r_o - r_j}{r_o} \right)^{1/7} \quad (B.7)$$

$$r_j^2 = (r_o - (j-1) * \frac{2r_o}{(J-1)})^2 \quad (B.8)$$

Where

u = Velocity of water within the pipe (m/s)

r_o = Radius of pipe (m)

r_j = Radius of element in pipe (m)

Q = Flow rate of water (m^3/s)

J = element number

B.3 MATLAB Code

B.3.1 Plug Flow Equation

```
function dcj=floweqnj(t, c)
global dx;
global de;
global d;
global uu;
global cc;
global r0;
global c;
global N;
global J;

c=zeros(N*J,1);

dc=zeros(N*J,1);

uu=0.033; %for plug flow

%uu=@(j)cc*((r0-(r0-(j-1)*2*r0/(J-1)))/r0)^(1/7);

for j=1:J
    for i=1:N
        if i==1
            dcj(i+(j-1)*N,1)=-(uu/dx+de)*c(i+(j-1)*N)+d;
        else
            dcj(i+(j-1)*N,1)=uu/dx*c(i-1+(j-1)*N)-(uu/dx+de)*c(i+(j-1)*N)+d;
        end
    end
end
end
```

B.3.2 Exponential Model Code

```
clear;

%define variables

global dx; %delta x
global de; %d/E
global d; %Ai*M/V
global N;
global J;
```

```

global r0;
global cc;
global c;

c=0;
N=5;
J=4;
dx=0.1;
M=0.03;
E=31
n=0;

lp = lognrnd(1,2,1,74);

for i=1:74 %monte carlo simulation
    d=2*3.14*dx*M*0.0127/(3.14*0.0127^2*lp(i));
    de=d/E;
    r0=0.0127; %radius in m
    Q=0.0000667; %flowrate in m3
    cc=Q/pi/(0.817*r0^2); %formula
    c0=zeros(N*J, 1);
    tspan=[0 15];

    [t c]=ode45(@floweqnplug040709,tspan, c0);
    %T(i)=t(i);

    C(i)=max(c(size(c,1),:));

    if C(i) >= 10
        n = 1 +n;
    end
end

n

%plot histogram
figure (3)
hist(lp,50);

figure(1)% one position at different time
%for k=1:J
    plot(t,c(:,J*N)) %plot CN1 CN2 CN3 CN4 with time
    %hold on
%end

```

B.4 London Pipe-Loop Study on the Calibration of the Zonal Model

The City of London conducted a series of pipe-loop tests to determine the effects of various pH levels on the lead concentration of water discharged from lead service pipes. Four lead service pipes (20 feet long) were removed from London properties, and were implemented in their study at different pH values (pH 7.1, 7.6, 8.0, and 8.4).

The City of London's pipe loop test data was used to derive the M and E values required for the zonal model. The pipe at a pH of 8.0 was chosen for this study since the pH value of the effluent water from the water treatment plants are approximately 8.1. Therefore, homes sampled during the community lead testing program are at this pH, and a proper comparison can be made between the validity of applying the pipe loop data to the zonal model and the actual results.

In the pipe loop #3 study, the stagnant unfiltered lead concentrations were used to derive the M and E values. The M value was derived using the equation below. The maximum 30-minute stagnation unfiltered lead concentration occurred on October 7, 2007 at 120 µg/L, and was chosen to represent the worst-case scenario. An average lead service line diameter of 0.0127 meters (0.5 inches) and a length of 15 meters from the home to the watermain were assumed for the City of Ottawa. The derivation of M is shown by Equation 4.1. The E value was estimated to be at 165 µg/L after 17 hours of stagnation.

$$M = \frac{[Pb] \times \text{Pipe Volume}}{\text{Internal Surface Area} \times 30 \text{ min}} \quad (\text{Equation B.1})$$

$$M = 120 \frac{\mu\text{g}}{\text{L}} \times \frac{1000\text{L}}{\text{m}^3} \times \frac{0.0019\text{m}^3}{0.5982\text{m}^2} \times \frac{1}{30 \text{ min}} \times \frac{\text{min}}{60 \text{ sec}} = 0.212 \frac{\mu\text{g}}{\text{m}^2 \text{ sec}}$$

