

**THE EFFECTIVENESS OF pH AND ALKALINITY ADJUSTMENTS IN
REDUCING LEAD AND COPPER LEVELS IN RECHLORINATED AND
CHLORAMINATED TAP WATER**

by
Kenneth C.H. Chan
B.A.Sc.(Honours), U.B.C., 1992

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE**

in
THE FACULTY OF GRADUATE STUDIES
Department of Civil Engineering

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
SEPTEMBER 1994
© Kenneth C.H. Chan, 1994

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

(Signature)

Department of Civil Engineering

The University of British Columbia
Vancouver, Canada

Date September, 1994

ABSTRACT

The effectiveness of pH and alkalinity adjustments in reducing copper and lead levels in rechlorinated and chloraminated tap water was assessed for a study area in Greater Vancouver. Standing cold water, running hot and cold samples were collected from 105 houses that were located in the study areas. The samples were analyzed in the laboratory for lead and copper concentrations, pH, and alkalinity.

After following an complex scheme of data manipulation, sorting, and statistical testing, comparisons of the copper and lead levels between the study areas were made.

This research study found that pH and alkalinity adjustments were definitely effective in reducing the copper levels in rechlorinated and chloraminated tap water. Lead levels were also reduced, but the magnitude of the reduction was statistically insignificant. The effects of pH and alkalinity adjustments on copper and lead levels did not appear to be different for rechlorinated and chloraminated tap water. Compared to houses with copper plumbing, houses with plastic plumbing and no-lead solder had extremely low levels of copper or lead in the tap water. This study also found that the age of a house, which was fitted with copper plumbing and was less than 15 years old, was not a significant factor in affecting lead concentrations.

TABLE OF CONTENTS

ABSTRACT	ii
LIST OF TABLES	viii
LIST OF FIGURES	ix
ACKNOWLEDGMENTS	x
1. INTRODUCTION	1
1.1 Greater Vancouver's Drinking Water	1
1.2 GVRD Initiatives	1
1.3 Study Area & Preliminary Results	2
1.4 Objective and Scope of Study	3
2. BACKGROUND AND LITERATURE SEARCH	4
2.1 Health Impacts of Lead	4
2.2 Health Impacts of Copper	4
2.3 Copper and Lead Regulations	5
2.4 Principles of Metallic Corrosion	5
2.4.1 Uniform Corrosion	6
2.4.2 Galvanic Corrosion	6
2.4.3 Crevice Corrosion	6
2.4.4 Pitting Corrosion	7
2.4.5 Concentration Cell Corrosion	7
2.4.6 Selective Leaching	7
2.4.7 Erosion Corrosion	7
2.4.8 Stress Corrosion	8
2.4.9 Microbiologically Induced Corrosion	8
2.4.10 Chemical Corrosion Mitigation	8

2.5 Previous Studies in Copper and Lead Levels	9
2.5.1 Seattle, WA	9
2.5.2 Boston, MA	10
2.5.3 Glasgow, Scotland	10
2.5.4 Portland, ME	10
2.5.5 Covewood Lodge, NY	11
2.6 Tap Water Sampling vs. Laboratory Simulations	11
2.7 Sources of Copper in Tap Water	12
2.8 Sources of Lead in Tap Water	12
2.9 Factors Affecting Tap Water Sampling Results	13
2.10 Factors Affecting Lead Leaching	16
2.11 Factors Affecting Copper Leaching	19
2.12 Plastic Pipes vs. Copper Pipes	19
2.13 Quality Control in Laboratory Tests	20
2.14 Reporting of Low Level Data	21
2.15 Considerations in Experimental Design	21
2.16 Sampling	23
2.17 Common Assumptions Made in Statistics	25
2.18 Measuring Central Tendency	26
2.19 Measuring Spread	27
2.20 Estimate	28
2.21 Coefficient of Variation	28
2.22 Skewness	28
2.23 Central Limit Theorem	28
2.24 Hypothesis Testing	29
2.25 Constructing Power Curves	30
2.26 Statistics of the Maximum	30

2.27 Systems of Measurement	31
2.28 Nonparametric Testing	31
2.29 Kolmogoroff-Smirnoff Comparison of Two Independent Samples	32
2.30 Median Test	32
2.31 Kruskal-Wallis H-Test	32
2.32 Confidence Intervals for the Difference Between 2 Means	34
2.33 Test for Equal Variance	34
2.34 Spearman Rank Correlations	35
2.35 Regression	36
2.36 One-way ANOVA	36
2.37 Theory of Causation	38
3. EXPERIMENTAL METHODS	40
3.1 Experimental Design	40
3.1.1 Controllable Factors	41
3.1.1.1 Direct Control	42
3.1.1.2 Indirect Control	43
3.1.2 Uncontrollable Factors	44
3.2 Arrangements with Governmental Agencies	46
3.3 Bottle Preparation	47
3.4 Sampling Package	49
3.5 Sampling Procedures	49
3.6 Participation of Homeowners	50
3.7 Bottle Pick-up	51
3.8 Lab Testing	51
3.8.1 Instruments	52

3.8.2 Testing Scheme	53
3.8.3 Data Recording	53
4. RESULTS AND DISCUSSION	55
4.1 Summary of Returned Bottles	55
4.2 Data Cross-check by GVRD	57
4.3 Reporting of Data	58
4.4 Data Used for Statistical Analysis	58
4.5 Non-Parametric Testing	60
4.6 Other Statistical Problems	61
4.7 Identifying Flushed Standing Samples	62
4.7.1 Rejected Samples for n,y,s,w	65
4.7.2 Rejected Samples for d	65
4.8 Simple Tests	66
4.9 Kruskal-Wallis H-Test (Copper)	67
4.10 Confidence Intervals for the Difference	
Between 2 Means	68
4.11 Median Test	68
4.12 Test for Equal Variance	68
4.13 Compliance with Regulations	69
4.14 Plot of Lead vs. Alk and pH	70
4.14.1 Spearman Rank Correlations	71
4.14.2 Regression of Alk and pH	71
4.14.3 Filling in Missing Data Points	73
4.15 Copper vs. pH	74
4.16 Lead vs. pH	75
4.17 ANOVA (Lead)	76
4.17.1 Using One-Way ANOVA	77

4.17.2 One-Way ANOVA grouped by area	78
4.17.3 One-Way ANOVA grouped by pH range with age as covariate	78
4.17.4 Residuals	79
4.18 Testing of Oldcopper and Plastic	82
4.19 Comparison of Flushed Cold and Flushed Hot	83
5. SUMMARY AND CONCLUSIONS	86
5.1 The Effects of pH/Alk Adjustment	86
5.2 Significance of Other Factors	86
5.3 Recommendations	87
6. REFERENCES	88
APPENDICES	
Appendix A Sampling Locations	92
Appendix B Written Sampling Instructions	93
Appendix C Cartoon Sampling Instructions	94
Appendix D Questionnaire	95
Appendix E GVRD Data Crosscheck	96
Appendix F Raw Data	97

LIST OF TABLES

1	Preliminary Copper and Lead Study Results (From 1988 to 1991)	2
2	Typical Data for a Single-Factor Experiment	37
3	The ANOVA Table for the Single-Factor, Fixed Effects Model	38
4	Results of Bottle Treatment Study	48
5	Summary Information of Returned Bottles	55
6	Detection Limits of Measurements	58
7	Summary of Simple Statistical Evaluation	66
8	Percentage Reduction from Delta (mean values)	67
9	Difference Between 2 Means	68
10	Test for Equal Variance	69
11	Regulation Compliance (as per EPA guidelines, 1991)	69
12	Regression Analysis of pH versus Alkalinity	72
13	Comparison of Oldcopper and Plastic with Main Data	83
14	Summary of All Statistical Testings	86

LIST OF FIGURES

1	Comparison of Data Types	60
2	Rejection Procedure	64
3	3D Plot of Lead, Alkalinity, and pH	70
4	Regression Plot of pH versus Alkalinity	73
5	Filling-in Missing Data for pH versus Alkalinity Data	74
6	Copper vs. pH	75
7	Lead vs. pH	76
8	Normal Probability Plot of ANOVA of Lead	80
9	Student t vs. Lead Estimate	81
10	Cook's Distance vs. Lead Estimate	82
11	Quantile-Quantile Plot of Cold & Hot Running Copper	84
12	Quantile-Quantile Plot of Cold & Hot Running Lead	85

ACKNOWLEDGMENTS

This research project was funded by a Natural Sciences and Engineering Research Council (NSERC) scholarship, by the UBC Civil Engineering Department, and by the Greater Vancouver Regional District (GVRD). I would like to thank Dr. Don Mavinic, and Prof. Jim Atwater of UBC, Mr. Doug Neden, Mr. Mark Ferguson, Ms. Judy Smith, and Mr. Indergit Singh of the GVRD for their help in the planning and analysis of this project. I want to thank the staff members at the City of Surrey and the Corporation of Delta for their assistance. My sincere appreciation to all the homeowners in North Delta, Newton, and South Surrey, who participated in this study, for taking the time to collect the water samples. I would also like to thank Ms. Susan Harper, Ms. Paula Parkinson, and Ms. Jufang Zhou of UBC, and Mr. Peter Zadorozny of the GVRD for their expert help in laboratory sample analysis. Soli Deo Gloria.

1. INTRODUCTION

1.1 Greater Vancouver's Drinking Water

The water supply of the GVRD comes from three watersheds on the north shore of the Burrard Inlet. These watersheds, covering a total of 585 squared km of land, are the Capilano, Seymour, and Coquitlam. Each watershed has its own major storage reservoir. The Cleveland Dam is constructed on the Capilano River, the Seymour Falls Dam on the Seymour River, and the Coquitlam Dam on the Coquitlam River.

The drinking water supply of the study areas for this research project mostly comes from the Seymour water source. The water from the Seymour reservoir is untreated except for the addition of chlorine. In 1992, the chlorinated source water was characterized by having an average pH of 6.0, dissolved oxygen content of 10.2 ppm, total chlorine residuals of 0.9 ppm as chlorine, total dissolved solids of 16 ppm as CaCO_3 , and total alkalinity of 2.3 ppm as CaCO_3 (GVWD, 1992). The natural copper and lead levels of the water in the reservoir was negligible.

1.2 GVRD Initiatives

A water with these characteristics is considered to have a high corrosion potential on metals. Since 1984, the GVRD has studied the bacteriological disinfection, and disinfection by-products of the Greater Vancouver's drinking water (GVWD, 1992). Studies have also been done on the corrosion aspects of the water quality improvement program of the GVRD. Corrosion can lead to green staining of porcelain fixtures and basins in bathrooms. It can also increase the copper and lead levels of the tap water. The economic impact of water corrosion is substantial.

Recognizing that the present water supply system is inadequate to meet future demands in Greater Vancouver, GVRD is planning a comprehensive program that will increase storage and transmission capabilities. At the same time, the GVRD's Drinking Water Quality Improvement Plan (DWQIP) is seeking to improve the quality of the

drinking water in order to consistently meet the Guidelines for Canadian Drinking Water Quality.

1.3 Study Area & Preliminary Results

In 1988, a monitoring study was initiated in South Surrey, Newton, and Delta to study the effects of secondary disinfectants on the water supply. Newton received secondary chlorine treatment, while South Surrey received chloramination. The effectiveness of the secondary treatments on controlling bacterial growth were compared to the results from the control area in Delta. Besides the disinfection initiatives, the study areas were also used to study the dynamics of corrosion control. The pH and alkalinity of the Newton and South Surrey areas were raised in order to make the water less corrosive. From 1988 onwards, the pH and alkalinity adjustments have been in continuous operation. It was hoped that collecting tap water samples from various locations in the three study areas would reveal whether or not pH and alkalinity adjustments were effective in reducing the lead levels of the drinking water.

About 15 tap water samples were collected in 1988, just prior to the introduction of pH and alkalinity adjustments. Three years later, in 1991, about the same number of samples were again collected. Of the samples, 6 (2 in Newton, 2 in South Surrey, and 2 in Delta) were collected from the same houses both in 1988 and in 1991. The data almost uniformly supported the conclusion that copper levels in the 1 liter standing samples were lowered after the introduction of pH and alkalinity adjustments. However, the lead data yielded inconclusive results (Table 1).

Table 1 Preliminary Copper and Lead Study Results (From 1988 to 1991)

Sample #	% change in copper	% change in Lead
1	-78	-32
2	-85	+177
3	-89	-38
4	-95	0
5	+16	+12
6	-9	+61

For half of the 6 houses sampled, the lead level increased in 1991 from 1988, whereas it decreased for the other half of the houses.

1.4 Objective and Scope of Study

The 6 data points that were collected in 1991 and 1988 did not give enough data to do any meaningful statistical analysis on the lead data. The main objective of this study, then, was to collect enough samples from the study areas so that meaningful statistical statements could be made on whether or not the pH and alkalinity adjustment program was effective in reducing lead levels in the tap water. Secondly, the copper levels of the collected samples were also analyzed to confirm the conclusion of the previous study that the copper level is reduced after the pH and alkalinity of the water is raised.

2. BACKGROUND AND LITERATURE SEARCH

2.1 Health Impacts of Lead

Lead is not a required trace metal for bodily functions. When taken up, it accumulates in the body. Lead is potentially poisonous to human beings, especially when there is continuous exposure to small amounts of it. Therefore, trace levels of lead in drinking water could become a problem to humans.

Lead has the most harmful effects on infants and young children, followed by adult females, and has the least effect, comparatively, on adult males (National Academy of Sciences, 1982). Upon entering the human body, some of the lead is absorbed in the blood stream and is excreted from the body through the kidneys and the intestinal tracts. Lead can also be deposited in soft tissues, hair and nails. However, most of the lead that stays in the body is found in the skeleton (Department of the Environment, 1977). Lead has a half life of 2 to 4 weeks in blood, about 4 weeks in soft tissues, and 27.5 years in bone (World Health Organization, 1984). Lead can enter the body through water, food, or air. It has been shown that the intake and the uptake of lead in drinking water can be a significant percentage of the total intake and uptake (Drill, 1979). When the amount of lead that has accumulated in the body has reached acute levels, the victim could suffer tiredness, abdominal discomfort, irritability, and anaemia (World Health Organization, 1984).

2.2 Health Impacts of Copper

In contrast to lead, copper is an essential trace metal that is required by the human for normal physiological functions. Long term exposure to copper at low levels does not have documented toxic effects on humans. But, the intake of very large dosages of copper could lead to severe mucosal irritation and breakdown, capillary damage, liver and renal damage, and central nervous system irritation, followed by depression (World Health Organization, 1984). When the body detects that it has an excessive amount of copper in its system, the person is involuntarily induced to

vomitting. This action helps to reduce the amount of copper in the body. Hence, copper poisoning is actually rarely found in humans. Copper is also of concern because it is toxic to fish at relatively low levels. In addition, at high levels, the formation of copper salts can cause blue green staining of plumbing fixtures.

2.3 Copper and Lead Regulations

The USEPA Lead and Copper National Interim Primary Drinking Water Regulations (1991) specified that lead levels in 1 liter standing samples should not exceed 15 ppb in 10% of the samples taken at the tap. Copper levels should not exceed 1.3 ppm in 10% of the samples. The samples are to be taken from the kitchen taps of a number of targeted residences. The public water utilities must show that the water supply does not exceed the prescribed levels for both copper and lead. Depending on the size of the distribution system, a number of samples have to be collected and analyzed in order to determine whether the supplied water meets the copper and lead regulations. When the regulations are shown to be exceeded, then the water utility must implement a corrosion control program. Alternatively, the utility must demonstrate that the existing treatment program has already maximized the level of treatment possible.

In Canada, the Guidelines for Canadian Drinking Water Quality propose different regulations for lead levels. The maximum acceptable concentration (MAC) for lead is 10 ppb (Health and Welfare Canada, 1989). However, this guideline applies to a thoroughly flushed sample. There is no MAC for copper, but it is recommended that copper level be kept below 1 ppm. It is not specified whether this aesthetic objective applies to standing samples or flushed samples.

2.4 Principles of Metallic Corrosion

Corrosion of metals means that the metal is gradually destroyed by chemical or electrochemical reactions with the environment. In almost all cases, metal corrosion in an aqueous environment is caused by electrochemical processes (Obrecht and Pourbaix,

1967). An electrochemical cell must have four important elements in order for the corrosion reaction to take place. First, there must be an anode; this is the place where the metal is oxidized. Electrons are generated from this place and are passed unto the cathode, which receives the electrons. At the cathode, corrosive substances, such as dissolved oxygen, chlorine, and hydrogen ions are reduced. Between the anode and the cathode, a conductor must exist. This is usually the metal pipe, which allows the electron to move from the anode to the cathode. Fourthly, an electrolyte must be present to provide a medium for moving the various ions involved in the oxidizing and reducing half reactions.

2.4.1 Uniform Corrosion

Uniform corrosion usually occurs in copper and lead pipes. In this form of corrosion, the corrosion uniformly penetrates the entire metal surface for a certain depth. Any given site on the metal surface could be anodic at one moment and be cathodic at another (Snoeyink and Kuch, 1985). This phenomenon is promoted when the metal being corroded is immersed in acid solutions or in water with high total dissolved solids (TDS) and with high electrical conductivity.

2.4.2 Galvanic Corrosion

Galvanic corrosion takes place when two metals of different electrode potentials come into contact with each other. The metal with the more positive electrode potential is the sacrificial anode and the metal with the more negative electrode potential becomes the cathode. Galvanic corrosion is a problem when copper pipe connections are soldered by lead solders. The lead solder is the anode, where the lead is converted into soluble ionic species (Oliphant, 1983).

2.4.3 Crevice Corrosion

Threaded junctions, screwed joints and inverted seams are places where crevice corrosion could occur. There is poor circulation and oxygen depletion at these crevices. Halides and sulfates can migrate into these crevices and combine with

dissolved metals to form strong acids. After the local corrosion process is initiated, the crevice becomes bigger, and the rate of corrosion accelerates.

2.4.4 Pitting Corrosion

Pitting corrosion or localized corrosion is a process where the anode remains at a fixed location. This type of corrosion generally occurs on ferrous surfaces. The fixed anodes could be imperfections in the metal or its oxide film. Regions of more highly stressed metal can also serve as permanent anodes. Because the anode is confined to a fixed spot, localized corrosion at that spot will eventually lead to a pin-hole leak in the pipe. Pitting corrosion also occurs where sediment has built up on bottom of copper pipe.

2.4.5 Concentration Cell Corrosion

In a concentration cell corrosion, different parts of the same metal are subject to different environmental conditions and have, therefore, different electrode potentials. The difference of electrode potential between different parts of the metal could be caused by minute differences in pH or concentration of dissolved oxygen or hydrogen ions.

2.4.6 Selective Leaching

Where the supply water is soft and aggressive, the lead component in brass can be selectively leached away. This leaves the copper with more pores and makes it soft and brittle. A similar phenomenon happens when tin is selectively leached from bronze in soft and aggressive water.

2.4.7 Erosion Corrosion

Erosion corrosion occurs when there is cavitation or impingement attacks. At the entrance to pipes, and sharp bends, such as joints and elbows of pipes, the velocity of the travelling water changes according to Bernoulli's Law. The resulting changes in water pressure at these locations may cause cavitation, where gas bubbles trapped in the water collapse and produces high localized pressure on the pipe surface. Impingement

attacks occur when the gas bubbles directly strike the metal surface. The energy that is released is sometimes sufficient to breakup protection films that have built up on the pipe surfaces.

2.4.8 Stress Corrosion

During the threading of pipe ends, the cold working of the metal often causes it have to dissimilar stress on different parts of the metal. This could lead to localized corrosion. The threaded ends of galvanized steel pipes are especially susceptible to this kind of corrosion mechanism.

2.4.9 Microbiologically Induced Corrosion

Microbiologically induced corrosion is, as yet, a poorly understood, but important form of corrosion. Bacteria can live on the surface of pipes. Nitrifiers, for example, use the ammonia in the water as a source of energy. During biochemical reactions, oxygen is used to oxidize the ammonia. Hydrogen ions are produced in these reactions. The resulting acidic environment that is produced encourages the reaction rate of the other forms of corrosion mentioned. Where chloramination is the choice of disinfectant, the availability of ammonia in the water system clearly encourages the activities of nitrifying bacteria. Microbiological corrosion can also be induced by iron and sulfur reducing bacteria.

2.4.10 Chemical Corrosion Mitigation

The majority of the corrosion mechanisms are influenced by such parameters as pH, dissolved oxygen, standing time, the buffering capacity of water, and the mineral content of the water. In general, a soft and aggressive water promotes corrosion, and a harder, less aggressive water decreases the potential for corrosion in the water supply system. Controlling corrosion, by making the water harder, is termed "neutralization". Alternatively, a passivation approach may be employed, where inhibitors, such as phosphate and silicate inhibitors, help to form a protective film on the pipe surface to block the contacts between the electrolytes, the anodes, and the cathodes. The

passivation approach is more expensive to operate than the neutralization approach. Using Zinc orthophosphate inhibitor appears to decrease copper corrosion but may actually increase lead corrosion (MacQuarrie, 1993).

The neutralization approach primarily involves adjusting the pH and alkalinity of the water to make it less aggressive. pH adjustment should always be accompanied by alkalinity adjustment, in order to provide enough buffering capacity to limit pH fluctuations. Due to the lowering of pH from carbon dioxide absorption, the pH of the water can drop after the neutralization step. The side effect of the neutralization approach are that raising the pH also increases the rate of THM formation and decreases the effectiveness of chlorine disinfection.

2.5 Previous Studies in Copper and Lead Levels

In previous years, other cities have tried to solve their copper and lead corrosion problems with pH and alkalinity adjustment programs. Based on the following studies, it has been shown that pH and alkalinity adjustments can reduce the lead levels at the tap by 35% to 75%.

2.5.1 Seattle, WA

The Seattle Water Department (SWD) provides drinking water to over one million people living in the Seattle Metropolitan Area. The water supplies come from the Cedar and the Tolt Rivers, which are characterized by low pH and alkalinity. In 1982, a corrosion control program was initiated to reduce corrosion and related aesthetic and economic problems. To the Cedar and the Tolt water supplies, 2 mg/L of calcium oxide was added. In addition, 9 mg/L of sodium carbonate was added to the Tolt supply (AWWARF, 1990). The effectiveness of the treatment program was extensively monitored throughout the areas serviced by the water supplies. Of the sampling sites, about half were randomly chosen, while the other half comprised of houses that made complaints about the water concerning rust stains, yellow water, and

metallic taste. Both standing and flushed samples were taken. The results of the monitoring program showed a lead reduction of 61 % to 68 %.

2.5.2 Boston, MA

Boston purchases its drinking water from the Metropolitan District Commission, which operates a surface water supply system. The water delivered to Boston had a pH between 5.9 to 6.8, alkalinity of 8 mg/L as calcium carbonate, and hardness of 12 mg/L as calcium carbonate (Karalekas et. al., 1983). In 1977, after unsuccessfully trying to control the lead corrosion problem by adding inhibitors, the pH of the water was raised to 8.5 by adding 14 mg/L of sodium hydroxide. Residences from areas that had lead service lines were chosen for monitoring the lead levels at the tap. Some of these residences also had interior lead plumbing. The average lead levels were reduced by 73 %, and the variability of the lead measurements also decreased significantly after the pH adjustment. The flushed samples exhibited highly skewed concentration frequency distributions.

