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Chloramination And Corrosion: Case Studies, Utility Experience, And Statistical Comparisons With Chlorination

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CHLORAMINATION AND CORROSION: CASE STUDIES, UTILITY EXPERIENCE, AND STATISTICAL COMPARISONS WITH CHLORINATION

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CHLORAMINATION AND CORROSION: CASE STUDIES, UTILITY EXPERIENCE, AND STATISTICAL COMPARISONS WITH CHLORINATION

JASON A. HEBERLING

CIVIL, CONSTRUCTION, AND ENVIRONMENTAL ENGINEERING

ABSTRACT

The United States Environmental Protection Agency (EPA) began implementing the Stage 2 Disinfectant By-products (DBP) Rule (Stage 2) in 2012. The purpose of this regulation is to protect water utility customers from potentially harmful DBP's, most importantly, total trihalomethanes (TTHM) and haloacetic acids (HAA). DBP's have been directly linked to health problems, especially bladder cancer. Regulated DBP's are formed by the chemical reaction of chlorine and naturally occurring organic matter. Chloramines do not produce TTHM's and HAA's and water utilities have used chloramines in place of chlorine in an attempt to meet Stage 2 rules. However, a possible problem of introducing chloramines to a distribution system is a potential increase of metal residuals, particularly lead. Any process or chemical that increases lead corrosion could raise lead concentrations in drinking water supplies leading to health concerns.

The following dissertation examines iron and lead corrosion data collected from a study performed for the Birmingham Water Works Board (BWWB); Birmingham, Alabama. The study was conducted to determine if the BWWB could switch their primary disinfectant from chlorine to chloramines, in an effort to combat DBP's, without contamination of drinking water from increased lead and iron residuals. Statistical comparisons are made between chloraminated and chlorinated drinking water collected from a flow-through rack constructed by the BWWB. This rack was comprised of lead pipes, cast iron pipes, and brass fixtures. Statistical analyses are performed on the data to compare and contrast corrosion potential of chlorinated and chloraminated drinking water treated with corrosion inhibitors.

The results of this study showed that chloramines, coupled with an orthophosphate based corrosion inhibitor did not increase metal residuals in cast iron pipes, lead pipes, and brass fixtures. Prolonged use of orthophosphates in the flow-through resulted in the continued drop of lead and cast iron residuals. However, one of the most important findings of this study was that corrosion inhibitors, which contain polyphosphates, do not reduce but actually increase water corrosivity in lead bearing features. Utilities with distribution systems that contain any lead bearing features run great risks for high lead residuals when using polyphosphates or polyphosphate blends for corrosion control.

Keywords: corrosion inhibitors, lead corrosion, iron corrosion, orthophosphate

DEDICATION

I dedicate this dissertation to my ever supportive and patient wife, Brenda L. Harrell. Her support was critical in the completion of this work.

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I wish to give a heartfelt thanks to the staff and management of the BWWB for the opportunity to pursue this study. The BWWB staff was instrumental in obtaining materials and installing the flow-through pipe rack. The expertise and assistance of the staff at the H. Y. Carson Filter Plant was essential. The BWWB Envirolab staff fielded hundreds of samples for laboratory analysis critical for the success of this investigation. I would also like to take the opportunity to thank Dr. Deborah Myers and Patty Barron who trained me on the use of equipment associated with this project.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AWWARF	American Water Works Association Research Foundation
BC	Brass Chlorine
BDL	Below Detection Limit
BNH	Brass Chloramines Orthophosphate
BP	Brass Chlorine Orthophosphate
BWWB	Birmingham Water Works Board
CFP	H.Y. Carson Filter Plant
CI	Cast Iron
c.u.	color units
DBP	disinfection by-product
DI	de-ionized water
DO	dissolved oxygen
EPA	United States Environmental Protection Agency
GAC	granular activated carbon
HAA	haloacetic acids
IB	Cast Iron Pipe Burn Out
IC	Cast Iron pipe Chlorine
IC30/70	Cast Iron Pipe Chlorine Polyphosphate 30/70
IC70/30	Cast Iron Pipe Chlorine Polyphosphate 70/30

ICO	Cast Iron Pipe Chlorine Orthophosphate
INH	Cast Iron Pipe Chloramines Orthophosphate
IDEQ	Idaho Department of Environmental Quality
KS	Kolmogorov Smirnov single sample test
KS2	Kolmogorov-Smirnov two-sample test
LB	Lead Pipe Burn Out
LC	Lead Pipe Chlorine
LCR	Lead and Copper Rule
LP	Lead Pipe Chlorine Orthophosphate
LNH	Lead Pipe Chloramines Orthophosphate
LRAA	locational running annual average
MCL	maximum contaminant level
NFESC	Naval Facilities Engineering Service Center
NORS	National Organics Reconnaissance Survey
PVC	polyvinyl chloride
TTHM	total trihalomethanes
UAB	University of Alabama at Birmingham
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WASA	District of Columbia Water and Sewer Authority
WRS	Wilcoxon Rank Sum test

INTRODUCTION

Chloramines have been used for nearly a century as a primary and secondary disinfectant for drinking water. Though chloramines pale in popularity to chlorine, recent interest in preventing disinfection by-products (DBP's) has rekindled interest in chloramines as a primary and secondary disinfectant for water purveyors worldwide. One reason for this incread popularity is the full promulgation of the United States Environmental Protection Agency's (EPA) Stage II Disinfection By-Product Rule (Stage 2). One strategy of meeting Stage 2 rules is to replace chlorine with chloramines as the primary (or in some cases secondary) disinfection. Chloramines do not produce the same regulated disinfection by-products as chlorine in drinking water.

However, chloramines are not without disadvantages. One of the biggest concerns is that chloramines may be responsible for producing higher metal residuals, through corrosion, relative to other disinfectants. These higher metal residuals can result in drinking water aesthetic problems, failure to meet government regulations (such as the EPA's Lead and Copper Rule), and health and safety concerns for utility customers. The possibility of increased lead corrosion is of particular concern.

Corrosion of metallic components in drinking water distribution systems cost utilities billions of dollars each year and decreases water quality [AWWARF, 2004]. Under extreme circumstances, corrosion endangers customer health and safety. Utilities that use or are considering chloramines as a primary or secondary disinfectant should be concerned about recent studies, which suggests chloramines increase metal corrosion relative to other disinfectants such as chlorine. Research over the last few decades has suggested that chloramines are particularly corrosive to lead-bearing elements in distribution systems and domestic plumbing. To mitigate potential corrosion problems, corrosion inhibitors are often introduced into a distribution system where chloramines are the primary or secondary disinfectant. Phosphate-based corrosion inhibitors have been successfully applied in several instances.

In anticipation of stricter disinfectant by-products (DBP's) regulations, the Birmingham Water Works Board (BWWB) investigated the feasibility of replacing their primary disinfectant, chlorine, with chloramines. A pipe rack flow-through pilot study rack was constructed by the BWWB to measure iron and lead corrosion rates in chlorinated and chloraminated drinking water. Corrosion inhibitors were employed to stabilize lead and iron corrosion in the flow-through rack's piping and fixtures. After testing three corrosion inhibitors, the BWWB eventually selected orthophosphate as the inhibitor employed in the corrosion study. One of the primary concerns addressed was the possibility of increased iron corrosion and "red water" from piping in the distribution system resulting from changing disinfectants. "Red water" is discolored water created from mineral release, particularly iron, in distribution systems and plumbing.

Samples were collected from lead pipes, cast iron pipes, and brass fixtures. Statistical analyses were used to determine if there were differences in drinking water treated with chlorine versus chloramines with respect to lead and iron corrosion. Likely the most important finding of this study is that polyphosphate blends proved ineffective in preventing and actually promoted lead corrosion in lead bearing features. This would indicate that polyphosphate blends are unsuitable for corrosion control in drinking water in most distribution systems. The study results suggested that there was no statistically significant increase in lead drinking water residuals when the primary disinfectant was changed from chlorine to chloramines or chloramines to chlorine when the finished water was treated with orthophosphate corrosion inhibitor. The findings of the flow-through study suggest that orthophosphates perform as well or better than polyphosphate blends in preventing iron corrosion and “red water”.

LITERATURE SEARCH

Chloramines are a group of chemical disinfectants formed by the reaction of ammonia with aqueous chlorine, used in primary and secondary drinking water treatment. Chloramines have advantages over chlorine, the most commonly used disinfectant, by having less taste and odor problems and greater stability in distribution systems. Chloramines are more effective than chlorine for controlling bacterial re-growth [USEPA, 1999]. Monochloramine is the most common form of chloramines used in disinfection. Dichloramine, trichloramine, and organic chloramines are produced in the generation of chloramines but at much lower levels than monochloramine. Organic chloramines are formed when chlorine reacts with organic nitrogen [AWWARF, 2004].

Chlorine has been the most popular drinking water disinfectant for over one hundred years. However, in the 1970’s, it was discovered that chlorinated organic compounds including disinfection by-products (DBP’s), byproducts of chlorinated water, might have deleterious health effects [Norman *et al.,* 1980]. Many water utilities are considering replacing secondary and even primary disinfectants with chloramines since chloramine treated water has demonstrated significantly smaller regulated DBP concentrations than water treated with chlorine [Brodtmann and Russo, 1979].

Chloramines are not without disadvantages. Chloramination alone may not be sufficient to control coliform in some distribution systems [Norton and LeChevallier, 1997]. Chloramines are toxic to aquarium flora and fauna and kidney dialysis patients. Granular activated carbon (GAC), used to destroy chloramines for kidney dialysis patients [Fairey *et al*., 2007], can be expensive to purchase and maintain. Autotrophic bacteria reacting with excess ammonia can result in nitrification, which can severely degrade water quality. If nitrification becomes extreme, it may be necessary to flush large sections of distribution pipes, drain and clean tanks, or re-introduce chlorine to the distribution system. This procedure is referred to as chlorine “burn out”. In addition, chloramines form DBP’s, different from ones formed in chlorinated water, which may be subject to future regulation. A great concern is that chloramines may be responsible for higher lead residuals relative to other disinfectants [Switzer *et al*., 2006]. The potential for chloramines treated water and lead corrosion is discussed later.

Chloramines: History

Chloramines were first discovered in 1811, and in 1905 the biocidal qualities of the compounds were documented. Chloramines were first used in Ottawa, Ontario (Canada) in 1916 and Denver, Colorado (USA) in 1917 as a drinking water disinfectant [Ngwenya *et al.,* 2013]. Before World War II, chloramines were used as the drinking water disinfectant in Greenville, Tennessee; Cleveland, Ohio; Springfield, Illinois; Lansing, Michigan; Lancaster, Pennsylvania and other municipalities in the United States and Europe. By the end of the 1930s, 407 of 2,541 utilities surveyed (sixteen percent) in thirty-six states in the US used chloramines [AWWARF, 1993]. Chloramines declined in popularity largely due to ammonia shortages during World War II [USEPA 1999].

By 1962, approximately 2.6 percent of US facilities used chloramines for disinfection. Between the 1960 and 1985, some utilities converted to chloramine to combat difficulties maintaining a disinfectant residual and to control taste-and-odor problems, particularly in warmer climates [Hoek *et al*, 2010]. By the 1980's, chloramines had again increased in popularity, largely due to the concern over DBP's [AWWARF, 1993]. Since the 1990's, several large utilities have converted to chloramine disinfection to help maintain a residual in their systems and reduce DBP's [Hoek *et al.*, 2010]. New United States Environmental Protection Agency (EPA) DBP rules implemented in 2012, have made chloramines an attractive choice to utilities worldwide, since chloraminated water does not produce the same regulated DBP's found in chlorinated water [AWWARF, 2004].

Chloramines: Chemistry

Chloramines are comprised of any combination of chemicals formed by the reaction of free chlorine and ammonia. These compounds are monochloramine (NH_2Cl), di-chloramine ($NHCl_2$) and trichloramine, or nitrogen trichloride (NCl_3). Monochloramine is the most popular of the forms because of its biocidal properties and minimal taste and odor [AWWARF, 2004].

$$HOCl + NH_3 \rightarrow NH_2Cl \text{ (monochloramine)} + H_2O \qquad (1)$$

$$HOCl + NH_2Cl \rightarrow NHCl_2 \text{ (dichloramine)} + H_2O \qquad (2)$$

$HOCl + NHCl_2 \rightarrow NCl_3$ (trichloramine or nitrogen trichloride) + H_2O (3)

Dichloramine and trichloramine produce unpleasant taste and odor. Organic chloramines, which can form during the chloramination process, are not effective disinfectants. Dichloramine is formed when the chlorine to ammonia-nitrogen weight ratio is greater than 5:1, however, this reaction is very slow. The combinations of the products are dependent upon pH, temperature, contact time, the ratio of Cl_2:NH_3-N, among other factors. Monochloramine (NH_2Cl) is the preferred specie because of its biocidal properties, relative stability, and few taste and odor problems. Optimum conditions for monochloramine formation are pH 8.3, 25^{o}C, and a 4:1 to 5:1 weight ratio of Cl_2:NH_3-N. Normally, at pH conditions of 6.5-9.0 and 10-25^{o}C, monochloramine forms within one to three seconds of initial mixing of chlorine and ammonia [AWWARF, 2004]. Ammonia excess should be avoided to prevent conditions, which promote nitrification.

Autotrophic bacteria reacting with excess ammonia cause nitrification, which can severely degrade water quality. If nitrification becomes extreme, it may be necessary to flush large sections of distribution pipes, drain and clean storage tanks, or re-introduce chlorine to the distribution system. This procedure is referred to as chlorine “burn out”.

Chloramines: Usage

Chloramines are being considered as an alternative to chlorine as a primary disinfectant for water utilities worldwide. A primary reason for the change, particularly in North America, is to comply with future, stricter drinking water regulations regarding DBP’s. DBP’s are known carcinogens and have been specifically linked to bladder cancer. Water purveyors have known for decades that water treated with chloramines produce significantly less regulated DBP's than chlorinated water. The drinking water standard for chloramines is four parts per million (ppm) measured as an annual average [AWWARF, 2004].

A 2006 survey of U.S. drinking water systems indicated that twenty-nine percent of utilities presently use chloramines for secondary disinfection. The most popular reasons for using chloramines were distribution system residual maintenance and DBP minimization. To comply with the recently promulgated EPA rules, the EPA predicts that an additional 4.5% of surface water systems and 2.5% of ground water systems will convert from free chlorine to chloramines to meet new EPA rules [AWWARF, 2006].

In addition to drinking water applications, chloramines are used for disinfection of wastewaters and in the control of biological fouling in cooling water systems and at the intakes and outlets of utilities and industries. One of the primary uses for biological control in intakes is the elimination of zebra mussels [Pasternak *et al.*, 2003]. However, for this dissertation, chloramines applications as a drinking water disinfectant will be the only focus.

Chloramines: Research

Several utilities worldwide have considered changing their primary or secondary disinfectant from chlorine to chloramines (switchover) to take advantage of the benefits provided by chloramines. However, a switchover can be a costly and risky venture if proper pilot testing is not performed. The following discussion describes various utilities experience with switchovers or pilot testing for switchovers and represents a range of expectations for utilities engaging in switchovers.

In 1974-1975, the EPA conducted a national eighty-city survey, the National Organics Reconnaissance Survey (NORS), to assess the extent of chlorinated organic compounds in drinking water in Huron, South Dakota. The NORS results discovered that Huron, South Dakota, did not meet minimum requirements for one regulated DBP. Chloramines were investigated as a viable alternative to chlorine to help reduce DBP's. In May of 1978, the Huron Treatment Plant switched to chloramines and was able to consistently meet coliform (bacteria) count requirements. After the switch, the utility reduced the distribution system problem DBP by seventy-five percent [Norman *et al.*, 1980].

The Indiana-American Water Company switched from chlorine to chloramines in the town of Muncie, Indiana. Chloramines were found to be as effective as chlorine in controlling HPC (heterotrophic plate count, a measurement of bacteriological activity), however, coliform counts increased. DBP rates decreased. No nitrification was detected in the distribution system [Norton and LeChevallier, 1997].

Pinellas County Utility (Tampa Bay, Florida) experienced both positive and negative outcomes from a switchover to chloramines. Chloramines proved a relatively inexpensive solution to high DBP residuals and a reduction of chlorine taste and odor complaints was a bonus. However HPC and coliform counts, as well as the frequency of remedial flushing, increased after the switch to chloramines. In addition, nitrification was discovered in storage tanks [Powell, 2004].

The Virginia American Water Company began a switchover to chloramines with the use of a temporary ammoniator (device used to introduce ammonia), in Hopewell, Virginia. Chloramines were found to be as effective as chlorine in controlling HPC. DBP rates decreased in the distribution system. No nitrification was detected in any distribution sampling [Norton and LeChevallier, 1997].

Willow Grove, Australia converted their disinfection from sodium hypochlorite (a chemical used to produce free chlorine) to chloramination in 1999. It was assumed that chloramine residual would be more stable and longer lasting than free chlorine and provided better protection against bacterial regrowth in systems with large storage tanks, dead-end water mains, and lower flow demands. This assumption was confirmed by April 2000 [Holt, 2002].

Stage II Disinfection By-Product Rule

The United States Environmental Protection Agency (EPA) implemented its the Stage II Disinfection By-Product Rule (Stage 2) in 2012. The purpose of this regulation is to protect water utility customers from potentially harmful disinfectant by-products (DBP's). The most importantly DBP's are total trihalomethanes (TTHM) and haloacetic acids (HAA), which are regulated under Stage 2. These DBP's have been directly linked to health problems, especially, bladder cancer [USEPA, 2003a]. Regulated DBP's are formed by the reaction of chlorinated water with organic matter found in typical drinking water distribution systems.

Stage 2 mandates that a utility maintain a maximum contaminant level (MCL) for TTHM at eighty parts per billion (ppb) and sixty ppb for HAA at designated sampling sites employing a locational running annual average (LRAA). LRAA calculations are determined by calculating the annual average of samples from all monitoring locations across a drinking water distribution system [USEPA, 2003b]. To comply with Stage 2, water providers identify the locations with high DBP concentrations in their distribution systems. These locations become the monitoring sites [USEPA, 2003a].

Lead and Copper Rule

The EPA's Lead and Copper Rule (LCR), regulations set forth to minimizing lead and copper levels in drinking water, was implemented to enhance public protection primarily by reducing water corrosivity. The LCR regulates lead and copper, metals often found in distribution systems and household plumbing. The LCR also requires the use of lead-free solder [Swistock *et al*., 2013]. Violation of the LCR can result in significant public health problems and can be a public relations disaster and cost a utility millions of dollars in treatment adjustment and pipe replacement

Lead and copper drinking water residuals are largely formed by service lines and household plumbing materials corrosion. Utilities are required to sample tap water at kitchen or bathroom taps, after at least a six-hour stagnation time of residences and other buildings. When distributions system samples exceed the MCL for lead of 15 ppb or copper concentrations exceeding 1.3 ppm, in more than ten percent of customer taps, the offending utility must implement corrosion control actions. [USEPA, 2008; USEPA, 2010].

Corrosion Basics

Corrosion is an electrochemical process where metal pipes are chemically oxidized. Corrosion can occur whenever there is a difference in electrical potential between two points on a metallic surface. The site with the higher electrical potential becomes the anode and the site with the lower electrical potential becomes the cathode [AWWARF, 1990a]. Most corrosion of metal is due to oxidation-reduction reaction between a metal and an oxidizing agent, such as dissolved oxygen [Landolt, 2007]. Internal corrosion in metallic drinking water distribution features results from complex drinking water chemistry. Alkalinity, pH, dissolved oxygen, and disinfectants all affect the degree and rate of corrosion [Larson and Skold, 1957].

The drinking water industry is concerned with three types of corrosion; galvanic, electrolytic, and chemical/biochemical [Shull, 1980]. Galvanic corrosion is accelerated corrosion due to formation of a corrosion cell with a metal or non-metallic conductor that exhibits higher corrosion potential. The difference in corrosion potential between the two metals of a galvanic cell drives galvanic corrosion [Landolt, 2007]. A galvanic cell can be created when unlike metals are connected, directly, without any non-conductive shielding. Electrolysis is the deterioration of metal by stray currents, which, can originate from a multitude of sources (underground wiring, grounded current, etc.) and in some cases can destroy metal piping at a rate of twenty pounds per ampere year [Shull, 1980]. Chemical corrosion is created by the action of dissolved chemicals in water such as oxygen and chlorine. Biochemical corrosion is caused by chemicals, which are the by-product of biological activity, usually by bacteria.

Corrosion creates economic, public health, aesthetic, and political problems for all water utilities. The most significant corrosion problems are [AWWARF, 1990a]:

- Deterioration of water quality;
- Accumulation of excessive concentrations of toxic heavy metals;
- Increased pumping costs;
- Reduced flow rates; and
- Structural deterioration of pipe leading to leaks, pressure loss, or pipe failure.

Pipe failure generally occurs with localized corrosion, and water quality deterioration and scale accumulation are associated with more uniform corrosion [AWWARF, 1990a]. Corrosion does occur anarobically most commonly by sulfate reducing bacteria, however, oxidation is the primary driving force behind corrosion in drinking water [Zhang and Edwards, 2007]. Corrosion scales form in pipe due to chemical oxidation. These pipe scales can obstruct flow, provide an environment for microbes, and become a source of chlorine demand [Sarin, 2002]. Most importantly for this research, pipe scales can degrade drinking water quality by release of toxic or non-aesthetic components previously absorbed by the scales.

Drinking water pipe corrosion (chemical) generally occurs in the following forms [Butler and Ison, 1966]:

- Uniform attack;
- Pitting;
- Tuberculation;
- Crevice attack;

- Dezincification; and
- Graphitization.

Uniform attack refers to corrosion by flowing water over entire surfaces. This form of corrosion is generally found in waters with a high concentration of dissolved salts. Pitting is a localized attack, which can result in pin-holes and even catastrophic rupture of pipe. Pitting is believed to be a result from activity of a small anodic region and a relatively large cathodic region. Tuberculation is the encrusting of oxides over the pipe's internal surface. These tuberculations, usually composed of ferric oxide, can reduce the carrying capacity of pipes. These growths usually protect metal beneath them from the corrosive effects of water. However, these coatings can trap reducing bacteria, which can exacerbate corrosion. Crevice attack involves corrosion in portions isolated from main flow. Dezincification is the selective corrosion of zinc, mainly of brass fixtures, which leaves behind a porous mass of brittle copper. Copper bearing waters, as little as 0.02 ppm, can locally dissolve iron, zinc, and aluminum. Graphitization, the corrosion of ductile and grey cast iron pipes, creates in graphite and iron oxide residues [Butler and Ison, 1966].