B.5: Pipe Loop Study Details

B.5.1: General Framework for Designing a Pipe Loop Study

Gagnon and Eisnor (2003) proposed a general framework for the implementation and design of pilot-scale distribution systems. Table B.1 provides a general summary of the factors that must be considered. Before implementing a pipe-loop study, clear

objectives must be established. Based on these factors, Table B.2 illustrates some preliminary details of a pipe-loop study that can be conducted to determine the M and E values for the zonal model.

Table B.1: Pipe-loop Factors

Factor	Description
Test Section Style	- Can use permanent pipes or pipe inserts - Use actual pipe sampled in the distribution system vs. using a new pipe (both are useful depending on the purpose)
Pipe rig flow configuration	- Water to flow through once or re-circulated - Flow-through more representative of real life
Flow velocities and stagnation	- Velocity affects corrosion in water distribution systems - Typical flow rate used is 0.3m/s - Longer stagnation periods result in higher lead levels until the oxidant concentration is depleted, and the lead concentration begins to stabilize
Pipe rig site location and duration	- Duration determined by time to maintain stable metal concentrations, and the number of samples required is based on the desired accuracy and confidence in the data result (6 months to 2 years) - Duration should be sited within existing facilities such as water treatment plants or laboratories and close to a water source
Measurement of corrosion and water quality parameters	- Corrosion can be measured by 3 general methods - o Specimen exposure testing (exposure followed by chemical) - o Physical examination and weight-loss measurement) - o Electro-chemical measurement

Table B.2: Preliminary Design for Pipe-Loop Study for Zonal Models

Study Design	Description	Purpose
Physical Characteristics: Test Section Style	Material: Lead pipe Pipe diameter > 25 mm Pipe length > 9m	To simulate residential plumbing conditions on lead release and corrosion control
Hydraulic Conditions	Flow-through (no re-circulation)	Necessary for simulating residential plumbing and lead concentrations at consumer's tap
	High velocity > 0.3m/s	Smaller diameter household tubing results in higher velocities
	Stagnation time at various times (1, 2, 4, 8, 16 hours)	Simulate on/off flow conditions in household plumbing and requires valves with timers or ongoing operator supervision.

B.5.2: Detailed Design of a Pipe Loop Study

A more detailed design was created based on the London Lead Service Pipe-Loop experiment to simulate the effect of different pH values on lead release. The data from this study can be used to derive the M and E values for the zonal model. Water with a certain pH value will be pumped through a pipe section over a 5-hour period for 7 weeks. The flowrate (60L/s) and pipe diameter (0.5" or 0.0127m) will result in approximately 800 litres of water to be pumped through each section daily to simulate an average household's daily water use. The average daily consumption in London is 796.94 litres per day per household based on 2005 National Water Wastewater Benchmarking data (Huggins, 2009). During the 7-week period, one pipe section will serve as control with no pH adjustment to the water. Another pipe section will be adjusted to the desired pH value using a 50% sodium hydroxide (NaOH solution). Samples of the water discharged from the pipe will be collected and analyzed for lead concentration. The pipe-loop will run from Monday to Friday. Each week will have a different pH value to determine the effect of pH on lead concentrations. A sample set of pH values is shown below based on the London study.

It is important to determine whether the control rack and the treatment racks will produce similar standing metal levels, which will provide assurance that all pipe racks evaluating treatment changes are consistent. First, control water can be run through all pipe racks under standard flow conditions. A series of standing samples can be collected to compare the results. If results are unacceptable, test loops should be reconstructed or dropped from the study. This approach can be used for 3-4 weeks depending on the condition of the pipe material

Before the pipe-loop study starts, there are also some recommended pipe rack start-up procedures. There is a need to flush the pipe rack thoroughly to remove debris and other contaminants in the system. Cold water (0 to 30°C) should be flushed for 15 minutes at a water velocity of 1.5 to 3.1 m/s. Following this step, the flushed test loops should be installed in the pipe rack and a programmable timer should be set to regulate the water flow.