2.5.3 Glasgow, Scotland

The water supply of Glasgow comes from Loch Katrine. The water is characterized by low alkalinity and a pH of 6.2. Due to the fact that there were extensive lead domestic plumbings, 50 % of random tap samples registered lead concentrations in excess of 100 ppb (Richards et. al., 1984). Beginning in 1978, lime was added to the Milngavie Treatment Works. The pH of the water supply was increased from 6.3 to 7.8. Random tap samples collected after the pH adjustment showed a decrease in lead concentrations to the point where more than 80 % of the samples had less than 100 ppb of lead. In another part of the distribution system, Kings Park (which is close to the end of the distribution system), the pH was increased to 9.0. The pH adjustments resulted in more than 83 % of the samples from this area having lead levels less than 100 ppb.

2.5.4 Portland, ME

The major source of water supply to the Portland Water District is the Sebago Lake. In addition, three well systems supplement this water supply. In 1986, the pH of the water was raised to 8.3 through the addition of sodium hydroxide (AWWARF, 1990). The reduction of copper levels in standing samples was 61 % to 85 %. The reduction of lead levels was about 69 %.

2.5.5 Covewood Lodge, NY

Covewood Lodge is a resort in upstate New York, and contains several cabins. A spring that has low pH and low alkalinity serves as the major water supply for this resort. In 1981, a baffled limestone contactor was constructed to treat the water of a few cabins at this resort. The dissolved calcium carbonate raises the pH of the water to 7.3 and the alkalinity to 28.5 mg/L (AWWARF, 1990). Over the next 2 years, 23 samples were taken and analyzed. It was found that the average lead level for the untreated cabins was 46 ppb and the average for the treated cabins fell to 18 ppb.

2.6 Tap Water Sampling vs. Laboratory Simulations

In order to assess whether a corrosion control strategy will improve the quality of supplied water so that it complies with the USEPA copper and lead rule, a field study or a lab simulation can be conducted. A properly designed tap water sampling survey can determine the level of lead and copper in the distribution system, and the effectiveness of a corrosion control program in reducing the level of lead and copper at the tap. The significant disadvantage to this approach is that any corrosion control experiment could actually adversely affect the quality of the supply water. A safer approach of determining the effectiveness of a corrosion control program is to do a laboratory simulation of the various corrosion control options. Pipe loops, and coupon testing have been used for a long time to assess corrosion rates and the relative impacts of various water treatment options. The major problem with using a laboratory simulation is that we do not know enough about the sources of lead, and the

mechanisms for lead mobilization, in order to accurately simulate an actual water distribution system.

2.7 Sources of Copper in Tap Water

Copper in tap water comes mostly from the leaching of copper from the water supply system. Leaching of copper can occur in the transmission or the distribution system. However, most of the copper leaching takes place in the household plumbings. The copper can be leached from the copper pipes and faucets. Copper leaching from brass faucets is the major source of trace copper in the tap water.

Copper might also be found in significant concentrations in the source water. Copper can be introduced into water from natural and anthropogenic sources. Through natural erosion, copper particles can be picked up and deposited in water sources by wind. Infrequent natural phenomena, such as volcanic eruptions, can also extrude a great deal of copper dust into the environment. Of the anthropogenic sources, copper is introduced into the environment in metal production, wood and fossil fuel combustion, and waste incineration activities (Environment Canada, 1981).

2.8 Sources of Lead in Tap Water

The lead found in tap water could be from the water supply source, the water treatment process, the transmission and the distribution system, or the service and household plumbings. The following is a list of potential lead sources (adapted from AWWARF, 1990).

Water source and water treatment:

- lead containing air pollutions, emitted by industries that are located near raw water sources
- deposits of lead-bearing materials that are naturally found in the watershed
- point sources of domestic wastewater or industrial discharges, located upstream from the water intake, that might contain lead

Transmission and distribution system:

- lead pipes in the distribution system
- large water meters or flow detector checks that have a lead counter weight inside
- lead-caulking compounds used to seal joints in the water mains
- lead gaskets used as flanges to join large valves

Service piping and household plumbing:

- resetters for meters that used 50:50 lead/tin solder as the joining material
- lead or lead-lined iron service lines or premise piping
- lead goosenecks or lead pigtails
- lead solder used to join copper service lines or copper premise piping
- brass fixtures and fittings or pipes with high lead contents
- water coolers that have lead components

2.9 Factors Affecting Tap Water Sampling Results

The variation of tap water results is caused by a number of analytical, chemical, and physical factors. Uncertainties of instrument calibration, and random instrument response errors are two of the most important analytical errors that could be made. In addition, there could be procedural errors, such as errors in dilution, and sample manipulations. The presence of potential interferences in the samples could also increase the analytical variability of data.

The lead levels at the tap are affected by the alkalinity, pH, and dissolved inorganic carbonate (DIC) of the supply water. For example, the equilibrium lead concentration in the pH range of 6 to 8 could vary by a factor of 5 to 10 per pH unit (Schock, 1980, 1985). The actual amount by which the equilibrium concentration varies is dependent on the type of solid that forms on the pipe surface.

Changes in any of the chemical characteristics of the water or in the chlorination practice, such as the chlorination dosage or the relative proportion of free and combined chlorine, could cause a subsequent change in the corrosivity of the water.

The initiation of corrosion treatment to the water supply could result in changes to the solubility and the adherability of the corrosion products to the pipe walls.

Likewise, the standing time of a sample is important. The amount of time the water is left standing in the pipe can affect the pH, chlorine residuals, dissolved oxygen level, temperature, calcium and magnesium hardness, and total and carbonate hardness of the water.

Physical factors can also influence the outcome of the lead levels at the tap. There are normally interconnecting lines within a plumbing system in a house. The water in the kitchen faucet is connected in some way to the faucets in the bathroom, utility room, and the exterior of the house. Any water usage from any of these faucets will cause some mixing of the water in the plumbing system.

When the faucet, from which the sample is taken, is turned on, a plug flow condition is created. As the water is drawn through the pipe, the shape and the length of the original plug of water flowing through the pipe is altered by the friction of the water against the pipe wall and by mixing due to turbulent eddies generated in the water. In almost all houses, the pipe diameter changes from the point where the service line connects with the house plumbing to where the interior plumbing connects with the faucet. At these junctures, there could be alterations to the shape of the original plug flow. The extent to which this occurs depends on the flow rate, the distance between joints, and the size and interior condition of the plumbing system (AWWARF, 1990). The amount of a plug of standing water that can be recovered in sample collection depends on the volume of samples taken relative to the diameter of the pipe, the size of the plug of standing water, and the degree of water mixing in the system. Therefore, even if the faucet from which the samples are taken has not been touched, the sampled water could still be effected by the mixed water.

The contribution of metals from the various parts of the plumbing system can be isolated by varying the volume of water sampled. The precision in identifying the

contribution from the faucets, for example, increases as the volume of water collected is decreased. The internal volume of the faucets differs according to the faucet design. Most kitchen faucets are usually about 90 to 120 mL (AWWARF, 1990). Bathroom faucets are smaller. Since standing samples are usually 250 to 1000 mL, measuring the contribution of the metals from the faucets requires collecting samples that have less volume than the volume for the standing samples. In comparing data from one sampling study to another, it is important to note the size of the samples collected.

It is important to consider the physical state of the lead which we want to measure. The popular mass transfer model of Kuch and Wagner (1983) deals with lead in its various aqueous forms of free ion, ionic complexes, and uncharged complexes. One study examined the size distribution of lead in tap water (AWWARF, 1990). The study found that 65 % to 84 % of the lead was less than or equal to $0.4\mu\text{m}$. The dissolved lead species are of most concern to sampling studies because they are easily taken up into the human body after being ingested.

The Kuch and Wagner model predicts the amount of lead picked up during steady-state turbulent flow through lead pipe. It can also calculate the concentration of lead in the water under no flow conditions in the water. To use the model for predicting lead concentrations in steady flow conditions, the experimenter must know the diameter of the pipe, the pipe length, the water temperature, and the volume rate of water flow. As well, an observed equilibrium lead level must be ascertained ahead of time by analyzing field samples. An estimate for the mass transfer coefficient and the diffusion coefficient of the Pb^{++} must also be made. However, the mass transfer coefficient is only important if the pipes have thick coats of scales that inhibit the diffusion of lead into the water.

In addition to the dissolved forms of lead, particulate lead is present in water distribution systems as well. Lead can be adsorbed onto foreign particles, such as iron oxides, corrosion products, or calcium carbonate particles. There can also be

adsorption or ion-exchange with sediment materials, colloidal hydrous ferric, and manganese oxides (AWWARF, 1990). The complicated reactions involving lead with other substances is probably regulated and influenced by the chemical characteristics of the supply water.

2.10 Factors Affecting Lead Leaching

The contact of water with lead soldered joints makes the water nearby the solder enriched in lead. The contact between the solder and the water allows the lead in any lead containing solder to migrate into the water by the process of simple diffusion. Depending on the amount of time the water is in contact with the solder, and the amount of lead containing solder that is present in the plumbing system, variable amounts of lead can be leached into the water.

Small differences in the amount of time water stands in a pipe containing lead can contribute to considerable differences in the degree of lead leaching. Differences of 10% to 30% in lead concentration is achieved in standing times that differ only 30 to 60 minutes. Lead leaching occurs at a faster rate in pipes of small diameters (USEPA Project Report).

Brass faucets contain lead that can leach out into the water. The amount of lead leaching from brass faucets depend on the stagnation (standing) time of the water in the faucet. The leachability of lead from brass probably decreases with the age of the faucet (Neff, 1987). The phenomenon is due to the fact that the leachable zone at the metal surface is depleted of lead, or because a passivating film is deposited on the metal surface (Sharrett, 1982; Britton et. al., 1981). A study that showed very high lead concentrations from standing samples implicated the brass faucet as an important lead source (Murrell, 1985).

The liberation of lead from brass faucets is due to dezincification. In areas where the free energy of the alloy is above the average value, dezincification can occur (Oliphant, 1978). These abnormal areas are the result of crystallographic dislocations,

distortion of the normal atomic array due to casting or drawing of the alloy, inhomogeneities in the alloy, or the presence of impurities. At these places, the zinc selectively dissolves and leaves the copper and any lead impurities behind. The contact between the lead impurities and the copper matrix can result in galvanic coupling and subsequent lead oxidation.

Numerous studies (Moore, 1973; Schaut, 1942; Gregory et. al., 1984) have shown that there is an approximately 2 to 3 fold increase in lead solubility when the temperature of the water is increased from 5 to 25 °C. Because temperature affects various dissociation, solubility, and complexation reactions, the actual amount of increase in lead solubility will also depend upon the pH of the water and its carbonate content.

Particulate lead can be formed through the precipitation of lead solids, which may deposit on the pipe surface as passivation film. However, if the velocity of the water flow through the pipe is too high, these lead deposits might slough off. Relatively large pieces of solder can also be dislodged from the solder mass. The solder will travel down the pipe until it is stopped by a bend, elbow, restriction, or the screen in the faucet. Through the mechanism of leaching, the continuous exposure of these particulate lead in the plumbing system can elevate the lead levels of tap water samples.

Many plumbing systems use components that are made of a variety of different materials. The service lines could be made of lead, the interior plumbing of copper, and the solder of lead and tin. In these situations, when the different materials come into contact with each other, such as when copper pipes are soldered together with lead/tin solder, a galvanic corrosion current is produced (Lyon et. al., 1977). This leads to the dissolution of the metals. Solder is shown to be anodic relative to copper pipes. Water acts as a bridge between the solder and the copper, the two poles of the corrosion cell. Galvanic corrosion at the solder joints can be a problem even if the

capillary joints are well made (Oliphant, 1983). The presence of chloride, and nitrate can increase the galvanic corrosion rates of soldered joints. The chloride penetrates and breaks down the protective films on the pipe surface. Nitrate stimulates corrosion activities at places where the protective film is exposed. The shift in pH changes the solubility constants, hence, the degree of protection, of the protective films. Furthermore, the overall corrosion rate at a soldered joint is determined by the aggressivity of the water supply.

Not all galvanic corrossions are due to the plumbing system itself. At least one study has shown that copper in the water supply can deposit on lead pipes and create a localized galvanic electro-potential cell (Britton et. al., 1981).

A newer house, with predominantly newer copper plumbing systems, gives rise to higher lead levels than do older houses. Age has a marginal effect on cold first-flush lead concentrations. However, hot water lead levels appear to be unaffected by age. Cold first-flush lead levels appear to be the same for copper and plastic plumbing systems. This result is the same for running hot water samples (Singh, 1990).

Lead exists in its elemental form in plumbing materials. In alloys, such as brass, the lead component is spread throughout the alloy matrix in particle form. The elemental lead is oxidized to the 2+ valence state when it comes into contact with water. This oxidation process enables the lead to become mobile and transportable into the water. These oxidation processes usually take place at the anodic areas of corrosion cells.

In potable water systems, dissolved oxygen and various chlorine species introduced through disinfection are the most common kinds of oxidizing agents for lead. The oxidation reaction is promoted by increases in the dissolved oxygen content, by decreases in pH, and by the complexation of free lead ions by ligands such as carbonate, hydroxyl, sulfate, and chloride (AWWARF, 1990). The effects of chlorine species on lead oxidation depends on the activities of hydrochlorous acid, hypochlorite

ion, chloramine species and chloride ion. One study showed that, under some circumstances, chloramination can solubilize more lead than chlorination with free chlorine. However, the rate of corrosion due to chloramination is slower than chlorination (Treweek, 1985). Also, the complexation of lead by hydroxyl and carbonate ions predominate in normal situations (Schock, 1985).

The rate of oxidation reactions goes up with increasing temperature; however, at the same time, the solubility of many film-forming solids goes down. As a result, the rate of lead oxidation might increase, while the diffusion of the oxidation products to the surface of the pipe scales could face inhibitions. The scouring action of water on the pipe scales can expose certain parts of the pipe to oxidation processes. This serves as a new source of solubilized lead and film-forming components.

2.11 Factors Affecting Copper Leaching

A newer house, with predominantly newer copper plumbing systems, gives rise to higher copper levels than do older houses. Age strongly influences cold first-flush copper concentrations; however, hot water copper levels appears to be unaffected by age. Cold first-flush has low copper concentrations for plastic pipe compared to that for copper pipes. This result also holds true for running hot water samples (Singh, 1990).

2.12 Plastic Pipes vs. Copper Pipes

In contrast to copper pipes, plastic pipes should have less problems with corrosion and metal leaching. For this reason, plastic pipes are now commonly installed in new homes as the preferred plumbing material (Economic and Engineering Services Inc., 1990).

Plastic pipe is made primarily of polymerized organic compounds. Some residual unpolymerized monomers may be present. PVC pipes are made by extruding thermoplastic PVC at temperatures between 150 to 200 °C. In order to make the process more stable, lead or tin compounds are commonly added. The presence of this

lead in the PVC pipes could contribute, but not necessarily, to minor levels of lead leaching. As well, there are other problems with using plastic pipes, such as the risk of leaching carcinogenic and other organic compounds.

2.13 Quality Control in Laboratory Tests

A sample validation process should be in place to make sure that a measurement is correctly reported for the sample from which it came. Where the samples are taken from a targeted population with known water characteristics, the samples should be analyzed for those characteristics to verify that they correspond to the expected values. If a sample does not meet the criteria for a good sample, it should be excluded from the database.

For analyses involving metal ions, samples should be acidified to pH of less than 2. The acidification of the samples minimizes the possibility of the metal ions precipitating or adsorbing onto the walls of the containers (Mancy, 1971).

The quality of sampling data depends heavily on the precision and the bias of the measurement methods and instruments used. If the samples are tested by several laboratories, the variability of measurements between the laboratories will be affected by the type of instruments and reagents used, the sampling handling techniques, the differing abilities of analysts, and the quality of laboratory support facilities.

Both quality control and quality assurance programs should be employed. Quality control refers to those activities, such as spiking, and calibration, that are used to assess the quality of the measurements. Quality assurance is the larger, overall management system that ensures that the quality control program is working effectively (Keith, 1991). Normally, quality control charts are drawn to measure the stability of the measurement instruments. Standards are periodically tested. The measurement process is out of control when a measurement of the standard is above the upper (UCL) and lower than the lower (LCL) control limits; these are defined to be plus and minus 3

sigma around the sample mean. When the process is out of control, the instrument has to be recalibrated and the samples reanalyzed.

2.14 Reporting of Low Level Data

Zero or negative values in measurements are usually considered to be outliers. This presents a problem when most of the measurements in a sampling program, such as found in this study, have true values that are expected to be close to zero.

Every measurement instrument has its detection limits. There are three basic expressions of the detection limit. Firstly, there is the limit of detection (LOD). This is the lowest concentration level that can be statistically determined to be different from a blank at a specified level of confidence. Secondly, there is the reliable detection level (RDL). This is the concentration at which we can say it is extremely likely that there is detection. Thirdly, there is the limit of quantitation (LOQ). This is defined as the level above which concentrations can be specified with a certain degree of confidence (Keith, 1991). The LOD is usually set at three times the standard deviation of the instrument precision (3σ). This ensures that we encounter "false" positives only 0.1% of the time, i.e., 99.9% level of confidence. If RDL is chosen to be 6σ , as is the convention, then the chances of having false negatives is also 0.1%. The LOQ is usually recommended to be set at 10σ . Values at the LOQ have an uncertainty of plus and minus 30% at the 99% confidence level.

A measurement that is lower than the LOD is sometimes not included in the data analysis because we can not be sure about the actual values of these very low level measurements. These measurements theoretically have finite, and positive values. Ignoring all data less than LOD might result in a left-censored data set. This means that the resultant database might be biased to the right. Some people prefer to retain all of the data as is, including all the values that are less than LOD (ASTM, 1984).

2.15 Considerations in Experimental Design

Most of the previous studies that looked at the metal levels in buildings or houses only reported the mean values of the metal levels. However, almost none of these same studies examined the variability of the metal levels in the system. It has been well documented (Bailey, 1986) that the mean lead level in one house can be significantly different from the mean lead level in another house of the same area. This result shows that the distribution of lead in the water supply system is a highly variable process. Not only is there a great deal of variability between the sampling sites, there is also a high degree of variability within the same site. Published field and laboratory studies of lead, solder, and brass corrosion (AWWARF, 1990) indicate that the equilibrium condition is usually not achieved in most samples taken. According to the Kuch and Wagner model of the lead stagnation curve, there is a sharp rate of change for lead before the equilibrium level is reached. This means that at concentrations much below the equilibrium, the level of lead in a standing sample could vary by a wide margin. In this case, it is clear that sampling should be repeated several times, for each house, in order to reflect the variability within each site.

To ascertain the effectiveness of a corrosion control strategy on reducing metal levels at the tap, detailed statistical analyzes should be performed. Some problems are common to statistical reporting (Study Group on Environmental Monitoring, 1977). These include: lack of statistical sophistication, no calculations of the precision of estimates, no statement of the test hypothesis, insufficient sample size, no description of the method of sample collection, no non-response mechanism, and no respondent bias mechanism.

Much effort should be paid to the selection of sampling sites to ensure that the sampling program yields the desired results. In general, the more sampling sites are included in the study, the more accurate will be the results. However, it is not easy to persuade some homeowners to provide standing samples. Due to budgets, any monitoring program will have constraints on how many samples can be collected and

analyzed. A crucial question to be considered at the start of the experimental design is what kind of gain in accuracy is there for every marginal increase in the sampling effort (Gilbert, 1987).

2.16 Sampling

Sampling means to select a few houses and to measure their metal levels, instead of doing the measurements for all the houses in the study area. The results we obtain from the few selected houses can also tell us something about the metal levels of the entire study area, through the process of statistical inference.

In a sampling survey, attention must be paid to all aspects and phases of the survey. Poor work in just one phase of the survey may ruin the results even if all the other phases have been done well.

Sampling survey theories have been developed extensively for normally distributed distributions. A large part of these theories is concerned with finding a formula for the means and variances of the distributions. The sample survey theory differs from the classical theory of sampling in that a population group in survey work contains a finite number of units, whereas the classical theory assumes an infinitely large population. For practical purposes, the difference between the two theories are seldom important.

Nonprobability sampling refers to those sampling methods that are not amenable to sampling survey theories because the selection of samples is not random. For example, the samples might be selected haphazardly, or the selection process might involve human judgment. In judgment, or purposive, selection, the sampler inspects a heterogeneous population and selects a typical unit, which the sampler deems to be close to the average of the population. Nonprobability sampling can yield useful results if good judgment is employed.

If the population has an underlying normal distribution, good sampling tends to make the sample distribution more normal. Bad sampling practice usually results in the

presence of many outliers, which potentially not only skews the sample distribution, but also increases the sample variance and decreases the precision. When possible, the cause of the outliers should be identified and the design of the sampling survey should be adjusted accordingly.

Nonresponse refers to not being able to measure some of the units in a selected sample group. As a consequence of nonresponse, the statistical estimates may be biased, since the nonresponse part of the population may be different from the part that did respond. Evidences from previous studies suggest that the magnitude of nonresponse bias varies widely from survey to survey (Cochran, 1977). Because the sample actually obtained is smaller than the size of the targeted sample, the variances of the estimates are increased.

Stratification sampling is an efficient way to sample a heterogeneous population, especially when it is possible to divide the population into subpopulations, each of which is internally homogeneous. Each subpopulation is called a "strata". Since each strata is homogeneous, an estimate of any stratum mean can be obtained from a small sample size. The estimates for the strata can be combined to form an estimate for the whole population group. When used properly, stratification almost always results in a smaller variance for the estimates than is given by a simple random sampling.

Quota sampling is basically stratified sampling with nonrandom selection of units within a stratum. Because the sample selection is not strictly random, the usual statistical formulae do not apply. Sampling continues until a targeted number of samples is attained.

Single-stage cluster sampling is type of stratified sampling. Here, instead of randomly selecting units within each stratum, only one cluster is randomly selected. All the units that are defined to be within the cluster will be sampled. Cluster sampling is the most economical way to do sampling if it is expensive to travel between the units, and the distance between the units is long.

Before any of the stratification sampling methods can be employed, the frequency distributions of the population must be known. This kind of information is either available from previous studies done on the same population group, or if not, can be obtained by doing a preliminary sampling. This technique is known as the double sampling or two-phase sampling. This method is useful only if the behaviour of the parameter to be measured in the population group does not change with respect to time; otherwise, the results of the preliminary sampling can not be used to define the strata for the later sampling stage. The accuracy of multiple-stage sampling improves as we increase the number of samplings. However, respondents who are repeatedly asked for the same information may not be willing to cooperate after a certain time.

