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AN ASSESSMENT OF LEAD AND COPPER IN SCHOOL DRINKING **WATFR**

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AN ASSESSMENT OF LEAD AND COPPER IN SCHOOL DRINKING WATER

A Project Presented

by

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Master of Science in Environmental Engineering

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MAY 2019

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

ACKNOWLEDGMENTS

First and foremost, I would like to express my sincere gratitude to my advisor, Dr. John Tobiason, for his continuous support, guidance, patience and immense knowledge which has brought this research to where it is today. I sincerely appreciate all his contributions that have made my research experience productive and stimulating.

I would like to thank Dr. David Reckhow for his insightful comments and encouragement for this study and for his support throughout the course of my graduate program. I would like to thank Ms. Sherrie Webb-Yagodzinski, our lab manager, who always went out of her way to be of assistance to me in the laboratory. I would also like to thank Ms. Jodi Ozdarski, the department's academic advisor, who has been of immense help with any administrative or academic counsel. I must express my profound gratitude to my parents and my grandparents, who have provided me with unfailing support and encouragement throughout my years of study. I also acknowledge and thank all my friends and my research group for their love, support and encouragement during my graduate studies. Lastly, I feel deeply indebted to all the faculty who have taught and shaped my scientific thinking during my stay at UMass Amherst. Thank you.

ABSTRACT

Metal contamination in drinking water, especially heavy metals such as lead, and corrosion issues, pose a threat to human health and have received increasing attention in recent years. This study reports on the results of 'The Massachusetts Assistance Program for Lead in School Drinking Water' and provides a better understanding of the dynamics of sampling protocols, premise plumbing and their influence on lead and copper concentrations. 'The Massachusetts Assistance Program for Lead in School Drinking Water' that was announced in April 2016, implemented tap-based water sampling for lead and copper at K-12 public schools and Early Education and Childcare centers in Massachusetts, thus targeting the most vulnerable populations to the health risks of lead and copper exposure. The Program funded by the Massachusetts Department of Environmental Protection (MassDEP) and implemented by both UMass Amherst and MassDEP, saw the collection and testing of about 68,000 water samples across 992 school buildings between June 2016 and December 2018. About 44% of school buildings had one or more samples exceeding the lead AL, 9% of school buildings had one or more samples exceeding the copper AL, and another 29% had exceedances of both the lead and copper ALs. Flushing was found to have a higher impact in decreasing lead concentrations as compared to the impact on copper concentrations. A decrease in lead concentration levels is seen in schools constructed later than the year 1990, possibly indicating the implementation of lead materials control following the regulations in the 1980s and the LCR.

1. INTRODUCTION

This chapter presents a general introduction and background information for this study, describing the motivation for this research and the scope of work covered.

1.1 Research Motivation

Clean and safe drinking water is an essential human right. However, contamination of tap water by metals is quite common. Lead and copper are two commonly occurring metals in tap water, both being potentially harmful to human health. The recent water crisis in Flint, Michigan has largely influenced the increased attention to lead in drinking water and many states are now conducting sampling at the point of use to detect levels of lead and copper in tap water (Rosen, Pokhrel & Weir, 2017).

A recent study estimates that approximately 400,000 deaths occur annually in the USA alone due to lead exposure, of which 250,000 are from cardio vascular disease attributed to elevated blood lead levels as a risk factor (Lanphear, Rauch, Auinger, Allen & Hornung, 2018). Although the use of lead in gasoline was phased out between 1973 and 1995, and the federal mandate in 1978 resulted in the removal of lead from paint as well, resulting in significantly decreased blood lead levels, recent studies have indicated that low-level exposures and blood lead levels can cause a number of serious health issues and can even lead to death. Drinking water is estimated to be responsible for about 20% of total daily lead exposure in a majority of the US population (Patrick, 2006). Moreover, childhood lead poisoning has been correlated belatedly with exposure to lead in drinking water (Triantafyllidou, Parks & Edwards, 2007).