PVC piping should be used for the manifold and all other portions of the pipe rack, with the exception of the test loops. The use of PVC pipe will prevent metals

contamination from non-test loop piping sections. Schedule 80 PVC is recommended for use in the manifold to provide additional rigidity to the model. PTFE tape rather than pipe joint sealing compounds is recommended, and PVC check values should be used.

The procedure for the operator is outlined below for each day. The pipe-loop experiment will be located close to a hydrant and there will be a tank that connects to each pipe section (Figure B.1).

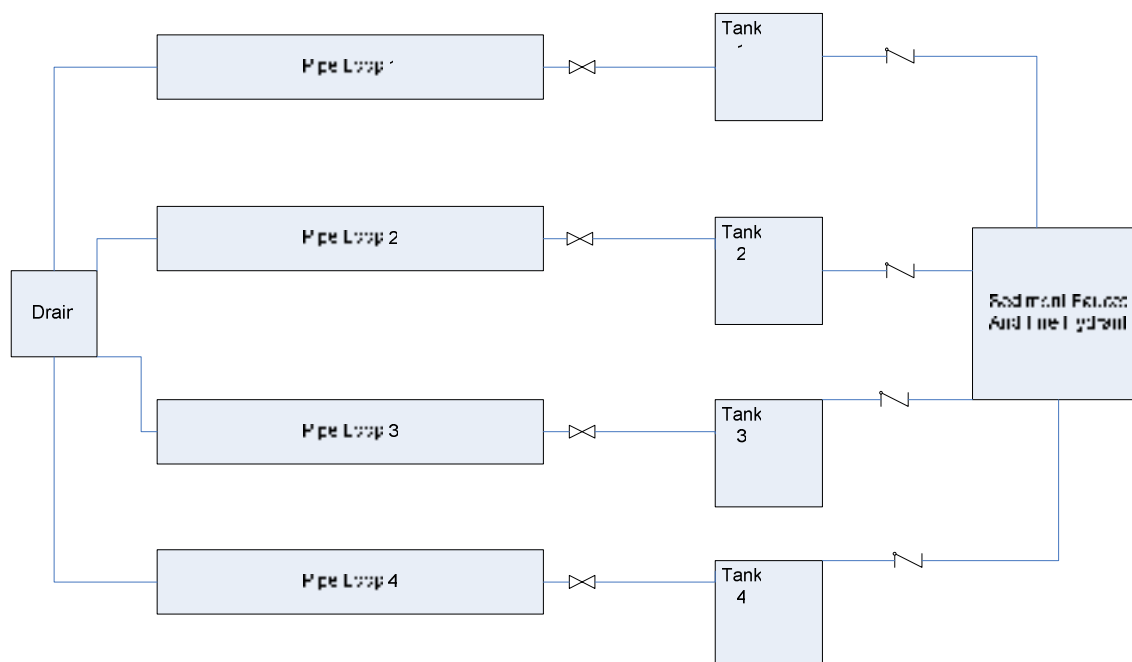


Figure B.1: Pipe-loop Schematic (Pipe Loop 1 is Control)

Steps to operate pipe loops:

- 1) Make sure to drain the water in tanks #1, 2, 3, and 4
- 2) Open the hydrant using a hydrant wrench
- 3) Open the sediment faucet connected to the hydrant port and ensure that the water appears to be clear
- 4) Close the sediment faucet
- 5) Open the tank filling valve
- 6) Open the gate valve that connects the hydrant port to the tank
- 7) Tank 1 will begin filling. When the tank is full, close the valve. Measure and record the pH and temperature using a portable pH meter and thermometer.
- 8) For Tanks 2, 3, and 4, pipette the amount of sodium hydroxide needed to make the desired pH (Table B.3)
- 9) Repeat step 7 to fill tanks 2, 3, and 4
- 10) Close the feed hydrant by turning the hydrant counter-clockwise using a hydrant wrench.