2.17 Common Assumptions Made in Statistics

Most of the standard statistical tests that have engineering applications are developed based on certain assumptions. First, the underlying distribution is usually assumed to be normally distributed. This assumption is often made because the analysis of non-normal distributions is highly difficult to compute. In cases where the underlying distribution is not normal, transformation routines can be applied to transform the original distribution into a normal one. Sometimes, non-parametric statistics have to be employed if the transformation routines are unsuccessful.

In theoretical statistics associated with the normal distribution, the population is considered to be infinite. In sampling statistics, the population is almost always finite. As long as the sampling population is large in comparison with the size of the samples, there is not much difference between theoretical and sampling statistics.

The selection of the samples from the population is usually assumed to be independent and random. In other words, the probability of selecting a certain sample is equal to, and not influenced by, the selection of another sample. To ensure that this assumption holds true, the population size must be large. Also, the selection of samples must follow a random scheme. In real life, the "random scheme" is actually

computed by a random number generator that gives numbers, within a predetermined range, with a equal degree of probability.

2.18 Measuring Central Tendency

The measurement error is composed of the random error plus the systematic error. The random error is related to the precision of the measurement process and the systematic error reflects the accuracy of the measurement. The systematic error is also called the bias, which is the difference between the expected value of the distribution and the population mean.

Of the systematic errors, blunders is one type. A blunder is a technical term meaning that a wrong sample is measured, or there is a misreading of the measurement scale, or a mistake in transcribing or transposing measured values. If large, a blunder may show up as an outlier. But once a blunder is made, it is next to impossible to recover the true value.

Due to the central limit theorem, we know that the magnitude of the random error decreases as the number of measurement increases. As n gets larger, the sample distribution also approaches the normal distribution. There is no safe rule available to predict the sample size needed to approximate the normal distribution. However, for samples that primarily deviate from normality due to positive skewness, a crude rule is $n > 25G_1^2$

where G_1 is Fisher's measure of skewness, and is equal to

$$G_1 = \frac{E(y_i - \bar{Y})^3}{\sigma^3}$$

This rule is designed so that a 95 % confidence probability statement will be correct 94 % of the time (Fischer, 1932).

For statistically independent variables, the expected value, E , has the property:
 $E(ax + by + cz + \dots) = aE(x) + bE(y) + cE(z) + \dots$

Also, if U is defined as

$U=ax+by+cz$, then the bias of U is

$$B(u)=aB(x)+bB(y)+cB(z)+\dots \text{ (Mandel, 1964).}$$

In statistical language, the central tendency is measured by a parameter, the most common of which are the mean, median, and the mode. The mean, or arithmetic mean, is defined as the sum of all the observations divided by the number of observations, i.e.

$$\bar{x} = \frac{1}{n}(x_1 + x_2 + \dots + x_n) = \frac{\sum x}{n}$$

The median, in a set of observations that is ranked or arranged in order of magnitude, is the middle observation. If the number of observations is even, then the median is the average of the two middle observations. As a measure of the central tendency, the median is not as prone to be affected by outliers as the mean measurement. The median is also easier to calculate than the mean, but, the mean has an advantage that it is always an unbiased estimate of the population mean (Kennedy, 1986). Mode is the value that occurs most frequently in a set of observations, or, in a continuous distribution, the value with the highest frequency.

2.19 Measuring Spread

For statistically independent variables, the variance, V , has the property:

$$V(ax+by+cz+\dots)=a^2V(x)+b^2V(y)+c^2V(z)+\dots$$

In statistics, the spread of a distribution is measured by the variance, which is defined as

$$\sigma^2 = \frac{\sum_{i=1}^n (x_i - \mu)^2}{n}$$

Because the variance has units of the square of the units of the variate, the standard deviation is often used in place of the variance. The standard deviation, σ , is defined as the square root of the variance, and has units the same as those of the variate.

When the mean value, μ , of the population is not known, an estimator can be used to estimate the standard deviation. The estimator is defined as

$$s = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

The estimator is almost the same as the standard deviation, except that the denominator is $n-1$ instead of n .

2.20 Estimate

The statistic that estimates a parameter of a population is called the estimate. A good estimate should be unbiased, consistent, efficient, and sufficient. Unbiased means that the estimate is the same value as the true value for the population. The estimate is consistent if it approaches the population value as the sample size increases. Efficiency refers to the variance of the estimate. A highly efficient estimate has a low estimate variance. Sufficient means the estimate has used all the information a sample contains about the parameter to be estimated.

2.21 Coefficient of Variation

Supposing that x can only be positive, the ratio of the standard deviation to the mean value is called the coefficient of variation, or coefficient of variability, c.v.

$$c.v. = \frac{s}{\bar{x}} \text{ for } x > 0.$$

The convenience of this quantity is that it is a dimensionless measure of dispersion, with the mean value as the measuring unit.

2.22 Skewness

There are many ways to measure skewness. In general, skewness is a measure of the asymmetry of the distribution, as opposed to the perfect symmetry of the normal distribution.

2.23 Central Limit Theorem

The central limit theorem proves that if we take independent samples from a population with a finite variance, all of size N , then the averages of these samples will result in a sample distribution that tends toward normal. This result is true regardless of the original population from which the samples were taken. Also, the larger the N , the greater will be this tendency towards normality.

2.24 Hypothesis Testing

Hypothesis testing has to do with making inferences about the population, based on the information from the samples. The hypothesis that a certain parameter of two population distributions agree with each other is called the null hypothesis, which assumes that the difference between the parameters is zero. The null hypothesis is tested against an alternative hypothesis. If the null hypothesis is tested to be not true, then the alternative hypothesis is said to be true, provided that the null hypothesis plus the alternative hypothesis cover all the possible outcomes.

One problem with almost all hypothesis testing is that we do not know the population distributions. Instead, we only have sample distributions that approximate the populations. The samples from any one population will have sampling variations. Therefore, hypothesis testing of two sample distributions will practically always yield a difference.

Hypothesis testing is meaningless unless we know the accuracy and the confidence intervals of the conclusions from the hypothesis tests. To determine whether or not the differences are due to the differences of the populations or the sampling variations, the probability of the conclusions being right must be stated. The null hypothesis is rejected when the testing indicates that there is only a small chance that the populations are the same.

The level of significance, α , of a hypothesis test is the maximum probability of rejecting a true null hypothesis. For most statistical tests, α is chosen to be 0.05. The

power, $1-\beta$, of a hypothesis test is defined as the probability of rejecting a false null hypothesis.

A test is unbiased if the probability of rejecting the null hypothesis, H_0 , when H_0 is false, is always greater than or equal to the probability of rejecting H_0 when H_0 is true, i.e., $\beta \geq \alpha$ (Conover, 1980).

A test is conservative if the actual level of significance of the hypothesis test is smaller than the stated level of significance.

Conclusions that are drawn from hypothesis testing are never sure. At best, they give us an indication of what might be true about the population. The conclusions from one hypothesis test can give us clues as to what other kinds of hypothesis tests ought to be performed. By properly structuring the hypothesis testings, we can hopefully find out what we want to know from the data that have been collected.

2.25 Constructing Power Curves

A power curve is a plot between the power of the test, $1-\beta$, and the sample size. It is very useful to be able to know the power of the test associated with the sample data being tested. However, the construction of power curves requires prior knowledge of the population means, which are usually not available for most studies (Yamane, 1964).

From the theoretical results of power curve analyzes, we know that, for the same level of significance, a one-tail test is always more powerful than a two-tail test.

2.26 Statistics of the Maximum

When we are sampling a population for the maximum values obtained over a defined time interval, we end up with a set of extreme values. The class of distribution functions that can describe this kind of distribution is called the "double exponential distribution function". Theoretically, it can be shown that the double exponential distribution is the limiting distribution of extreme values of large samples taken from populations such as Gaussian (Kinnison, 1985). Many types of environmental pollution

problems, including tap water sampling, can be viewed as an extreme value problem. The "maximum value" statistics should be used if we want to know the most likely maximum values to be obtained in a sampling program that spans across various times and locations.

2.27 Systems of Measurement

We normally measure things using the system of real numbers. For example, we say that a certain pen is eight inches long or a chair across the room weighs five pounds. This type of measurement is sometimes also called the ratio scale of measurement. The main characteristic of this measurement system is that there is a true zero point. In systems where the zero point is only arbitrarily set, such as in a thermometer measurement, the measurement is defined in terms of an interval scale. In such a system, the intervals between the numbers have an empirical meaning, but the ratio between numbers do not. Certain other measurements are not as easily quantifiable. Licence plate numbers and zip codes of addresses, for example, are defined rather arbitrarily. These measurements are said to be nominal. In a taste test, a panel of judges are asked to rank the flavor of chlorine in drinking water samples. On a scale from 1 to 5, one being no chlorine detectable and five being strong chlorine taste detected, only the relative order or position of the parameter of interest is important. This system of measurement is called "ordinal".

2.28 Nonparametric Testing

It is hard to handle sample distributions that are not normal or log normal because most statistical tests are designed on the basis of the normal distribution. Whenever a nonnormal distribution is encountered, it can potentially be transformed into a normal distribution by the log function or the function $f(x) = x^q$, where q belongs to the set of real numbers. The most common transforming functions of this form are the square root, the negative reciprocal, and the negative reciprocal square root (Tukey, 1977).

However, in situations where even the transformation procedure can not transform the actual distribution into one that is normal or log normal, the nonparametric testing method should be used. Nonparametric statistical methods are those that can be used on data based on almost any measurement system, such as nominal, ordinal, interval, and ratio data. It can also be employed when the distribution function of the random variable producing the data is either unspecified, or is specified but has a large number of unknown parameters.

2.29 Kolmogoroff-Smirnoff Comparison of Two Independent Samples

The Kolmogoroff-Smirnoff test can tell us if two independent samples from populations with continuous or discrete distributions, but both of the same type, are drawn from the same population. This test is robust against differences in the shape of the distribution, especially differences in the mean, median, dispersion, and skewness.

The maximum difference between the cumulative distribution functions, F , of the two populations serves as a test statistic, D .

$$\hat{D} = \max \left| \left(\frac{F_1}{n_1} - \frac{F_2}{n_2} \right) \right|$$

The critical D value, for an aggregate sample size of 35, can be approximated by

$$D_\alpha = K_\alpha \sqrt{\frac{n_1 + n_2}{n_1 n_2}}$$

If $n_1 = n_2$, $K_\alpha = 1.36$ when $\alpha = 0.05$ (Sachs, 1982). If $\hat{D} > D_\alpha$, then there is a significant difference between the distribution of the two populations.

2.30 Median Test

The median test examines whether the sample sets being tested come from populations that have the same median. However, the underlying populations need not be identical when the H_0 is true.

2.31 Kruskal-Wallis H-Test

The Kruskal-Wallis H-Test is the extension of the Mann-Whitney Test for Two Independent Samples. Where there are k random samples, each of which is possibly from a different population, the H-Test tests the null hypothesis of whether or not all of the populations are identical. The alternative hypothesis is that one or more of the populations tend to give larger values than the other populations, i.e., not all the populations have identical means.

The H-Test is similar to the median test. However, the H-test uses more information contained in the observations than the median test. Therefore, the H-test is usually more powerful than the median test. The disadvantage of using the H-test is that all the observations have to be ranked in the combined sample. For a large data set, the H-test involves more work than the median test.

The assumptions of this test are that all samples are random samples from their respective populations. In addition to independence in each sample set, the various sample sets must be mutually independent from each other. Also, the measurement scale of the data must be at least ordinal.

The test statistic, T, is defined as

$$T = \frac{1}{S^2} \left(\sum_{i=1}^k \frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4} \right)$$

S is defined as

$$S^2 = \frac{1}{N-1} \left(\sum R(X_{ij})^2 - N \frac{(N+1)^2}{4} \right)$$

N is equal to the total number of samples of all the sample groups. And R is the aggregate rank, across all the sample groups, of each observation. The null hypothesis is rejected for $T > T_\alpha$. For k=3, and n>5 for each sample group, T_α can be found in a table (Conover, 1980).

If, and only if, the null hypothesis is rejected, we can determine each pair of the compared populations differ from each other. The test statistic is

$$\left| \frac{R_i}{n_i} - \frac{R_j}{n_j} \right| > t_{1-(\alpha/2)} (S^2 * \frac{N-1-T}{N-k})^{1/2} (\frac{1}{n_i} - \frac{1}{n_j})^{1/2}$$

Population i is said to be different from population j if the inequality holds true.

2.32 Confidence Intervals for the Difference Between 2 Means

The confidence intervals of the difference between 2 means can be computed by the non-parametric method that bears the same name. In this method, it is assumed that the two distributions being compared are identical except for a difference in the location of the mean. If n denotes the number of samples in distribution A, and m denotes the number of samples in distribution B, then we calculate an intermediate, $k = w_{\alpha/2} - n(n+1)/2$, where $w_{\alpha/2}$ is a function of n and m (Conover, 1980). For all possible pairs of (X_i, Y_j) , the kth largest difference, U, and the kth smallest difference, L, are the respective upper and lower limits of the confidence interval for the difference between 2 means, i.e.,

$$P[L \leq E(X) - E(Y) \leq U] \geq 1 - \alpha$$

2.33 Test for Equal Variance

The test for equal variance is designed to test whether or not population X has the same variance as another population, Y. If the populations of X and Y have normal distributions, the F test should be used in place of the nonparametric test for equal variance. However, the F test is extremely sensitive to the assumption of normality. Even if the true underlying distribution is a double exponential distribution, which can resemble the normal distribution, the true level of significance may be two or three times as large as it is supposed to be. Therefore, the F test is not safe to use unless we are sure that the populations are normal. The A.R.E. of the Squared Ranks Test for Equal Variance is 0.76 (Conover, 1980) if it is used instead of the F test, when the populations are actually normal. But, for other distributions, the A.R.E. increases and approaches unity.

In addition to the usual assumptions of independence, and randomness, the test for equal variance also assumes that the measurement scale is at least interval. For a two-tail test, the null hypothesis is $\text{Var}(X) = \text{Var}(Y)$.

Let n denote the number of samples in distribution X , and m denote the number of samples in distribution Y . The absolute deviation of each observation from the mean is $U_i = |X_i - \mu_x|, i = 1, \dots, n$; and $V_j = |Y_j - \mu_y|, j = 1, \dots, m$.

The ranks 1 to $n+m$ are assigned to the combined sample of U s and V s. In situations where several U s and V s are exactly equal to each other, the average of the ranks, if there are no ties, are assigned to each value. The rank of each observation is denoted by $R(U_i)$ and $R(V_j)$.

The test statistic is

$$T_1 = \frac{T - n\bar{R}^2}{\left[\frac{nm}{N(N-1)} \sum_{i=1}^N R_i^4 - \frac{nm}{N-1} (\bar{R}^2)^2 \right]^{1/2}}$$

where $N = n + m$, and,

$$\bar{R}^2 = \frac{1}{N} \left\{ \sum_{i=1}^n [R(U_i)]^2 + \sum_{j=1}^m [R(V_j)]^2 \right\}; \quad \sum_{i=1}^N R_i^4 = \sum_{i=1}^n [R(U_i)]^4 + \sum_{j=1}^m [R(V_j)]^4$$

The null hypothesis for a two-tail test is rejected if T_1 is less than $\alpha/2$ or greater than $1 - \alpha/2$ (Conover, 1980).

2.34 Spearman Rank Correlations

Where the data consists of pairs of numbers (x, y) , a measure of correlation between the two numbers can be calculated. Correlation estimates the degree of dependence between x and y . The Spearman measure of correlation in ranked data is defined as

$$\rho = \frac{\sum_{i=1}^n \left[R(X_i) - \frac{n+1}{2} \right] \left[R(Y_i) - \frac{n+1}{2} \right]}{n(n^2 - 1) / 12}$$

The correlation measure only assumes values between -1 to +1. The correlation is closer to +1, if the larger values of X tend to be paired with the larger values of Y. If the larger values of X tend to pair with the smaller values of Y, the measure of correlation tends to -1. If there the pairing of X and Y do not follow any predictable pattern, then the correlation should be close to zero.

2.35 Regression

As opposed to correlation methods, regression methods are used to inspect more closely the relationship between x and y in bivariate data sets. One important objective of regression methods is to predict a value of y where only the value for x is known. This is done based on the information we obtain from existing (x,y) data sets.

The variables used for regression analysis should be carefully selected. Also, we should know beforehand whether the form of the fitting function is linear or nonlinear. A linear regression function is in the form $y=a+bx$, where a is the intercept, and b is the slope of the regression line. Both the a and b regression coefficients have physical meaning. Therefore, given that the data can be fitted by a linear regression line, the most important task is to determine the values for the a and b coefficients.

The best empirical fit of the data points may not necessarily be accurate. It is possible to develop, between variables, relationships that are completely meaningless in a practical sense (Montgomery, 1991).

Regression relationships are only valid for the range of values in the original data. Regression models should never be extrapolated to predict values outside of the range of the original data.

2.36 One-way ANOVA

The analysis of variance, ANOVA, seeks to determine if the differences between groupings of data are significant. Data is classified into groups based on the distinguishing features of the data. In the analysis of water samples, the chemical

parameters of the samples can be used to group data. Lead samples with low pH and low alkalinity can be grouped together, and samples with higher pH and higher alkalinity grouped separately. In this illustration, pH and alkalinity are said to be the ANOVA factors of the lead analysis. If the analysis reveals significant differences in the lead concentrations between the various pH and alkalinity data groupings, we can say that the pH and alkalinity factors significantly influence the lead data. This illustration is also an example of a two-way ANOVA because there are two factors: pH and alkalinity. In an one-way ANOVA, the data is grouped based on only one factor (Montgomery, 1991).

The study of ANOVA is an extremely vast and complicated field of study in statistics. For the purposes of this particular research study, it will suffice to explain the simplest case.

A typical data table for a single-factor experiment is presented in Table 2.

Table 2 Typical Data for a Single-Factor Experiment

Treatment Level			Data		Totals	Averages
1	y11	y12	...	y1n	y1	\bar{y}
2	y21	y22	...	y2n	y2	\bar{y}_2
.
.
.
a	ya1	ya2	...	yan	ya	\bar{y}_a

From the data table, we can calculate the total of the treatment level totals, y

$$y = \sum_{i=1}^a \sum_{j=1}^n y_{ij}; \text{ and the average of the averages is, } \bar{y} = y / N.$$

In addition to these, we can calculate other important quantities, such as:

$$SS_T = \sum_{i=1}^a \sum_{j=1}^n (y_{ij} - \bar{y})^2; \quad SS_E = SS_E = \sum_{i=1}^a \sum_{j=1}^n (y_{ij} - \bar{y}_i)^2; \quad SS_T = SS_{treatments} + SS_E;$$

$MS_{treatments} = \frac{SS_{treatments}}{a - 1}$; and $MS_E = \frac{SS_E}{N - a}$. We summarize these important derived

variables in the one-way ANOVA analysis table (Table 3).

Table 3 The ANOVA Table for the Single-Factor, Fixed Effects Model

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F _o
Between treatments	SS _{treatments}	a-1	MS _{treatments}	$F_o = \frac{MS_{treatments}}{MS_E}$
Error (Within treatments)	SS _E	N-a	MS _E	
Total	SS _T	N-1		

The most important part about this whole table is the F_o. If the computed Fisher value exceeds the critical Fisher value, then we conclude that the between treatment factor is significant.

2.37 Theory of Causation

Statistical methods can function to demonstrate the relationships, the interrelatedness, or the correlations between variables; however, no statistical methods can prove that there is certain causation. Suppose we find a positive relationship between the number of books a high school student purchases and the grade point average the student receives. We can demonstrate through the use of statistics that a student who purchases a lot of books also receives a high grade point average. However, it is not valid to, therefore, say that buying a lot of books will ensure the student of a high grade point average. There may be other factors involved here. For example, the students who purchased a lot of books may also have spent a lot of time in reading those books. As a result of their reading efforts, their increased knowledge of the school subject matters has helped them to excel in examinations. We see, then, it is in fact reading books, not purchasing them, that affects grade point averages. A poor student who does not have the money to purchase books, but assiduously pours through

volumes borrowed from the local library, may do better in examinations than students who buy a lot of books but do not read them.

In certain cases, the presence of correlation between variables has no meaning in terms of causal relationships. For example, we find that there is a strong correlation between the length of the right and the left arm, and the height and body weight of a person (Sachs, 1982).

There is another class of noncausal relationship called the inhomogeneity correlation. Consider a population that has three subgroups. When we measure two quantities: A and B, they may not be correlated in each of the subgroups, but a correlation may be found when all the three subgroups are analyzed together as one population.

Although we do not know for certain if there is a causal relationship between correlated variables, but we can make this conclusion once we have excluded other possibilities. This method of proving causality is only useful if we have an exhaustive list of all the possible types of noncausal correlation relationships. Furthermore, we must have a way of detecting these relationships.

3. EXPERIMENTAL METHODS

3.1 Experimental Design

The study areas of this research project are located in North Delta, Newton, and South Surrey of the Greater Vancouver Regional District. North Delta is the control area. Due to bacteriological and chemical chlorine demand within the distribution system, the supply water from the Seymour Reservoir is stripped of chlorine residuals by the time the water reaches North Delta. In North Delta, no chemicals are added to the water to adjust for pH and alkalinity. The Seymour water supply also feeds Newton and South Surrey. In Newton, the water is rechlorinated and adjusted for pH and alkalinity. In South Surrey, the water is chloraminated and also adjusted for pH and alkalinity levels.

The major water feeder main for Newton comes into the distribution grid at the intersection of 128th Street and 64th Avenue. Similarly, 144th Street and 32nd Avenue is the feed point for South Surrey. As the water enters into the distribution grid, the chemical characteristics of the feed water, such as residual chlorine levels, pH, and alkalinity, change according to the physical, chemical, and biological conditions of the distribution grid. In general, as the water travels farther away from the feed point, the residual chlorine levels drop. The change for pH and alkalinity is harder to predict because the interactions between the supply water and the distribution pipes could lead either to increases or decreases of pH and alkalinity.

By collecting tap water samples from North Delta, Newton, and South Surrey, we can compare the copper and lead levels in Newton and South Surrey against those in the control area. The comparison tells us if pH and alkalinity adjustments are key factors in lowering copper and lead levels in tap water. Because pH, alkalinity, and residual chlorine levels vary in Newton and South Surrey, each area has to be studied internally to see if there are significant internal differences.

Samples from the control area should have fairly homogenous pH, alkalinity, and residual chlorine measurements. Therefore, random aerial sampling (taking samples from locations randomly distributed throughout the control area) would be the best way to assess the copper and lead levels. In contrast to North Delta, Newton and South Surrey will have pH, alkalinity, and residual chlorine measurements that span a wide range. Simply taking random aerial samples from each of these two districts would not reveal significant differences, if there were any, in copper and lead levels within each district. Assuming that water with higher residual chlorine levels also has higher copper and lead levels, areas closer to the feed points should have the highest metal levels in Newton and South Surrey and areas farther in distance from the feed points should have the lowest metal levels. By getting a representative set of samples from an area closest to and another set of samples farthest from the feed points, we have an excellent chance of finding any significant differences in metal levels between the two areas. Due to the spatial variations in water quality parameters, we cannot travel too far away from one sampling site to another before we find substantially different pH, alkalinity, and residual chlorine levels. Hence, cluster sampling is the best way to get the two sets of representative samples from Newton and two sets from South Surrey (Appendix A).