Corrosion Pilot Study Designs

Metal corrosion in pilot studies is generally measured using the following means; metal coupons, pipe racks (also called a flow-throughs), and pipe loops. Occasionally, both coupons and piping are used simultaneously. In coupon studies, corrosion rates are determined from coupon lost mass or from instrumentation that instantaneously measures corrosion rate. Pipe studies examine the concentrations of metals from water, in either a recirculating loop or a flow-through system, constructed from a material of interest [AWWARF, 1994].

A flow-through system is a tested approach to measure metal leaching in water distribution piping, fixtures and coupons. A flow-through system differs from a pipe loop in that a loop recirculates the same water over a given time period. A flow-through allows water to pass as an effluent and does not recirculate water through the system. In addition, a pipe loop focuses on material deterioration and does not effectively mimic the behavior of a distribution system or domestic plumbing [AWWARF, 1994]. Alternative names for flow-through systems include flow through, flow-through rack, and pipe rack.

The American Water Works Association Research Foundation (AWWARF) pipe rack development study, performed in 1994, provided the first attempts to consistently and comprehensively evaluate metals leaching in drinking water supplies. A flow-through system was selected, as opposed to a pipe loop, because a flow-through is a closer approximation to a drinking water distribution system. The AWWARF pipe rack was developed for demonstration testing with an emphasis on comparing the effect of various corrosion treatments on metals residuals. Pipe racks can be used to detect differences in lead and copper levels associated with different types of treatments and can be used to determine optimum treatment approaches. Pipe racks can also assess the secondary impacts of a treatment on a system's overall water quality and regulatory compliance. Results from the 1994 AWWARF study indicated that drinking water metal concentrations may respond quickly to changes in incoming water quality due to treatment interruptions. Additionally, a flow-through system can be used as a tool for demonstrating potential problems resulting from operational changes on metals levels in the distribution system after full-scale treatment is implemented [AWWARF, 1994].

Lead Use, Toxicity, and Occurrence

Lead's low melting point and malleability has proved useful to humanity for millennia. Unfortunately, lead's versatility is matched by its pervasive toxicity. Lead is extremely toxic to body tissues and can be particularly dangerous to infants and children. Lead affects developing nervous systems as well as intellectual and behavioral development. In 1991, the Center for Disease Control adopted a blood lead level of concern for children of ten micrograms per deciliter (μg/dL) in response to evidence associating adverse health effects with blood lead levels above that level. Recent studies that blood lead levels below ten μg/dL also may be associated with negative effects on children's intellectual development [Tiemann, 2005].

The practice of using lead pipe and lead-based solders in home plumbing systems was eliminated in 1986 (per LCR). In addition, all pipes and fittings were required to be constructed of "lead-free" material, which, by legal definition, contain less than 8% lead. However, lead piping and solder are commonplace in many distribution systems particularly ones dating before World War II when lead piping was commonplace. Most utilities have a lead piping removal policy in place, which greatly reduces the threat of lead residuals in drinking water [USEPA, 1996].

Even if a utility manages to free itself of all lead bearing features, many older homes still have lead piping and solders within their plumbing. A survey conducted in 1988 of ninety-four water companies concluded that lead solder, with a small contribution from leaded brass fixtures, contributed to a majority of lead residuals collected in water tap samples [Lee *et al*., 1989]. Lead solder was also discovered to be a major source of lead residuals in a survey performed by the Connecticut State Department of Health and Connecticut Water Utilities [Birden *et al*., 1985]. Many homes, even new construction, have brass fixtures, which can contain lead. Any brass fixture with less than 8% brass is considered, under the LCR, to be "lead free" [USEPA, 1996]. Recent legislation in several U.S. states has tightened regulation of lead content in the components of potable (drinkable) water treatment systems. Other states may well be considering similar moves [Gutierrez, 2010].

Lead Corrosion Basics

Dissolved lead in potable water is usually derived from dissolution of lead mineral scales on surfaces of lead pipe, lead solder, or brass while particulate lead results from detachment of lead from scales via mechanical processes. Often lead contaminated matter is trapped in faucet aerators [Nour *et al*., 2007].

Lead corrosion control using pH, hardness, and alkalinity adjustment is achieved primarily by forming a passive film of lead carbonate coating the inside of distribution pipes. Calcium hardness adjustment may have limitations because the protective coating may be too soft or porous to provide needed protection [Lyons *et al*., 1995]. Corrosion inhibitors reduce the corrosion rate by interfering with the movement of molecules between an anode and cathode. Inhibitors may also alter the electrical potential of the surface and lower the driving force of chemical reactions [AWWARF, 1990a].

Chloramines and Lead

Several studies have provided conflicting evidence on the relationship between chloramines and lead corrosion. It has been observed that a change in primary disinfection to chloramines caused lower lead concentrations [AH Environmental Consultants, 2005]. When chloramines have been applied to water treated with orthophosphate corrosion inhibitors, lead residuals have remained the same or even reduced relative to the same source water treated with chlorine [AWWARF, 2004]. However, studies have also suggested that chloramines facilitate higher lead corrosion residuals relative to other disinfectants [Switzer *et al.*, 2006]. One case study from Washington D.C., indicating that chloramines exacerbate lead corrosion, has been examined in great detail.

Incident in Washington D. C.

Like many major U.S. cities, Washington D. C. has lead features in its distribution system (and in service lines). In July 2002, the District of Columbia Water and Sewer Authority's (WASA) routine tap samples for lead exceeded the lead MCL of fifteen ppb. The following monitoring period, ending June 30, 2003, WASA again exceeded the action level with a concentration of forty ppb, requiring continuation of a public education program implemented in 2002 and lead service line replacement program. WASA was required, as well, to continue with the full routine tap monitoring. In the spring of 2003, the EPA hired an independent corrosion expert to assist with their investigations [USEPA, 2004b].

In January 2004, the Washington Post reported that the WASA had found elevated lead levels in the drinking water of more than 4,000 homes in Washington, DC during 2003 testing [Tiemann, 2005]. Discovery of increased lead residual in WASA drinking water occurred in conjunction with a switch from chlorine to chloramines, as the primary disinfectant, in 2001 [Edwards and Dudi, 2004]. After exceeding the lead MCL from 2002 through 2004, WASA conducted full monitoring for lead and copper at customers' taps yearly [USEPA, 2008]. This incident at WASA brought to the forefront potential problems associated with changing a water utilities primary disinfectant chlorine to chloramines (switchovers) and spurred a great deal of research into switchovers.

Subsequent research indicated that chloramines were likely responsible for the increased lead residuals. It was postulated that lead is more soluble in chloraminated water versus chlorinated water. It is also possible that brass, which can contain significant amounts of lead, is less chemically stable in chloraminated drinking water (compared to chlorinated water). In addition, nitrogen-loving bacteria, which can thrive in chloraminated water where ammonia is present, may augment lead residuals through biologically driven chemical reactions [Edwards and Dudi, 2004].

Brass Corrosion

Brass is an alloy, comprising of predominately copper, used in plumbing fixtures. Though brass can be a source of significant copper corrosion, one of the biggest concerns of corroding brass is the creation of excessive lead residuals. Even newly cast brass fixtures can contribute enough lead to exceed MCL's [Gardels and Sorg, 1989]. Factors such as variations in water chemistry and temperature, physical features of the brass fixtures, and mechanical operation (which may dislodge protective films), can result in measurable lead residuals. [AH Environmental Consultants, 2005].

The EPA claimed, in 1991, that there is limited data to suggest that leaded brass contributes significantly high lead residuals. The LCR states, "Until additional data can be collected that provide a clearer indication of the rate of dissolution from brass faucets under a variety of conditions, the extent to which faucets contribute to the total tap water lead levels will remain difficult to quantify". It was assumed that contributions brass made to lead exposure would be transient (i.e., limited to the first few weeks or months after installation) and that the rate of lead dissolution would drop below the lead MCL, then stabilize [Kimbrough, 2007]. Several studies since the promulgation of the LCR have found that brass is a significant source of lead drinking water contamination [USEPA, 1996; Kimbrough, 2007; Heberling *et al.*, 2009; AWWARF, 2010; and Elfland *et al.*, 2010].

Copper Basics and Corrosion

Copper piping first became popular in the United States in the 1920's. One of the biggest concerns to utilities is the corrosion of copper piping which results in increased replacement cost and water loss. Dissolved copper has also been implicated in health problems. Copper in water can cause abdominal pains, nausea, vomiting, diarrhea, headache, dizziness and even cirrhosis [Fabbricino *et al.*, 2005]. High dissolved copper deteriorates aluminum utensils and galvanized steel fittings and can adversely affect wastewater treatment [Fabbricino *et al.*, 2005]. Dissolved copper is rare in nature and therefore, dissolved copper found in drinking water often originates from the distribution system, mostly from household plumbing fixtures. High amounts of dissolved color gives a metallic taste and can discolor drinking water. Excessive copper residuals can color drinking water green or blue [Zhe and Pehkonen, 2004].

Iron Corrosion and "Red Water"

Iron corrosion induced water quality problems are the most common complaint received by water utilities. Such problems as discolored water, staining, and taste / odor problems are associated with iron corrosion. Tubercles, a product of iron corrosion in distribution system, may provide sites for microbial regrowth. Iron corrosion directly consumes disinfectants, which can lead to reduced disinfectant residuals. Released ferrous iron reacts with monochloramine [Huang *et al.*, 2005] as follows:

$$NH_2Cl + 2H^+ + 2Fe^{2+} \rightarrow 2Fe^{3+} + NH_4^+ + Cl^- \quad (4)$$

Corrosion of iron pipe is influenced by many different factors including water quality and composition, flow conditions, and biological activity [McNeill and Edwards, 2002].

"Red water" is discolored water created from mineral release, particularly iron in distribution systems and plumbing. "Red water" is caused by improperly treated source water that contains iron, or from the corrosion of iron-containing distribution pipes. "Red water" can stain porcelain, glass, and clothes [AWWARF, 2002]. Chlorine has been discovered to be less likely than chloramines to create "red water" [Zhang and Edwards, 2007]. The Tampa Bay Water Department experienced a "red water" episode during a drought in late 1999. The likely culprit was high concentrations of dissolved solids in supplemental groundwater [Brodeur *et al.*, 2006].

Chloramines Research / Corrosion Studies

One of the most researched and documented changeovers was the District of Columbia Water and Sewer Authority's (WASA) conversion from chlorine to chloramines. The switch was made in an attempt to meet The United States EPA regulations and ended poorly when routine tap samples for lead exceeded the action level of 15 ppb [USEPA, 2004b]. WASA began application of an orthophosphate corrosion inhibitor as a method to reduce the drinking water lead levels. The lead levels significantly reduced over a period of several months to below lead MCL's [USEPA, 2008].

A pilot plant study, for the Portland (Oregon) Bureau of Water Works, was constructed using domestic pipe material. The pilot plant used 220 feet of copper piping with lead inserts with tin and lead solder. Corrosion rates reached equilibrium after six to eight months of the pilot plant operation. Samples collected, after a stagnation period, showed no corrosion rate differences between chlorinated and chloraminated copper and galvanized pipes. The lead inserts showed twenty percent more corrosion in chloraminated water than chlorinated water. While samples with chloraminated water showed lead levels above the MCL's, chlorinated samples were below MCL's for lead [Treweek *et al.,* 1985].

A pipe loop was set up to evaluate the impact of secondary disinfectants on internal corrosion and water quality in old, unlined cast-iron distribution pipes for low pH and alkalinity raw water in Halifax, Nova Scotia. A pipe loop is a re-circulating system used to measure pipe reaction to water of a particular quality. The disinfectants compared for this study were free chlorine, chloramines, chlorine dioxide, and chlorite. The pipe loops were operational for 220 days and samples were evaluated for corrosion rate, total and dissolved iron, and turbidity. Overall results suggested that chlorine dioxide and chlorite reduced corrosion rates while chloramines and chlorine increased corrosion rates. In addition, chloramines showed a higher corrosion rates on many non-metal components such as rubber rings [Eisnor and Gagnon, 2004].

A six-month, continuous pipe loop study and an annular reactor study were performed to anticipate possible problems of switching New York City water disinfectant from chlorine to chloramines. Parameters investigated included copper and lead leaching; corrosion of iron, brass and bronze; and microbial re-growth potential. The goal of the study was to determine if the proposed conversion to chloramines would allow New York City to avoid violation of the lead and copper rule and continue to provide safe drinking water. Each group of pipe rigs had a total of seven identical, one-meter long rigs tested in parallel. The groups included three rigs exposed to chlorine, three rigs exposed to chloramine, and a single control rig exposed to deionized (DI) water. The New York water had low alkalinity and a pH near 7.2. The results from the first phase of pipe rig studies indicate that chloramines, prepared with a chlorine to nitrogen ratio of 3:1 and a pH that ensures complete monochloramine formation, will not result in increased lead and copper leaching at any greater rate than what is experienced with chlorine disinfection [Sharp *et al.*, 2007].

Corrosion Inhibitors

A common method of reducing metal corrosion is the use of corrosion inhibitors. Corrosion inhibitors are used in a wide variety of industries and only a small number are applicable to drinking water. Chemicals commonly added to potable water for corrosion control are carbonate-containing chemicals, which encourage growth of protective calcium carbonate or metal carbonate scales, including orthosilicates, polysilicates, orthophosphates, polyphosphates, and zinc [AWWARF, 1990a].

Phosphate Based Corrosion Inhibitors

Phosphate-based corrosion inhibitors have been used in the drinking water industry for decades. For over seventy years, hexamataphosphates ability to prevent calcium carbonate deposition and inhibit iron corrosion has been documented [Hatch and Rice, 1939; 1940]. However, definitive data on the effectiveness of corrosion inhibitors was sparse. Before collection of extensive quantitative data, the effectiveness of inhibitors was often based on such qualitative information as reduction in consumer complaints about “red water” or metallic staining [AWWARF, 1990b]. A primary disadvantage of hexametaphosphate is that it appears to increase release of both particulate and soluble lead [Hatch, 1941; Edwards and McNeill, 2002].

Phosphates salts, produced for use in potable water treatment, are derived from phosphoric acid. Phosphoric acid is produced from (1) elemental phosphorous or (2) a purified wet acid process. In the first process, phosphate ore is mixed with coke and silica in a furnace and elemental phosphate is distilled and burned in water to form phosphoric acid. In the second method, the phosphate ore is extracted with sulfuric acid.

The phosphoric acid produced by either method is reacted with potassium, sodium, or zinc to produce the desired phosphate product [Pacholec and Weidemann, 1995].

Phosphate corrosion inhibitors arrest metal corrosion in two ways; sequestration and passivation. Sequestration is the prevention of metallic ion precipitation by forming a compound that remains dissolved in water. Since the compound remains in solution no discoloring from precipitation occurs. This phenomenon is particularly important in preventing “red water”, discoloration derived from corrosion of iron pipes. Passivation is the formation of an inorganic film, which essentially coats the inner surface of a metal component. Passivation is analogous to the application of paint to protect surfaces from reactive environments [AWWARF, 1990b; Mishra and Kommineni, 2007]. Effectiveness of corrosion inhibitors is dependent on water quality. Phosphate inhibitors have been shown to be more effective in low alkalinity and low hardness water, since higher alkalinity and hardness waters often provide ample corrosion reduction from passive calcium carbonate scales, thus rendering phosphate inhibition largely redundant. [Edwards and McNeill, 2002].

Phosphate-based corrosion inhibitors also have potential drawbacks including accelerated biological activity and associated corrosion [Edwards and McNeill, 2002; Mishra and Kommineni, 2007]. Phosphorus is an essential nutrient for bacteriological growth and can lead to increased biofilm formation. It has been suggested that high doses of phosphate inhibitors can contribute to outbreaks of disease causing pathogens such as *legionella pneumophillia,* which is responsible for Legionnaire’s disease [Crespí and Ferra, 1997]. Phosphate-based inhibitors (ranging from 1 to 4 mg/L total phosphorus) increased biological activity in drinking water with high organic carbon content (> 8.0 mg/L measured as total organic carbon). However, low concentrations of phosphate inhibitors (<8.0 mg/L total phosphorus) do not seem likely to increase biological activity and biofilm in drinking water with low organic carbon content [Gouider *et al*., 2009; Park *et al*., 2008] and some research suggests that low levels of phosphate-based inhibitors actually (under two ppm) reduce bacteriological growth [Teasdale *et al*., 2007]. Stannous chloride has been used in place of phosphate inhibitors when bacterial counts are excessive [Hozalski *et al.,* 2005].

Phosphate inhibitors are a source of the nutrient phosphorus, which can lead to algal blooms and other phenomenon hazardous to the natural environment. The amount of phosphorous contributed to drinking water by corrosion inhibitors is small compared to phosphorus present in wastewater and runoff from other sources. However, deliberately placing phosphorous in drinking water can have huge public relations implications for a utility [USEPA, 2003a].

Zinc Phosphates

Several utilities have found success with using zinc phospates for corrosion control [Swayze, 1983]. Zinc-orthophosphate reduce metal residuals, particularly copper at dosages below 1.0 part per million (ppm) [Bancroft, 1988; Pacholec and Weidemann, 1995] and have been used in chlorine versus chloramines comparisons [Woszczynski *et al*., 2013]. Zinc orthophosphate has limitations at high doses. Zinc orthophosphate creates problems for wastewater treatment plants since higher zinc levels make treatment to remove zinc more costly. Land application rates for biosolids derived from plants with high zinc waste may be limited. In addition, some industrial users of treated water cannot tolerate zinc levels above certain thresholds [Ramaley, 1993]. The Springfield Massachusetts water system introduced zinc orthophosphate in February of 1992 to the distribution system as a corrosion inhibitor. They were forced to switch to orthophosphate in September of the same year when zinc concentrations in composted sludge increased almost 300% nearly reaching the federal zinc action limit [Lyons *et al.,* 1995].

Studies have revealed that reducing or eliminating zinc from corrosion inhibitors does not decrease performance in lead residual reduction [Schneider *et al.*, 2007; Ryder *et al.*, 1994]. Since zinc phosphates are potentially toxic and reducing in popularity worldwide, this dissertation will concentrate on research dealing with polyphosphates, polyphosphate blends, and orthophosphates.

Polyphosphates, Polyphosphate Blends and Orthophosphate

Three popular types of phosphate based corrosion inhibitors are polyphosphate, polyphosphate blends (blends) and orthophosphate. Polyphosphate is a composite of different types of phosphates (other than orthophosphate), usually dominated by sodium phosphate. Polyphosphates are generally effective at neutral pH [Boffardi, 1991]. Orthophosphate corrosion inhibitors are pure phosphoric acid, diluted in water to a desired strength. Blends are a mixture of orthophosphate and polyphosphates. Blends have the advantage of utilizing sequestration and passivation chemistry to reduce metal corrosion. Generally the polyphosphate component acts as the sequestering agent while orthophosphate forms the passivity coating. Blends are usually described as a percentage polyphosphate versus orthophosphate [AWWARF, 1990b].

Polyphosphate, Blends, and Orthophosphate - Lead/Copper Corrosion

Evidence from experimentation suggests that polyphosphates are capable of dissolving lead and copper from stagnant drinking water pipe scales [Holm and Schock, 1991; Edwards and McNeill, 2002; Heberling *et al*., 2009]. Similar results were found with hexametaphosphates, an active component of many polyphosphates [Hatch, 1941; Edwards and McNeill, 2002]. In an experiment with three-year old pipes (source water at a pH of 7.2 and an alkalinity of 45 mg/L as $CaCO_3$), hexametaphosphates increased lead residuals by 3500 percent over the same system treated with orthophosphate [Edwards and McNeill, 2002]. It has been speculated that the sequestering nature of polyphosphates creates higher lead residuals [AWWARF, 1990b].

Plenty of evidence also suggests that blends, which often contain hexametaphosphate, are ineffective in lead corrosion prevention and even exacerbate lead residuals by releasing dissolved and particulate lead [Edwards and McNeill, 2002; USEPA, 1993; Holm and Schock, 1991; Cantor *et al.,* 2000; Hozalski *et al*., 2005; Heberling *et al*., 2009]. However, some chemical producers are marketing blends of polyphosphate and orthophosphate as effective lead corrosion inhibitors. Research indicates that 70-30 blends and 30-70 blends (70-30 being a mix of 70% polyphosphate and 30% orthophosphate [mass ratio]; 30-70 being 30% polyphosphate and 70% orthophosphate) increase lead corrosion in drinking water [Edwards and McNeill, 2002; Heberling *et al*., 2009].

Unlike polyphosphates, orthophosphates have proven successful in reducing lead corrosion [Edwards and McNeill, 2002; USEPA, 2006a; Cook, 1996; Atassi *et al*., 2004;

Ryder *et al.*, 1994; Hozalski *et al.,* 2005]. However, Orthohosphate has shown mixed results when used to inhibit copper residuals [Dartmann *et al.*, 2005; Becker, 2002; Rezania and Anderi, 1995]. Some studies suggest that orthophosphate does not prevent copper corrosion [AWWARF, 1990a]

Polyphosphate, Blends, and Orthophosphate - Iron Corrosion

Studies have indicated that use of polyphosphate reduces iron corrosion [McNeill, 2000], which leads to “red water”. Polyphosphates ability to sequester iron and manganese ions has historically made it a favorite choice of utilities for combating “red water” [Holm and Schock, 1991]. Blends have been used to counter the perceived red water problems with orthophosphate, while still employing orthophosphate’s passivity [USEPA, 1993]. Polyphosphates effectiveness diminishes below a pH of 7.0 [AWWARF, 1990b] and polyphosphate is more effective in newer pipes. In older pipes polyphosphates can dissolve scales leading to red water [Brodeur *et al.*, 2006]. One other variable to consider is the potential increased biological activity resulting from use of polyphosphates or orthophosphates. Increased biological activity can lead to greater iron corrosion [Li *et al.*, 2010].

Research and Utility Experience with Chloramines and Corrosion Inhibitors

Orthophosphates were used in Washington D.C. to reduce excessive lead residuals in the municipal distribution system after a change in primary disinfectant from chlorine to chloramines. Lead levels decreased dramatically within a few weeks after the application of orthophosphate to the distribution system. Application of orthophosphate before the switchover from chlorine to chloramines likely would have prevented a potential public health and public relations incident [USEPA, 2004b].