- 11) Measure and record the pH and water temperature in each solution tank using a portable pH meter
- 12) Turn on each discharge pump connecting to each tank
- 13) Establish the desired flow rate by adjusting the pipe discharge valve
- 14) Record the start time of the desired flowrate for each pipe section
- 15) Collect a discharge water sample in a clean beaker for each pipe section, measure pH and temperature of each sample
- 16) When the final flow period has ended for each pipe section, close the pipe discharge valves and record the stop times
- 17) Transfer all readings to a spreadsheet
- 18) Make sure all the valves are closed
- 19) In the morning (after 12 hours of stagnation), fill a 125mL lead sample bottle immediately after the flow rate of 3 to 4L/minute is established to capture water that had been sitting stagnant in the lead pipe to capture water that had sitting stagnant in the lead pipe section
- 20) Record the sample date and time on the label and calculate the stagnation time since the flow rate ended on the previous day (to the nearest 15 minutes)
- 21) The Sample I.D. is to be recorded as "Pipe # X - Y Hours, Z minutes Stagnation.
- 22) Begin the Daily Flow Routine
- 23) Sample each pipe section again during Flow Rate #1.
- 24) The Sample I.D.s for these samples are to be recorded as "Pipe # X – Flow Rate #Y. Also record the Sample Dates and Times.
- 25) After the final flow rate has been completed, the pipe sections will be left stagnant for a period of 30 minutes and then one sample will be taken from each pipe, using the Stagnant Sample procedure described above

Table B.3: Average Volumes of 50% NaOH Required for pH Elevation in 900 L of Water

Target pH	7.1	7.5	7.6	7.8	8.0	8.1	8.4	8.7	9.0	9.3	9.6
mL of NaOH	0	7	9	10	12	13	15	18	22	26	31

Adapted from Braam et al. (2009)

B.6 Recommendations for Statistical Evaluation of Corrosion Control Study Data

There are several statistical techniques that can be used to evaluate the pipe-loop data. First, there is a need to determine data normality. One can use a 1-sample Kolmogorov-Smirnov test to determine whether the distribution is normal. If the distribution is normal, parametric tests should be used. However, if the distribution is not normal, non-parametric tests should be used. Second, there is a need to evaluate data outliers. High lead values should be kept unless there is documented evidence that the sampling or analytical technique for those particular samples was in error

There is also a need to test for stabilization if new lead pipes are being used. Pipe loops constructed of a new pipe material tend to exhibit a decreasing trend in lead over time as the materials age. Hence, there is a need to determine when these levels stabilize if the incoming water quality is consistent. Only data that have reached stabilization should be used when determining impact of treatment on lead levels. Stabilization can be determined by visual examination of the data or calculating an estimated trend line for the data. Another method is to observe if an estimated trend line with a slope equal to 0 since that means metals have stabilized. To determine treatment differences, one can use the Mann-Whitney U-test. One can also use box and whisker plots to determine differences in average lead concentrations between control and experimental pipe sections.

The length of the study depends on the objectives. The total length of the pipe rack study must be determined by the time required to maintain stable metal levels. The number of samples needed to achieve desired accuracy and confidence in data results is shown in Table B.4. It may take 3 to 9 months for lead levels to stabilize in either lead loops or lead-soldered copper loops. The AWWARF pipe loop study conducted by Kirmeyer et al. (1994) recommended operating for 12 months to take into account seasonal variations. When considering water quality sampling and frequency of sampling, this can be divided into 2 major categories: standing samples for corrosion-related parameters and running samples for influent water quality characteristics and operational consistency.

Table B.4: Number of samples required for a certain accuracy level

Accuracy Level	90% Confidence Level	95% Confidence Level
25%	44	62
20%	68	97
15%	121	171
10%	271	385

¹It is recommended that a minimum of 30 samples be collected if possible, for statistical reasons

²Based on a 1:1 ratio of standard deviation to mean

Adapted from (Kirmeyer, 1994)