3.1.1 Controllable Factors

Besides pH, alkalinity, and residual chlorine levels, there are other factors that could influence the copper and lead levels in tap water. Most of these factors can be controlled directly or indirectly. By direct control, we mean that we can control the quantity or quality of the parameter of interest. For example, we can control the pH, alkalinity, and residual chlorine levels inside the rechlorination station. By indirect control, we mean that we cannot control the parameter of interest, but we can use other techniques to influence the outcome of a variable. Outside of the rechlorination station, the pH, alkalinity, and residual chlorine levels begin to vary in an unquantifiable way

because we do not have precise information on every part of the entire distribution grid. But, if our objective were to collect tap water samples that have a similar level of residual chlorine, we can indirectly achieve this objective by taking our water samples from houses that are very close to each other. This way, although we cannot say "a priori" that the levels of residual chlorine in all the samples will be exactly the same, the chances are that they will be similar.

3.1.1.1 Direct Control

The age of the house, from which the water sample is collected, is a factor that can be controlled directly. This study investigated the worst potential copper and lead problems, which previous studies have shown to be houses plumbed with copper piping that are less than ten years old. Therefore, the houses selected for this study had to be less than ten years old. Some very old houses may have been renovated in the past ten years with new copper plumbing. But, since it is nearly impossible to find out which old house has new plumbing, it was much easier to target for houses built in the past ten years.

A problem arises with using this strategy because some of these very new houses had plastic plumbing. These houses are not likely to have a problem with metal leaching into the tap water, and these houses were not included in this study. The residents of the houses were asked whether their plumbings are plastic or copper. If they were not sure, we could check the water service pipes underneath the kitchen sink. Most houses that have plastic plumbing inside the house will also have plastic service pipes. However, this method of determining the predominant type of plumbing material used in the house is at best tenuous. On the other hand, this was probably the only method available, if the residents are not sure what type of plumbing is in the house.

Samples were collected both from houses that have plastic and houses that have copper plumbing. The data from houses plumbed with plastic pipes had to be analyzed

separately from those with copper pipes. Results from the two separate data sets were compared with each other to confirm that houses with plastic pipes indeed did not have a metal leaching problem.

All tap water samples were collected from the kitchen tap of houses (single family dwellings). The metal levels in the tap water from the same house will vary, depending on from which tap the water is collected. This is due to the fact that the tap faucets contribute to the metal leaching problem. Not only are different faucets in a house of different sizes, but they may be of different makes and have a different percentage mixture of metallic components that are susceptible to leaching. Collecting water samples only from the kitchen tap minimizes the variation in tap water metal levels due to the variation in the faucets.

This study targeted houses, rather than apartments or buildings, because the different types of dwelling cannot be studied together. Previous studies have shown that the type of building will influence lead levels in tap water. Apartments and buildings have, in general, higher levels of lead than houses. Apartments or buildings have much longer internal plumbing loops than houses. The average residence time of water in the plumbing system of a house is much less than in an apartment. Therefore, there is less contact time between water and the leachable metals in the plumbing system of a house (Singh, 1990).

For the past few years, on-line water purification devices have become popular in the market. The house residents were asked if they have installed such devices on their kitchen taps. In cases where they had, they were instructed to turn off those devices during the sampling process. Some of these water purification devices are very effective at removing metals in the water. The failure to consider this variable could be detrimental to this study.

3.1.1.2 Indirect Control

The natural level of lead and copper in the supply water could be a problem if they were much higher than the levels leached from the distribution and plumbing systems. Fortunately, GVRD data show that the natural lead and copper levels in the Seymour source water is extremely low. Hence, the background metal levels were not expected to "mask" the effects of pH and alkalinity adjustments on copper and lead leaching. Furthermore, there could be a problem if the drinking water of North Delta, Newton, and South Surrey was supplied from water sources that have different water chemistry. Having anticipated this problem, the drinking water of all the study areas were supplied exclusively from the Seymour reservoir.

The type of solder and the lengths and sizes of pipes used in the plumbing system were variable in each house. Even though the old type of lead/tin solder has been prohibited in municipal plumbing codes for many years, they are still sometimes used illegally due to the ease of handling lead/tin solder. Houses that have more of the lead/tin type solder, rather than the newer tin/antimony solder, in the house plumbing will probably also have higher lead levels at the tap. Unfortunately, there is no way to quantify the amount of lead/tin solder present inside the house or in the distribution system. The technique of sampling a number of houses instead of a few houses solves this problem. Sampling ensures that some houses sampled have more lead/tin solder and some houses have less. The average of the lead concentration of the sampling group will then reflect an averaged amount of lead/tin solder.

The temperature of the supply water in the various areas of the distribution system could also affect the rate of metal leaching from the pipes, solders, and faucets. However, considering the close proximity of the various sample locations, and the fact that solar heating of the supply water is retarded by the soil cover on top of the entire distribution system, the temperature variation across the sampling sites was not expected to significantly affect metal levels.

3.1.2 Uncontrollable Factors

There is one very important factor of copper and lead leaching that is completely uncontrollable in a field study. This factor is the standing time of the water samples. This study examined standing cold water, flushed cold water, and flushed hot water; however, the focus of the study was on the standing cold water samples because they are likely to have the highest levels of copper and lead. Standing samples are also important because they are used to determine the compliance of trace copper and lead levels in USEPA regulations.

In a laboratory or coupon study, the standing time of water can be controlled. In a field study, however, the standing time cannot be controlled precisely. The standing time is the time between the last use of water in the house before the occupants go to sleep and the time the sample is collected first thing in the morning, i.e., before any water is used in the morning. There are at least four potential problems with the control of standing time. One, not everybody participating in this study would sleep the same amount of time. Two, one or more of the residents may have to use the bathroom sometime during the night. When this happens, some of the standing water is flushed out of the plumbing system. This has the effect of decreasing metal levels in the house plumbing, and hence, decreasing the effective standing time. Three, when the occupants wake up first thing in the morning, they may use the bathroom or the kitchen before they remember to do the sampling. This is probably the most serious problem, and this scenario is more likely to happen if there are many occupants living in the house. The larger the household, the higher is the chance of having at least one of the occupants forgetting about the sampling study. Four, some houses have one or more leaky water taps. The faucets may be getting too old or someone may forget to shut-tight a tap, which causes continuous slow leakage of the standing water. Depending on the degree of leakage, the effective standing time could drop insignificantly or a great deal.

The participants of this research project were instructed about these potential problems. But human behaviour is hard to predict and impossible to control. Therefore, we can predict that the samples come from a wide variation of standing time. Since we wanted our standing cold water samples to have remained in the pipes for at least six or seven hours, samples that had an effective standing time less than that will significantly bias the copper and lead data toward the low side. We also expected that a lot of the scatter in the copper and lead data could be attributed to the standing time problem.

There are two possible ways to get around this problem. Both are highly imperfect. Assuming that most people sleep more than six hours and that the water leakage problem is insignificant, we can ask the participants if they used any water between the time they went to sleep and the time they collected the samples. Some participants who know that they have made a mistake may not be willing to admit it. Also, the person who is asked this question may not know whether or not another person in the household has used any water before collecting the water samples. This method of determining if the standing sample from a particular house has been flushed or not is seriously flawed.

The second way to solve this problem is to identify the flushed standing samples by using statistics. This approach, while imperfect, is nevertheless more scientific than the first approach described earlier. This research project adopted this approach (refer to section 4).

3.2 Arrangements with Governmental Agencies

Before the samples were collected, various levels of government were consulted. In particular, the GVRD, the Municipality of Delta, and the City of Surrey gave this researcher permission to solicit houses, within their jurisdictions, for collecting tap water samples. Assistance was also offered by these government

agencies to provide letters of recommendations, in the event that the home owners had doubts about the legality of this project.

From the archives of these government agencies, it was possible to locate the addresses of about two hundred houses that were newer than ten years old, plus a few more houses that were between ten to fifteen years old. These houses, located throughout the five sample areas (one in North Delta, two in Newton, and two in South Surrey), were the target houses for collecting water samples. The GVRD assisted in mailing out letters to these homeowners, informing them that this researcher might come to their house to ask for their cooperation in this study and to provide tap water samples from their kitchens.

3.3 Bottle Preparation

All the bottles used in this study were brand new plastic bottles that were delivered to the UBC laboratory sealed in the original packaging. This was the first step toward minimizing the potential of metal contamination of the bottles due to air particulates, solvents, or chemicals in the lab. Because the degree of existing contamination due to copper or lead particles on the inside surface of the bottles was unknown, a bench test was performed. Six different kinds of bottle preparation techniques were tested. Three bottles were prepared for each bottle treatment. Each copper measurement was repeated five times, and lead three times.

The first set of bottles (NT) were the controls. Only deionized distilled water was poured into the bottles, and no pretreatment was given. The second set of bottles (A1D) were pretreated by acid washing with 10% nitric acid for one minute and then rinsing with deionized distilled water. The third set (A5D) was similar to the second set, except that the acid wash time was five minutes; the fourth set (A90D) had a ninety minute acid wash time; the fifth (AOD) had the acid stay in the bottle for overnight. The sixth set of bottles (SDAOD) were pretreated by the method recommended by the Standard Methods (17th edition). The bottles were soaped, rinsed by deionized

distilled water, acid washed overnight (about eight hours), and then rinsed again by deionized distilled water. This last method is extremely labor intensive. To wash all the bottles needed for this study (about 600) by this method would have required approximately 2 months for one person. If any of the first five shorter methods proved to be equally as effective as the method recommended by the Standard Methods, then that method was adopted by this study.

Table 4 Results of Bottle Treatment Study

Treatment Method	Average Copper (ppm)	Average Lead (ppb)
NT	0.023	0
A1D	0.000	0
A5D*	0.016	0
A90D	0.016	0
AOD	0.016	0
SDAOD	0.000	0

The results of the bottle treatment study (Table 4) shows that the deionized distilled water used for this study was free of lead. Also, the zero level of lead detection, regardless of the treatment method employed, means that the bottles had no lead contamination.

The detected levels of copper were extremely low compared with the range of copper concentrations that one would expect to find in the collected tap water samples. Therefore, it did not really matter which treatment method was chosen. The method recommended by Standard Methods worked the best; but, for the purposes of this study, is inconsequential. All the treatment methods resulted in a lower level of copper contamination. A decision could have been made not to treat any of the bottles. However, to avoid the unlikely possibility that excessive amounts of lead or copper particulates might be found in some of the bottles due to chance, it was decided to acid wash all the bottles used in this study for five minutes, followed by rinsing with deionized distilled water.

3.4 Sampling Package

The sampling packages that were to be delivered to the homeowners were prepared beforehand, at the UBC lab. The package was a large ziplock bag that had, sealed within it, a 1L bottle, two 125 mL bottles, a copy of the letter that the GVRD helped to send to the homeowners beforehand, and two instruction sheets. The one liter bottle was marked with the number "one". This bottle was used to collect the standing cold water sample. The metal levels in this sample came primarily from the interior home plumbings, soldered joints, and faucets (AWWARF, 1990). One liter was chosen to be the size of the standing sample because the one liter sample size was recommended by the USEPA in the May 1991 Lead and Copper National Interim Primary Drinking Water Regulations.

One of the two 125 mL bottles was marked with the number "two" and was used to collect the flushed cold water sample. The other 125 mL bottle was marked with the number "three" and was used to collect the flushed hot water sample. All three bottles were empty and capped. The flushed samples measured the metal levels in the water distribution system. The sample volume for the flushed samples was not an important issue, assuming that the kitchen tap had been adequately flushed before the sample collection. Since the metal levels in the distribution system have less variation compared to those inside the house plumbings (AWWARF, 1990), collecting a large or a small does not make much of a difference. A relatively small sample size was chosen, making storage and transportation more convenient.

The first page of the instruction sheets was a concise written explanation of the sampling procedures (Appendix B). The second page was a self explanatory cartoon that helped the homeowner to visualize the sampling procedures, in case the instructions on the first page was unclear to them (Appendix C).

3.5 Sampling Procedures

Two identical ziplock bag packages were delivered to each house that participated in this study. One was marked bag "A" and the other bag "B".

On the first morning after being contacted by the researcher, the homeowner was to take the three bottles out of bag "A" and place them, in order of their numbering, on the counter beside the kitchen sink. First thing in the morning, before any water was used in the house, the homeowner was to turn on the cold water tap and fill bottle number 1. The cold water tap was left on, until the water became cold, before filling bottle number 2. When the water from the cold water tap turned cold, it was a sign that water came from the distribution pipes outside the house plumbing. After the flushed cold water sample was collected, the cold water tap was turned off, and the hot water tap was turned on. Bottle number 3 was filled after the water became hot. All three bottles were to be capped tightly, and sealed in the ziplock bag for pickup. On the next morning, the second morning after being contacted, the same procedure was repeated for bag "B".

3.6 Participation of Homeowners

The participation and cooperation of the homeowners in this study was absolutely crucial to its success. First, the homeowner had to be willing to participate in the study. Second, the homeowner had to follow the sampling procedures correctly.

In order to obtain a database of sufficient size, there was a target of enlisting 35 houses in each of North Delta, Newton, and South Surrey to participate in the study. Having 35 data points for each area allowed the researcher to do statistical comparisons between the study areas with an acceptable degree of confidence (see Section 4), while keeping the sampling and lab testing efforts at a manageable level. Quota sampling was employed for this study. Targeted homeowners, who had been contacted previously by mail, were contacted personally by door knocking. They were asked if they were willing to participate in the study. Those who were willing were given the sampling packages and were instructed about the sampling procedures. The

homeowners were also asked a series of questions regarding their houses (Appendix D). For a variety of reasons, a portion of the homeowners who were contacted did not want to participate in the study. Enough homeowners on the list of targeted addresses were asked until 35 homeowners in each study area agreed to participate.

By far the biggest error in this study was due to the homeowners not following the sampling instructions. The most common error was the use of water in the house prior to sampling. Other less common, but equally serious, errors included: not letting the cold water flush enough when collecting bottle number 2, not letting the hot water get hot before collecting bottle number 3, and mixing the order of collecting the samples.

3.7 Bottle Pick-up

The sample bottles, sealed in the ziplock bags "A" and "B", were left outside the houses after the second morning of sampling. The bottles were picked up in the afternoon and brought back to the UBC lab for analysis. Due to the large number of samples that had to be delivered and picked up, the sampling process took place over a three week period between September 20th to October 10th, 1994. Each bottle was tracked so that the bottles from each house could be picked up right after the second morning of sampling.

3.8 Lab Testing

The pH, alkalinity, and chlorine residuals in tap water deteriorated quickly. To determine the values of these parameters for the houses, the standing sample from bag "B" of each house was measured in the lab on the same day that it is picked up. The copper and lead metals did not deteriorate as quickly as the other measured parameters. Therefore, the measurement on copper and lead levels was deferred for a few weeks after all the bottles were picked up from the houses. Copper and lead were measured for all the bottles from bags marked "A" and bags marked "B".

After the bottles were brought into the UBC lab, each bottle was coded so that one could identify later on where each bottle came from. The pH, alkalinity, and chlorine residuals were measured before acid was added to preserve the water samples. Preservation with acid was necessary for measuring lead and copper. Copper ions had a tendency to adsorb onto the bottle surface and, thus, the addition of acid de-adsorbed the copper ions. For lead analysis, the acid added served as a matrix modifier that reduced interferences (Standard Methods, 17th edition). Nitric acid at 2.5% was selected as the preserving acid. Normally, a concentration of 0.3% would have been used. To make the copper and lead testing feasible in terms of time, the samples were not digested before measuring the metal levels. A higher concentration of acid was added to the samples in order to compensate for this deficiency. This did not mean that total metal was recoverable without going through the digestion step; however, at least all of the dissolved metals could be recovered.

In essence, this procedure measured and analyzed the dissolved copper and lead. This study focused on the dissolved metals, since they account for most of the total metals in tap water (AWWARF, 1990). Also, dissolved copper and lead have more potential harmful effects on humans than the particulate counterparts, since the human body can uptake the dissolved forms much more easily. In the past, studies that were strictly concerned with dissolved lead species filtered the samples through a member filter of 0.4 or 0.45mm pore size. This procedure was not effective because the dissolved lead tended to adsorb onto and was retained by the filter material (Schock, 1983).

3.8.1 Instruments

The pH of the samples were measured by a Fisher glass electrode and a Bechman pH meter. Because tap water has a low ionic strength, an orion buffer solution was added to the water to give more stable readings. The pH meter was calibrated by pH buffer solutions. Total alkalinity was determined by the titration

method (Standard Methods, 17th edition). The free and total chlorine levels were measured by the DPD Colorimetric Method.

Copper was analyzed by a Thermo Jarrel Ash Atomic Absorption Spectrophotometer, using lean acetylene fuel. Samples were aspirated directly out of the sample bottles in order to avoid contamination in the measurement stage. Standard solutions, in the range of copper concentrations we expected to find, were made. 2.5% nitric acid was added to the standards in order to make them equivalent to the samples. The AAS instrument was recalibrated against these standards for every ten samples measured. All measurements were repeated five times. Only the averages of these repeated measures were reported.

Lead was determined by atomic absorption graphite furnace. Lead samples were poured into pre-rinsed sampling cups before the graphite furnace instrument tested them with the autoanalyzer. The quality control procedure was the same for lead as for copper.

3.8.2 Testing Scheme

Five percent of the standing samples were cross-checked by the GVRD water quality lab. Interlaboratory testing could help to determine whether or not the equipment at the UBC lab was working properly and was in good condition.

Because there were roughly six hundred samples that had to be measured for copper and lead, it took two months to complete the testing for all the samples. During this testing period, the working conditions of the instruments changed according to the environmental conditions of the lab, on any given day. The same sample that was measured on one day might have a different reading than on another day. The variations of the instruments could have been purely random or may have had systematic trends. Besides the technique of constant recalibration, the instrument effect was taken care of by selecting the sample to be tested in a random sequence.

3.8.3 Data Recording

There were inevitably some errors in the process of reading, recording, and transcribing data. The validity of the databank would be in jeopardy if the rate of these kinds of error was high. There should not have been any reading and recording errors for the lead and copper measurements because the test instruments automatically printed out the data on paper. To assess the rate of transcription error made in the process of translating the data into the computer databank, the data in the databank was cross referenced with the data tapes. The rate of error that could not be corrected was found to be 0.1%.

4. RESULTS AND DISCUSSION

4.1 Summary of Returned Bottles

Of the 105 houses that agreed to provide samples for this study, 92 of them returned bottles. Thirteen houses did not return any bottles. The 88% return rate was high for a study of this type. Participants of this study were informed about the potential dangers of consuming water with excessively high levels of copper and lead. They were told that their participation was vital to the success of identifying the safety of the water supply in their area. Those who wanted to know about the outcome of this study received the conclusions of this study after it was completed. Personal communication with the house owners, and linking this study to their health and safety, were the main ingredients of obtaining a substantial number of samples. A summary of the information about the returned bottles is provided in Table 5.

Table 5 Summary Information of Returned Bottles

Area	code	#	pH**	alk**	free chlorine*	chloramine*	sampling
Delta	d	19	n	n	.01	.01	random
Newton1	n	31	y	y	.28	.05	cluster
Newton2	y	10	y	y	.91	.10	cluster
S.Surrey1	s	19	y	y	.29	.27	cluster
S.Surrey2	w	13	y	y	.33	.44	cluster

* GVRD data (avg for Sept 20- Oct 10)

** The presence of pH or alkalinity adjustments

The samples from the 92 houses were collected from the five different sampling areas. The North Delta area had 19 bottle returns. As expected, free chlorine and chloramine residuals were almost zero because all of the chlorines had been oxidized in the system by the time the supply water from Seymour travelled to North Delta. North Delta was given a shortform "d" in sample identification and statistical analysis. The first of the two sample areas of Newton, "n", registered levels of chlorine residuals much higher than the Delta area. Comparing the second of the two sample areas of Newton, "y", to "n", we clearly see that the free chlorine residuals of "y" was much

higher than "n". This was expected since "y" was closer geographically to the water supply feedpoint than "n".

Chloramine was added to the two South Surrey study areas. The first of the two sample areas of South Surrey, "s", had higher levels of free chlorine and chloramine residuals than "n" or "y". The second of the two sample areas of South Surrey, "w", had chloramine levels that were even higher than "s" because "w" was closer to the feedpoint than "s". pH and alkalinity tests on the samples from the five study areas showed the addition of chemicals had substantially raised the pH and alkalinity of the water in Newton and South Surrey. In all, measurements of the four water quality parameters: pH, alkalinity, free chlorine residuals, and chloramine residuals, agreed well with the expected levels.

The results of this statistical analysis will be valid only for the range of the water quality parameters detected in the samples of this study. The conclusions of this study do not apply to ranges of water quality parameters that are above or below those in the study samples. Conclusions based on statistical statements are also specific to the study areas. Lead and copper levels in the other areas of the Greater Vancouver Water District have to be examined separately, because the water quality characteristics and the water distribution systems might be significantly different from those in this study. However, the same methods and analysis techniques can be applied when studying these other regions of Vancouver.

Although the chlorine levels of the samples were measured in the UBC lab, none of these measurements were used in the data analysis. All the measured chlorine values were very low in comparison with the GVRD chlorine data.

There was a time gap of several hours between the time the homeowners took the water samples and the time the chlorine levels were measured in the UBC lab. Because chlorine is a very volatile gas, much of it escapes from the bottles even if the bottles are tightly capped. For any chlorine measurement to be valid, the analysis must

be carried out concurrent with the time of the actual sampling. Fortunately, the GVRD regularly monitors various water quality parameters from many places in the Greater Vancouver. There was at least one of these GVRD monitoring sites in each of the five study areas. The reported chlorine residuals in this study were the time averaged (Sept 20 to Oct 10) values of all the monitoring stations in each area.

4.2 Data Cross-check by GVRD

The accuracy of the measurement data from the UBC lab was cross-checked by the GVRD lab (Appendix E). Because the standing samples constituted the focus of this research, only standing samples were selected for cross-checking interlaboratory accuracy. Of the 177 standing samples from bags "A" and bags "B", fifteen percent, or 28, of the samples were randomly selected and sent to the GVRD lab. Copper and lead were measured by the GVRD lab using the same principles of measurement as those in the UBC lab.

The GVRD and the UBC lab data for the 28 samples revealed some differences. While the copper values for the two data sets were remarkably similar, 9 out of 28 of the lead measurements appeared to be significantly different. If the UBC and the GVRD data sets were significantly different from each other, then either the UBC or the GVRD lab or both labs had a problem with measurement accuracy. The Kolmogorov-Smirnov test was employed to test for a statistical difference between the two data sets. The UBC data set was randomly drawn from the pool of standing samples, which was the population of values measured by the UBC instrument. The null hypothesis of the test was that the GVRD data set belonged to the same population of values as the UBC data set. The rejection of the null hypothesis meant that the GVRD data set differed significantly from the UBC data set. If this were the case, more interlaboratory testing had to be conducted to identify the sources of the measurement inaccuracies.