The City of Highland Park Water Utilities in Illinois and the Minneapolis Water Works in Minnesota both utilize chloramines for disinfection. Both utilities have added polyphosphate blends to their distribution systems to stave off potential LCR violations. Each water purveyor has been able to comply with LCR regulations and have not seen increased lead and copper corrosion associated with chloramines or polyphosphate blends [AWWARF, 2009].

STATISTICAL METHODS

As confirmed by exhaustive literature searches, precious little information about drinking water pipe corrosion statistical data is available. However, statistical methods employed in environmental sampling have shown promise for pipe corrosion data [Wysock *et al.,* 1995; AWWARF, 2010]. Similar parameters, collection techniques, and pitfalls (such as what to do with non-detects) are present in environmental data and pipe data. Proper statistical evaluation of data is critical to determining the best methods of corrosion control. Statistical analysis is often given only perfunctory analysis. Often, these cursory analyses take the form of using Students t-test (*t*-test) and the Analysis of Variance (ANOVA) test as the primary means of statistical comparisons between treatments.

Comparison of means tests using techniques such as ANOVA and *t*-tests are often inadequate for laboratory and field corrosion data [Wysock *et al*., 1995]. There are five problems with the t-test that make it less applicable for general use than other tests such as the nonparametric rank-sum tests. These problems include: 1) lack of power when applied to non-normal data, 2) dependence on an additive model, 3) lack of applicability for censored data (non-detects), 4) assumption that the mean is a good measure of central tendency for skewed data, and 5) difficulty in detecting non-normality and inequality of variance for the small sample sizes common to water resources data [USGS, 2002]. When dealing with corrosion data, the biggest concerns are the *t*-tests unpredictability with non-normal data sets (since corrosion data rarely follows a normal distribution) and populations with large amounts of censored data [Wysock *et al.*, 1995]. The inability to apply non-detects can be particularly problematic with pipe corrosion data since data below detection limits can make up a significant fraction of points in a data set. In addition, outliers often cannot be readily dismissed. Unfortunately, many statistical analyses employed in corrosion studies are geared toward data that follow normal (or log-normal) trends. Non-parametric methods are generally more successfully employed when analyzing non-normal data [Helsel, 2012].

Collecting corrosion data is expensive and time consuming, therefore, careful attention must be taken when the data is examined statistically. When comparing data from two or more corrosion data populations, it is critical to examine the following:

1) The distribution symmetry (normality) of the collected data sets,

2) The addressing of outliers and censored data (non-detects),

3) Variance similarity of the sets,

4) Data trends,

5) Statistical differences between sets, and

6) Graphical analysis and representation.

Following these six steps makes selecting the best possible statistical methods appropriate for the data collected more likely. Choosing the appropriate statistical methods increases the likelihood of selecting the best methods for corrosion control and can greatly reduce costly pilot study time and protect public health by eliminating practices that threaten drinking water quality [Wysock *et al.*, 1995].

Determination of Population Normality

The first step in corrosion statistical analysis should be to determine which data sets displayed a normal distribution [IDEQ, 2009]. Normality is defined as the level of agreement a data set has with a Gaussian or normal distribution. A normal distribution is a bell-shaped graphical representation of data, which is symmetrical about the mean, median, and mode. Determining if a data set has a normal distribution is critical to selecting appropriate statistical tests. Parametric tests are statistical tests, which are more effective when a data distribution is approximately normally distributed. When data significantly deviates from a normal distribution a non-parametric statistical test is appropriate. A common type of normality tests is goodness of fit tests, which are models used to determine if a population closely approximates a statistical distribution (such as normality) [Rao and Scott, 1981].

Corrosion and other environmental information rarely follow normal or log-normal data patterns [Helsel, 2012; Cantor *et al.*, 2003; Wysock *et al.*, 1995]. Outliers (observations distant from collected data) and censored data (non-detects) skew data to the left (censored data) or to the right (outliers). Often censored data and outliers are discarded to make a distribution appear closer to a normal distribution. However, outliers and non-detects are often treated as valid, even critical, data points in corrosion studies. Censored data and outliers can rarely be discarded without seriously compromising the analysis' validity. As mentioned earlier, non-parametric methods are generally more successfully employed when analyzing skewed or otherwise non-normal data sets [Helsel, 2012]. In addition, smaller data sets usually exhibit non-normal behavior and are best suited for non-parametric methods [AWWARF, 1994]. Dissolution within drinking water pipes behaves in a non-linear fashion with respect to time, which would require analysis using non-parametric methods [Wysock *et al*. 1995]. Often data collected in corrosion studies reflects a non steady-state situation, which creates non-normal data sets [AWWARF, 1996]. When data is collected from non steady-state environments or there are outliers in the data, non-parametric test methods are most appropriate for evaluating treatment differences [AWWARF, 1996]. Smaller data sets (generally below fifty data points) are usually non-normal and should be analyzed using non-parametric methods [Huston and Juarez-Colunga, 2009; AWWARF, 1994].

One of the most popular analyses to determine normality is the Shapiro-Wilk test. The Shapiro-Wilk test is based on the premise that if the sets of data are normally distributed then the ordered values should be highly correlated with corresponding quantiles taken from a normal distribution [Shapiro and Wilk, 1965; IDEQ, 2009]. The Shapiro-Wilk tests the null hypothesis (H_0) that a set of data comes from a normal distribution or, more precisely, the graphical representation of the data set mimics a normal distribution curve. The alternative hypothesis would state that the distribution is non-normal or non-parametric. The Shapiro-Wilk test compares ordered sample values with a corresponding order statistics from a specified distribution [Shapiro and Wilk, 1965]. Though a powerful method, the Shapiro-Wilk test is most effective when used with data sets with populations under 50 sampling points [NFESC, 2003; Chou, 2004; IDEQ, 2009].

D'Agostino's skewness test is recommended by the USEPA to determine normality in sets with greater than fifty members [USEPA, 2006b], particularly 50 – 1000 points [USEPA, 2006c]. Basically, under the D'Agostino's skewness test, the null hypothesis ($H_{0)}$ stipulates that the value of skewness and kurtosis of a data set is close to zero. A sample population that shows low (near zero) skewness and kurtosis is highly likely to display a normal distribution [D'Agostino *et al*., 1990]. Skewness is a shift left or right of a distribution curve indicating a large number of data points above the mean (positive or right skewed) or a large number of points less than the mean (negative or left skewed). Kurtosis is the variability of data directly about the mean and describes how great the values are around the mean. It is also described as the sharpness (or height) of a distribution curve and can also describe the size of tails. The tails are the high and low extremes of a data set graphically represented in a distribution set [Healy, 1996].

The Kolmogorov Smirnov single sample test (KS) is another test for normality, which is more powerful with data populations over fifty, though it is effective with small samples [Lilliefors, 1967]. The KS can be modified to perform a goodness of fit test, specifically a normality test. Samples are standardized and compared with a standard normal distribution by setting the mean and variance of the reference distribution equal to the sample estimates [USEPA, 2002]. The Anderson Darling test (a modified Kolmogorov-Smirmov test) gives more weight to the data distribution tails than the Kolmogorov-Smirmov test [Stephens, 1974]. The Anderson Darling test is commonly used for determining normality in sets of greater than fifty data points and has been recommended for use with corrosion data [Wysock *et al.*, 1995]. The Anderson-Darling test applies specific distributions in calculating critical values. An advantage is that this allows a more sensitive test. A disadvantage is that critical values must be calculated for each distribution [Stephens, 1974].

The Anscombe-Glynn test, another normality statistical test, measures for normality by determining the kurtosis of a distribution. The Anscombe-Glynn test tests for normality by determining the size of tails relative to the normal distribution. If data fails the Anscombe-Glynn test, the conclusion is that the underlying distribution has non-normal kurtosis. That is, if the tails don't match the expected tail size for a normal distribution, the test fails [Okten, 2002].

The Jarque-Bera test is a goodness of fit test, which determines if a data set skewness and kurtosis displays a normal distribution. The null hypothesis is a joint hypothesis of a zero value for skewness and kurtosis. The Jarque-Bera test loses power with small sample sets, but is popular because of its power with larger sample sets [Mantalos, 2010]. To clarify, a population of more than fifty members can be considered large [Huston and Juarez-Colunga, 2009].

However, using a normality test as the sole basis for selecting a non-parametric test may be a dubious practice. Normality tests, as discussed earlier, are sensitive to population sizes. Often the discarding of outliers and non-detects or a data transformation can move a population to a more normal distribution. Since a distribution rarely follows an ideal bell-shaped curve, determining the barrier between normal and non-normal distributions is arbitrary [GraphPad, 2013]. A careful selection of the appropriate method can reduce the likelihood of a Type I error in a normality test. A Type I error is defined as the rejection of the null hypothesis (H_0) when H_0 is actually true [Navidi, 2008]. Since outliers and non-detects are rarely discarded in corrosion data and also since corrosion data populations do not consistently follow normal distributions, a normality test is recommended.

Addressing Outliers and Censored Data

Outliers

Discarding outliers is common practice in statistics and is tempting when evaluating corrosion data. However, ignoring high metal residuals is a dubious practice, which encourages misleading results. High residuals are formed by chemical reactions present in active distribution systems. Corrosion data should only be discarded if there is a suspicion of sampling or testing error [Wysock *et al*., 1995]. Also, the lead and copper rule makes no allowances for rejecting outliers [USEPA, 2004a]. Unless there is tangible evidence of sampling or equipment error, outliers should not be discarded, since outliers likely represent valid data points.

Censored Data

There are many strategies to incorporate non-detects. Substitution methods are often employed, by replacing the censored data with zero, the detection limit, or the average of the detection limit and zero. Under the LCR, non-detects are 0.0. However, there appears to be no justification for this convention [Krishnamoorthy *et al.,* 2009]. Using the detection limit to replace the censored data overstates the mean and can give misleading results. Replacing all non-detects with zero has the opposite effect by understating the mean [Hewett and Ganser, 2007]. Direct substitution, generally, has demonstrated limitations and is without theoretical basis [Huston and Juarez-Colunga, 2009; Hewett and Ganser, 2007; Helsel, 2005; Helsel, 1990].

Comparison of Variance

Certain statistical comparison tests lose effectiveness when the variances of compared sets are dissimilar. Heterogeneous variances in compared groups increase the likelihood of Type I errors when applying the Wilcoxon Rank Sum test [Pappas and DePuy, 2008]. Other non-parametric tests such as the Kolomogorov-Smirnov two sample test and Welch's *t*-test are less likely to succumb to the same errors as the Wilcoxon Rank Sum test when data sets have a wider spread of variances [Welch, 1947; McElduff *et al.*, 2010; Wysock *et al.*, 1995].

When populations have normal distributions, the *F*-test can be used to determine equality of variance [Navidi, 2008]. The *F*-statistic is a ratio of the variances of two sample populations. Independent random samples drawn from populations with equal variances will display a probability distribution known as an *F*-distribution. The *F*-test measures the compared population to an expected *F*-distribution to determine similarity of variances [Johnson, 1984]. The assumption of the data possessing an *F*-distribution is the null hypothesis [Navidi, 2008]. However, corrosion data often does not display a normal distribution behavior and therefore the *F*-test may not apply. The Levene's test is considered less powerful than the *F*-test for normal distributions. However for non-normal sets the non-parametric Lavene's test is recommended over the *F*-test [Allingham and Rayner, 2011]. The Levene's test is a variance test that applies the F-test to the absolute deviations of the observations from the compared group means. The null hypothesis assumes variances are equal [Gastwirth *et al.*, 2009]. Historically, the Levene's test had the advantage of being simpler to use. This is rendered irrelevant by the availability of statistical software packages [Hayes, 2005].

The Brown Forsythe test has been reported as a superior variance comparison test versus the Levene's test and the Brown-Forsythe is more likely to reduce Type 1 error versus the Levene's test [Conover *et al.*, 1981]. The Brown–Forsythe test is a statistical test for variance equality based on ANOVA using a transformation of dependent or independent variables. The underlying difference between the Levenen's and Brow-Forsyth is that the former examines differences in the means while the latter determines differences in the median. The Brown-Forsythe is considered more robust, i.e., able to perform under a wide range of variables and assumptions, compared to the Levene's test [Hayes, 2005].

Data Trends

Examining trends in corrosion studies is critical to determining if corrosion data sets have stabilized. Generally, when using some type of corrosion control strategy, two years is recommended to ensure stabilization of data [AWWARF, 1997], though due to factors such as water chemistry, stabilization may never occur [Cantor *et al.*, 2000; Wysock *et al.*, 1995]. If compared data sets have at least one population that has not stabilized, the statistical comparisons could be flawed. A population of data points from an un-stabilized system may not reflect the true chemical and physical nature of the system. Any comparisons between stabilized and un-stabilized data should be considered at least somewhat suspect.

Three popular trend analyses are the Mann-Kendall test, the Thiel Sen trend estimate and the coefficient of determination (R^2). The Mann-Kendall test is a non-parametric test for that compares the relative magnitudes of sample. Since it is a non-parametric test, the data does not need to conform to a normal distribution [Khambhammettu, 2005]. More specifically the Mann-Kendall determines if the median changes over time. The Mann-Kendall test does not assume any particular distribution and can accommodate values below detection limits by assigning a common value. The Mann-Kendall can be modified to deal with multiple observations and multiple sampling locations [USGS, 2002].

The Theil-Sen trend estimate (TSE) is a slope estimated as the median of all possible slopes between pairs of data. The TSE is also a non-parametric method [Huston and Juarez-Colunga, 2009]. The TSE is also known as the Theil–Sen estimator, Sen's slope estimator, slope selection, the single median method, and the Kendall robust line-fit method. The TSE is a trend estimator that selects the median slope among all lines through pairs of sample points. The TSE is useful with data sets containing a high percentage of censored data [USGS, 2002].

R^2 linear regression is a commonly used trend analysis familiar to many users of spreadsheet applications. The R^2 is a parametric method and therefore may have some limitations when applied to corrosion data. R^2 indicates the interdependent association between x and y data point co-ordinates without suggesting specific dependency between x and y [Feinstein, 1996]. Since the R^2 linear regression is parametric, the applications to corrosion data may be limited [USGS, 2002].

Statistical Differences Between Sets

While percentiles are used in parametric methods [AWWARF, 1996], some common non-parametric methods used in water analysis are based on data ranks. Data values are ordered from lowest to highest and ranked according to their list position [IDEQ, 2009]. Table 1 lists commonly used rank analysis and their parametric equivalents.

Table 1.

Commonly used rank analysis and their parametric equivalents.

Non Parametric Method	Parametric Equivalent
Wilcoxon signed-rank test	one- sample t-test
Wilcoxon rank-sum test (Mann-Whitney's test)	two-sample t-test
Kruskal-Wallis test	ANOVA

The USEPA recommends non-parametric test methods for unstabilized data, sets with data spikes, or small numbers of data points [AWWARF, 1994; 1996]. Also, the USEPA also acknowledges the effectiveness of non-parametric methods for stabilized pipe loops [Cantor *et al*., 2000]. The Wilcoxon Rank Sum test (WRS), also called the Mann-Whitney test, is a commonly used non-parametric test to determine if two data populations are statistically different. Historical application to pipe loop studies makes the WRS a popular choice when analyzing corrosion data [Cantor *et al*., 2000]. The WRS is a method to compare the means or medians of two independent populations to determine differences in the sets [Fagerland and Sandvic, 2009]. The WRS is the non-parametric alternative to the two-sample t-test. The WRS test uses ranked data instead of actual numerical data. Numerical data is transformed to ranks in combined groups. The ranks from the combined groups are compared to the sums of the ranks in the two groups [Kang and Harring, 2012].

To be clear, use of the WRS has its weaknesses. In particular, small differences in variances and moderate skewness can produce large deviations from the nominal Type I error rate. It has been recommended that the variances should be within a ratio of 1.5 for WRS to be applied and it has been reported that the Wilcoxon method loses power under low homoscedasticity (homogeny of variance) [Fagerland and Sandvik, 2009]. Populations that show significantly different distribution patterns, even when non-normal, may not be best interpreted by the WRS [Kang and Harring, 2012].

Another commonly used comparison test is the Welch's *t*-test. The Welch's *t*-test performs well with data showing no homoscedasticity and out performs the Wilcoxon test under conditions of unequal variances [Zimmerman and Zumbo, 1993]. However, the Welch's *t*-test assumes Gaussian populations, which are often not found in corrosion data sets [USEPA, 2006c]. The Welch's *t*-test is a modification of the Student's *t*-test (*t*-test), which is a statistical comparison test to determine if two sets of data are significantly different. The Welch's t-test compensates for data sets with unequal variances, while the *t*-test is better suited for data sets with similar variances [Welch, 1947; USGS, 2002].

Another non-parametric test often employed data population comparison is the Kolmogorov-Smirnov two-sample test (KS2). The KS2 test is more powerful with populations of greater than 50 members and is applicable with a wider range of variances.

The KS2 test is a sample population comparison test that determines if two data sets come from the same distribution. The distribution is not specified, therefore not dependent on a particular distribution (like, for example, a normal distribution) [USEPA, 2006c].

The Kruskal-Wallis test is a rank-based test, which compares the sum of the ranks and the expected sum of the ranks for each group [Derryberry *et al*., 2010]. The Kruskal Wallis test is essentially the non-parametric equivalent of the ANOVA and the equivalent of the WRS for comparison tests of over two groups. The Kruskal-Wallis test ranks data and performs a parametric test on the ranks, which are calculated by using a chi-square distribution approximation [USGS, 2002]. The Kruskal-Wallis test does not test a null hypothesis using a population's mean or median [Sokal and Rohlf, 1995]. The Kruskal-Wallis test does have drawbacks. If the total sample size is seven or less, the Kruskal-Wallis test will always return a p-value greater than 0.05 no matter how the groups differ [Motulsky, 1998]. It has been suggested that, like the WRS, the Kruskal-Wallis test provides good Type I error control and power when variances were equal, however, Type I error rates became severely inflated when variances were unequal [Cribbie and Keselman, 2003]. This error is likely to occur when a low number of ranks are compared [Cribbie and Keselman, 2003].

Graphical Analysis and Representation

Often, a graphical representation of compared data can provide a convincing illustration of differences between sets. Graphical illustrations should not provide the only avenue of data analysis, particularly since many statistical packages and calculators are readily available, some free of charge on various websites. One of the most popular ways to graphically represent non-parametric data is to use box plots. Box plots can be placed side by side for visual comparisons of several populations. Box plots clearly indicate outliers, which in the case of corrosion data are often considered viable data points. Box plots are a useful way to visually illustrate differences between corrosion rates in different disinfection practices, corrosion control measures, and water treatment methods.

BWWB FLOW-THROUGH PILOT STUDY

In anticipation of stricter disinfectant by-products (DBP's) regulations, the Birmingham Water Works Board (BWWB) investigated the feasibility of replacing their primary disinfectant, chlorine, with chloramines. The BWWB wanted to determine if chloramine usage could have a deleterious effect on the BWWB distribution system in the form of increased metal residuals. A pipe rack pilot study (flow-through) was constructed to measure lead and iron corrosion rates in chlorinated and chloraminated drinking water. Corrosion inhibitors were employed to stabilize lead corrosion in lead pipes and brass fixtures. After testing three corrosion inhibitors, orthophosphate was selected as the inhibitor employed in the chlorine versus chloramine corrosion study.

Though the BWWB and many utilities worldwide have made a concerted effort to remove lead piping from distribution systems, some lead features still remain. In addition, many older homes in water utility service areas have lead service lines and plumbing as well as brass fixtures, which often contain lead. Any process or chemical that increases lead corrosion could raise lead residuals leading to potential health concerns [Heberling *et al*., 2009].

The Birmingham Water Works Board (BWWB) constructed a flow-through equipped with cast iron, brass, and lead piping and fixtures. The rack was designed to mimic a distribution system with twelve-hour flow (approximately 3000 gallons) and twelve hours stagnation (zero flow condition). Finished water and phosphate-based corrosion inhibitors were introduced to the pipe rack. The twelve-hour on and off cycle was chosen to represent a distribution system with high flow and stagnation periods. Though a functioning distribution system would not show a completely balanced stagnation versus high flow periods, twelve hours of stagnation allowed a greater time for leaching of residuals. Weekly samples were collected from the brass fixtures and lead pipes and analyzed for total and dissolved lead using approved Environmental Protection Agency (EPA) sampling and detection methods. The cast iron pipes were sampled for total and dissolved lead [Heberling *et al*., 2009].

Phosphate inhibitor introduction was intended to stabilize metal residuals in the flow-through pipes. Unfortunately, lead levels steadily increased after introduction of the corrosion inhibitor. A possible culprit in the lead residual rise may have been a reaction with the polyphosphate blend marketed and recommended in its literature as a lead corrosion inhibitor. The BWWB tested two additional phosphate inhibitors (including pure orthophosphate) to determine performance in such areas as lead residual. More than 2.5 years of data was collected comparing the three corrosion inhibitors. In addition, statistical tests have been employed to determine if there are significant differences in lead corrosion of chloramines treated drinking water versus chlorine treated drinking water. The BWWB selected a stagnation time of twelve hours for the flow through study to roughly mimic a stagnation time found in a distribution system and provide a convenient schedule for sampling [Heberling *et al*., 2009].

H.Y. Carson Filter Plant

The H.Y. Carson Filter Plant (CFP), located in Pinson, twenty miles north of Birmingham, Alabama (USA) was the setting for this research. Built in 1972, the CFP supplies BWWB customers with up to 25.9 million gallons per day (mgd) of finished drinking water. CFP's water source is Inland Lake, a low turbidity and alkalinity reservoir located twenty miles north of Pinson, Alabama (approximately thirty miles northeast of Birmingham). Raw water supplied to the CFP flows through a sixty-inch transmission line. The lake has a typical pH range of 7.0 to 7.5 at intake level. The water has low alkalinity (less than 25 mg/L as $CaCO_3$) with trace amounts of dissolved iron and manganese. The CFP staff assembled a flow-through pipe rack with a primary goal to assess corrosion potential of chloramine introduction.