A two sided test was performed, with $n=28$, $\alpha=0.05$, and $D_{critical}=0.36$. For copper, $d=0.07$. Because $d < D_{crit}$, the null hypothesis was retained. For lead, $d=0.33$. The null hypothesis was also retained in this case. The resulting conclusion was that the GVRD data set validated the accuracy of the UBC data set.

4.3 Reporting of Data

Various methods of reporting laboratory data have been employed by different groups of people. For this study, since most of the data was around zero, the practice of reporting and using only data that was above the LOD (level of detection) would have resulted in too little information left for statistical analysis. On the other hand, the suggestion that reporting all the data as it was, including the negative values (ASTM, 1984), might have led to negative bias in the data set.

For computational purposes, this study reported all negative values as zero. Also, all values below the LOD were reported and used in the statistical analyses.

The sigma, standard deviation (precision), for copper was 0.01ppm and sigma for lead was 1 ppb. So the LOD for copper was 0.03 ppm and for lead was 3 ppb. The LOQ for copper was 0.10ppm and for lead was 10 ppb (Table 6).

Table 6 Detection Limits of Measurements

Metal	σ	LOD	LOQ
copper (ppm)	.01	.03	.10
lead (ppb)	1	3	10

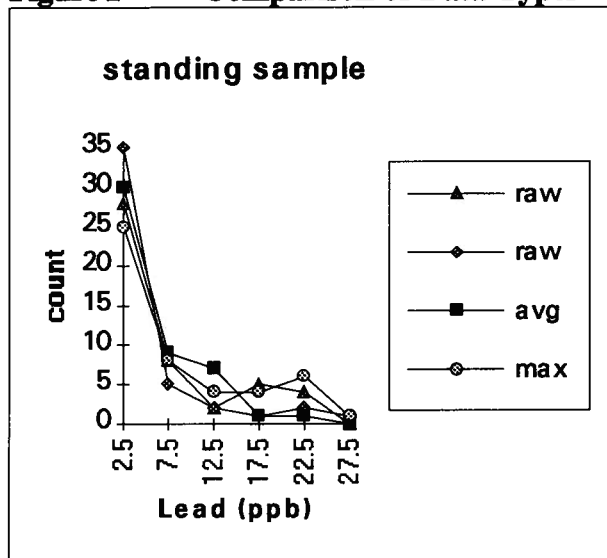
4.4 Data Used for Statistical Analysis

A choice had to be made as to how to analyze the raw data (Appendix F). Raw data consisted of measurement data of the samples in bags "A" or of the samples in bags "B". Previous studies that characterized the metal levels at the tap used the average values of the raw data (Karalekas, 1983). Although this has been the most widely employed method of comparing metal levels, this study had used another measure of comparison. Instead of averaging the "A" and "B" values, the maximum

value of the two was chosen for performing subsequent analyses. The rationale for using this method was that the metal level for the sample with the highest standing time should be known. Due to the inevitability of human error, it was anticipated that certain homeowners collected the samples improperly for one of the two sets of samples they had to collect. In such cases, choosing the sample with the maximum metal level was equivalent to throwing out bad data. In a situation where both "A" and "B" samples had been collected properly, one of the two samples was likely to have a longer standing time than the other. Here, picking out the maximum value improved the chance that this databank reflected the highest metal levels at the tap during the sampling period. If samples from both mornings had been collected improperly, it would not have mattered if the maximum method or if the averaging method had been used.

The method of using the maximum value had implications for the statistical analyses. If, other than "A" and "B" values, many more sampling repetitions were present, then the metal level frequency distribution of the maximum values should have approached a double exponential distribution, as the number of repetitions approach infinity (Kinnison, 1985). In other words, it would be expected that the copper and lead histograms for the various study areas would follow the double exponential distributions instead of the normal or log-normal distributions. This would have added complications to the statistical analyses, because most of the available statistical methods have been developed for normal distributions. For this study, the number of sampling repetitions was two. Since this number did not even come close to approaching infinity, the problem of having to deal with double exponential distributions was only a theoretical concern. Examining the lead standing sample histograms (data combined for study areas "s", "n", "w", and "y"), it can be seen that the irregular distribution of the maximum value histogram is not substantially different from the shape of the average value histogram (Figure 1).

Figure 1 Comparison of Data Types



It can also be noted that the maximum value histogram has less low value data points and more of the higher value data points. This result was predicted by the theory of the maximum value method.

4.5 Non-Parametric Testing

The frequency distribution of lead of all the study areas exhibited highly irregular patterns. Although some were close to being log-normal, most of them were highly skewed to the left and had bi- or multi-modal tendencies. These kinds of distributions were not amenable to the common statistical tests that were developed for normal or log-normal distributions. To get around this problem, it was common to transform the existing distribution into a normal or log-normal distribution and then to perform the usual analyzes. This researcher tried to apply the square root, logarithmic, and reciprocal transformations. Using SYSTAT, testing was carried out to see if the distributions obtained after the transformations deviated significantly from the normal distribution, at $\alpha=0.05$. Using the Lilliefors Test, it was found that the transformation procedures were not successful in converting our distributions into ones that were insignificantly different from the normal distributions (SYSTAT, 1992). As a last means, non-parametric statistical tests have been used to analyze the data.

Non-parametric testing is not only particularly suited to ill-behaved distributions, but it is also a powerful method. In fact, the asymptotic relative efficiency (A.R.E.), a measure of power, of a non-parametric test to its parametric counterpart, is greater than 90% for most of the tests used in this study. In order to increase substantially the power of the test, the number of samples collected has to be increased. For a given number of samples, there is a very little loss of power by using the non-parametric rather than the parametric method.

4.6 Other Statistical Problems

The statistical significance of this study has to be qualified by certain disclaimers. First, the so-called spatially random or cluster sampling techniques employed in this study were not really random or cluster in the true statistical sense. In a truly random sampling, a population would be well defined. A random sample would then be randomly picked out of the population group. Similarly, in a cluster sampling, there would be clearly identifiable sub-populations. One of the sub-population group would be picked from the whole population and all of the units in the selected sub-population group would be sampled.

In this study, the governing factors of copper and lead levels were chemical parameters that could not "a priori" be known with certainty. Therefore, it was not possible to clearly identify population or sub-populations groups. The sampling techniques employed in this study were the best that could have been employed under the circumstances. Engineering judgment, based on general knowledge of water chemistry in a distribution system, was used to decide, roughly, the sample population and sub-population boundaries. This type of sampling belongs to a type of non-probability sampling called the "judgment or purposive selection" (Cochran, 1977).

The quota sampling technique which was employed, in order to obtain a minimum number of samples for analyses, violated the principle of true random selection.

The 13 households that did not return bottles presented a problem with non-response bias. Non-response bias would have occurred if the non-returns came from houses that had very clean or very contaminated water, in relation to the houses that returned bottles. For the houses that had ultra-clean water, the homeowners may not have bothered to return bottles, because they did not feel this study could benefit them in any way. For the houses that had very contaminated water, the homeowners may have been embarrassed to disclose the fact that they had a water quality problem. Non-response may have contributed to a high or a low bias in our database.

Although modern statistical research is progressively finding better techniques to deal with this type of non-ideal sampling scheme, no one method could have accounted for all of these statistical problems at the same time. However, just because these problems existed did not mean that our analyses were completely invalid. The results were still useful; but one must be extra careful in interpreting the conclusions drawn from these analyses.

4.7 Identifying Flushed Standing Samples

To obtain a valid characterization of the copper and lead levels in the study areas, the researcher had to identify the flushed standing samples and to reject them from the database before performing statistical analyses. Including these results in the analyses would have grossly biased the sample distributions to the low side.

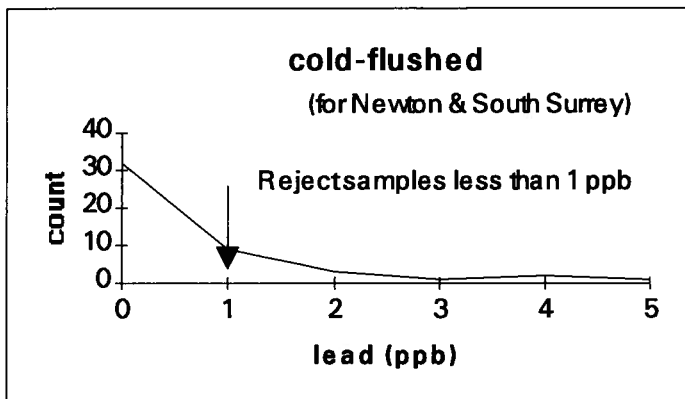
Flushed samples were treated as outliers that had very low values in comparison to the rest of the population group. Normally, these outliers could have been identified by outlier identification procedures such as the Rosner's Test for Detecting Up to k Outliers or the Dixon Test (Gilbert, 1987). Alternatively, a general rule in statistics is that, given a data set with at least 10 values, a value that lies outside 4σ from the mean of the data set can be treated as an outlier (Sachs, 1982). The problem with using these conventional methods is that they assume that the number of outliers is small compared to the number of data in the data set.

In a field study, such as this one, the percentage of flushed samples was not small. Hence, one had to base a rejection criterion on something other than the set of standing samples. The flushed cold water samples could be used as a baseline to compare with the standing sample values. A flushed standing sample should have had a lead value that was very similar to the value of a flushed cold water sample. Therefore, as long as one could establish the criterion of similarity between the flushed cold water samples and the flushed standing samples, there existed an objective way to assess which data point should have been rejected. Due to a different water chemistry, flushed cold water samples may have had higher copper concentrations than 1 liter standing samples. To avoid a possible conflict between a rejection criterion based on lead and one based on copper, one metal was finally chosen. Since the emphasis of this study was to clarify the extent of lead problems in the study areas, lead was chosen to be the basis for establishing a rejection criterion.

Using the flushed cold water samples as the baseline, the simplest way to identify outliers was to take the difference between the flushed cold water value and the standing sample value for each house. A distribution of the differences between the values could have been plotted, and the outliers could have been identified by the Rosner or the Dixon Tests. However, this method would be invalid if there were a large number of true outliers.

The rejection procedure that was used was slightly different. This rejection procedure could be illustrated by looking at the histogram of the flushed cold water lead values for the Newton and South Surrey areas (Figure 2).

Figure 2 Rejection Procedure



About 90% of the flushed cold water values were less than 2.5 ppb, although there were a few values as high as 5 ppb. Suppose one wanted to know if a particular standing sample with a lead value of 20 ppb had been flushed or not. Knowing that 20 ppb was higher than the highest flushed cold water level found in the study areas, one could confidently say that this particular standing sample had not been flushed. On the other hand, it would have been concluded that the standing sample had been flushed if it measured 0 ppb. However, a standing sample with a value between zero to five ppb would make it harder to decide. Therefore, one needed to find a cut-off value below which all standing samples would be classified as flushed and, above which, classified as unflushed. If the cut-off was chosen to be at 5 ppb, the chances were that one would reject some standing samples that legitimately had low standing lead levels. As one lowered this cut-off, the opposite problem was encountered, of not rejecting some of the flushed standing samples. Committing the error of not rejecting flushed standing samples would be worse than rejecting legitimate standing samples, because the presence of a low outlier in the database would cause more bias to the database than the absence of a good piece of data. Therefore, the strategy was to choose the cut-off as high as possible, while making sure that enough data remained to be analyzed statistically.

This rejection procedure was performed once for the samples that came from the Newton and South Surrey regions. The procedure was repeated separately for the samples that came from the Delta region, because Delta did not receive any corrosion treatment. Failing to analyze the two groups of data separately would have resulted in rejecting too many unflushed standing samples that came from Newton and South Surrey, and not rejecting enough of the flushed standing samples from Delta.

4.7.1 Rejected Samples for n,y,s,w

The flushed cold water samples were, just like the standing samples, sampled from a larger population group. Therefore, the quantification of the cut-off point was itself subject to statistical uncertainties. The cut-off point could be quantified as a quantile of the set of flushed cold water samples. If one chose 5 ppb as the cut-off point, then the cut-off was at 100 quantile of the flushed cold water sample set. But, in the larger population group, from which the samples were taken, the real 100 quantile was most probably higher than 5 ppb. Stating that 5 ppb was at the 100th quantile of the population group should be qualified by a certain level of confidence.

The statistical test that was perfectly suited to this type of task was a non-parametric test called the "quantile test". In the Newton and South Surrey areas, there were 48 standing samples that had to be tested for flushing. This researcher performed an upper-tail quantile test, with $n=48$, $\alpha=0.10$, and choose the 65th quantile. There were 18 standing sample data rejected, and 1 ppb was the cut-off point. Choosing a higher quantile to be the cut-off point would have resulted in rejecting almost all of the standing samples.

4.7.2 Rejected Samples for d

The rejection scheme for the standing samples of Delta had to be the same as that for Newton and South Surrey, i.e., $\alpha=0.10$, and $p=0.65$. Standardizing the rejection scheme ensured that the unrejected data from the different areas could be compared on an equal basis. There were 12 standing samples that had to be tested.

Given $\alpha=0.10$, and $p=0.65$, and $n=12$, 5 ppb was calculated to be the cut-off point, and three standing samples were rejected.

4.8 Simple Tests

After the rejection procedures, there were 14 unrejected standing samples from South Surrey, 16 from Newton, and 9 from Delta (Table 7).

Table 7 **Summary of Simple Statistical Evaluation**

	South Surrey		Newton		Delta	
	copper	lead	copper	lead	copper	lead
mean	.129	12.3	.174	10.8	1.439	16.3
σ	.031	7.9	.127	7.9	0.736	6.2
$\sigma_{\bar{x}}$.008	2.1	.032	2.0	.245	2.1
c.v.	.24	.6	.726	.7	.512	.4
median	.12	10.0	.135	6.5	1.780	14.0

Note: Copper measured in ppm, Lead in ppb

The values had significant figures equal to the detection limit plus 1 decimal place. For copper, the detection limit was 0.01 ppm, and the significant figures were therefore given in units of 0.001 ppm. For lead, the detection limit was 1 ppb, and the significant figures were in units of 0.1 ppb. The coefficient of variations, a measure of the standard deviation divided by the mean, were under 1 for all the categories of copper and lead measurements.

A coefficient of variation that is under 1 is considered to be low in comparison with other studies of copper and lead levels in tap water (AWWARF, 1990). A low variability of copper and lead measurements indicates that the sampling areas were indeed homogeneous. Therefore, we can be sure that whatever statistical statements we make from our analysis will not be distorted by having taken samples from inhomogeneous sampling areas. Furthermore, a low coefficient of variation excludes the possibility that there were serious procedural or laboratory errors. In short, a low variability in copper and lead measurements confirms the soundness of the entire sampling strategy employed in this study.

One can also do a cursory examination for the skewness of our data sets. Mean values should theoretically be higher than median values for a positively skewed distribution (Lapin, 1983). The more skewness there is, the farther is the distance between the mean and the median.

Based on this reasoning, the set of lead measurements for Newton is probably highly skewed in the positive direction. This is an indication that the sampling distribution for this set of data, even after having rejected the flushed standing samples, is still not transformable into a normal or log-normal distribution. By the same reasoning, the other data sets are probably transformable. Because transformed data cannot theoretically be compared with untransformed data, non-parametric statistical methods should be used to analyze the data after the flushed samples have been rejected.

Using the mean value as the measure of central tendency, it can be seen that both the mean copper and lead values are lower in Newton and South Surrey than in the control Delta area (Table 8).

Table 8 Percentage Reduction from Delta (mean values)

	lead (ppb)	copper (ppm)
to Newton	34 %	88 %
to South Surrey	25 %	91 %

The copper values are reduced dramatically, while the lead values are marginally reduced.

4.9 Kruskal-Wallis H-Test (Copper)

The result of the comparison between the mean copper values strongly suggests a statistically significant difference between the copper levels of the different study areas. To investigate this further, the Kruskal-Wallis H-Test was conducted. For $n=39$, $\alpha=0.05$, the null hypothesis is that the samples from Newton, South Surrey, and Delta all belong to the same population. This null hypothesis is rejected, which

means that at least one of the three sample sets is significantly different from the other sets. Using the Kruskal-Wallis multiple comparisons method, it was discovered that the copper levels in Delta were significantly higher than South Surrey and Newton. Copper levels in South Surrey were statistically equivalent to those in Newton.

4.10 Confidence Intervals for the Difference Between 2 Means

The difference between the expected copper level of Delta and Newton or Delta and South Surrey is subject to statistical uncertainties. The 95% confidence interval of the differences can be calculated by a non-parametric method. The differences between Delta and the two test areas are similar. The lower bounds hover around 1 ppm and the upper bounds around 1.8 ppm (Table 9).

Table 9 Difference Between 2 Means

	lower bound (ppm)	upper bound (ppm)
Delta minus South Surrey	1.01	1.82
Delta minus Newton	.92	1.80

4.11 Median Test

The median test tests the null hypothesis that the samples from Delta, Newton, and South Surrey all come from population groups that have the same median. For $n=39$, $\alpha=0.05$, the null hypothesis is rejected. This result corroborates with the results from the Kruskal-Wallis H-Test.

A similar analysis on lead samples did not reveal any statistically significant differences between the study areas.

4.12 Test for Equal Variance

This non-parametric test tests if the variances of the study areas are equal. For $n=39$, $\alpha=0.05$, the test shows that the variances of the sample sets from South Surrey and Newton were less than samples from Delta (Table 10).

Table 10 Test for Equal Variance

	copper	lead
South Surrey vs Delta	less variance	Ho ok
Newton vs Delta	less variance	Ho ok

This piece of evidence further proves that pH and alkalinity treatment in the South Surrey and Newton areas are changing the copper levels at the tap. In contrast, the variances for the lead samples from the study areas are statistically equivalent.

4.13 Compliance with Regulations

The most up-to-date copper and lead guidelines from the USEPA was issued in 1991. The guidelines stipulated that 90% of the samples in a monitoring program should have less than 15 ppb of lead and 1.3 ppm of copper. For the samples in this study, this researcher analyzed the effectiveness of pH and alkalinity adjustments in reducing copper and lead levels in terms of regulation compliance (Table 11).

Table 11 Regulation Compliance (as per EPA guidelines, 1991)

	Newton/South Surrey		Delta	
	copper	lead	copper	lead
Cold Standing	ok	no	no	no
Cold Flushed	ok	ok	ok	no
Hot Flushed	ok	ok	ok	no

Copper is out of compliance in the control area, but is in compliance in areas with pH and alkalinity adjustments. Lead in the standing samples is out of compliance both before and after pH and alkalinity adjustments. The flushed cold and hot lead samples are also out of compliance. However, these comply after the adjustments are in place. It was concluded that pH and alkalinity adjustments do not significantly help lead to comply with the regulations.

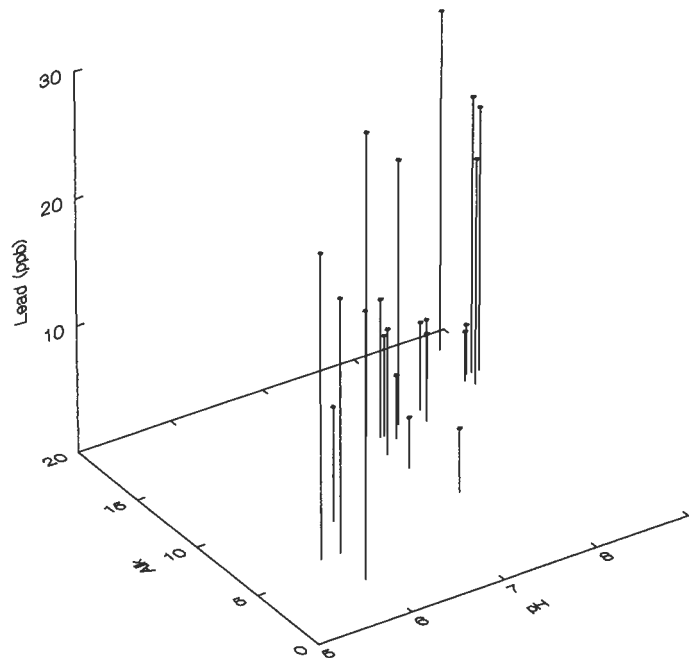
The copper and lead guidelines in Canada are much more lenient than the USEPA guidelines. The USEPA guidelines are chosen as the compliance benchmark because most of the Canadian Drinking Water Regulations follow the lead of the

USEPA. Secondly, the present Canadian lead and copper regulations do not have well specified sampling protocols (Environment Canada, 1981).

4.14 Plot of Lead vs. Alk and pH

From the previous statistical analysis, it is abundantly clear that pH and alkalinity adjustments work to reduce copper levels at the tap. The effects on lead is much less clear. In order to investigate the relationships between pH and alkalinity with lead, this researcher started the data exploration (Tukey, 1977) by making a 3-D plot of pH, alkalinity and lead (Figure 3).

Figure 3 3D Plot of Lead, Alkalinity, and pH



From this graph, we see that there is a strong correlation between pH and alkalinity. However, there does not seem to be a pattern of increase or decrease of lead with rising pH or rising alkalinity.

4.14.1 Spearman Rank Correlations

The extent of the correlation between pH and alkalinity can be quantified by calculating the Spearman Rank Correlation coefficient between the two variables. The calculation indicates that there is a 0.917 correlation between the pH and the alkalinity, with 1.000 being perfect correlation.

4.14.2 Regression of Alk and pH

Basic water chemistry tells us that pH should be related to the amount of alkalinity in the water. Therefore, it is not surprising to find confirmation of this prediction from the Spearman Rank Correlation Test. If the regression test shows a equally strong relationship between the two parameters, then we can simplify the subsequent statistical analyses by eliminating one variable. A three dimensional problem can then be reduced to a two dimensional problem: copper or lead versus pH.

Because of the amount of work that had to be accomplished during the sampling period (a period of three weeks), only selected samples were picked for measuring pH or alkalinity or both. Of the 39 samples that were not rejected by the procedure that weeded out flushed standing samples, only 21 were measured for both pH and alkalinity.

Using SYSTAT, a regression analysis was undertaken, with pH as the independent variable and alkalinity as the dependent variable (Table 12).

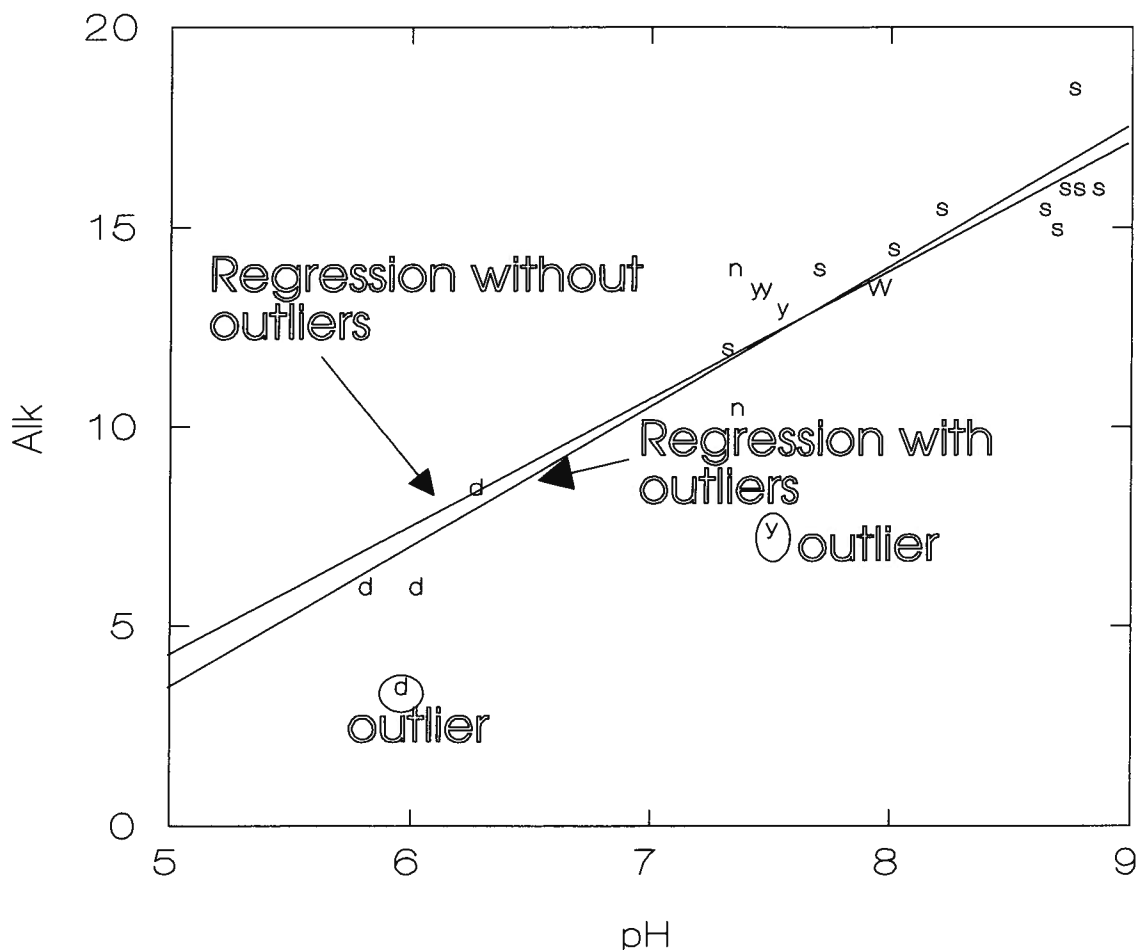
Table 12 Regression Analysis of pH versus Alkalinity

DEP VAR: ALK N: 21 MULTIPLE R: 0.911 SQUARED MULTIPLE R: 0.830						
ADJUSTED SQUARED MULTIPLE R: .821 STANDARD ERROR OF ESTIMATE: 1.692						
VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	-16.106	2.995	0.000	.	-5.378	0.000
PH	3.745	0.389	0.911	1.000	9.626	0.000
ANALYSIS OF VARIANCE						
SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P	
REGRESSION	265.133	1	265.133	92.658	0.000	
RESIDUAL	54.367	19	2.861			

The regression analysis gives us a squared multiple R of 0.830. This means that 83.0% of the total variation in alkalinity can be accounted for by a linear equation involving pH. The adjusted squared multiple R of 0.821 is the expected value for the squared multiple R if the same analysis was performed on another set of 21 samples taken from our study areas (SYSTAT, 1992). A squared multiple R of 1.000 means we can fit a perfect linear line through the alkalinity versus pH data. Our computed squared multiple R of 0.830 suggests that there is a good empirical linear relationship between pH and alkalinity. This linear relationship has a slope and an intercept on the abscissa. The slope of the linear fit is 3.745 and the intercept is -16.106. Two-tail student t tests at $\alpha=0.05$ show both the intercept and the slope to be statistically significant. The Analysis of Variance Test also tells us that the overall regression model is significant at $\alpha=0.05$.

The regression analysis also tests each piece of data individually to see if it is an outlier in the linear regression model. Two, one point from Delta and one point from study area "y", of the 21 points are outliers (Figure 4).

Figure 4 Regression Plot of pH versus Alkalinity



After these outliers are taken away, the regression modeling can be repeated for the remaining 19 data points. The regression estimate is improved slightly, with the new adjusted squared multiple R being 0.887. By visual inspection, the outliers do not seriously affect the linear regression line.

4.14.3 Filling in Missing Data Points

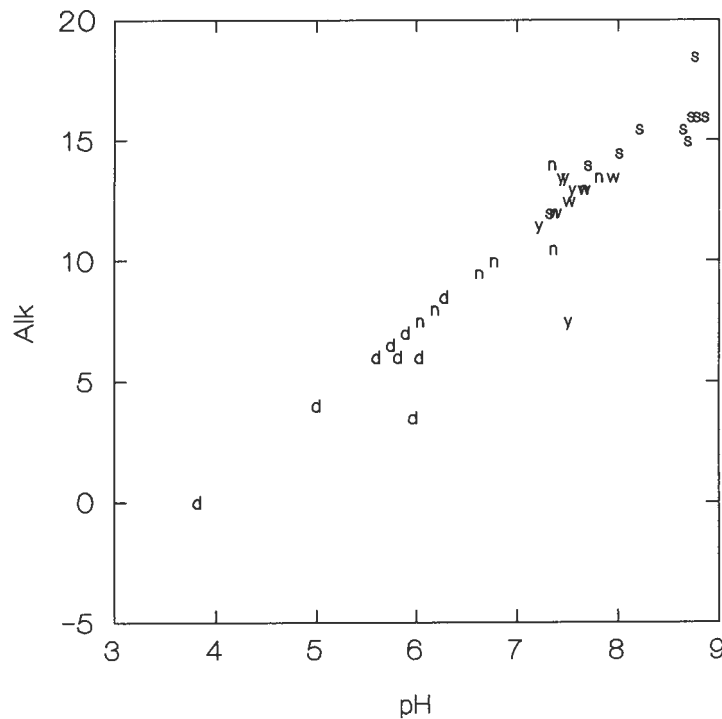
The regression analysis demonstrates that we can approximate the relationship between pH and alkalinity by the equation

$$\text{Alkalinity} = -12.893 + 3.379 \cdot \text{pH} \dots \dots \dots (1)$$

Having demonstrated the validity of this relationship, we may analyze the copper and lead patterns with respect to only pH.

Having only 21 data points with pH measurements may not be good enough for performing subsequent statistical tests. To increase the number of available data points, one may exploit the knowledge of the relationship between pH and alkalinity. All 18 of the 39 standing samples that do not have a pH measurement do have an alkalinity measurement. By using Equation 1, one can predict the pH of those 18 standing samples by knowing their alkalinity measurements (Figure 5).

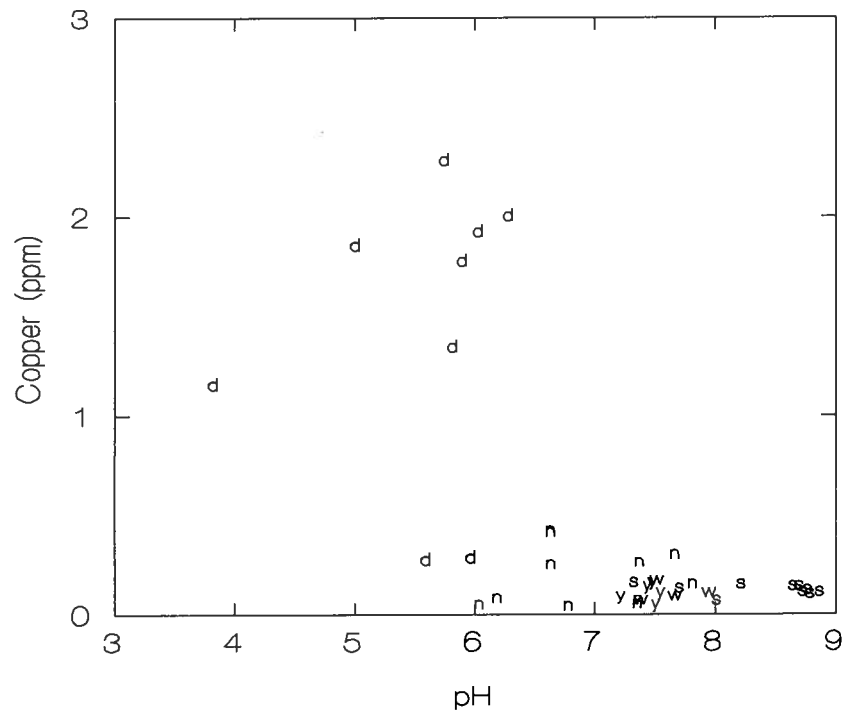
Figure 5 Filling-in Missing Data for pH versus Alkalinity Data



4.15 Copper vs. pH

The copper levels of the standing samples can now be plotted against their respective pH values (Figure 6).

Figure 6 Copper vs. pH

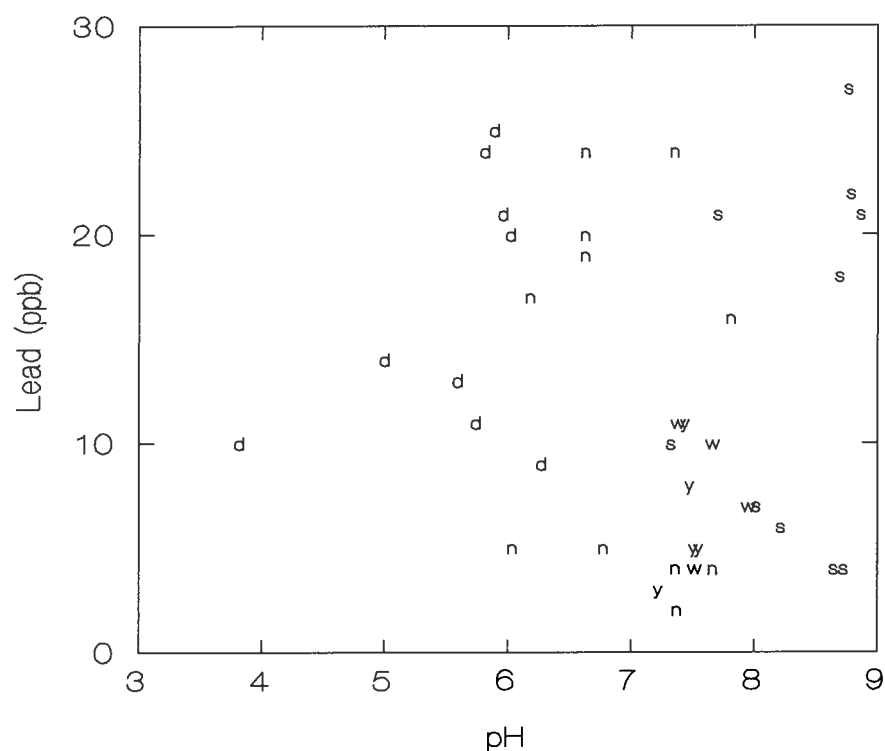


A visual inspection dramatically underscores the difference in copper levels between samples from Delta and the samples from the areas with pH and alkalinity adjustments.

4.16 Lead vs. pH

One can also plot the lead levels of the standing samples against their respective pH values (Figure 7).

Figure 7 Lead vs. pH



Unlike the copper vs. pH graph, this figure does not show an obvious trend in lead reduction, in sampling areas that have pH and alkalinity adjustments. However, there are three interesting observations in this figure that may be of significance. First, the lead levels are confined to a narrow interval in the samples that have pH less than about 6. Secondly, from pH of 6 and above, there is a wide scatter in the lead levels. This scatter is probably attributable to the standing time, which is the only uncontrollable factor in this study. Thirdly, there is a window between pH of 8 to 8.5 where there appears to be a drop in the sample lead levels.

4.17 ANOVA (Lead)

So far, the evidence has conclusively proven that pH and alkalinity adjustments reduce copper at the tap. For lead, there appears to be some reduction, but preliminary

tests do not indicate these reductions to be statistically significant. Further analysis of the lead data can be done with ANOVA (the analysis of variance) because it is a powerful statistical tool that can analyze the significance of a large number of different factors at the same time.

ANOVA is a technique that is highly sensitive to nonnormally distributed data (Sachs, 1982). There is no readily applicable ANOVA technique that can handle nonparametric data. However, it is possible to make the ANOVA technique more robust, more able to accommodate distribution free data without substantially losing the true level of significance or the true power (A.R.E.) of the test (Conover, 1980). The technique requires transforming the measurement data into ranked data, and then to apply the ANOVA tests on the ranked data. This technique is employed for the analyzes in this research study.

4.17.1 Using One-Way ANOVA

There are many types of ANOVA tests. Since we want to know the effects of pH on lead levels, one-way ANOVA appears to be the most appropriate method. In one-way ANOVA, the lead values are separated into groups based on a factor. The factor that determines which group a data point belongs to could be the study areas, i.e., "d", "s", "n", "y", "w", or pH separated into different ranges of values. For both of these methods of grouping lead data, the experimental design is considered unbalanced. This means that not all groups have the same number of data points. Also, the ANOVA we have employed uses the random effects model. Although all the data from each group are characterized by the same factor, the factor itself is not fixed and is subject to variations. For example, the data points in study area "d" all have slightly different pH, alkalinity, and chlorine residual levels. SYSTAT has incorporated both the unbalanced design and the random effects model in its algorithms. SYSTAT can also do split-plot analysis. This routine is usually required if the sequence of data measurements is not randomized. Since our database was

measured using a randomized sequence, it is not necessary to include the split-plot design in these analyses.

4.17.2 One-Way ANOVA Grouped by Study Area

This researcher analyzed the lead pattern of the standing samples by one-way ANOVA, grouped by study area. There are five groupings, namely "d", "s", "n", "y", and "w". Although the samples from the Delta region have lower pH than the samples from the other areas, the pH of samples from the other study areas have some overlap. The primary purpose of this test, then, is not so much to investigate the effects of pH alone, as it is to investigate all of the factors, including chlorine residuals, at the same time. The Fisher Test probability is $p=0.131$ for this model. At $\alpha=0.05$, this model is not considered to be significant. The conclusion from this test is that pH, alkalinity, and chlorine residuals are not effective in reducing lead levels at the tap.

4.17.3 One-Way ANOVA Grouped by pH Range with Age as Covariate

The plot of lead vs. pH gave this researcher some clues as to the effects of altering the pH of the water on the lead levels at the tap. Chlorine residuals have been ignored from this analysis. If the chlorine residual in the water is a significant factor, then it would have shown up in the one-way ANOVA grouped by area.

In the pH analysis, we are most interested in examining the two zones that appear to be anomalies: pH less than 6 and pH between 8 and 8.5. For this analysis, then, the lead data has been separated into bins. Each bin contains data that have pH measurements falling into a certain range. The five bins are: pH between 3 to 6, 6 to 7, 7 to 8, 8 to 8.5, and 8.5 to 9. No pH measurements recorded less than 3 or more than 9; thus, the reason for selecting pH of 3 and 9 as the minima and maxima of this analysis is a sound one.

Besides pH, the age of the house from which the sample is taken, might also affect the concentration of lead in the standing samples. With one-way ANOVA analysis, it is possible to isolate the effects of house age from the effects of pH on the

lead values. pH, then, is the grouping parameter, and age is the covariate of the analysis.

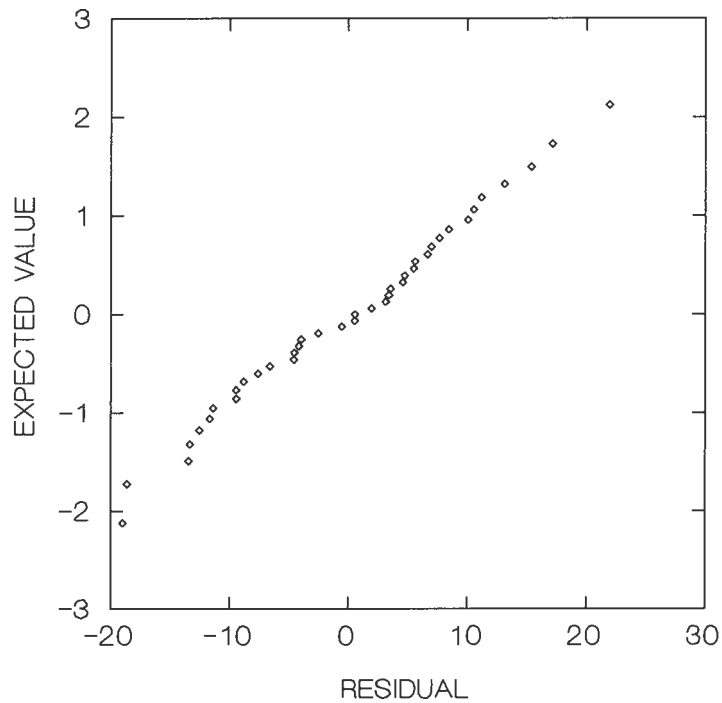
The ANOVA analysis indicated that the covariate, $p=0.685$, and the pH bins, $p=0.072$, are not statistically significant at $\alpha=0.05$. The Tukey HSD Multiple Comparisons (SYSTAT, 1992) show that the pH range 8 to 8.5 is not significantly different from the data from the other four pH bins.

4.17.4 Residuals

The residuals for all the ANOVA analyzes have been examined. The results fully confirmed that none of the essential assumptions of the ANOVA method have been violated by the data sets. As an example of residual examination, the residuals for the pH range ANOVA analysis will be looked at closely.

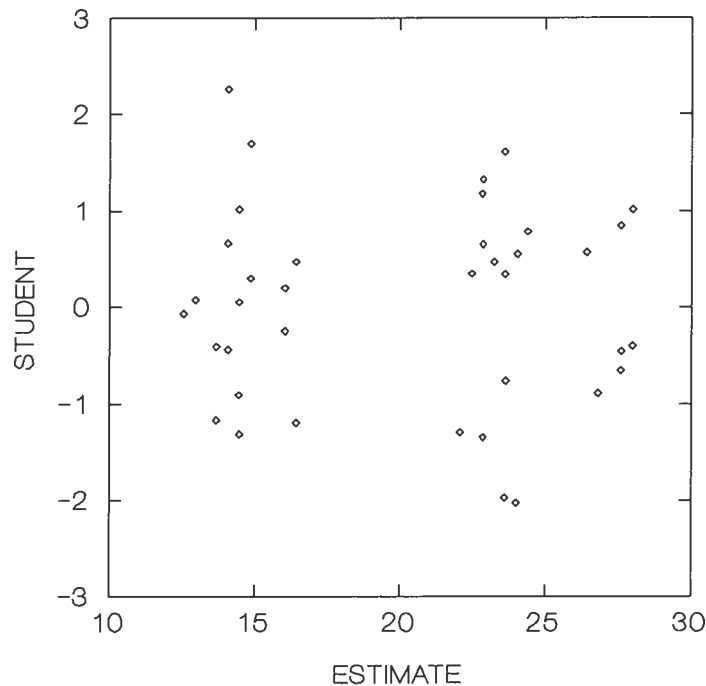
Firstly, the residuals should follow a normal distribution, for the ANOVA method to be valid. Although the measurement data of the lead values deviate highly from the normal distribution, the same data, after being ranked, do closely follow the normal distribution (Figure 8).

Figure 8 Normal Probability Plot for ANOVA of Lead



We know this is the case because the expected normally distributed values plot in a relatively straight line against the data residuals. Secondly, the plot of the student t versus the ANOVA estimates of the lead values (Figure 9) tells us that the errors of the estimates are not dependent on each other.

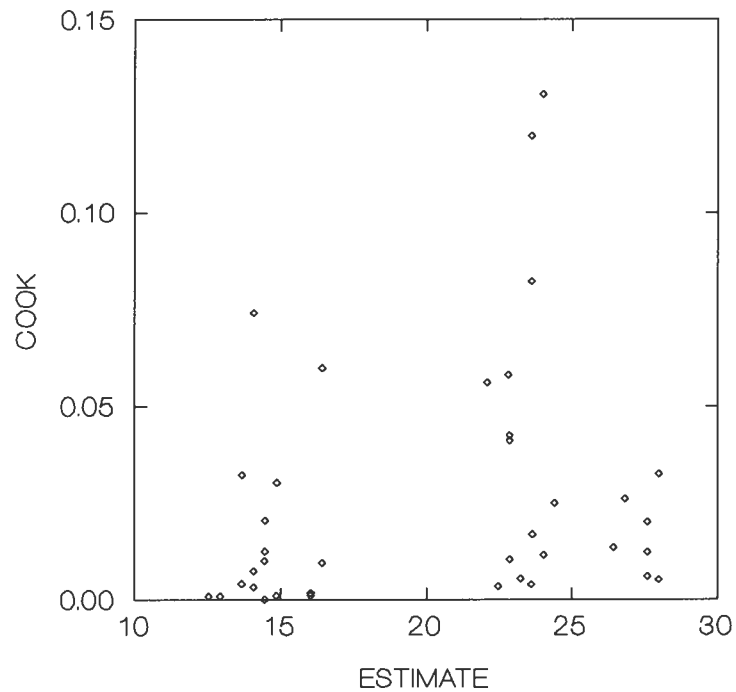
Figure 9 Student t vs. Lead Estimate



We know the errors are independent because the student t values are randomly scattered above and below zero in this figure. Dependent errors would show a definite pattern or trend. Also, we note from this figure that all the points fall between plus and minus 3 standard deviations of the student t distribution. The absence of a widening range of errors means that the variance of the lead values is constant with respect to the magnitude of the lead measurement.

Finally, the plot of the Cook's distance versus the lead estimate (Figure 10) shows all of the datapoints do have a Cook's distance of much less than 1. This means that all the datapoints used in the ANOVA analysis belong to and are adequately described by the statistical model. The residual analysis shows that the ANOVA method employed here is a valid way to analyze the lead data.

Figure 10 Cook's Distance vs. Lead Estimate



4.18 Testing of Oldcopper and Plastic

Of the 92 houses that returned bottles to this study, 6 houses had a house age of between 11 to 15 years old (Oldcopper), and 25 houses had plastic plumbing (plastic). These data were not included in the previous analyzes. The Oldcopper and the plastic data are divided into the Delta, South Surrey, and Newton areas and compared against the main data from the same study areas (Table 13).

Table 13**Comparison of Oldcopper and Plastic with Main Data**

Oldcopper(N=6)

Plastic(N=25)

	copper	lead	copper	lead
South Surrey	same	same	lower	lower
Newton	same	same	lower	lower
Delta	same	higher (1 pt)	lower	lower

Almost all the Oldcopper copper and lead data are in the same range as the main data set. The only exception is the lead data of the Delta area, where the Oldcopper lead value is higher than the main data. This particular comparison may not be valid because there was only one Oldcopper data in the Delta area. We can say, in general, that the copper and lead levels at the tap are not significantly different between houses with copper pipes that are 11 to 15 years old and houses with copper pipes that are 10 years old or less.