Purpose of the BWWB Study

The primary purpose of this study was to determine if chloramines use would have an adverse effect on a large utility distribution system's cast iron and lead features. That is, would chloramines increase metal residuals when replacing chlorine as the primary disinfectant. The BWWB wanted to determine if a chloramines changeover (from chlorine) would result in the same public health and public relations problems experienced by WASA and if so, how these problems could be prevented. The study was also set up to investigate the effectiveness of corrosion inhibitors in preventing metal residuals in cast iron pipes and leaded pipes/features, as well as determine if previous research suggesting polyphosphates exacerbate lead residuals in drinking water could be replicated. This study was also concerned with determining if nitrification reduction strategies (i.e., the use of a chlorine "burn out") would be increase metal residuals in the BWWB distribution system and customer plumbing. Data was statistically analyzed to determine if chloraminated drinking water was more likely to cause metal corrosion relative to chlorinated drinking water (in drinking water treated with a corrosion inhibitor). A comparison of effectiveness of corrosion inhibitors was also tested for the cast iron pipes.

Design of Flow-Through System

A pipe flow through was selected as opposed to a pipe loop because the pipe flow is better designed to mimic an actual water distribution system and the focus of this project was to determine potential metal residuals that could be created in a distribution system under similar conditions. The CFP was selected largely because of the low alkalinity water treated by the plant. Low alkalinity increases the aggressiveness of the treated water and provides a scenario where higher corrosion can take place.

Lead and cast iron pipes were directly excavated from the BWWB distribution system. Spray paint was applied to each pipe section, before removal, indicating flow direction. Each pipe section was cut at a 90^{o} angle perpendicular to the pipe center-line with a diamond edged saw. Disturbance of each pipe was kept to a minimum and each pipe was removed and rinsed to prevent contamination from shavings. The external surfaces and ends of the pipes were cleaned with wire brushes. Each pipe was filled with water, capped, and sealed. The pipes were transported to the CFP cushioned and covered to minimize disturbance, exposure to ultraviolet radiation, and avoid temperature extremes.

The frame for the flow-through system was constructed of a plywood face attached to a lumber frame. The frame was constructed before the harvest and arrival of the pipes. The plywood face, angled at 75^{o} (from the back of the flow through to the floor), was composed a 5 foot wide and 10 foot long piece connected to a five foot by five foot piece. Pipes and fixtures were mounted to the face making up the pipe rack. The pipes and fixtures consisted of unlined cast iron pipes in service for approximately fifty years, lead service lines greater than fifty years of age, and brass fixtures purchased as new specifically for the study. The pipe sections were filled with water during installation.

The pipe rack was divided into five sections, each consisting of one ten-foot pipe of unlined cast iron pipe (two inch inner diameter), three 2.5-foot pipes of lead service line pipe (one inch inner diameter), and an assembly of brass fixtures. Each brass fixture assembly consisted of six, two-inch brass connectors with one-inch inner diameters. Five of the connectors were valved. The brass valves remained open for the duration of the study. The cast iron pipes were designated Cast Iron 1-5 from the top of the rack to the bottom. The lead pipes were labeled Lead 1-1, Lead 1-2, Lead 1-3, Lead 2-1 … Lead 5-3. The brass fixture arrays were labeled Brass 1-5 (Figure 1). Brass fixtures were selected for the flow through because brass can have up to 8% lead and still be considered “lead free” [USEPA, 1996]. Each section was tapped with sampling valves for each pipe and assembly. Additional valves separated the pipes during sampling. Valves were installed between each pipe section for pressure release during sampling. This pipe rack design was intended to give the best possible approximation of settings and materials found in the BWWB distribution system.

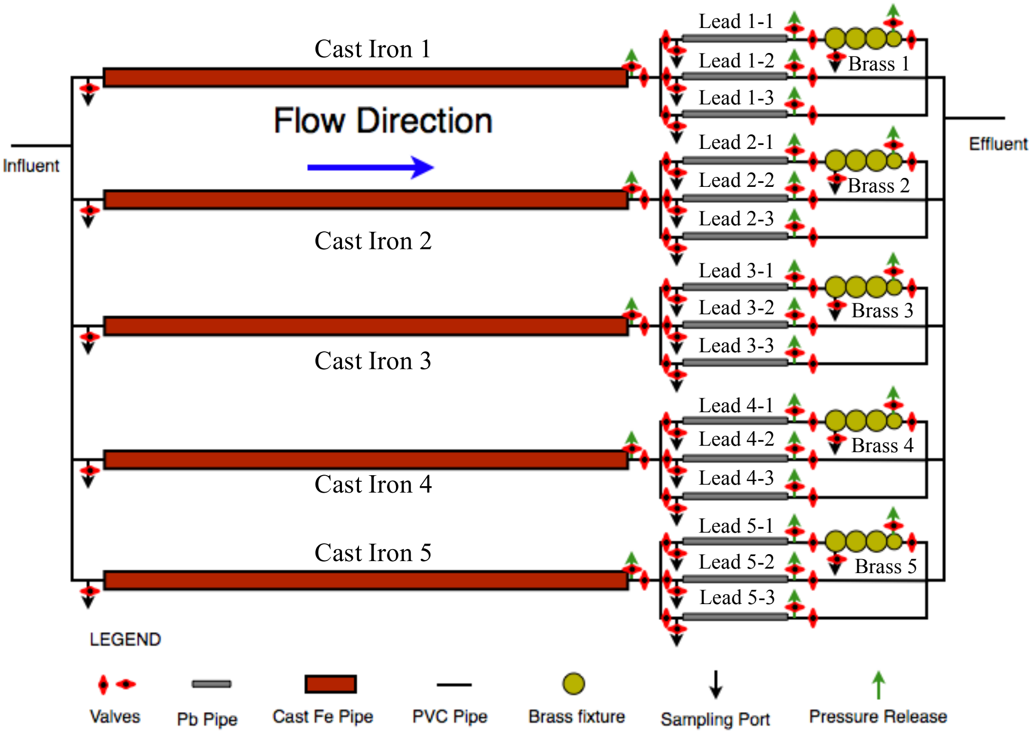

Figure 1. H. Y. Carson Filter Plant (CFP) Pipe Rack Schematic [Heberling and Barron, 2012].

Flow introduced into the pipe rack was unidirectional west to east (left to right in Figure 1). The cast iron pipes divided the influent into five sections (Figure 2). The flow subsequently branched into fifteen lead pipes (Figures 3 and 4). Ten of the branches fed directly to effluent two inch polyurethane tubing. The remaining five branches fed directly to the five assemblies of brass fixtures (Figure 5) and then into two inch polyurethane effluent tubing. Each pipe and brass section was tapped with sampling valves. These valves separated the pipes during sampling, which occurs toward the end of the twelve-hour off (stagnation) cycle. The on/off cycle was controlled by a twelve-hour timer, which suspended flow between active and stagnant periods. The pipes and fixtures are filled with water present in the pipes during the second which flow is suspended. All water exited through effluent pipes measured by residential water meters. All five sections showed similar flow volume (within 1% total effluent volume) throughout the project (approximately 600 gallons over a twelve hour flow period). No measurable

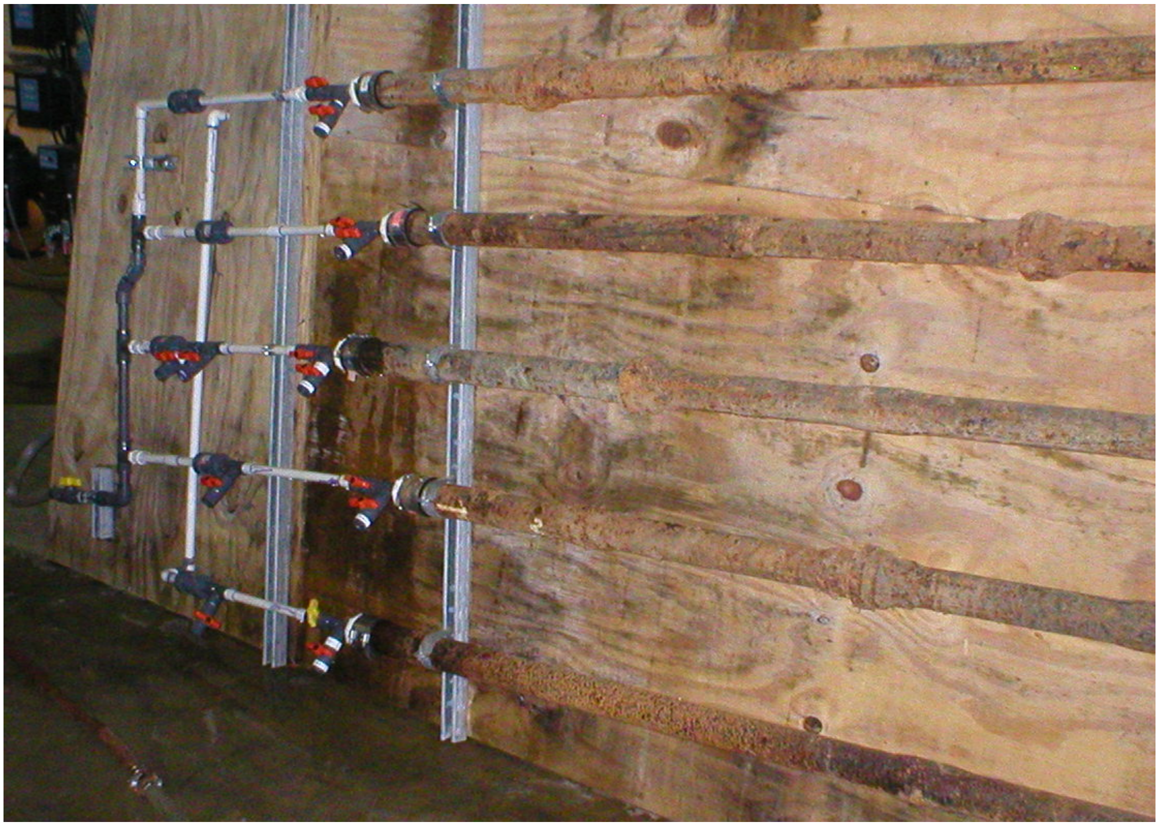

Figure 2. Cast influent pipes feeding cast iron pipes for the BWWB flow-through system.

leakage was noted throughout the study. A reservoir and pump introduced chemicals before the water enters the rack piping. The design was inspired by the AWWARF study described previously [AWWARF, 1994].

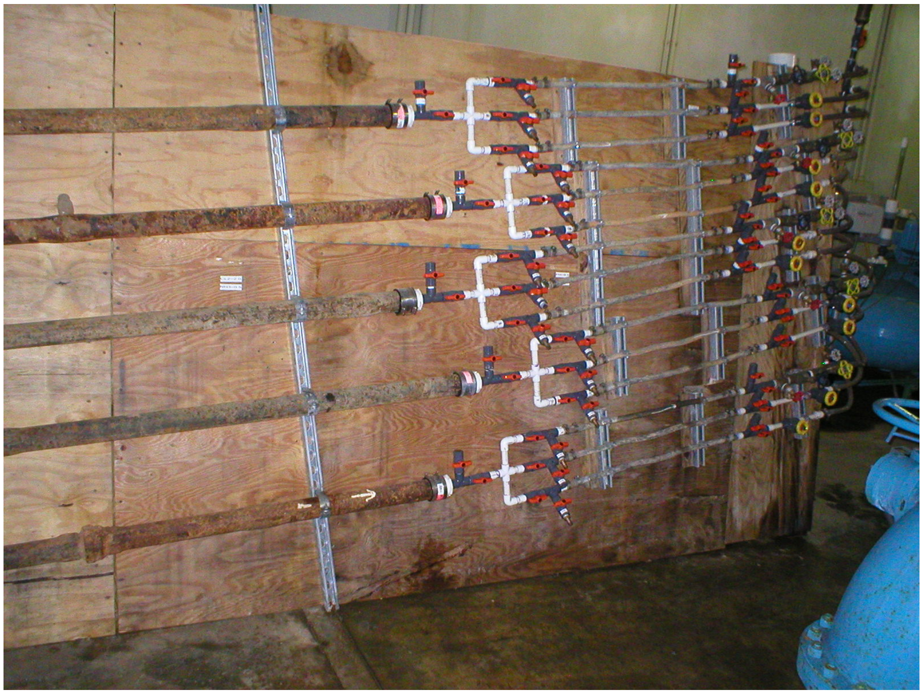

Figure 3. Cast iron pipes feeding into lead pipes, BWWB flow-through system.

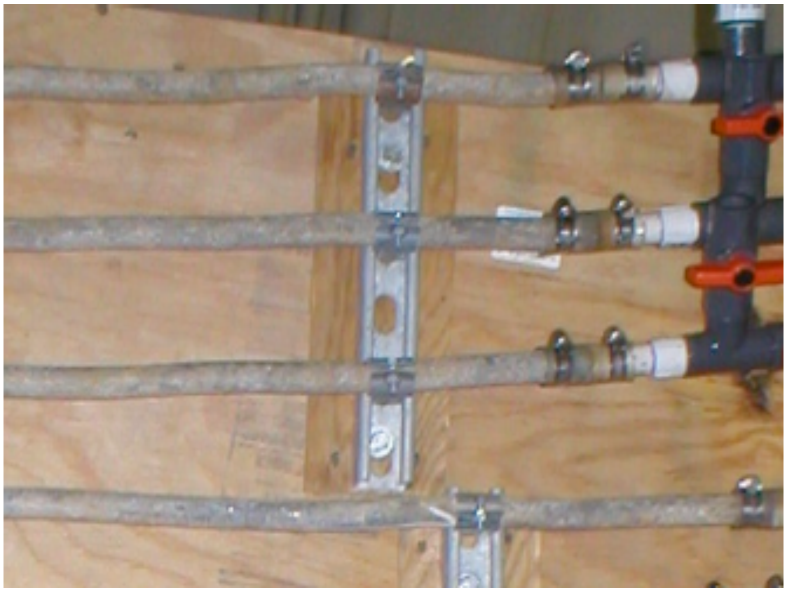

Figure 4. Lead pipes, BWWB flow-through system.

Figure 5. Brass fixtures for the BWWB flow-through system.

This orientation of the flow-through system was chosen out of necessity due to limited space in the pipe gallery. The flow-through system received CFP finished drinking water influent from an active tap approximately seventy three feet west of the western edge of the rack. All flow through sections received water from an identical source, providing treated CFP water. The influent flowed into a polyvinyl chloride (pvc) pipe, which branched into five additional PVC pipes leading to the cast iron pipes. Reynolds number calculations determined that the flow was laminar and that the scaling inside the pipe was not subject to turbulent water (range Re 640 - 1110). The Langelier saturation index (LSI) ranged between 0.6 and 0.9 (95th percentile) indicating that the water is saturated with respect to $CaCO_3$ and tended to form scale. The order in which water flowed through the rack was identical to the regime found in the field. That is, water flows from cast iron distribution pipes to lead service lines and through copper and brass features in a typical home. The arrangement of the pipes reduced head loss and decreased potential turbulence. The water flowed from the five cast iron pipes to the lower volume lead pipes. There were five assemblies of brass fixtures, which were attached to the east end of the rack.

During the flow through study, source water was treated in the following order:

- Chlorinated water (6 months);
- Chlorinated water with a 70/30 (70% polyphosphate / 30% orthophosphate) Polyphosphate blend corrosion inhibitor (3 months);
- Chlorinated water with a 30/70 polyphosphate blend corrosion inhibitor (5 months);
- Chlorinated water with orthophosphate (6 months);
- Chloraminated water with orthophosphate (6 months); and

- Chlorinated water with orthophosphate introduced after six months of chloraminated water (chlorine "burn out") (2 months).

The pipes and fixtures in Section 4 consistently delivered water samples with 175% or higher turbidity (measured in Nephelometric Turbidity Units [NTU]) than samples from other sections. The source of the higher turbidity was particulate iron dislodged from pipe scales in pipe Cast Iron 4. One possibility for the higher turbidity may have been cast iron pipe damage during unearthing. Regardless, the high turbidity persisted in section 4 for the duration of the 2.5-year study. It has been demonstrated that high turbidity waters reduce the effectiveness of phosphate based corrosion inhibitors [Schock, 1989; LeChavillier *et al.*, 1993; Lytle and Schock, 2000] including orthophosphate [Lytle and Snoeyink, 2002]. With this in mind, the group 4 lead pipe, cast iron pipe and brass assembly data was not compared with the low turbidity samples.

The data in Sections 1, 2, 3, and 5 are grouped together, since these sections have similar turbidities and all sections are fed identical source water. Data from the cast iron pipes in Sections 1, 2, 3, and 5; the lead pipes in Sections 1, 2, 3, and 5; and the brass assemblies in Sections 1, 2, 3, and 5 have been analyzed as sets providing hundreds of data points for study.

The cast iron pipes were sampled weekly for total and dissolved iron. The lead pipes and brass fixtures were sampled for total lead on the same weekly schedule. The BWWB Envirolab provided the bulk of the analyses using a Perkin Elmer Elan 6000 Plasma Spectrometer. Occasionally when Envirolab was constrained, samples were shipped to Guardian Services in Greensboro, North Carolina [USEPA, 2004a]. With exceptions depending on sampler and laboratory availability, samples were taken weekly.

All lead and iron samples collected were analyzed using EPA method 200.8 (plasma mass spectrometry) with accredited equipment and techniques (Table 2) [USEPA, 2004b]. EPA Method 200.8 is described in Appendix F.

Table 2.

EPA methods for metal sample analysis.

Parameter	EPA Method
Dissolved Lead	EPA 200.8 (USEPA, 2004b)
Total Lead	EPA 200.8 (USEPA, 2004b)
Dissolved Iron	EPA 200.8 (USEPA, 2004b)
Total Iron	EPA 200.8 (USEPA, 2004b)

All pipes were sampled weekly field parameters including: pH, temperature, dissolved oxygen, turbidity, true color, and apparent color. Table 2 shows the equipment used to measure field parameters. Samples collected were analyzed using EPA methods and approved equipment and techniques (see Table 3). The purpose of sampling field parameters is to determine any major fluctuations in water quality occur during the study. All field parameters showed stability and little fluctuation throughout the project. However, as mentioned earlier, turbidity values were consistently high in all pipes and features in Section 4 of the flow-through system.

Table 3.

Field parameter equipment.

Parameter	Instrument
pH	Fisher Scientific Accumet XL 15 Meter
Temperature	Fisher Scientific Accumet XL 15 Meter
Dissolved Oxygen	YSI 85 Meter
Turbidity	Hach 2100N Turbidimeter
True Color	Hach DR 890 Chlorimeter
Apparent Color	Hach DR 890 Chlorimeter

Sampling Procedures and Protocols

Samples were collected weekly from the flow through after 11.5 hours of stagnation time. Valves separating the pipes and fixtures were closed separating the stagnant water in each pipe and brass assembly. Valves for releasing pressure release were opened. Water from each cast iron pipe was poured from sampling ports into 500 milliliter (mL) bottles. Each lead pipe and brass assembly was drained of its content from sampling ports into 250 mL bottles. Temperature and pH readings were taken from each bottle immediately after sampling and valves of the flow through were returned to the on position. Pressure release valves were closed. Each container was tested for pH and temperature by direct submerging the probe of a Fisher Scientific Accumet XL 15 Meter directly into each bottle. The probe was rinsed with de-ionized (DI) water between each reading.

Dissolved Oxygen (DO) was sampled by submerging a YSI 85 meter probe into each bottle. The probe was rinsed with DI water between each reading. Water from each sample was placed into a clean cell of a Hach 2100N Turbidimeter and measured for turbidity. Samples were collected from each 500 mL bottle to measure free chlorine, total chlorine, apparent color and true color using a Hach DR 890 Chlorimeter. All protocols for sampling and calibration were followed with all equipment before sampling (according to USEPA Method 330.5). After field sampling was completed, samples were delivered to the BWWB Envirolab for analysis of total and dissolved iron for samples collected from the cast iron pipes; and total and dissolved lead for samples collected from the lead pipes and brass fixtures. Water in a flow-through system spends very little time in the rack during flow periods.

A vast majority of chemical interactions between pipes and water occurs during the stagnation period. Carry over effects from one pipe to another was likely negligible since the contact time of the water prior to entering a pipe or fixture (less than two seconds) compared to a twelve-hour stagnation time was significantly less. Particles dislodged from one pipe to another feature are possible. This condition is to be expected in a functioning distribution system, therefore the same condition present in a pilot system is simply another realistic element in the study.

The flow-through study was designed to investigate the following:

- The impact of corrosion inhibitor addition to pipe scale stability in chlorinated water,
- The impact of chloramines on pipe scale stability, and
- The impact of nitrification control strategies (chlorine “burn out”) on pipe scale stability.

The proper implementation of the study depended on the stabilization of metal residuals in the stagnant water in the flow-through pipes, after the introduction of the corrosion inhibitor. Unfortunately, lead levels in sampled water were steadily increased. Within ten months, lead residuals in the brass fixtures were well above the MCL of 15 ppb and steadily rising, in some cases to the double-digit ppm range. More alarming was the rapid increase of lead residuals in the samples from the lead pipes. Some readings were as high as 30 ppm (2000 times the MCL). A likely culprit in the lead residual rise may have been a reaction with a polyphosphate blend, marketed and recommended in its advertised literature as a metal (including lead) corrosion inhibitor. Polyphosphate blends have been shown to increase lead residuals [Hozalski *et al.,* 2005; Cantor *et al*., 2000; Edwards and McNeill, 2002; Lytle and Schock, 2005; USEPA, 2010].

Polyphosphate blends were used as a corrosion inhibitor after three months of sampling with no corrosion inhibitors. Corrosion inhibitors were introduced into the flow through from a reservoir by way of a pump. A 70/30 polyphosphate blend (70% polyphosphate and 30% orthophosphate) was initially introduced to the flow through as a corrosion inhibitor. Pure orthophosphate was not initially considered due to a reputation for creating “red water”. The 70/30 blend was introduced to the finished water at 4 parts per million (ppm) as recommended by the distributor. Within two weeks, the lead residuals rose above 30,000 times the lead MCL (Figure 6). A 30/70 polyphosphate blend (30% polyphosphate and 70% orthophosphate), added at 4 ppm, replaced the 70/30 blend. It was hoped that the reduction of polyphosphates would decrease lead residual yet prevent “red water”, which was believed to be a concern with orthophosphates. Lead residuals thousands of times the lead MCL were also present in samples treated with the 30/70 blend, also For this reason, the lead results from the polyphosphate blend data are not discussed because the poor performance rendered polyphosphate blends inappropriate for use in drinking water systems with any leaded features. However, the data collected from the cast iron pipes, while polyphosphates were introduced to the flow-through, has been statistically examined. The use of polyphosphate blends was terminated after eight months due to the high lead residuals in the lead pipes and brass fixtures of the flow-through system. For three weeks, the pipe rack did not have any corrosion inhibitor introduced into the effluent and sampling was halted. After the three-week period to evaluate options, orthophosphate was introduced to the pipe rack, at 2 ppm, and sampling continued.