For the plastic data, the copper and lead values in all the study areas are substantially lower than the main data. This shows that houses that use plastic pipes as the plumbing material do not have the same copper and lead problems as the houses plumbed with copper pipes.

4.19 Comparison of Flushed Cold and Flushed Hot

So far, almost all of the analyses completed apply to the standing samples. We know that the flushed cold water samples have very low metal values compared with the standing samples. Previous studies (Singh, 1990) have shown that flushed hot water samples have higher copper and lead levels than the flushed cold water samples. This researcher has subsequently plotted the flushed cold water data versus the flushed hot water data for copper (Figure 11) and lead (Figure 12) measurements.

Figure 11 **Quantile-Quantile Plot of Cold & Hot Running Copper**

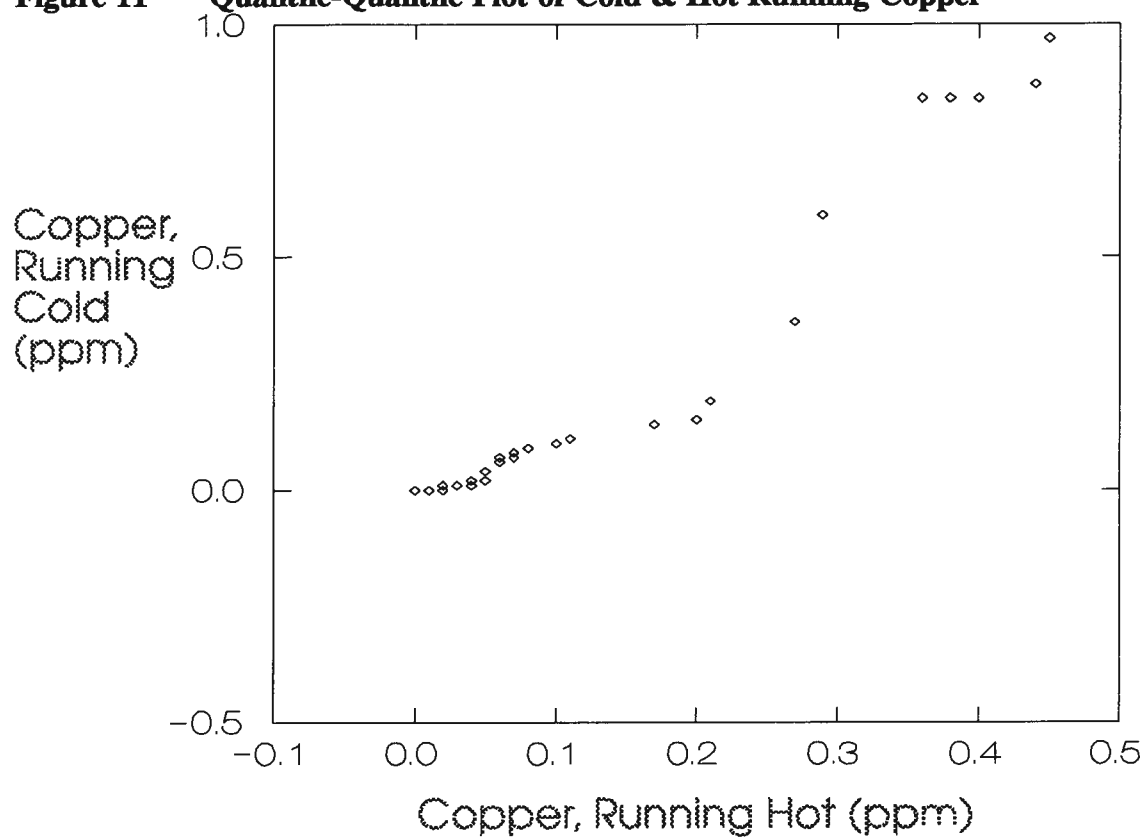
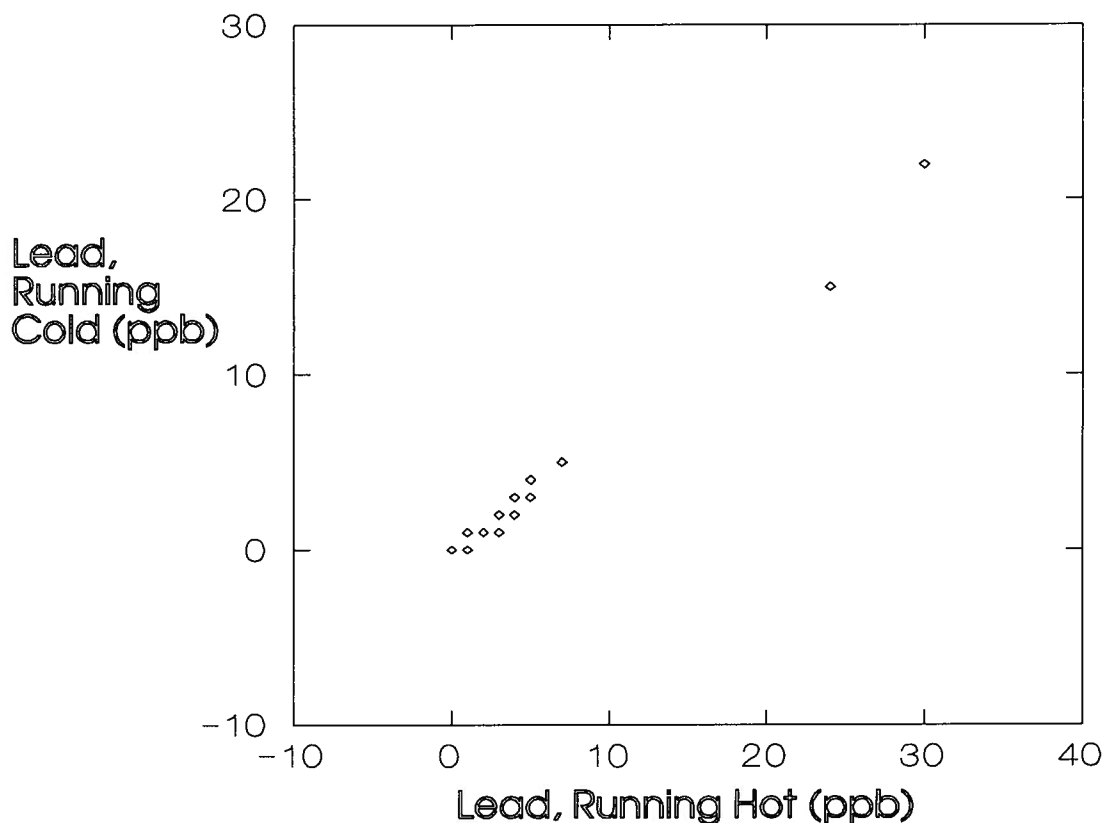


Figure 12 Quantile-Quantile Plot of Cold & Hot Running Lead



These are non-parametric quantile-quantile plots, i.e., the largest flushed cold water data is paired with the largest flushed hot water data, and the smallest with the smallest, and so forth. For copper, it can be seen that the flushed hot samples have less copper concentration than the flushed cold samples. The flushed cold samples also exhibit a larger variability than the flushed hot samples. For lead, although the flushed hot samples have marginally higher lead values than the flushed cold samples, one can still say that they are much less than the standing samples. The variability of both the hot and cold flushed samples are roughly the same. Because the flushed hot samples do not give us substantially different information from the flushed cold samples, future studies should not waste the effort in collecting flushed hot water samples. The effects of pH and alkalinity adjustments on running cold and hot copper and lead levels did not appear to be different for rechlorinated and chloraminated tap water.

5. SUMMARY AND CONCLUSIONS

5.1 The Effects of pH/Alk Adjustments

The results of the various statistical tests on the effectiveness of pH and alkalinity adjustments in reducing lead and copper are summarized in Table 14.

Table 14 Summary of All Statistical Testings

	copper	lead
simple test	reduction	reduction
H test	reduction	-
median test	reduction	no reduction
equal variance	reduction	no reduction
USEPA regulations	compliance	no compliance
Canadian regulations	compliance	compliance
ANOVA(code)	-	no reduction
ANOVA(pH range)	-	no reduction

The pH and alkalinity adjustments are definitely effective in reducing the copper levels in rechlorinated and chloraminated tap water. The same adjustments appear also to marginally reduce the sample lead levels. However, the reduction is so slight that it is not statistically significant.

5.2 Significance of Other Factors

In the ANOVA analysis, age (houses fitted with copper pipes that are 1 to 10 years old) as a covariate was calculated to be insignificant as a factor on lead concentrations at the tap. Furthermore, the analysis involving Oldcopper data also showed that houses fitted with copper pipes that were 10 to 15 years old yielded lead concentrations that were indiscernible from the main data set. In general, then, it is concluded that the age of a house, which is fitted with copper plumbing and is less than 15 years old, is not a significant factor in affecting lead concentrations at the tap in systems with or without pH and alkalinity adjustments. The effects of pH and alkalinity adjustments on copper and lead levels did not appear to be different for rechlorinated and chloraminated tap water.

5.3 Recommendations

For the houses in the study areas that are fitted with copper plumbing, and are less than 15 years old, pH and alkalinity adjustments are not effective in reducing lead levels at the tap. More research should be done to ascertain why pH and alkalinity adjustments by themselves are not effective treatment methods. As fundamental research in the behavior of lead chemistry in the distribution systems and house plumbings is improved, it should be possible to develop more effective methods to reduce the level of lead concentrations at the tap.

For the same level of significance, obtaining more samples will also improve the power of the statistical tests that have been used to analyze the databank of this study. Because non-parametric tests are conservative, increasing the power of the tests might make the outcome significant for certain tests that were close to being significant.

One has to remember that the results of this research project are valid only for the range of chlorine residuals that were measured for the samples during the sampling period. Since the levels of the chlorine residuals change from day to day (GVWD, 1992), the effects of the change in chlorine residuals in the system could be investigated to assess its impact on the lead levels at the tap. In addition, the effects of rechlorination could be compared with the effects of chloramination, for all the different levels of chlorine residuals.

Finally, it has been mentioned that some of the assumptions of the statistical methods employed in this study have been violated due to a number of practical issues. New advances in statistical research, especially in quota sampling, non-response problems, and sampling from non-definable population groups, could be applied to the statistical analysis.

6. REFERENCES

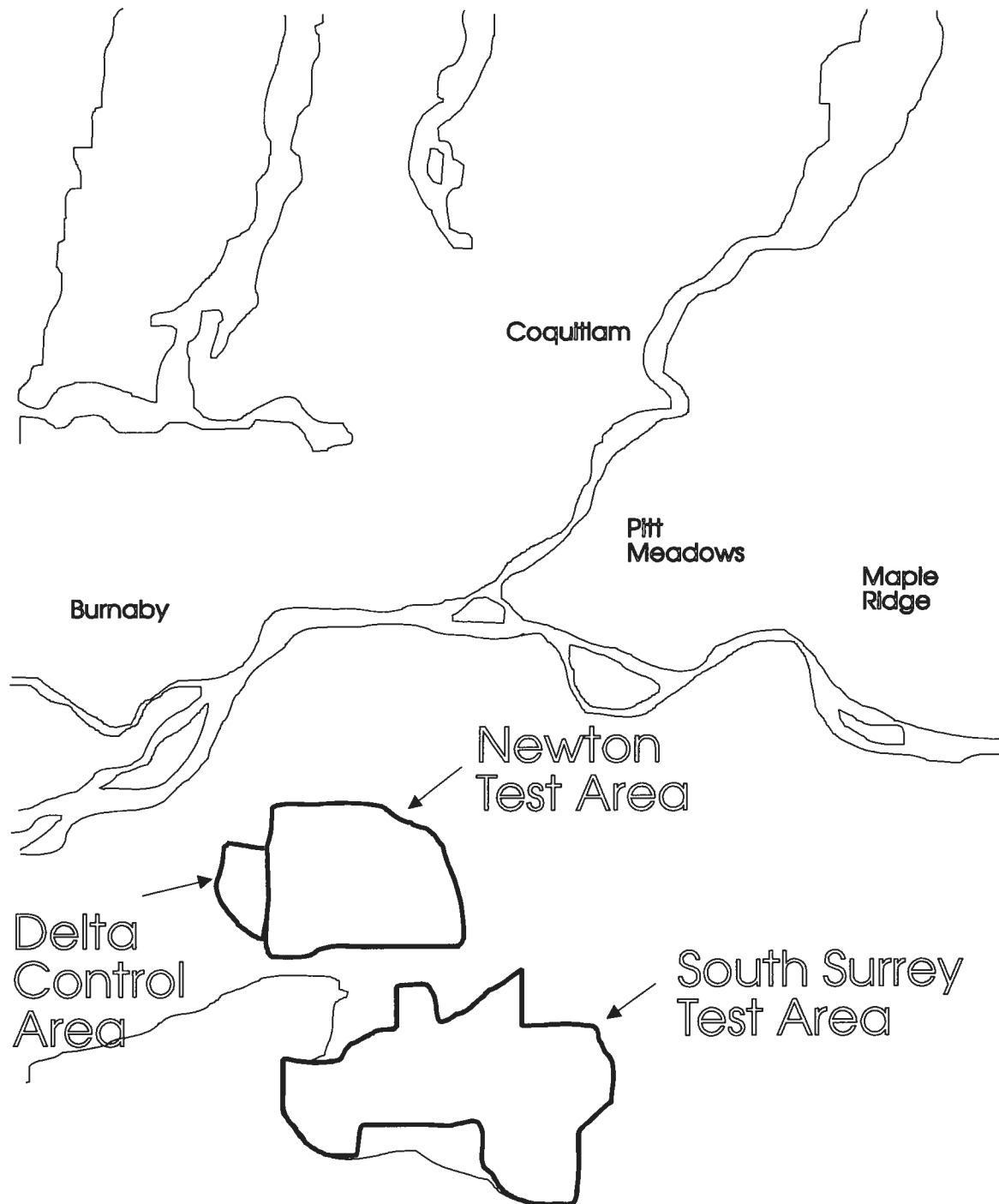
1. American Society for Testing and Materials. *Annual Book of ASTM Standards*, vol. 11.01. Designation: D4210-83. ASTM, 1984.
2. American Water Works Association Research Foundation. *Lead Control Strategies*. American Water Works Association, Denver, 1990.
3. APHA-AWWA-WPCF, 1989. *Standard Methods*, 17th edition.
4. Bailey, R.J., et. al. "Lead Concentration and Stagnation Time in Water Drawn Through Lead Domestic Pipes". Water Research Center Technical Report , TR243, 1986.
5. Britton, A., and Richards, W.N. "Factors Influencing Plumbosolvency in Scotland". Journal of Institute of Water Engineers and Scientists, Vol. 35, Apr 81.
6. Cochran, W.G. *Sampling Techniques*. Wiley, New York, 1977.
7. Conover, W.J. *Practical Nonparametric Statistics*. Wiley, New York, 1980.
8. Department of the Environment. Lead in Drinking Water. A Survey in Great Britain, 1975-1976. Report of an Interdepartmental Working Group. Pollution Paper No. 12, London, England, 1977.
9. Drill, S. et. al. *The Environmental Lead Problem. An Assessment of Lead in Drinking Water from a Multimedia perspective*. Washington, D.C., USEPA, 1979.
10. Economic and Engineering Services Inc. *Greater Vancouver Regional District Water Quality Improvement Program: Final Corrosion Control Report*. March, 1990.
11. Environment Canada. *Guidelines for Surface Water Quality. Vol.1. Inorganic Chemical Substances*. Inland Waters Directorate, Water Quality Branch, Ottawa, Canada, 1981.
12. Fisher, R.A. *Statistical methods for research workers*. Oliver and Boyd, Edinburgh, 1932.
13. Gilbert, R.O. *Statistical Methods for Environmental Pollution Monitoring*. Van Nostrand Reinhold, New York, 1987.

14. Greater Vancouver Water District, 1992. *Quality Control Annual Report*.
15. Gregory, R. and Jackson, P.J. "Central Water Treatment to Reduce Lead Solubility". Proceedings of AWWA Annual Conference, Dallas, TX, June 1984.
16. Health and Welfare Canada. *Guidelines for Canadian Drinking Water Quality*. Federal-Provincial Advisory Committee on Environmental and Occupational Health, Ottawa, 1989.
17. Karalekas, P.C., C.R. Ryan, and F.B. Taylor. "Control of lead, copper, and iron pipe corrosion in Boston". Journal AWWA, Vol. 75, No. 2 (Feb 83), pp 92-95.
18. Keith, L.H. *Environmental Sampling and Analysis: A Practical Guide*. Lewis Publishers Inc., Chelsea, MI, 1991.
19. Kinnison, R.R. *Applied Extreme Value Statistics*. Battelle Press, Columbus, Ohio, 1985.
20. Kuch, A., and Wagner, I. "A Mass Transfer Model to Describe Lead Concentrations in Drinking Water". Water Res., Vol. 17, Oct 83.
21. Lapin, Lawrence L. *Probability and Statistics for Modern Engineering*. PWS Publishers, Belmont, California, 1983.
22. Lyon, T.D.B., and Lenihan, J.M.A. "Corrosion in Solder Jointed Copper Tubes Resulting in Lead Contamination of Drinking Water". Br. Corrosion Journal, Vol.12, Jan 77.
23. MacQuarrie, Doug M. *GVWD Corrosion Control Initiative - Phase II: Inhibitor Chemical Testing at Seymour Dam*. M.A.Sc. Thesis, Department of Civil Engineering, University of British Columbia, 1993.
24. Mancy, K.H. editor. *Instrumental Analysis of Water Samples*. Ann Arbor Science Publishers, 1971.
25. Mandel, J. *The Statistical Analysis of Experimental Data*. Interscience-Wiley, New York, 1964.
26. Montgomery, Douglas C. *Design and Analysis of Experiments, 3rd edition*. John Wiley & Sons, Inc., 1991.
27. Moore, M.R. "Plumbosolvency of Waters". Nature, Vol. 243, 1973.

28. Murrell, N.E. "Summary of Impact of Metallic Solders on Water Quality, Plumbing Materials and Drinking Water Quality". Proceedings of a Seminar, Cincinnati, Ohio, May 16-17, EPA 600/9-85/007, 1985.
29. National Academy of Sciences. *Drinking Water & Health*. Safe Drinking Water Committee. National Academy of Sciences, Vol. 4, Washington, D.C., 1982.
30. Neff, C.H., Schock, M.R., and Marden, J.I. "Relationships between Water Quality and Corrosion of Plumbing Materials in Buildings". Project report for Grant No. CR8085660101, USEPA, EPA/600/S2-87/036, 1987.
31. Obrecht, Malvern F. and Marcel Pourbaix. "Corrosion of Metals in Potable Water Systems". Journal AWWA, Vol. 59, No. 8, August 1967.
32. Oliphant, R.J. "Lead Contamination of Potable Water Arising from Soldered Joints". Water Supply, Vol. 1, 1983.
33. Oliphant, R.J. "Dezincification by Potable Water of Domestic Plumbing Fittings: Measurement and Control". Water Research Center Technical Report TR88, 1978.
34. Richards, W.N. and M.R. Moore. "Lead Hazard Controlled in Scottish Water Systems". Journal AWWA, August, 1984.
35. Sachs, L. *Applied Statistics: A Handbook of Techniques*. Springer-Verlag, New York, 1982.
36. Schaut, G.G. "The Action of a Chlorinated Water Supply upon Lead Pipe". American Journal of Pharm., 1942.
37. Schock, Michael R. "Factors Affecting the Temporal Variability of Lead Concentrations in Domestic Plumbing Systems". Project Report for USEPA Order No. 7W-7480-NASA in partial fulfillment of USEPA Order No. 7W-7425-NASX.
38. Schock, Michael R. "Response of Lead Solubility to Dissolved Carbonate in Drinking Water". Journal AWWA, Vol. 72, Dec 80.
39. Schock, Michael R. and Wagner, I. *Internal Corrosion of Water Distribution Systems*. AWWARF/DVGW-Forschungsstelle Cooperative Research Report, 1985.
40. Schock, M.R. and Gardels, M.C. "Plumbosolvency reduction by high pH and low carbonate-solubility relationships". Journal AWWA, Vol. 75, Feb 1983.

41. Sharrett, A.R. et. al. "Daily Intake of Lead, Cadmium, Copper, and Zinc from Drinking Water: The Seattle Study of Trace Metal Exposure". Environmental Research, Vol. 28, 1982.
42. Singh, Inderjit. *Significance of Building Plumbing Specifics on Trace Metal Concentrations in Drinking Water*. MASC Thesis, Dept. of Civil Engineering, University of British Columbia, August, 1990.
43. Snoeyink, V.L. and A. Kuch. *Principles of Metallic Corrosion in Water Distribution Systems*. AWWARF. Denver, Colorado, 1985.
44. Study Group on Environmental Monitoring. *Analytical Studies for the US Environmental Protection Agency: Environmental Monitoring*. National Academy of Sciences, 1977.
45. *SYSTAT for Windows, Version 5 Edition*. Evanston, IL: SYSTAT, Inc., 1992.
46. Treweek, G.P., et al. "Pilot Plant Simulation of Corrosion in Domestic Pipe Materials". Journal AWWA, Vol. 77, Oct 85.
47. Tukey, J.W. *Exploratory Data Analysis*. Addison-Wesley, Reading, Massachusetts, 1977.
48. USEPA. *Lead and Copper National Interim Primary Drinking Water Regulations*. May 1991.
49. World Health Organization. *Guidelines for Drinking Water Quality*. Vol. 2. Health Criteria and Other Supporting Information. Geneva, 1984.
50. Yamane, T. *Statistics: An Introductory Analysis*. New York, 1964

Appendix A Sampling Locations



Appendix B Written Sampling Instructions

Dear Resident:

Thank you for your participation. You are given two Ziploc bags. Please fill the bottles in bag "A" tomorrow morning (morning 1). And fill the bottles in bag "B" the second morning (morning 2).

SAMPLING INSTRUCTIONS

Morning 1 (Fill the bottles in bag "A")

1. Please take all samples from the kitchen tap first thing in the morning, BEFORE you use the showers, toilets, etc.
If you use a water purifier, please turn it OFF during sampling.
2. Put bottles #1, #2, and #3 on the kitchen counter in order.
3. Take off the caps of bottles #1, #2, and #3.
4. Bottle #1 has to be filled first. Place bottle #1 under the kitchen tap. Turn on the cold water and fill up bottle #1 completely.
5. Turn on the cold water full blast and let it run until the water becomes really cold. Fill up bottle #2 completely. Turn off cold water.
6. Turn on the hot water and let it run until the water becomes hot. Please don't burn yourself. Fill up bottle #3 completely. Turn off hot water.
7. Cap bottles #1, #2, and #3 tightly and put them in the Ziploc bag.
8. Leave the Ziploc bag and everything in it outside your front door.