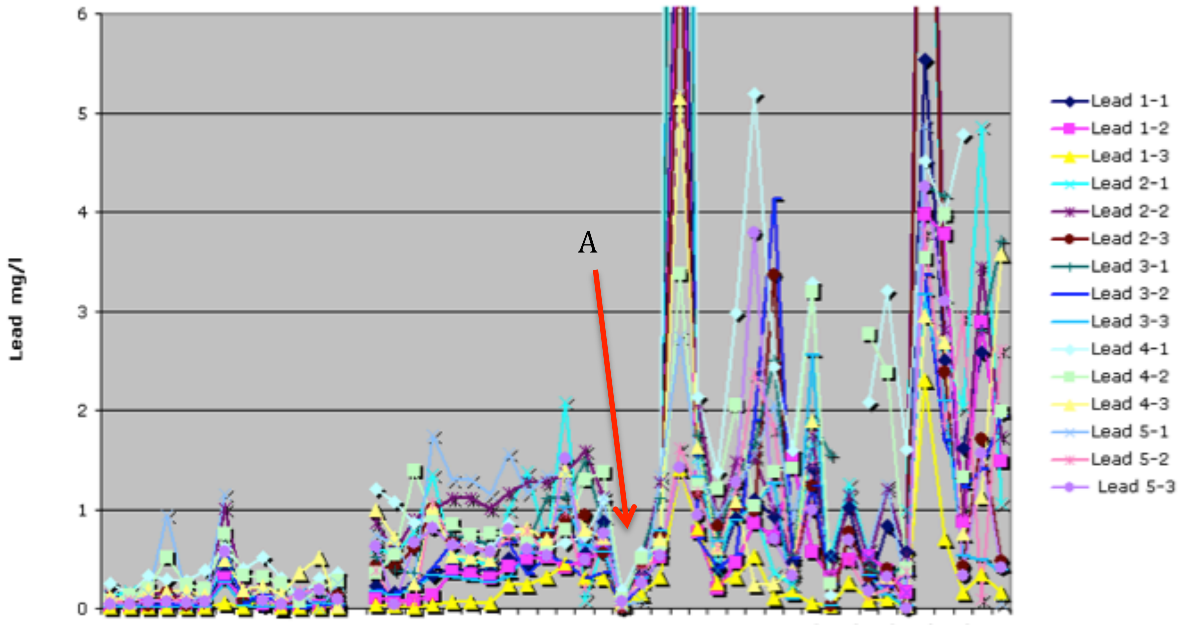

Figure 6. Increase of lead residuals after introduction of polyphosphate blends in lead pipes (mg/L).

Orthophosphate has been employed successfully at utilities in Washington DC and Greensboro, North Carolina [AH Environmental Consultants, 2005]. Other studies have showed that orthophosphate-based corrosion inhibitors are superior to other chemicals in controlling the leaching of lead from brass faucets [AH Environmental Consultants, 2005] as well as lead piping [Edwards and Triantafyllidou, 2007]. The introduction of orthophosphate showed immediate results in the BWWB flow through and lead residuals were consistently near or below the MCL's on the majority of samples collected from the lead piping and brass fixtures [Heberling and Barron, 2012; Heberling *et al.*, 2009].

Six months after the introduction of pure orthophosphate to the flow-through system, chlorine was converted to chloramines using liquid ammonia injected into the flow-through system from the same reservoir used to introduce the corrosion inhibitors. An excess of ammonia was intentionally created to produce an environment conducive to nitrification. The ammonia excess was between 1.0 and 1.5 mg/L since this was greater than 10 times the optimal maximum ammonia excess of 0.1 mg/L yet well below the EPA advisory level of 30 mg/L [AWWARF, 2004]. There was no evidence of growth of nitrifying bacteria when the chlorine "burn out" was initiated. Six months after the introduction of chloramines, ammonia injection was terminated to allow a chlorine "burn out" condition to commence. The "burn out" was achieved by discontinuing introduction of ammonia in the flow-through rack thus resuming chlorine as the primary disinfectant. This is the standard procedure for eliminating nitrifying bacteria in a chloraminated distribution system [Heberling *et al.,* 2009]. Samples were collected for an additional two months and the flow-through procedure was terminated. The last condition was terminated after only two months because the CFP was instituting valve replacement activity, which could not be postponed and the flow-through system created an obstruction to the work [Heberling *et al.*, 2009].

There were no gaps in data collection between the introduction of orthophosphate and the termination of the project. Though allowing a stabilization of treatment is a common practice, this was avoided in order to simulate conditions found in water treatment after the initialization of new treatment methods. In the water industry, production may not be terminated to customers to allow optimal conditions. Destabilization resulting from changing methods must be considered when implementing new treatment methods.

As mentioned earlier, the section of cast iron pipe, lead pipes and brass fixtures designated as Section 4 had high turbidity readings and were not compared with low turbidity data. The data set designated Brass "Burn Out" was not analyzed using any statistical method. This data set was over 90% non-detect data points, meaning, a majority of points were below the detection limit of the sample method. There is no recommended analysis for data sets exceeding 90% non-detects [USEPA, 2006c; Antweiler and Taylor, 2008].

Water samples were collected from piping and brass fixtures. The water in the lead pipes and brass fixtures were sampled for total lead. The cast iron pipes were sampled for total iron. It has been suggested that high turbidity waters reduce the effectiveness of phosphate-based corrosion inhibitors [Schock, 1989; LeChavillier *et al.*, 1993; Lytle and Schock, 2000] including orthophosphate [Lytle and Snoeyink, 2002]. With this in mind, the group 4 lead pipe, cast iron pipe and brass fixture data was not compared with the rest of the lead data, since these samples had very high turbidity.

True and apparent color was analyzed throughout the flow-through study. When corrosion inhibitors were used for a period of more than four weeks, true color never exceeded 30 Color Units (c.u.), which is the maximum allowed under the EPA color nuisance regulations. The use of c.u. is the most popular standard measure of color and is based on the cobalt platinum color scale [DFAS, 2004]. Throughout the study, there was no evidence of "red water" or noticeable particles or sediments in the low turbidity samples.

Innovations of the BWWB Flow-Through Study

This study has made many specific contributions and discoveries to the study of corrosion and corrosion inhibitors that were sparsely investigated or absent from literature. In particular, this investigation used elements directly harvested from an active distribution system. Using field-weathered elements provides insight into physical and chemical behaviors that cannot be replicated using metal slugs or coupons. Simultaneous observations were made of metal components found in a distribution system. Water flowed through cast iron into lead and brass components, as would happen in an active distribution system. The low alkalinity source water used in this study encouraged maximum possibility for corrosion as a result of the water's aggressiveness.

Rigorous statistical methods applying tests specifically designed for non-parametric data sets were used in this study. Too often, default tests, not specifically, applicable to corrosion data sets are chosen for analysis (such as ANOVA). The data in this study was examined taking into consideration data distribution, variance, and non-detects when selecting tests. The method for selecting statistical tests is more rigorous than methods applied in the literature.

Direct comparisons were examined between three types of phosphate corrosion inhibitors. Collected evidence was examined to determine if orthophosphate encourages "red water" as sometimes suggested by corrosion inhibitor distribution representatives. Several hundred data points for contrasting lead residuals in chlorinated water (with and without orthophosphate) and chloraminated water (with orthophosphate) were collected. Burn out conditions were created to examine the consequences of nitrification control strategies on distribution pipes and fixtures.

This study provided evidence to confirm previous studies that polyphosphate inhibitors can drastically increase lead residuals in lead bearing plumbing features. Also, the study was not reactive. Corrosion inhibitors and chloramines were tested as a pilot study, before any consideration of implementation in the BWWB distribution system. Therefore, at no time, was BWWB water quality or customer public health in any potential danger from the activities in this study.

Description Data Sets / Lead Pipes and Brass Fixtures

Total lead samples were collected and analyzed from stagnant water samples in the lead pipes and brass fixtures of the BWWB flow-through system. The data sets are grouped into the following categories representing four treatment conditions applied to the BWWB flow-through system. Samples were collected in the lead pipes and brass fixtures for each condition. As mentioned earlier, samples from sections 1, 2, 3, and 5 were grouped excluding high turbidity samples from Section 4. The abbreviations listed for each condition will appear in subsequent tables. Water samples were collected weekly.

Lead Pipe Chlorine, Brass Chlorine (LC, BC)

The data points were collected before any corrosion inhibitor was introduced to the flow-through system. For six months, chlorinated finished water from the H.Y Carson Filter Plant (CFP), untreated with inhibitors, passed through the flow-through system.

Lead Pipe Chlorine Orthophosphate; Brass Chlorine Orthophosphate (LP, BP)

After ten months of an unsuccessful attempt to apply polyphosphates as a corrosion inhibitor, orthophosphate was introduced to the chlorinated finished water from the CFP passing in the flow-through system.

Lead Pipe Chloramines Orthophosphate; Brass Chloramines Orthophosphate (LNH, BNH)

Following a stabilization of six months, ammonia was added to the flow through for an additional six months. Samples were collected to examine the effects of introducing chloraminated CFP water (treated with orthophosphate) to the piping and fixtures of the BWWB flow-through system.

Lead Pipe Burn Out (LB)

For the last two months of the flow-through project, ammonia was no longer introduced and chlorinated finished water from the CFP, treated with orthophosphate, entered the flow-through system. The brass fixture samples had over 90% non-detects and the data was not statistically analyzed as previously described.

Description of Data Sets / Cast Iron Pipes

Total iron samples were collected and analyzed from stagnant water samples in the ten-foot cast iron pipes of the BWWB flow-through system. The data sets are grouped into the following categories representing six treatment conditions applied to the BWWB flow-through system. As mentioned earlier, samples from Sections 1, 2, 3, and 5 were grouped excluding high turbidity samples from Section 4. Water samples were collected weekly.

Cast Iron Pipe Chlorine (IC)

Data was collected before any corrosion inhibitor was introduced to the flow-through system. For six months, chlorinated finished water (untreated with inhibitors) passed through the flow-through system.

Cast Iron Pipe Chlorine Polyphosphate 70/30 (IC70/30)

For three months, samples were collected from stagnant water in the cast iron pipes that was treated with a corrosion inhibitor containing a polyphosphate blend of 70% polyphosphate and 30% orthophosphate.

Cast Iron Pipe Chlorine Polyphosphate 30/70 (IC30/70)

For five months samples were collected from stagnant water in the cast iron pipes that was treated with a corrosion inhibitor containing a polyphosphate blend of 30% polyphosphate and 70% orthophosphate.

Cast Iron Pipe Chlorine Orthophosphate (ICO)

After a three-week suspension of corrosion inhibitors, orthophosphate was introduced to the chlorinated finished water passing in the flow-through system for six months.

Cast Iron Pipe Chloramines Orthophosphate (INH)

Ammonia was added to the flow-through system for an additional six months. Samples were collected to examine the effects of introducing chloraminated water (treated with orthophosphate) to the cast iron pipes of the BWWB flow-through system.

Cast Iron Pipe Burn Out (IB)

For the last two months of the flow-through system project, ammonia was suspended and chlorinated finished water, treated with orthophosphate, entered the flow-through system. This condition was intended to mimic the procedure of a chlorine "burn out."

STATISTICAL ANALYSIS OF THE BWWB FLOW-THROUGH DATA

The data collected from the BWWB study was statistically analyzed to determine differences in metal corrosivity between chloraminated and chlorinated water flowing through the BWWB flow-through system. No data collected with polyphosphate blends as a corrosion inhibitor are compared, for lead pipe and brass fixture data, since the high lead residuals in samples from water treated with polyphosphates suggest that polyphosphate blends should never be used in drinking water distribution systems with any leaded features. The incredibly high residuals produced by finished water treated with polyphosphate blends confirmed previous study findings that polyphosphates should not be used in distribution systems with lead containing elements [Edwards and McNeill, 2002; USEPA, 1993; Holm and Schock, 1991; Cantor *et al.,* 2000; Hozalski *et al*., 2005]. This includes lead piping, solder, brass alloyed with lead, and lead containing pipe scales. In addition, since virtually any home may have lead containing fixtures in their plumbing system, polyphosphate blends can prove harmful even in new or rehabilitated distribution systems. Samples from the cast iron pipes were statistically examined for the three corrosion inhibitors used in the study; two polyphosphate blends and orthophosphate. All statistical packages and software used in this analysis are listed in Appendix A.

Normality

The tests for normality postulate a null hypothesis (H_0), that the data sets display a more symmetric distribution the higher the *p* value [Healy, 1996]. Six statistical methods used to determine normality for this study are: the Kolmogorov-Smirmov Single Sample test, The Anderson Darling test, the Anscombe-Glynn test, the Jarque-Bera test and the D'Agostino's skewness test [Shapiro and Wilk, 1965; Anderson and Darling, 1952; Anscombe and Glynn, 1983; Jarque and Bera, 1980; and D'Agostino *et al*., 1990]. As mentioned previously, The Shapiro-Wilk test is not recommended for a population of over 50 members [Shapiro and Wilk, 1965]. Data sets LC. LP, LNH, and LB all contained greater than 50 points and were therefore, not analyzed using the Shapiro-Wilk Test.

None of the *p* values for any lead data set, using any of six normality tests, are at or above 0.01 (see Table 4). Only the *p* values for IC 70/30 exceeded 0.01 (see Table 5). The *p*-values for the data set IC 70/30 indicated that the set likely follows a normal distribution. However, none of the other iron data sets can be considered to exhibit a normal distribution. Therefore, none of the lead data sets and only one cast iron data set can be considered to have a normal distribution, i.e., the H_0 for a normal distribution is rejected in all but one set. This is important because it has been demonstrated that non-parametric comparison methods have stronger power when contrasting data from non-normal sets or non-normal versus normal sets. Therefore, a non-parametric statistical comparison method may be more applicable for all data (i.e, not a *t*-test or ANOVA) [Bridge and Sawilowsky, 1999]. Histograms for the collected data can be found in Appendix D.

Table 4.

Normality tests p-*values for lead pipes and brass fixtures.*

	Shapiro Wilk	Kolmogorov Smirmov	Anderson Darling	Anscombe Glynn	Jarque Bera	D'Agostino
LC	N/A	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$
LP	N/A	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$
LNH	N/A	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$
LB	N/A	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$
BC	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$
BP	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$
BNH	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$

Table 5.

Normality tests p-*values for cast iron pipes.*

	Shapiro Wilk	Kolmogorov Smirmov	Anderson Darling	Anscombe Glynn	Jarque Bera	D'Agostino
IC	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$
IC 70/30	$p= 0.75$	$p= 0.61$	$p= 0.57$	$p= 0.52$	$p= 0.57$	$p= 0.69$
IC 30/70	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$
ICO	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$
IHN	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$
IB	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$	$p<0.01$

Addressing Outliers and Non-Detects

All BWWB flow-through data has been analyzed using substitution with zero for all censored data and the detection limit for all data reported as non-detects (censored data). Normally, a non-parametric substitution would be recommended for this data. However, there was no difference in the level of significance (for $\alpha = 0.10, 0.05, 0.01$) in any of the data sets whether all censored data was replaced by zero (i.e., the minimum p value possible) or the detection limit (i.e., the maximum p value possible). Therefore, the substitution method used had no bearing on the analysis. All p-values given were achieved using a substitution value of 0.00 for censored data.

Comparison of Variance

Variance similarities among compared sets influence which statistical methods are more applicable for a comparison test. The F, Lavene's, and Brown Forsythe tests, briefly described earlier, were applied to the lead and brass data sets. The results, assuming a null hypothesis (H_0) stating that the variances are equal, found that each of the variance comparisons for each test had p values below 0.01. The low p values indicate that the H_0 for similar variance should be rejected. Therefore, a non-parametric method, that is less sensitive to wide ranging variances, should be used for comparing the data populations.

The *F*, Lavene's, and Brown Forsythe tests were applied to the cast iron data sets, as well. The results, assuming a null hypothesis (H_0) stating that the variances are equal, found that each of the variance comparisons with, the exception of two pairs of data sets, had *p* values below 0.01. The two sets that showed similar variances are listed in Table 6, along with Lavene's and Brown Forsyth tests *p*-value results. The F-test results are not displayed since all but one data set was non-normal and the *F*-test is a parametric test. The low *p* values (<0.01) for the remaining comparisons indicate that the H_0 for similar variance should be rejected.

Table 6.

Test results for comparisons determined to have similar variances.

Data Sets Compared	*p* - value of Variance Test Lavene's Test	 Brown Forsyth Test
IC and ICO	0.524	0.610
INH and IB	0.186	0.145

Trend Analysis

Trend analyses were performed using the Mann-Kendall test, the Thiel Sen test and a linear regression coefficient of determination (R^2) [USGS, 2002; Healy, 1996]. None of the tests determined a trend in any of the data sets; lead pipes, brass fixtures, or cast iron pipes for any tested condition.

Statistical Comparison of Data

The lead data populations for the lead pipes and brass fixtures showed no symmetry characteristic of a normal distribution. Only one data set from the cast iron pipes showed symmetry consistent with a normal distribution. Commonly used statistical comparison tests such as ANOVA and its companion test for two populations, the Student's *t*-test, are not as powerful when analyzing data populations that do not display a normal distribution [Helsel, 2012; Wysock *et al.*, 1995]. The Welch's *t* test, briefly described previously, is an adaptation of the *t*-test for comparing data sets with different population sizes and variance [Welch, 1947]. However, like the *t*-test, the Welch's *t*-test performs better in comparisons of data with Gaussian distributions [Allingham and Rayner, 2011]. The data displayed little homoscedasticity (homogeny of variance) and it has been reported that the Wilcoxon method loses power under those conditions [Fagerland and Sandvik, 2009]

Since the data population, were determined to not be Gaussian, and variances were unequal, the two sample Kolmogorov-Smirnov test (KS2) is likely, the most appropriate comparison test for the lead corrosion data. The KS2 provides an additional advantage since most of the data sets had populations of over 50 points. Tables 7 and 8 show the *p*-values from the KS2 test for the lead pipes and brass fixtures. Table 9 shows the KS2 results for cast iron data. Each value in the cells represents a comparison between the condition listed in each row and column.

Table 7.

Comparisons of the four treatment conditions in lead pipes of the BWWB flow-through system (using the Kolomogorov Smirnov two sample test).

	LC	LP	LNH	LBO
LC		$p<0.0001$	$p<0.0001$	$p<0.0001$
LP	$p<0.0001$		$p=0.002$	$p<0.0001$
LNH	$p<0.0001$	$p=0.002$		$p<0.0001$
LBO	$p<0.0001$	$p<0.0001$	$p<0.0001$	

Table 8.

Comparisons of the four treatment conditions in brass fixtures of the BWWB flow-through (using the Kolomogorov Smirnov two sample test).

	BC	BP	BNH
BC		$p<0.0001$	$p= 0.026$
BP	$p<0.0001$		$p= 0.383$
BNH	$p= 0.026$	$p= 0.383$	

Table 9.

Comparisons of the six treatment condition p-values in the cast iron pipes of the BWWB flow-through study (using the Kolomogorov-Smirnov two sample test).

	IC	IC70/30	IC30/70	ICO	IHN	IB
IC		$p<0.0001$	$p<0.0001$	$p<0.0001$	$p<0.0001$	$p<0.0001$
IC70/30	$p<0.0001$		$p=0.974$	$p=0.004$	$p=0.001$	$p=0.005$
IC30/70	$p<0.0001$	$p=0.974$		$p=0.015$	$p=0.004$	$p=0.009$
ICO	$p<0.0001$	$p=0.004$	$p=0.015$		$p<0.0001$	$p<0.0001$
IHN	$p<0.0001$	$p=0.001$	$p=0.004$	$p<0.0001$		$p=0.931$
IB	$p<0.0001$	$p=0.005$	$p=0.009$	$p<0.0001$	$p=0.931$	

The null hypothesis (H_0) for the KS2 states that the compared sets are not statistically different. Only one population comparison for the lead pipes and brass fixtures (Brass Chlorinated with Ortho [BP] versus Brass Chloraminated with Ortho [BNH]) was statistically identical ($\alpha > 0.05$) and all other lead pipe and brass fixture comparisons were statistically different.

The data was analyzed using the Kolmogorov-Smirmov two-sample test to determine if the lead pipes and brass fixtures data sets were statistically different. Introduction of chloramines to the finished water treated with orthophosphate resulted in no statistically significant increase of lead residuals in the brass fixtures (relative to chlorinated water with orthophosphates) and a statistically significant decrease in lead residuals in the lead piping upon the introduction of chloramines. The reduction continued when the chlorine "burn out" condition was initiated in both the lead pipes and brass fixtures. The lead residuals in the pipes and brass fixtures were consistently below the MCL's for lead in drinking water. There was no indication of nitrification as a result of producing chloramines with an excess of ammonia. Therefore, the burn out condition was essentially a change from chloramine as the primary disinfectant to chlorine, without the destruction of nitrifying bacteria. It is also possible that the lower numbers in the "burn out" condition were simply a result of the continued application of the orthophosphate and greater stability of pipe scales, regardless of disinfectants used.

Using the KS test, it was determined that results from the conditions of IC 30/70 and IC 70/30 were not statistically different. This suggests that there was no difference in effectiveness between the two polyphosphate blends in reducing iron corrosion. In addition, according to the KS test, the conditions of INH and IB also show no statistical difference. This implies that there is no difference in performance between orthophosphate treated chloraminated water versus chlorinated water (when switched following chloraminated water). The comparisons of IC versus ICO and INH versus IB were also compared using the Wilcoxan Signed Rank test (WSR), since these paired data sets had similar variances. The outcomes generated from the *p*-values of the WSR did not differ significantly from the conditions found with the KS2 test therefore, supporting the findings of the KS2 test, meaning that each test produced similar results.

Graphical comparison

The box plots in Figures 7 and 8 compare the conditions for the lead pipes and brass fixtures of the BWWB flow through study. Conditions studied earlier in the project are to the left, and later in the study to the right. The pipe scales were relatively stable before the introduction of polyphosphates. These box plots show the lead concentrations from samples collected for the given conditions. As discussed earlier, the polyphosphate treated water was not included in the analysis because the lead residuals from drinking water treated with polyphosphates was consistently hundreds to thousands of times above drinking water lead MCL for the pipes and dozens to hundreds of times the MCL for the brass fixtures. Six months of polyphosphates were used before the inhibitors were abandoned in favor of orthophosphate. An increase in lead residuals was noted following the replacement of polyphosphate blends with orthophosphate. Lead residuals continued to drop in the lead pipes, following the introduction of orthophosphate, as the study progressed.

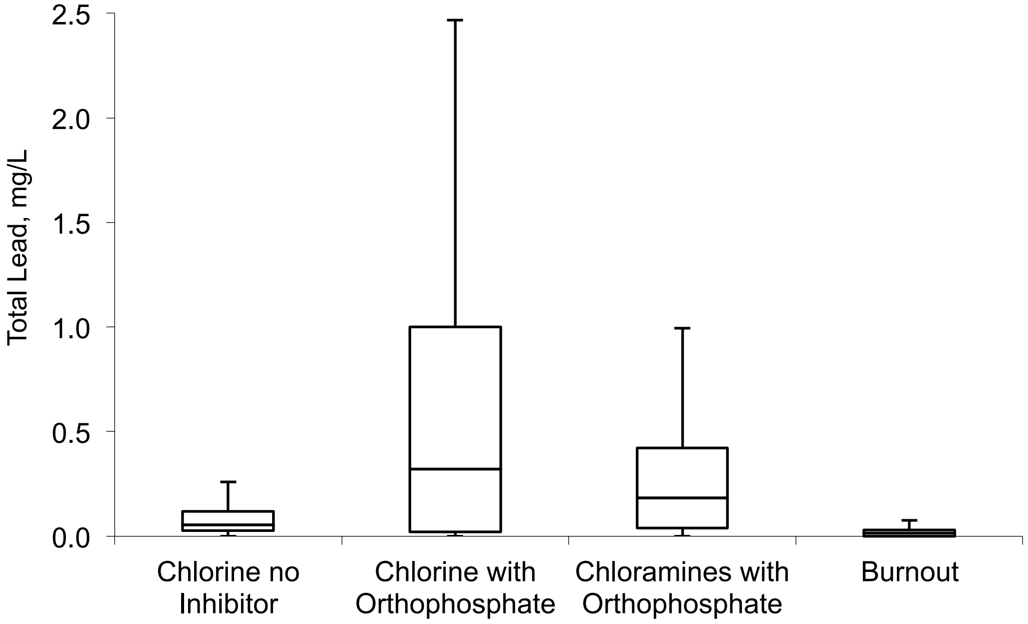

Figure 7. Box plot comparison of the lead corrosion data for the BWWB flow through (lead pipes).

Figure 8 shows box plot data from brass assembly lead residual data. The box plots illustrate the statistical similarity between the conditions of chlorine and chloramines (both coupled with orthophosphates) in the brass assemblies. The condition for burn out is not shown in figure 8 because over 90% of the data points were non-detects. Therefore, the brass fixtures during the burn out phase showed virtually no lead residuals in the brass assembly. The prolonged use of orthophosphate coincided with the reduction of lead residuals in the brass fixtures.

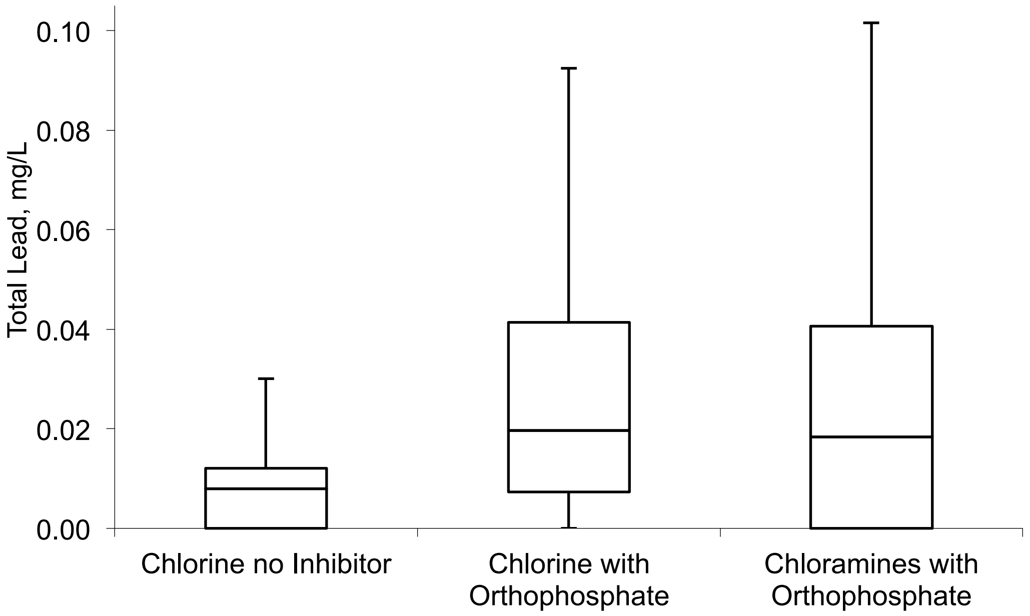

Figure 8. Box plot comparison of the lead corrosion data for the BWWB flow-through study (brass fixtures).

The increased lead residuals present in the chlorine with orthophosphate may have been a result of the use of the polyphosphate blends, before the introduction of orthophosphate. The polyphosphate blends may have destabilized the pipe scales resulting in higher residuals, even after orthophosphate was introduced to the flow-through. Continued use of orthophosphate coincided with a reduction in lead to the point where lead residuals were statistically less than chlorinated water without corrosion inhibitors (Figure 9). The residuals were on average, below the MCL for lead (0.015 mg/L) before the introduction of corrosion inhibitors.

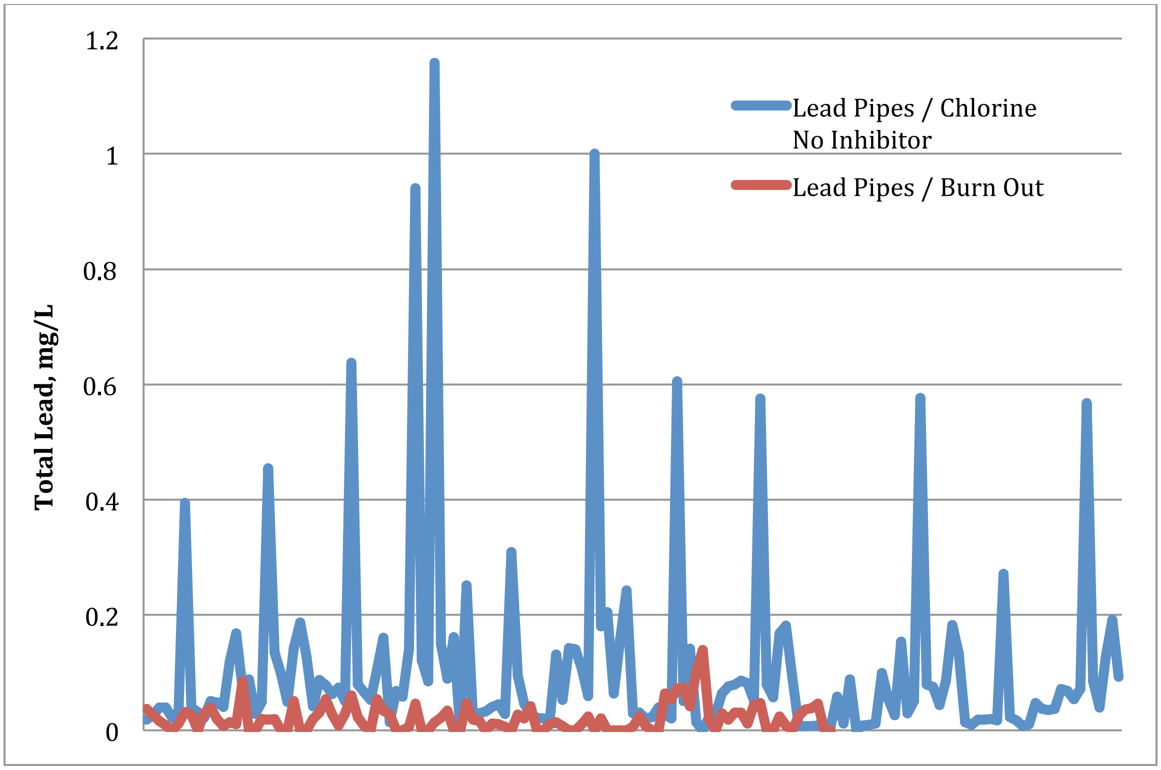

Figure 9. Total lead LC versus LBO (mg/L).

With the introduction of chloramines (coupled with orthophosphate) lead residuals continued to decrease compared to the chlorinated water with orthophosphate (Figure 10). Replacement of chloramines with chlorine in the burn-out phase showed a large reduction in lead residuals. In fact, the termination of chloramine generation with a return to chlorination resulted in a greater than 75% reduction (on average) in the lead piping (Figure 11). As a result, the BWWB determined that chloramines, coupled with orthophosphate, could be introduced to the distribution system as a viable option for DBP control [Heberling *et al*., 2009].

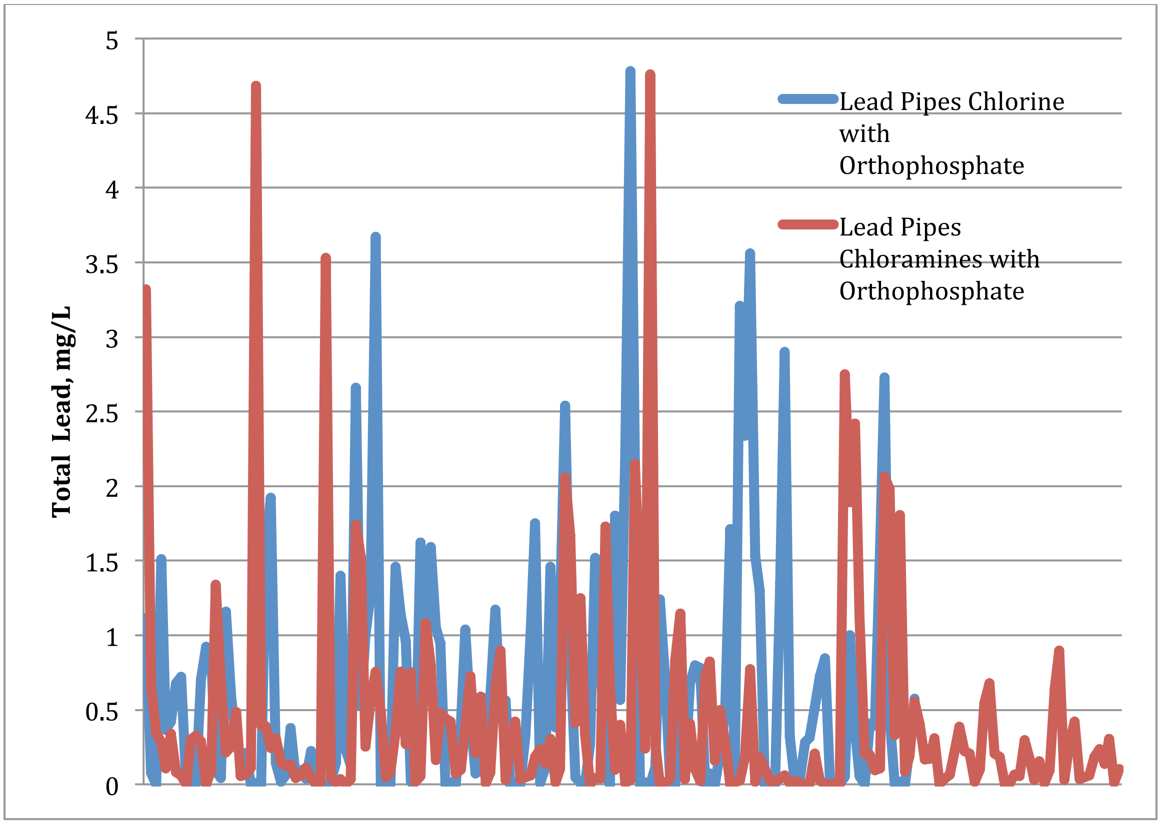

Figure 10. Total lead LP versus LNH (mg/L)

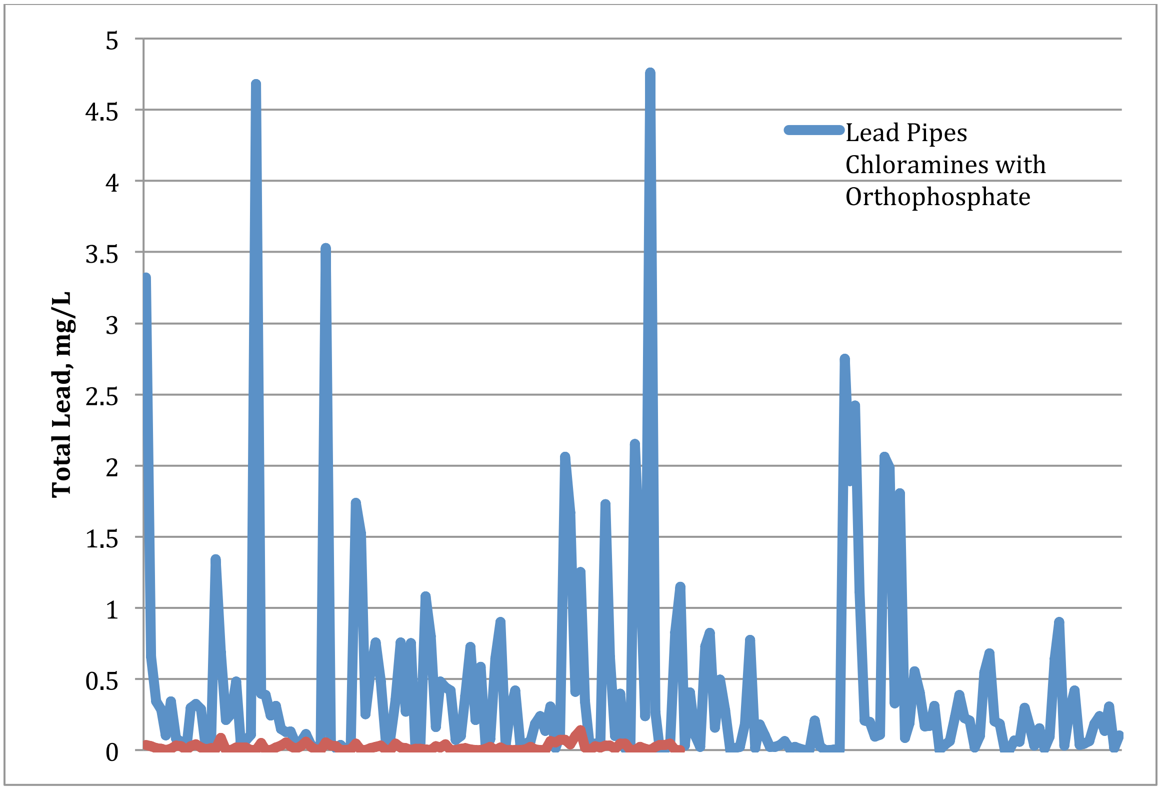

Figure 11. Total lead LNH versus LBO (mg/L)

The primary reason for the BWWB study was to determine if a switch to chloramine from chlorine, as the primary drinking water disinfectant, would result in increased lead residuals in lead piping and brass fixtures. In addition, the study was to investigate if a nitrification control strategy, chlorine burn-out, would result in increased lead residuals in samples collected from the BWWB flow-through system. In both cases, the evidence from this study suggests that chloramination, coupled with an orthophosphate corrosion inhibitor, does not lead to higher lead residuals. It would be unwise to compare effectiveness between the two treatments (orthophosphate and chlorine versus orthophosphate and chloramines, before the burn-out) since orthophosphates were introduced in chlorinated water after a significant time period when no corrosion inhibitor was used. The polyphosphate blends also likely destabilized scales in the lead piping and brass fixtures. However, the data clearly showed that chloramines did not increase lead residuals, which has been suggested in other studies [USEPA, 2004b].

The box plots in Figures 12 and 13 compare the conditions for the cast iron pipes of the BWWB flow-through study. The *y*-axis represents the concentration of total iron in collected samples. Conditions studied earlier in the project are to the left, and conditioned studied later in the project to the right. For reference, the USEPA maximum contaminant level for iron in drinking water is 0.3 mg/l [USEPA, 2006a].

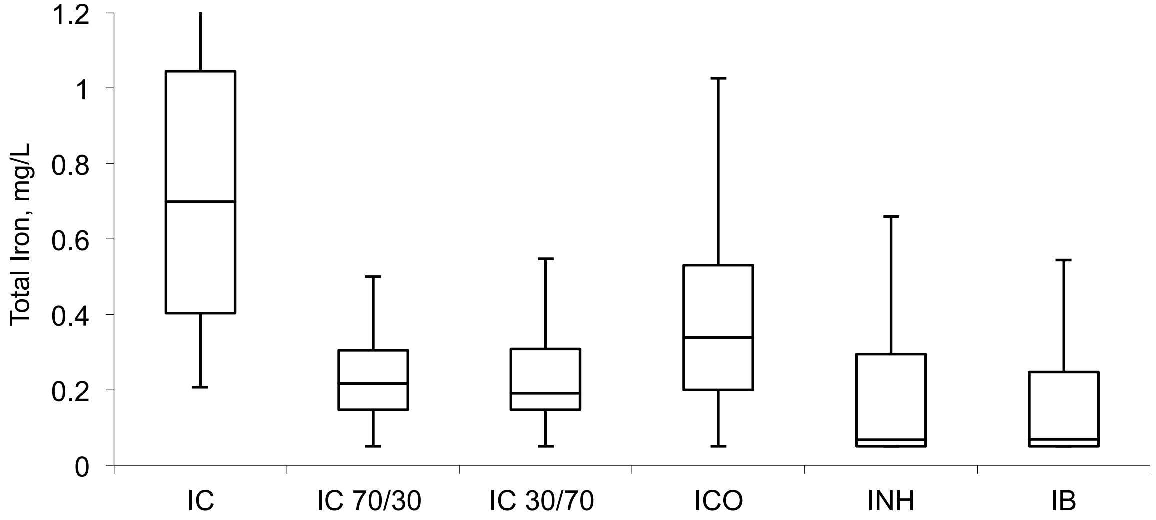

Figure 12. Box plot comparison of the iron corrosion data for the BWWB flow-through study (cast iron pipes).

The findings illustrated in Figure 12 suggest that corrosion is reduced when a corrosion inhibitor (polyphosphate blend or orthophosphate) is introduced in chlorinated or chloraminated water, relative to untreated chlorinated water. The polyphosphate blends performed equally as well and were superior to the chlorinated water with orthophosphates. This may be due to the three-week suspension of polyphosphate blend corrosion inhibitors before the introduction of orthophosphates. The orthophosphates were not outperformed by the polyphosphate blends when chloramines were generated and during the burn-out stage. There was no statistical difference in the performance of orthophosphate during chloramination or the burn-out phases. When chloramines were first generated, the iron residuals dropped, on average, by fifty percent relative to the residuals found in the chlorinated water.

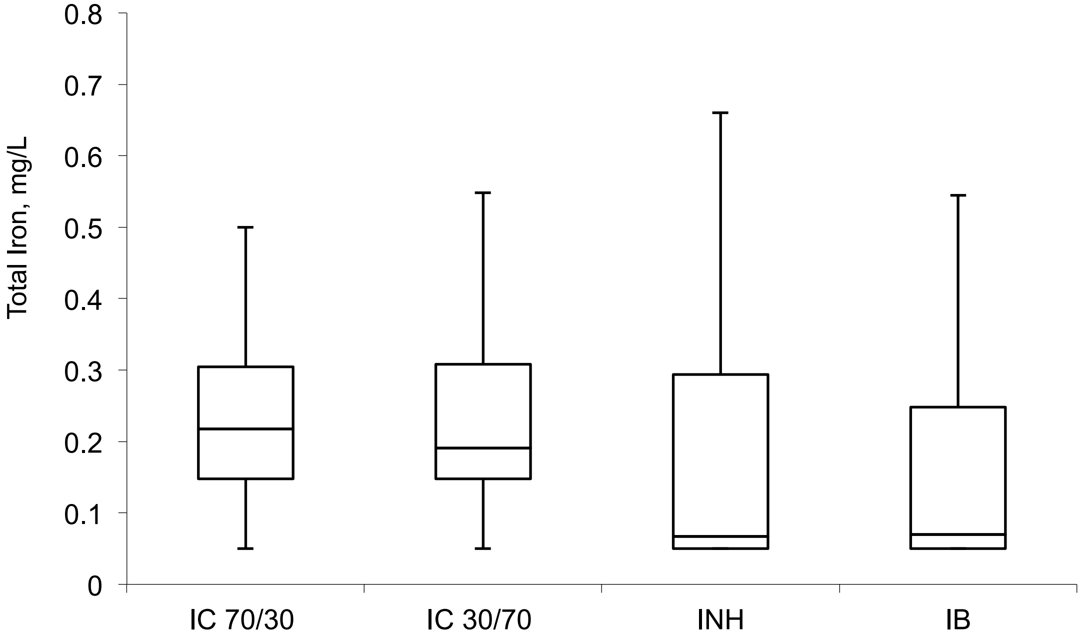

Figure 13. Box plot comparison of the iron corrosion data polyphosphate blends versus orthophosphates.

Figure 13 compares the box plot data for the conditions with polyphosphate corrosion inhibitors and orthophosphate (after weeks of stabilization). Though polyphosphate blends showed a consistent tendency to reduce iron corrosion, as mentioned previously, polyphosphates and polyphosphate blends should never be used in potable water distribution systems if there is the potential for any lead-bearing elements.