Morning 2 (Fill the bottles in bag "B")

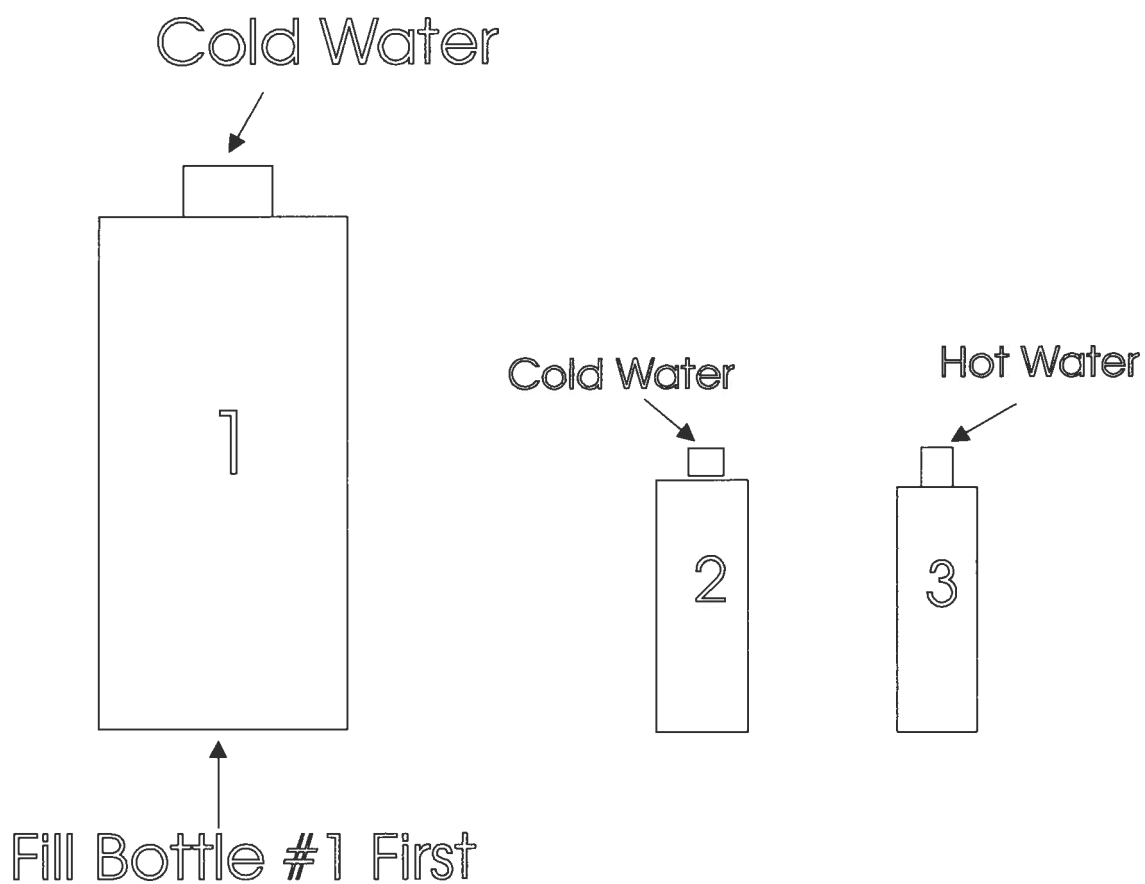
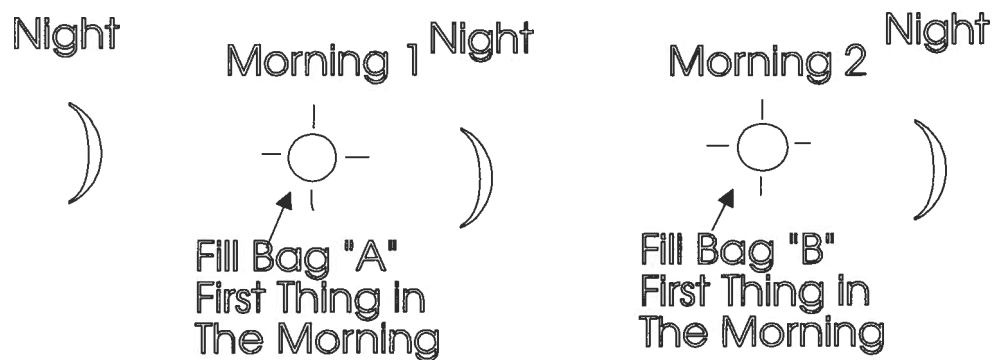
Repeat steps 1 through 8.

I will come by to pick up both bags outside your front door.

If you have any problems, please do not hesitate to call Ken Chan at 430-2420. Thank you for your cooperation.

Appendix C Cartoon Sampling Instructions

SAMPLING INSTRUCTIONS



Appendix D Questionnaire

WATER QUALITY STUDY QUESTIONNAIRE

1. May I have your name please?
2. May I have your telephone number please?
3. Do you use a water purifier on your kitchen water tap? y/n
4. What is the type of plumbing material in your house?
Look at the water pipe (it is a thin pipe) underneath the kitchen sink.

<u>Type</u>	<u>Color</u>
a) copper	bronze
b) plastic	could be any color
c) galvanized metal	grayish
d) other	

5. Has the plumbing been replaced in the past? y/n
6. Would you like a summary of the study results? y/n

Please return this questionnaire with the bottles. Thank you for your cooperation.

Appendix E GVRD Data Crosscheck

sample	ubc	gvrđ	ubc	gvrđ
	copper	copper	lead	lead
	ppm	ppm	ppb	ppb
a1d19	0.06	0.13	3	4
a1d20	1.76	1.98	9	8
a1n11	0.14	0.2	< 1	2
a1n47	0.06	0.11	24	9
a1n55	< 0.02	0.04	< 1	1
a1nx10	0.06	0.11	5	5
a1s16	0.1	0.14	< 1	9
a1s18	0.09	0.12	< 1	250
a1s26	0.16	0.2	10	10
a1s33	< 0.02	0.05	5	6
a1s49	x	0.02	x	2
a1sx13	0.16	0.2	< 1	12
b1d14	0.23	0.29	5	5
b1d16	1.9	0.13	3	3
b1d21	1.76	1.79	17	17
b1d5	0.42	0.49	29	9
b1d9	1.32	1.39	4	8
b1n1	0.42	0.49	20	21
b1n11	0.04	0.08	1	5
b1n18	0.02	0.08	< 1	3
b1n38	< 0.02	0.05	< 1	2
b1n75	0.24	0.29	< 1	7
b1n79	0.23	0.3	< 1	6
b1n83	< 0.02	0.02	< 1	< 1
b1nx2	< 0.02	0.02	< 1	< 1
b1s19	0.11	0.14	< 1	5
b1s20	< 0.02	0.02	3	5
b1s24	0.14	0.13	< 1	18
b1s24-A	x	0.16	x	9
b1s33	< 0.02	0.04	1	2

Appendix F Raw Data

id#	street	house#	plumbing	age of house(yr)
sx1	142st	3149	c=copper	3
sx2	142st	3105	p=plastic	4
sx3	142st	3113	p	3
sx4	31aave	14133	c	4
sx5	29ave	14149	c	1
sx6	141st	2948	p	1
sx7	30ave	14130	c	1
sx8	141st	3086	c	2
sx9	31aave	14148	c	3
sx10	31aave	14153	p	3
sx11	31aave	14230	c	4
sx12	31aave	14229	c	3
sx13	31aave	14252	p	4
sx14	31ave	14245	c	3
nx1	68aave	12630	p	1
nx2	68aave	12706	p	1
nx3	129ast	6149	c	8
nx4	129ast	6157	c	11
nx5	129ast	6175	c	10
nx6	129ast	6783	c	10
nx7	129ast	12922	c	7
nx8	129ast	12938	c	10
nx9	129ast	12930	c	12
nx10	129ast	12910	c	9
nx11	131ast	13128	c	9
nx12	131ast	13152	p	10
nx13	131ast	13168	p	4
nx14	131ast	13176	p	12
s4	140ast	1935	c	8
s5	140ast	1927	c	8
s6	140ast	1833	p	10
s8	140ast	1817	c	11
s11	140ast	1826	c	10
s16	140ast	1761	c	10
s17	140ast	1739	p	6
s18	140ast	1740	c	6
s19	140ast	1731	p	7
s20	140ast	1699	p	7
s22	140ast	1687	p	7
s24	140ast	1667	c	7
s25	140ast	1659	c	7
s26	16bave	14041	c	7

id#	street	house#	plumbing	age of house(yr)
s27	16bave	14035	c	6
s30	16aave	14097	c	7
s32	16aave	14096	c	5
s33	16aave	14137	p	6
s44	19aave	14125	c	8
s49	19aave	14175	c	9
s51	19aave	14203	c	8
n1	137ast	8007	c	8
n3	137ast	8025	c	8
n4	137ast	8031	c	8
n7	137ast	8046	c	8
n11	137ast	8012	c	8
n18	138st	8129	c	10
n33	138st	8035	p	7
n34	138st	8029	c	8
n35	138st	8023	p	8
n36	138st	8017	c	7
n37	80aave	13802	c	9
n38	80aave	13806	c	9
n42	80aave	13836	c	8
n43	80aave	13844	c	9
n44	80aave	13852	c	7
n46	80aave	13876	c	9
n47	80aave	13884	c	9
n49	80aave	13887	c	9
n50	80aave	13879	p	7
n51	80aave	13871	c	8
n53	80aave	13847	c	8
n55	80aave	13831	p	6
n59	138ast	8073	c	8
n60	138ast	8063	p	7
n61	138ast	8085	c	8
n65	80bave	13881	c	10
n74	80bave	13967	c	10
n75	80bave	13975	c	10
n77	80bave	13991	c	10
n79	80bave	13966	c	14
n81	80bave	13954	c	15
n83	80bave	13922	p	7
n84	80bave	13914	c	8
n85	80bave	13908	p	7
n87	80bave	13888	p	8

id#	street	house#	plumbing	age of house(yr)
d1	woodridge cres	11930	c	10
d2	woodridge cres	11926	c	9
d3	woodglen st	6444	c	5
d4	woodlynn ct	11802	c	12
d5	woodlynn ct	11838	c	5
d6	woodlynn ct	11857	c	7
d7	woodlynn ct	11858	c	7
d8	alderwood cres	11877	c	9
d9	beechwood ave	11938	c	7
d10	woodridge cres	11916	c	7
d11	doncaster cr	10742	c	6
d12	doncaster cr	10714	c	5
d13	doncaster cr	10778	p	6
d14	83aave	11115	p	4
d15	83aave	11125	p	4
d17	uppercanyon rd	11081	p	4
d16	uppercanyon rd	11084	p	5
d18	uppercanyon rd	11116	c	6
d19	cherrylane	10874	p	4
d20	cherrylane	10847	c	6
d21	cherrylane	10834	c	6

id#	pH	alk
sx1	7.38	
sx2		
sx3	7.24	11.00
sx4	7.95	13.50
sx5	7.89	12.50
sx6		13.00
sx7		0.00
sx8		14.00
sx9	8.07	13.50
sx10		10.50
sx11		13.00
sx12	7.67	7.50
sx13		11.50
sx14		12.50
		0.00
nx1		0.00
nx2	7.41	12.00
nx3	7.48	13.50
nx4	7.52	13.00
nx5	7.55	13.00
nx6		11.50
nx7		0.00
nx8		0.00
nx9	7.62	12.50
nx10	7.51	7.50
nx11	7.44	13.50
nx12		14.50
nx13		11.50
nx14		0.00
		0.00
s4	8.69	15.00
s5	8.76	18.50
s6	8.35	14.00
s8	8.16	15.00
s11	8.78	16.00
s16	7.29	12.00
s17		0.00
s18	8.86	16.00
s19	8.72	15.50
s20	7.05	9.00
s22		0.00
s24	7.70	14.00
s25	8.21	15.50
s26	7.32	12.00

id#	pH	alk
s27	8.01	14.50
s30	8.64	15.50
s32	8.72	0.00
s33	8.91	14.00
s44	8.72	16.00
s49	8.95	14.00
s51	8.50	14.00
		0.00
n1		9.50
n3		13.50
n4		10.00
n7		9.50
n11		9.50
n18		12.50
n33		11.50
n34		13.00
n35		10.00
n36	7.28	8.50
n37		14.00
n38		8.00
n42		10.00
n43		0.00
n44		9.50
n46		8.00
n47	7.35	14.00
n49		0.00
n50		10.50
n51		12.00
n53		0.00
n55		7.00
n59		9.50
n60	7.33	10.00
n61	7.36	10.50
n65		7.50
n74		12.50
n75		10.00
n77		0.00
n79		9.00
n81		11.50
n83	7.36	12.50
n84		10.00
n85		8.50
n87		11.00

id#	pH	alk
d1	5.96	3.50
d2		0.00
d3		5.00
d4		6.00
d5	5.75	4.00
d6		6.00
d7	5.92	5.00
d8		0.00
d9	5.81	6.00
d10		6.50
d11		0.00
d12	6.02	6.00
d13	6.25	5.00
d14	6.24	5.00
d15	6.19	5.00
d17	6.35	0.50
d16	4.75	5.00
d18		4.00
d19		0.00
d20	6.27	8.50
d21		7.00

id#	a1C*	a2C*	a3C*	b1C*	b2C*	b3C*	a1P*	a2P*	a3P*	b1P*	b2P*	b3P*
sx1	0.08	0.01	0.11	x	x	x	11	-1	3	x	x	x
sx2	x	x	x	x	x	x	x	x	x	x	x	x
sx3	0.11	0.02	0.03	0.12	0.01	0.03	11	-1	2	-1	-1	-2
sx4	0.09	0.01	0.03	0.12	0.01	0.05	7	-2	-2	5	-1	-1
sx5	0.1	0.03	0	0.12	0.01	0.07	-3	-2	0	-1	-2	-2
sx6	0.11	0.02	0.01	0.11	0.04	0.02	-2	-2	-2	-1	-1	-1
sx7	0.09	0.01	0.05	x	x	x	-1	-1	-1	x	x	x
sx8	0.16	0.01	0	0.13	0	0.02	-4	1	0	-1	1	-2
sx9	0.16	0	0.03	0.15	0	0.03	0	-1	0	-1	0	-2
sx10	0	0	0	0	0	0	-4	0	0	-1	0	0
sx11	0.1	0	0	0.08	0	0	6	0	1	10	0	3
sx12	0.16	0.02	0	0.14	0.01	0	-1	-1	0	-2	0	0
sx13	0.16	0.06	0.03	0.09	0	0.09	7	11	10	4	1	6
sx14	0.18	0.01	0.01	0.17	0	0	0	-2	1	4	0	0
nx1	x	x	x	x	x	x	x	x	x	x	x	x
nx2	0	0	0	0	0	0.02	-1	-2	-2	-1	0	-1
nx3	0.11	0.06	0.02	0.17	0.07	0.03	6	2	-1	8	-2	-2
nx4	0.15	0	0	0.16	0	0	2	1	0	-1	0	0
nx5	0.09	0	0	0.12	0.01	0	-1	0	-1	5	1	-2
nx6	0.1	0	0.02	0.09	0	0.04	3	-1	-1	3	-1	-1
nx7	x	x	x	x	x	x	x	x	x	x	x	x
nx8	x	x	x	x	x	x	x	x	x	x	x	x
nx9	0.12	0	0	0.16	0	0	10	-2	-2	16	-2	-1
nx10	0.06	0	0.03	0.02	0.07	0.1	5	1	-1	4	5	2
nx11	0.11	0.19	0	0.15	0.15	0.08	4	1	-1	11	2	-2
nx12	0.15	0	0.01	0.15	0	0.01	12	0	-1	18	-1	-1
nx13	0	0	0	0	0	0	-1	-1	0	0	-1	-1
nx14	x	x	x	x	x	x	x	x	x	x	x	x
s4	0.15	0.01	0.05	0.14	0.01	0.04	18	-1	1	1	1	1
s5	0.11	0.02	0.04	0.13	0	0	18	1	1	27	-2	-1
s6	x	x	x	0.07	0.02	0.02	x	x	x	1	0	1
s8	0.1	0	0.03	0.13	0	0.01	9	-1	1	10	1	1
s11	0.11	0	0.04	0.05	0	0.36	22	1	1	0	0	3
s16	0.1	0.02	0.03	0.07	0.01	0.04	-4	0	1	-2	0	1
s17	x	x	x	x	x	x	x	x	x	x	x	x
s18	0.09	0	0	0.12	0	0	-5	3	4	21	-2	2
s19	0.09	0	0.02	0.11	0.01	0	-5	0	0	-3	-2	-2
s20	0	0	0	0	0	0	-5	-2	-1	3	0	-2
s22	x	x	x	x	x	x	x	x	x	x	x	x
s24	0.12	0.02	0	0.14	0.02	0.02	21	1	-1	-2	0	0
s25	0.13	0.02	0	0.16	0.04	0.04	6	1	-1	-2	1	1
s26	0.16	0	0.01	0.17	0	0.01	10	1	1	0	1	3

id#	a1C*	a2C*	a3C*	b1C*	b2C*	b3C*	a1P*	a2P*	a3P*	b1P*	b2P*	b3P*
s27	0.08	0	0.02	0.08	0	0.07	5	0	-2	7	-2	3
s30	0.15	0	0	0.11	0	0	4	-1	-1	4	-1	-1
s32	0	0.02	0.02	0	0.02	0.02	1	0	0	1	0	0
s33	0.01	0	0	0	0	0	5	1	-1	1	0	-1
s44	0.12	0.02	0.04	0.09	0	0	4	0	0	3	-1	0
s49	x	x	x	x	x	x	x	x	x	x	x	x
s51	0	0.02	0	0	0.01	0	-3	0	0	-3	0	0
n1	0.4	0.1	0.06	0.42	0	0.01	19	-3	0	20	-3	-3
n3	0.15	0	0.03	0.16	0.08	0.01	16	-1	-1	-5	-3	-3
n4	0.23	0.02	0.04	0.23	0.01	0.01	-5	-1	-3	-6	-2	-3
n7	0.4	0.06	0.04	0.43	0.09	0.06	24	0	-3	-5	-1	-1
n11	0.14	0.03	0	0.04	0.13	0.06	0	-2	-3	1	-1	-1
n18	x	x	x	0.02	0	0.03	x	x	x	-2	0	0
n33	0	0	0.02	0	0	0.01	-6	-1	-3	0	-1	-1
n34	0.23	0.01	0.05	0.31	0.01	0.02	4	-1	-1	3	-4	-3
n35	0.35	0	0	0.34	0.02	0.04	-5	-3	-3	13	-1	0
n36	0	0.01	0	0	0.01	0	-3	-1	0	-3	-1	0
n37	0	0.01	0.09	0	0	0.09	-1	0	0	1	-4	-2
n38	0.07	0	0	0.01	0	0	-4	-3	-2	-4	-1	-2
n42	0.18	0.05	0.04	0.18	0.02	0.06	-4	0	-1	1	-1	0
n43	x	x	x	x	x	x	x	x	x	x	x	x
n44	0.26	0.04	0.02	0.18	0.06	0.01	-2	4	0	19	-3	-1
n46	0.08	0.02	0.05	0.09	0	0.07	17	-1	0	8	-2	-2
n47	0.06	0.11	0.02	0	0	0	24	4	-1	-4	-3	-3
n49	x	x	x	x	x	x	x	x	x	x	x	x
n50	0	0	0	0	0	0	-3	-1	-1	2	0	-1
n51	0.27	0.02	0.03	0.04	0	0.02	2	0	1	-1	0	0
n53	x	x	x	x	x	x	x	x	x	x	x	x
n55	0	0	0.01	0	0	0	-3	1	-2	-1	-1	0
n59	0.13	0	0.09	0.14	0.03	0.03	-1	-1	3	-1	-1	0
n60	0	0	0	0.01	0.01	0	-1	-1	0	-2	0	0
n61	0.08	0	0.01	0.07	0.02	0	4	0	1	-2	-1	-1
n65	0.06	0	0	0.06	0	0.03	5	-1	5	0	-1	1
n74	0.06	0.03	0.07	0.02	0.03	0.01	-4	2	0	-3	2	2
n75	0.2	0.01	0	0.24	0	0.06	-1	1	-3	-4	-3	1
n77	x	x	x	x	x	x	x	x	x	x	x	x
n79	0.22	0.04	0.05	0.23	0.04	0.05	15	1	0	-4	0	0
n81	0.12	0.02	0.08	0.19	0.03	0.03	7	0	0	-3	1	-2
n83	0	0	0	0	0	0.02	-1	-3	-2	-4	54	2
n84	0.05	0	0.04	0.05	0	0.03	5	-2	2	-3	-1	0
n85	0	0.01	0.03	0	0	0	0	0	0	1	-3	-1
n87	0	0.02	0	0	0	0	-1	0	-2	-1	-3	-2

id#	a1C*	a2C*	a3C*	b1C*	b2C*	b3C*	a1P*	a2P*	a3P*	b1P*	b2P*	b3P*
d1	0.24	0.15	0.18	0.29	0.11	0.2	21	1	24	5	2	5
d2	x	x	x	x	x	x	x	x	x	x	x	x
d3	0.91	0.13	0.23	0.23	0.11	0.13	1	-1	2	-1	0	0
d4	1.4	0.5	0.32	1.45	1.22	0.35	3	2	4	29	20	5
d5	0.4	0.2	0.21	0.42	0.18	0.22	-1	1	3	4	5	2
d6	0.17	0.11	0.17	0.28	0.36	0.15	-2	3	7	13	3	5
d7	0.19	0.08	0.14	0.08	0.21	0.16	6	6	4	-2	3	4
d8	1.16	0.84	0.21	x	x	x	10	22	4	x	x	x
d9	1.35	0.59	0.27	1.32	0.34	0.27	24	2	3	4	1	3
d10	2.29	0.24	0.37	2.01	0.84	0.38	8	1	5	11	2	4
d11	x	x	x	x	x	x	x	x	x	x	x	x
d12	1.87	0.11	0.38	1.93	0.14	0.4	20	2	30	18	1	8
d13	0.2	0.07	0.04	0.06	0.07	0.11	12	2	3	2	2	18
d14	0.29	0.16	0.26	0.23	0.08	0.26	2	0	4	5	1	1
d15	0.64	0.43	0.22	0.55	0.29	0.22	3	0	1	5	-1	1
d17	0.08	0.09	0.27	0.07	0.52	0.48	-1	2	13	9	4	10
d16	2.12	0.09	0.09	1.9	0.07	0.06	3	1	1	3	0	0
d18	1.81	0.84	0.23	1.86	0.29	0.29	7	-2	4	14	0	-2
d19	0.06	0.01	0.18	0.17	0.02	0.11	3	0	8	0	-2	2
d20	1.76	0.42	0.45	2.01	0.97	0.42	9	-2	5	6	15	3
d21	1.78	0.87	0.44	1.76	0.2	0.39	25	2	-2	17	3	3

*

a (sample collected from morning 1)

b (sample collected from morning 2)

1 (standing sample)

2 (running cold sample)

3 (running hot sample)

C (copper, ppm)

P (lead, ppb)