Figure 13 excludes ICO because the three-week suspension of corrosion inhibitor may have led to an increase in residuals. What becomes immediately apparent from the BWWB flow-through data is that cast iron pipes left untreated with corrosion inhibitors displayed higher iron residuals than any other treatment condition tested. This may have been a factor in the slightly higher residuals found in the orthophosphate with chlorine (ICO) relative to other conditions with corrosion inhibitors. The three weeks without any corrosion inhibitors may have destabilized pipe scales before the introduction of orthophosphate. After several weeks of stabilization, orthophosphate proved to be an effective corrosion inhibitor in chlorinated water (INH) or water under conditions of chlorine burn-out (IB). While orthophosphate has a reputation of exacerbating iron corrosion, the evidence from this study suggested otherwise. In fact, orthophosphate decreased iron residual greatly reducing the likelihood of “red water” in cast iron pipes. It would be misleading to compare effectiveness between the two treatments (orthophosphate and chlorine versus orthophosphate and chloramines before the burn-out) since orthophosphates were introduced in chlorinated water after a significant time period with no corrosion inhibitor in the flow-through system. The longer orthophosphate was applied, the greater the reduction in iron residuals. Regardless, polyphosphate blends and orthophosphate both consistently lowered iron residuals below the EPA MCL of 0.3 mg/L.

The prevailing wisdom, particularly from chemical vendors, has been that polyphosphate and polyphosphate blends out perform pure orthophosphate in preventing iron residuals in drinking water distribution piping. The evidence from the BWWB study suggest this is not the case and that orthophosphates actually reduce iron residuals after six month stabilization, in chloraminated and chlorinated water. This may be a result in the chemical behavior of the inhibitors. The polyphosphates tendency to sequester iron may lead to increased residuals in the blends relative to pure orthophosphate.

Table 10 displays average values for iron and lead residuals for lead pipes, cast iron pipes, and brass fixtures for all conditions applied to the BWWB flow through. The raw data is listed in Appendix C.

Table 10.

Average values for iron and lead residuals for lead pipes, cast iron pipes, and brass fixtures; BWWB flow-through.

	LC			LP	LNH	LBO
Average Total Lead (mg/L)	0.11			0.65	0.43	0.02
	BC			BP	BNH	
	0.02			0.05	0.01	
Average Total Iron (mg/L)	IC	IC 70/30	IC 30/70	ICO	INH	IB
	0.84	0.23	0.38	0.44	0.20	0.18

In summary, the BWWB flow-through study results indicated the following:

- Polyphosphate blends are unsuitable for drinking water with any lead bearing features;

- Chloramines, coupled with an orthophosphate corrosion inhibitor, will not increase lead residuals in lead bearing features (relative to chlorinated water treated with orthophosphates);

- Changing primary disinfectant from chloramines back to chlorine (while applying an orthophosphate corrosion inhibitor) does not result in increased lead residuals;

- The lowest consistent lead readings occurred during the "burn-out" condition of the flow-through project;

- Drinking water treated with a corrosion inhibitor reduces total iron residuals relative to drinking water without corrosion inhibitors;

- There is no statistical difference between 70/30 and 30/70 blends in their ability to reduce iron corrosion;

- Even temporary suspension of corrosion inhibitors can lead to a rapid and significant increase in iron residuals, which require several weeks of inhibitor re-treatment to reverse;

- Polyphosphate blends and orthophosphate both consistently reduce iron below the EPA MCL of 0.3 mg/L;

- When applied for several months, orthophosphates are statistically more effective than polyphosphate blends in reducing iron residuals;

- There is no statistical difference in the reduction of iron residuals between chloraminated drinking water and chlorinated water (after chloramination is suspended) treated with pure orthophosphate,

- The addition of orthophosphate in the flow-through system did not result in any evidence of "red water" production due to increased iron residual; and

- Prolonged addition of orthophosphate reduces iron and lead residuals whether chlorine or chloramines are used as the primary disinfectant.

FINDINGS

One of the most important observations of this study was a verification of other research, which determined that polyphosphate blends increase lead residuals in lead bearing plumbing features and distribution systems. Introduction of the polyphosphate blends coincided with increased residuals in the BWWB study. The same observations were observed in Edwards and McNeill, 2002; USEPA, 1993; Holm and Schock, 1991; Cantor *et al.,* 2000; and Hozalski *et al*., 2005. Once again, it is important to recognize, that several studies have come to the same conclusions that polyphosphates do not decrease lead corrosion but actually create higher lead residuals. However, polyphosphate blends did show a reduction in iron residuals, from cast iron pipes in the BWWB flow through. These findings were similar to observations by Hatch and Rice, 1939 and 1940; AWWARF, 1990b; and Myers, 2006.

The study did not show any increase of metal residual as a result of the introduction of chloramines in finished water treated with orthophosphate. There was no indication that chloramines showed any measurable tendency toward higher corrosion potential than chlorinated water. In fact, in all tested situations metal residuals dropped when chloramines were added and orthophosphate was kept at a constant concentration. This parallels the findings of the WASA study [USEPA, 2004b]. Water treated with orthophosphates showed lowered residuals in iron and lead as the pilot study progressed. Orthophosphates did not produce “red water” during the study. These findings suggested that chloramines could prove a viable alternative, when coupled with orthophosphate, to chlorine as a primary disinfectant.

The replacement of chloramines with chlorine in the burn-out phase did not increase lead residuals. In fact, the termination of chloramine generation with a return to chlorination resulted in a greater than 95% reduction (on average) of lead residuals in the lead piping. The conditions of chlorine and chloramines (both coupled with orthophosphates) in the brass fixtures were statistically identical. The condition for burn-out is not shown because over 90% of the data points were non-detects. The prolonged use of orthophosphate coincided with the reduction of lead residuals in the brass fixtures.

The findings suggest that iron corrosion is reduced when a corrosion inhibitor is introduced in chlorinated or chloraminated water relative to untreated chlorinated water. The polyphosphate blends performed equally as well and were superior to the chlorinated water with orthophosphates. This may be due to the three-week suspension of polyphosphate blend corrosion inhibitors before the introduction of orthophosphates. The orthophosphates performed better than the polyphosphate blends when chloramines were generated and during the burn-out stage. There was no statistical difference in the performance of orthophosphate during chloramination or the burn-out phases. When chloramines were first generated, the iron residuals dropped, on average, by fifty percent relative to the residuals found in the chlorinated water treated with orthophosphate. The lead residuals continued to drop on average, another 10% during the burn-out phase. The significant reduction of iron residuals may have been due to the prolonged use of orthophosphate during the study.

No “red water” conditions were observed in orthophosphate treated water. This is contrary to research seen in previous studies [AWWARF, 1990b]. More importantly, this is contrary to recommendations given by vendors who recommend polyphosphates because of a perceived “red water” problem with orthophosphates.

SIGNIFICANCE AND CONTRIBUTIONS OF STUDY

As indicated earlier, chloramines have several advantages over chlorine which are appealing to water purveyors. One in particular is that chloramines do not create the same regulated DBP's as chlorine. However, chloramines have been linked to higher metal corrosion, particularly lead. This study has demonstrated that chloramines, coupled with orthophosphate corrosion inhibitors, do not exacerbate lead corrosion under the conditions tested. For the BWWB, this means that chloramines are now a viable solution to combatting DBP's generation and ensuring compliance. With concerns of elevated lead residuals quelled, the BWWB is free to pursue chloramines as an alternative for chlorine.

Also significant are the observations about polyphosphate blends, which confirmed findings in other research. This study provides more evidence that polyphosphate blends are not suited for use in distribution systems where any lead features are present. This research has added to the growing body of knowledge, which indicates that polyphosphates are a public health risk when applied to drinking water, which is distributed through lead bearing plumbing and distribution lines.

Orthophosphates reputation as a generator of "red water" was shown to be unfounded under the conditions of this study. In fact, orthophosphates were superior to polyphosphates in preventing iron corrosion in cast iron pipes. This is important because orthophosphates used as a corrosion inhibitor are superior to polyphosphates in distribution systems with leaded features. The fact that orthophosphate may not encourage "red water" gives utilities an opportunity to consider orthophosphate without concern for increased iron corrosion.

CONCLUSIONS

One of the most important conclusions that can be drawn from the BWWB study was related to the performance of polyphosphate corrosion inhibitors. According to the findings of this study, under no circumstances should polyphosphate corrosion inhibitors be used in any distribution system that may contain leaded elements. Many systems worldwide, even if lead piping has been abandoned for decades, have some leaded features. In addition, many brass fixtures manufactured today worldwide, may contain up to 8% lead. The BWWB flow-through study confirmed what several studies have already postulated; polyphosphates can draw dissolved and particulate lead from leaded plumbing features [Edwards and McNeill, 2002; USEPA, 1993; Holm and Schock, 1991; Cantor *et al.,* 2000; Hozalski *et al*., 2005]. Before the introduction of the polyphosphate blends, the lead residuals were, on average, below the MCL for lead in the brass features and lead pipes

There is a perception that chloramines may lead to increased corrosion, particularly in lead-bearing features. This perception was spurred by an incident in Washington DC involving lead in drinking water during a changeover from chlorine to chloramines as the primary disinfectant. Data collected by the Birmingham Water Works Board (BWWB) from a pilot study using chloramines (coupled with phosphate-based corrosion inhibitors) were statistically examined. These findings were determined using a rigorous and novel method for statistical analysis, which has applications in drinking water corrosion studies in general. Corrosion analysis creates challenges that make cursory statistical analyses inadequate, misleading, or incorrect.

The BWWB study found no statistical difference in corrosivity between chlorinated water treated with orthophosphate versus chloraminated water with orthophosphate in brass fixtures. Nor was there any statistical difference between the two polyphosphate blends in the reduction of iron corrosion. All other compared sets were determined to be statistically different. When applied for several months, orthophosphates are statistically more effective than polyphosphate blends in reducing iron residuals.

Comparisons between the corrosivity of chlorinated water versus chloraminated water (both treated with orthophosphate) were difficult to discern because of a temporary suspension of corrosion inhibitors before the introduction of orthophosphate. Even temporary suspension of corrosion inhibitors can lead to a rapid and significant increase in metal residuals, which require several weeks of inhibitor re-treatment to reverse. However, chloramines, coupled with an orthophosphate corrosion inhibitor, did not increase lead residuals in lead bearing features (relative to chlorinated water treated with orthophosphates). In fact, prolonged use of orthophosphates reduced lead and iron corrosion in the BWWB flow-through system. In addition, orthophosphates did not demonstrate any propensity for creating “red water” problems. In fact, orthophosphate was equally effective in reducing iron and lead corrosion. This was clearly visible in the “burn-out” stage (suspension of chloramines and return to chlorination). Metal residuals under “burn-out” conditions were the lowest for the entire flow-through study.

APPLICATIONS AND RECOMMENDATIONS

Though each utility has its own unique water chemistry and treatment characteristics, the findings of this research study are applicable to utilities worldwide, particularly those with piping fifty years or older with cast iron pipes and lead bearing elements. The source water for this study had an atypical low alkalinity. This means that the water used for this study is more aggressive and more likely to induce corrosion compared to most drinking waters. Therefore, the methods and findings of this study are applicable to a wide range of drinking water chemistries. It should be noted that before a change in water treatment is implemented, rigorous pilot testing is recommended regardless of the findings of this or any other study. The layout of the flow-through system is ideal for utilities interested in pilot studies for chloramines and corrosion inhibitors. A utility can replace or select additional elements for study such as copper piping or ductile iron pipes, for example. Also, a utility can collect additional data on chloraminated water samples allowing for more time for nitrification to occur. A burn-out under conditions of nitrification is likely to give additional information not available from this study, since there was no indication of nitrification in the BWWB flow-through study.

The findings of this dissertation can provide a guide to consultants and drinking water purveyors when considering choices in disinfectants and corrosion inhibitors. The method proposed for statistical investigation may help engineers and researchers select statistical tests appropriate for their collected data. In a business where public health and millions of dollars can be at risk, information provided from the findings of this dissertation may help prevent costly mistakes.

After the conclusion of the BWWB flow-through study, it was determined that under no circumstances should polyphosphates, or polyphosphate blends be used in the BWWB distribution system or any distribution system where lead components are present. As a result of this study, the BWWB discontinued any further testing of polyphosphate and polyphosphate blends and will not consider their use in the future.

The results of this study confirmed that chloramines, coupled with orthophosphate as a corrosion inhibitor, could replace chlorine as the primary disinfectant with no discernable disruption (due to water quality degradation). Any changes in disinfection would need to be phased in gradually to prevent any problems not detected by the pilot flow-through study. Additionally, protocols to prevent nitrification would need to be implemented before full-scale replacement of chlorine with chloramines. The findings of this study have given the BWWB another option in combatting DBP’s in its distribution system.

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APPENDIX A

Statistical Packages Used

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GraphPad Software, Inc. 2013. All rights reserved.

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APPENDIX B

Specific contributions by Dissertation Author

This appendix describes in detail the specific contributions of the author to the dissertation. This includes such aspects as project as maintenance, sampling, chemical feeding, and disassembly of the pilot study. This is by no means complete, since many minor daily tasks were also performed and a detailed description would prove tedious. However the major activities are described in the following paragraphs.

I was not directly involved with the unearthing of pipes, selection of bass fixtures, or construction of the Birmingham Water Works Board (BWWB) flow-through system. These tasks were supervised, recorded, and described to me by Dr. Deborah Myers, who was the primary investigator during the construction of the flow-through system. One month after construction, Dr. Myers found alternate employment and I became the primary investigator in every phase of the project. At this point, I enlisted the help of Dr. Robert Peters of the University of Alabama at Birmingham (UAB) as a primary advisor (along with supervisors at the BWWB). Dr. Peters has collaborated with me in several presentations and conference proceedings papers detailing results from the flow-through study.

The flow-through system was designed with five different sections, which were intended to measure four water treatment conditions with one control simultaneously. However, one section, section four, showed consistently higher turbidity than the other four sections. Upon receiving full command of this project, I decided that all section would receive drinking water under identical conditions starting with water untreated with a corrosion inhibitor. Samples collected from the four lower turbidity sections were analyzed together, giving a significantly larger population of data points. The high turbidity samples were analyzed separately, giving an opportunity to compare and contrast high turbidity water data with lower turbidity water data. Data analysis for section four pipes and features were not described for this dissertation.

A critical juncture in the project was the introduction of polyphosphate blend corrosion inhibitor. Dr. Myers intended to introduce a 70/30 polyphosphate / orthophosphate blend to the flow through pilot study at start up. She was unsuccessful after one month due to a pump maintenance problem. When I inherited this project, I was able to successfully address the pump problems. I elected to wait an additional two months before introducing the corrosion inhibitor in order to obtain three months of data before the introduction of corrosion inhibitors or ammonia.

After four weeks of the introduction of the polyphosphate blend, a significant increase in lead residuals was found in all lead pipes and brass fixtures. I immediately determined, through an extensive comprehensive literature review, that the likely culprit was the polyphosphate blend chemically reacting with the lead pipes and brass fixtures. I immediately recommended the polyphosphate blend be replaced with pure orthophosphate. The BWWB elected to use a 30/70 blend (polyphosphate and orthophosphate). After two weeks, it became clear that the 30/70 blend encouraged similar high lead residuals and was replaced with orthophosphate, my original recommendation. Though the polyphosphate blends were replaced with orthophosphate, eight months of valuable data was collected regarding iron corrosion and polyphosphate blends. Samples collected from the lead pipes and brass fixtures, which were treated with polyphosphates, showed incredibly high residuals. These residuals were not statistically compared since the concentrations were, in some cases, thousands of times above the Environmental Protection Agency's (EPA) maximum contaminant level (MCL)

I collected over 90% of all samples and performed all statistical analyses and comparisons. I was responsible for generation of chloramines using aqueous ammonia pumped into chlorinated water. I was responsible for all maintenance of the flow-through system and supervised its demolition.

All laboratory sampling was performed by the BWWB's accredited lab, Envirolab. I was trained by laboratory staff in the operation of all equipment used in determining metal concentrations in collected samples including the mass spectrometer. I performed 90% of all collected samples field parameters. I coordinated with the BWWB QA/QC manager and obtained reports for all quality control for sample analyses.

I performed all statistical analyses using various software packages (See Appendix A). Selection of statistical methods was based on literature reviews and guidance from dissertation committee members. I created all figures and tables for this dissertation or other referenced publications. All sections of this dissertation were written for this dissertation with input and editing from the dissertation committee.

APPENDIX C

Raw Data

Table C1.

Lead Pipe and Brass Fixture Data Chlorinated Water – No Corrosion Inhibitors, mg/L

Lead 1-1	0.019	0.026	0.039	0.040	0.022	0.033	0.395	0.04	0.032	0.022	0.051	0.048	0.041
Lead 1-2	0.021	0.030	0.033	0.041	0.045	0.028	0.309	0.095	0.046	0.026	0.022	0.021	0.018
Lead 1-3	0.007	0.007	0.007	0.008	0.011	0.007	0.058	0.012	0.088	BDL	0.009	0.010	0.012
Brass 1	0.082	0.007	BDL	BDL	0.012	BDL	0.011	0.012	0.010	BDL	0.006	0.000	
Lead 2-1	0.119	0.168	0.073	0.088	0.028	0.050	0.454	0.135	0.098	0.050	0.143	0.187	0.127
Lead 2-2	0.132	0.053	0.143	0.141	0.107	0.059	1.001	0.180	0.205	0.064	0.158	0.243	0.029
Lead 2-3	0.100	0.054	0.026	0.154	0.030	0.051	0.577	0.080	0.075	0.044	0.086	0.183	0.134
Brass 2	0.002	0.008	0.008	0.011	0.011	0.009	0.035	0.026	0.017	BDL	0.007	BDL	0.007
Lead 3-1	0.042	0.087	0.078	0.063	0.074	0.051	0.638	0.080	0.066	0.053	0.105	0.161	0.014
Lead 3-2	0.031	0.021	0.023	0.039	0.027	0.021	0.605	0.051	0.142	0.014	0.000	0.023	0.028
Lead 3-3	0.014	0.010	0.018	0.019	0.020	0.017	0.271	0.023	0.017	0.007	0.011	0.047	0.037
Brass 3	0.007	BDL	BDL	BDL	0.021	0.007	0.058	0.010	0.009	0.007	0.000	0.000	0.010
Lead 5-1	0.068	0.058	0.140	0.940	0.122	0.085	1.160	0.149	0.089	0.162	BDL	0.252	0.014
Lead 5-2	0.064	0.076	0.079	0.086	0.082	0.052	0.576	0.080	0.057	0.168	0.182	0.092	0.028
Lead 5-3	0.035	0.037	0.072	0.068	0.054	0.072	0.568	0.085	0.040	0.130	0.191	0.093	0.037
Brass 5	0.016	0.027	0.024	0.015	0.038	0.01	0.346	0.041	0.036	0.040	0.071	0.007	0.010

BDL – Below Detection Limit

Table C2.

Lead Pipe and Brass Fixture Data Chlorinated Water – Orthophosphate Corrosion Inhibitors, mg/L.

Lead 1-1	1.117	0.078	BDL	1.510	0.364	0.421	0.679	0.722	BDL	0.027	BDL	0.705	0.923
Lead 1-2	0.877	0.091	0.042	1.160	0.597	0.280	0.181	0.209	BDL	0.007	BDL	1.570	1.920
Lead 1-3	0.143	0.019	0.066	0.379	0.044	0.094	0.038	0.225	BDL	0.020	BDL	0.023	0.146
Brass 1	0.019	BDL	0.026	0.050	0.040	0.041	0.025	BDL	BDL	0.021	0.011	0.022	

Lead 2-1	1.400	0.233	0.131	2.660	0.525	1.000	1.280	3.67	BDL	0.033	BDL	1.460	1.140
Lead 2-2	0.962	0.017	0.067	1.620	0.851	1.590	1.050	0.949	BDL	0.013	BDL	0.387	1.040
Lead 2-3	0.457	0.074	0.094	0.578	0.579	1.170	0.512	0.562	BDL	0.015	BDL	0.329	1.010
Brass 2	0.014	0.007	0.275	0.044	0.010	0.052	0.100	0.032	BDL	BDL	BDL	0.007	0.013

Lead 3-1	1.750	0.009	0.113	1.460	0.384	1.170	2.540	0.924	0.045	0.011	BDL	0.272	1.520
Lead 3-2	0.888	0.051	BDL	1.800	0.568	2.240	4.780	2.160	BDL	0.014	BDL	0.118	1.240
Lead 3-3	0.725	0.033	BDL	1.130	0.052	0.675	0.799	0.780	BDL	0.074	BDL	0.210	0.484
Brass 3	0.017	0.780	0.049	0.975	0.047	0.054	0.060	0.061	0.023	BDL	BDL	BDL	0.022

Lead 5-1	1.710	0.322	0.360	0.026	1.710	0.322	0.360	0.026	1.710	0.322	0.360	0.026	1.710	0.322
Lead 5-2	0.049	0.008	0.057	0.023	0.049	0.008	0.057	0.023	0.049	0.008	0.057	0.023	0.049	0.008
Lead 5-3	3.210	0.045	BDL	0.129	3.210	0.045	BDL	0.129	3.210	0.045	BDL	0.129	3.210	0.045
Brass 5	2.340	0.285	0.410	0.065	2.340	0.285	0.410	0.065	2.340	0.285	0.410	0.065	2.340	0.285

BDL – Below Detection Limit

Table C3.

Lead Pipe and Brass Fixture Data Chloraminated Water – Orthophosphate Corrosion Inhibitors, mg/L.

Lead 1-1	3.320	0.660	0.344	0.283	0.106	0.341	0.084	0.0615	BDL	0.300	0.327	0.290	BDL	0.096
Lead 1-2	1.340	0.689	0.214	0.254	0.484	0.0575	0.0663	0.111	4.683	0.396	0.389	0.245	0.310	0.148
Lead 1-3	0.126	0.132	0.0441	0.0605	0.112	0.0383	0.0149	0.0155	3.529	0.0483	0.0148	0.0358	BDL	0.0339
Brass 1	0.024	0.057	0.0302	0.0209	BDL	BDL	0.00755	0.0841	0.0332	0.0198	0.0202	BDL	0.049	BDL

Lead 2-1	1.740	1.520	0.253	0.557	0.755	0.481	0.049	0.085	3.500	0.757	0.269	0.753	0.019	0.057
Lead 2-2	1.080	0.804	0.164	0.483	0.443	0.419	0.073	0.099	0.383	0.726	0.212	0.588	0.009	0.079
Lead 2-3	0.644	0.899	0.032	0.275	0.421	0.036	0.047	0.062	0.185	0.238	0.138	0.305	0.013	0.103
Brass 2	BDL	0.061	0.008	0.017	0.032	0.387	BDL	0.021	0.252	0.016	0.009	BDL	BDL	BDL

Lead 3-1	2.060	1.670	0.411	1.250	0.341	BDL	0.045	0.039	1.73	0.652	0.098	0.398	0.009	0.031
Lead 3-2	2.150	1.330	0.240	4.760	0.266	BDL	0.007	0.037	0.831	1.147	0.033	0.408	0.103	0.024
Lead 3-3	0.728	0.826	0.158	0.498	0.278	BDL	0.013	0.025	0.185	0.773	0.017	0.18	0.103	0.022
Brass 3	0.022	0.038	0.0624	0.008	0.0231	0.011	BDL	0.007	0.208	0.027	BDL	BDL	0.007	BDL

Lead 5-1	2.75	1.89	2.420	1.117	0.208	0.200	0.094	0.108	2.064	1.984	0.329	1.806	0.088	0.188	2.750	1.890
Lead 5-2	0.555	0.404	0.166	0.171	0.310	BDL	0.038	0.064	0.232	0.386	0.226	0.206	0.017	0.101	0.555	0.404
Lead 5-3	0.547	0.680	0.205	0.185	BDL	BDL	0.070	0.058	0.297	0.166	0.033	0.155	0.009	0.094	0.547	0.680
Brass 5	BDL	0.080	0.043	0.013	0.012	0.405	0.009	0.015	0.025	0.060	0.027	0.042	BDL	0.014	BDL	0.080

BDL – Below Detection Limit

Table C4.

Lead Pipe and Brass Fixture Data Chlorinated Water Burn Out, mg/L.

Lead 1-1	0.0373	0.0260	0.0159	0.00793	BDL	0.0115	0.0316	0.02700	BDL
Lead 1-2	0.0293	0.0398	0.02	0.00705	0.0135	0.0102	0.0845	BDL	BDL
Lead 1-3	0.0199	0.0182	0.0197	BDL	BDL	0.0507	BDL	BDL	0.0190
Brass 1	BDL	BDL	BDL	BDL	BDL	0.0872	BDL	BDL	BDL
Lead 2-1	0.0312	0.0536	0.0275	0.00806	0.028	0.0603	0.0232	0.00764	BDL
Lead 2-2	0.0545	0.0336	0.0281	BDL	BDL	0.00601	0.0460	BDL	BDL
Lead 2-3	0.0138	0.0222	0.0335	BDL	BDL	0.0470	0.0189	0.0157	BDL
Brass 2	BDL	BDL	BDL	BDL	BDL	0.0826	BDL	BDL	BDL
Lead 3-1	0.0118	0.0107	0.00600	BDL	0.0270	0.0210	0.0419	BDL	BDL
Lead 3-2	0.0103	0.0139	0.00699	BDL	BDL	0.0102	0.0237	BDL	0.02084
Lead 3-3	BDL	BDL	BDL	BDL	0.00615	0.0243	0.00738	BDL	BDL
Brass 3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Lead 5-1	0.0635	0.0539	0.0728	0.0744	0.0421	0.102	0.139	0.0184	BDL
Lead 5-2	0.029	0.0185	0.0307	0.0304	0.012	0.0437	0.0472	BDL	BDL
Lead 5-3	0.0245	0.00871	BDL	0.0251	0.0361	0.0382	0.0459	BDL	BDL
Brass 5	BDL	BDL	BDL	BDL	BDL	0.014	BDL	0.012	BDL

BDL – Below Detection Limit

Table C5.

Total Iron Cast Iron Pipe Data Chlorinated Water – No Corrosion Inhibitors, mg/L.

CI 1	0.26	1.09	1.00	0.774	0.600	1.265	0.692	0.713	0.56	0.375	0.364	0.455	0.701	0.378	0.26	1.09
CI 2	0.633	0.853	2.65	2.32	2.276	1.341	1.902	1.33	1.15	0.498	0.471	0.76	0.767	1.57	0.633	0.853
CI 3	0.627	0.744	0.833	0.416	0.269	0.859	0.699	0.527	0.321	0.278	0.213	0.207	0.376	0.318	0.627	0.744
CI 5	0.337	3.57	1.51	1.19	1.089		1.156	1.48	0.804	0.705	0.961	0.558	0.725	0.528	0.806	0.578

Table C6.

Total Iron Chlorinated Water – 70/30 Polyphosphate Blend Corrosion Inhibitors, mg/L.

CI 1	0.37	0.4	0.42	0.182	BDL	0.250	0.156	0.074
CI 2	0.29	0.36	0.5	0.269	BDL	0.215	0.303	0.359
CI 3	0.25	0.15	0.24	0.150	BDL	0.103	0.197	0.098
CI 5	0.16	0.22	0.27	0.140	0.191	0.114	0.310	0.351

BDL – Below Detection Limit

Table C7.

Total Iron Chlorinated Water – 30/70 Polyphosphate Blend Corrosion Inhibitors, mg/L.

CI 1	0.167	0.184	0.331	0.174	0.198	0.564
CI 2	BDL	0.173	0.238	0.222	0.171	0.389
CI 3	0.0653	0.144	0.149	0.070	0.131	0.581
CI 5	BDL	0.297	0.311	0.276	0.307	3.80

Table C8.

Total Iron Chlorinated Water – Orthophosphate Corrosion Inhibitor, mg/L.

CI 1	0.505	0.337	0.783	0.738	0.544	0.059	0.587	0.383	0.738	0.435	0.488	0.064	BDL	BDL	BDL
CI 2	0.406	0.607	0.331	0.58	0.526	0.263	0.674	0.672	0.279	0.476	0.775	0.517	0.625	0.279	0.336
CI 3	0.281	0.387	0.49	4.62	0.340	0.265	0.444	0.263	0.170	0.229	0.314	0.204	0.184	0.356	0.249
CI 5	0.437	0.315	BDL	BDL	0.425	0.113	BDL	0.617	0.455	0.389	0.332	0.471	0.492	0.377	0.443

BDL – Below Detection Limit

Table C9.

Total Iron Chloraminated Water – Orthophosphate Corrosion Inhibitor, mg/L.

CI 1	0.505	0.337	0.783	0.738	0.544	0.059	0.587	0.383	0.738	0.435	0.488	0.064	BDL	BDL	BDL	0.505	0.337
CI 2	0.406	0.607	0.331	0.580	0.526	0.263	0.674	0.672	0.279	0.476	0.775	0.517	0.625	0.279	0.336	0.406	0.607
CI 3	0.281	0.387	0.490	4.620	0.340	0.265	0.444	0.263	0.170	0.229	0.314	0.204	0.184	0.356	0.249	0.281	0.387
CI 5	0.437	0.315	BDL	BDL	0.425	0.113	BDL	0.617	0.455	0.389	0.332	0.471	0.492	0.377	0.443	0.437	0.315

Table C10.

Total Iron Chlorinated Water (Burn out) – Orthophosphate Corrosion Inhibitor, mg/L.

CI 1	BDL	BDL	0.053	0.210	BDL	0.204	0.190	BDL	BDL
CI 2	0.148	0.100	0.520	0.622	0.186	0.233	BDL	BDL	BDL
CI 3	0.135	BDL	0.312	0.300	0.063	0.293	0.055	BDL	BDL
CI 5	0.384	0.392	0.896	0.424	0.058	BDL	0.076	BDL	BDL

BDL – Below Detection Limit

APPENDIX D

Histograms

Note: All metal concentrations are in mg/L (*x*-axis). The *y*-axis represents population of selected ranges of metal concentration.

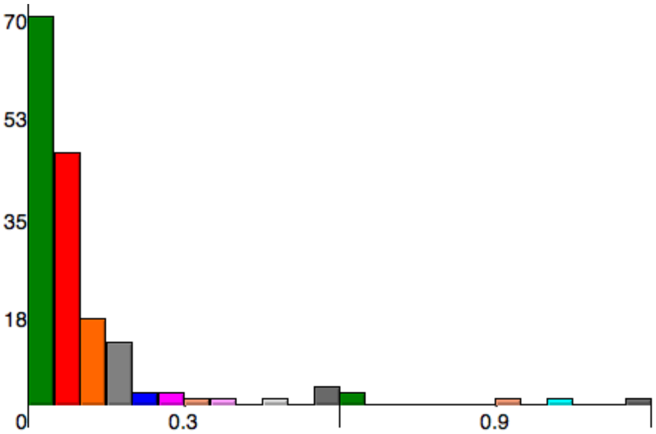

Figure D1. Condition LC total lead, mg/L.

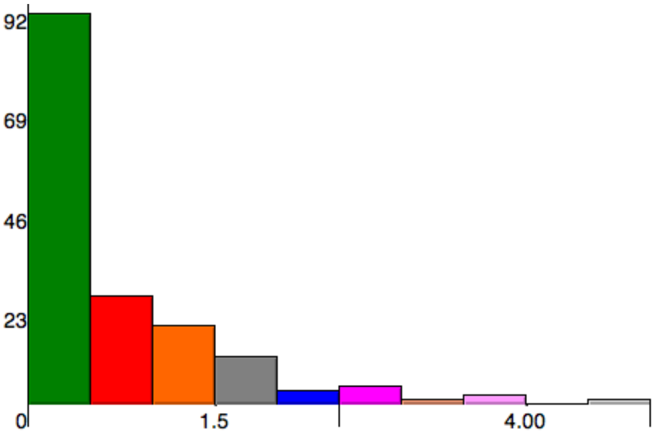

Figure D2. Condition LP total lead, mg/L.

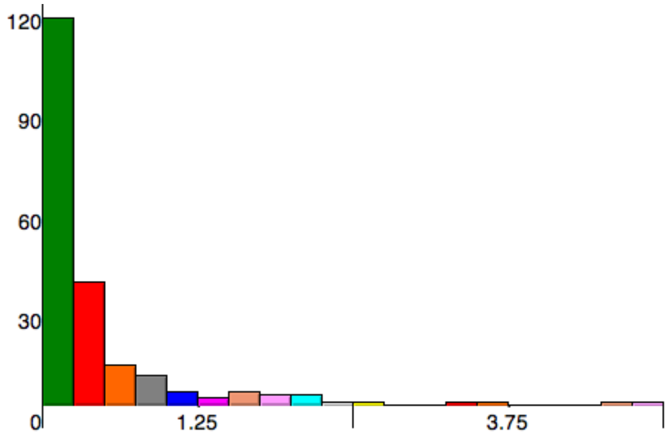

Figure D3. Condition LNH total lead, mg/L.

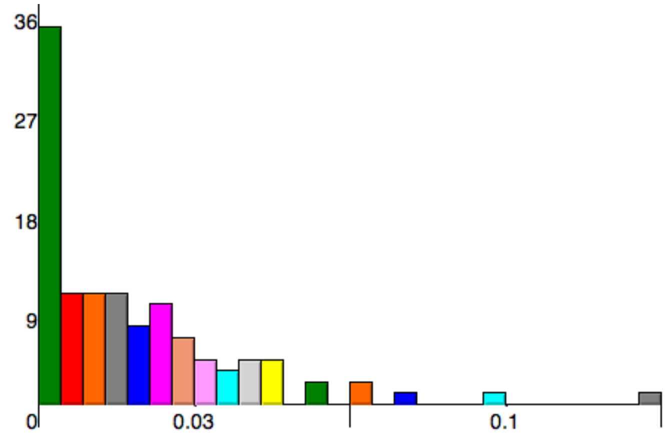

Figure D4. Condition LBO total lead, mg/L.

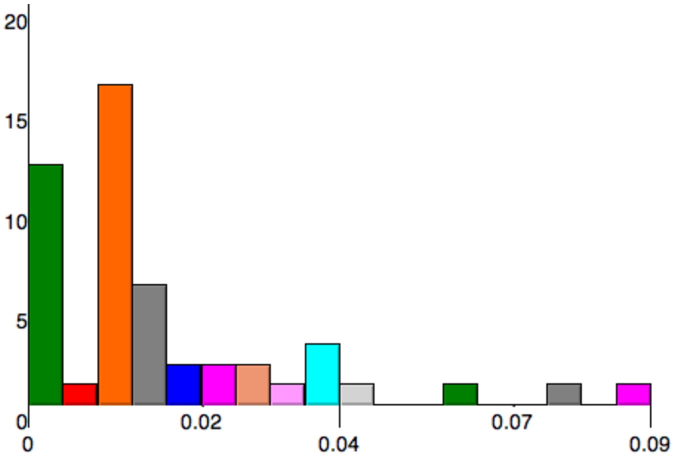

Figure D5. Condition BC total lead, mg/L.

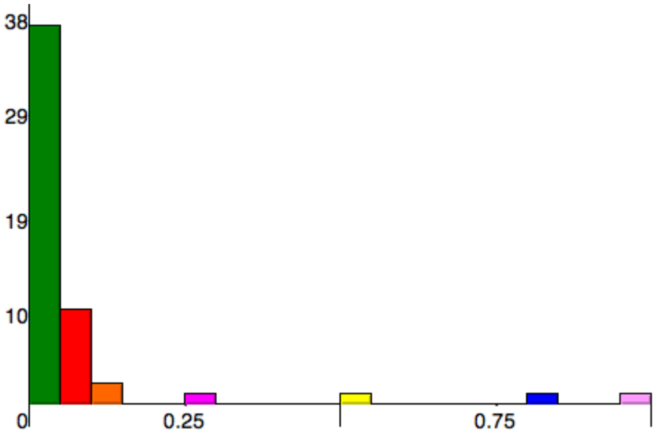

Figure D6. Condition BP total lead, mg/L.

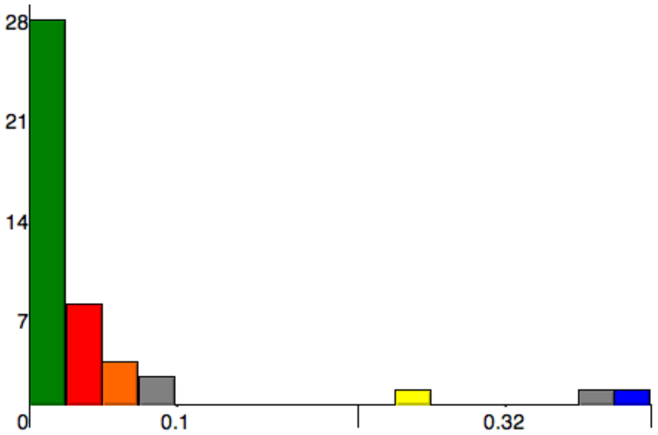

Figure D7. Condition BNH total lead, mg/L.

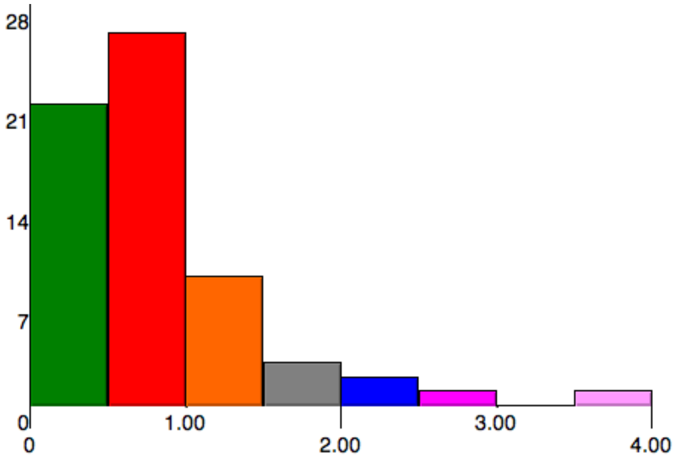

Figure D8. Condition IC total iron, mg/L.

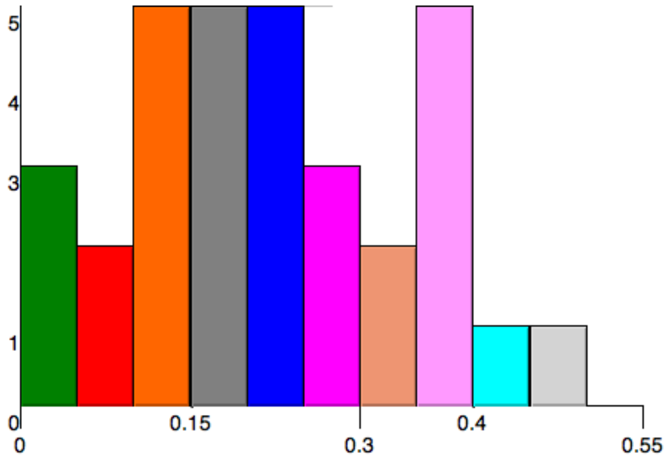

Figure D9. Condition IC 70/30 total iron, mg/L.

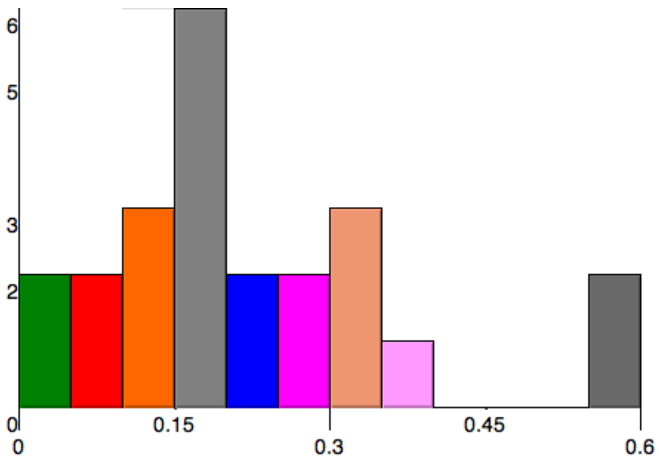

Figure D10. Condition IC 30/70 total iron, mg/L.

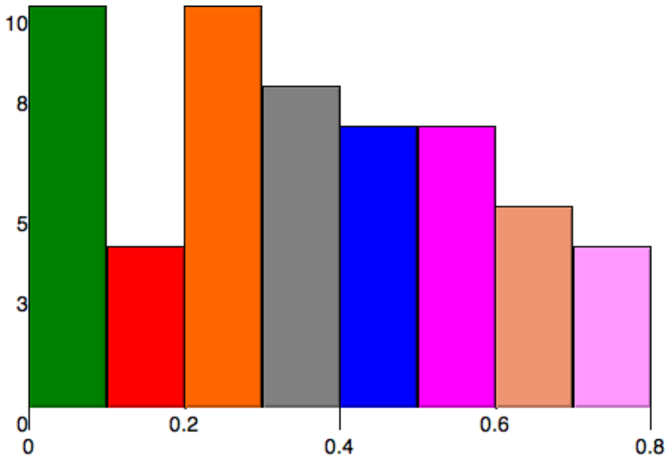

Figure D11. Condition ICO total iron, mg/L.

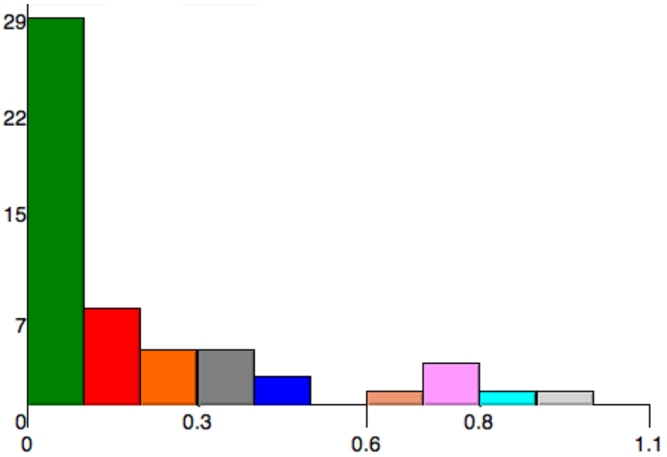

Figure D12. Condition INH total iron, mg/L.

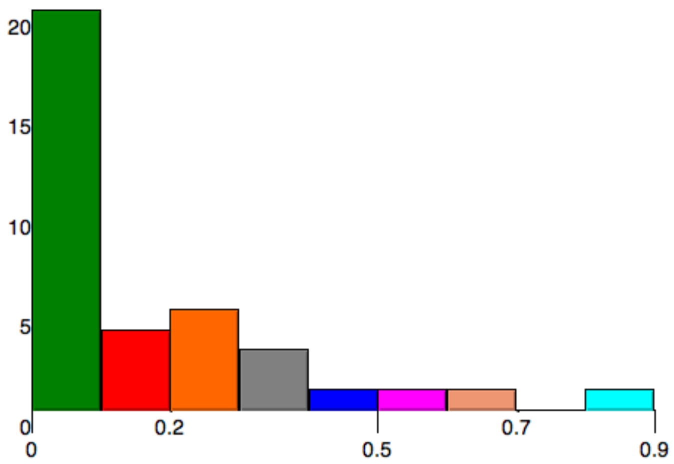

Figure D13. Condition IB total iron, mg/L.

APPENDIX E

T-TEST RESULTS

Table E1.

t-test results for lead pipe data.

	LC	LP	LNH	LBO
LC		$p<0.0001$	$p<0.0001$	$p<0.0001$
LP	$p<0.0001$		$p=0.0123$	$p<0.0001$
LNH	$p<0.0001$	$p=0.0123$		$p<0.0001$
LBO	$p<0.0001$	$p<0.0001$	$p<0.0001$	

Table E2.

t-test results for brass fixture data.

	BC	BP	BNH
BC		$p=0.040$	$p= 0.1186$
BP	$p=0.040$		$p= 0.2864$
BNH	$p= 0.1186$	$p= 0.2864$	

Table E3.

t-test results for cast iron pipe data.

	IC	IC70/30	IC30/70	ICO	IHN	IB
IC		$p<0.0001$	$p=0.0049$	$p<0.0001$	$p<0.0001$	$p<0.0001$
IC70/30	$p<0.0001$		$p=0.2630$	$p=0.0527$	$p=0.5994$	$p=0.2695$
IC30/70	$p=0.0049$	$p=0.2630$		$p=0.1031$	$p=0.3352$	$p=0.0157$
ICO	$p<0.0001$	$p=0.0527$	$p=0.1031$		$p=0.0102$	$p=0.0157$
IHN	$p<0.0001$	$p=0.5994$	$p=0.3352$	$p=0.0102$		$p=0.837$
IB	$p<0.0001$	$p=0.2695$	$p=0.0157$	$p=0.0157$	$p=0.837$	

APPENDIX F

EPA METHOD 200.8

The EPA method can be reviewed in its entirety (including quality control) at:

http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_200_8.pdf