As children and young adults are the most vulnerable populations to lead and copper concentrations in drinking water, it is important to estimate and quantify exposure from schools

and early education centers, since children spend a considerable amount of their time in these institutions. In late April 2016, the 'Massachusetts Assistance Program for Lead in School Drinking Water' was announced by the Commonwealth to fund the implementation of tap-based water sampling at K-12 public schools and early education and childcare (EECs) centers in Massachusetts.

1.2 Scope of Work

This study analyzes and quantifies lead and copper levels in school drinking water, from the data obtained through the MassDEP Assistance Program. Water was sampled at schools to determine lead and copper concentrations in the water and a comparison with Action Levels (ALs) was performed once the results were obtained. The data were examined, using both a building perspective and an all samples perspective. The results for different sample types, first draw (P) and flush (F), are compared. Concentration trends are discussed, and the data are also analyzed based on fixture type. The influence of building age on lead and copper concentrations is also evaluated.

The goal of this report is to analyze the results of the MA DEP Assistance Program and present an assessment of levels of lead and copper in school drinking water, to better understand the impacts of premise plumbing and sampling protocols on lead and copper concentrations.

2. LITERATURE REVIEW

This chapter provides background information on certain key topics related to this study. The section is divided into six parts: 1) lead, 2) copper, 3) incidences of elevated lead and copper levels, 4) distribution systems and premise plumbing, 5) sampling methods, 6) summary of literature.

2.1 Lead

2.1.1 Chemical Properties

Lead is the most widely studied occupational toxin (Gidlow, 2004). Lead is a toxic heavy metal found naturally in the Earth's crust and is denser than most common materials. Although a minor constituent, it is widely distributed in low concentrations in sedimentary rock and soils (Hem & Durum, 1973). Lead metal is bluish white and lustrous and is a relatively poor conductor of electricity. It has the symbol Pb and has an atomic number of 82. The mass stable isotopes of lead are 208Pb, 206Pb, 207Pb and 204Pb with abundances of 52.4%, 24.1%, 22.1% and 1.4% respectively. Lead is easily extracted from its ores and is soft, malleable, dense and has a relatively low melting point (Brown & Margolis, 2012; Flora, Gupta & Tiwari, 2012; Markowitz, 2000). Lead is highly ubiquitous on Earth and also possesses properties of high ductility and resistance to corrosion but tarnishes upon exposure to air. It is a potent occupational toxin and is non-biodegradable, and therefore is persistent in the environment (Flora et al., 2012; Papanikolaou, Hatzidaki, Belivanis, Tzanakakis & Tsatsakis, 2005).

Lead exists in three forms: metallic lead, inorganic lead and lead compounds (or lead salts), and organic lead (containing carbon) (Sanders, Liu, Buchner & Tchounwou, 2009). The reactivity of lead is important in understanding the pathways of lead leaching and exposure to humans. Lead

metal can get oxidized to Pb (II) and Pb (IV), both having some solubility in water, forming various dissolved species and solid phases. Lead in the environment is rarely found in its elemental state and lead compounds are usually found in the $+2$ oxidation state rather than the $+4$ oxidation state (Cartier et al., 2013; Sanders et al., 2009). Lead and lead oxides react with acids and bases and tend to form covalent bonds.

Lead is present in drinking water in two main forms; as dissolved lead and as particulate lead. Dissolved lead is a result of dissolution of lead surfaces and lead mineral scales from lead pipes, lead solder and brass elements (Cartier et al., 2011; Cartier et al., 2012). Particulate lead is formed from sloughing off and transport of particles that are released from plumbing materials (Cartier et al., 2011). Particulate lead may be lead that is adsorbed onto iron oxides, calcium carbonates or corrosion products (Schock, 1990). Particulate lead has in many cases been shown to be present at as much or more significant levels than dissolved lead in drinking water but can however be overlooked by typical sampling and analysis protocols (Masters & Edwards 2015; Triantafyllidou et al., 2007).

2.1.2 Uses of Lead

Lead is ubiquitous in its presence, found in food, water, air, soil and in many items applicable to our daily lives (Payne, 2008). Lead's properties, high abundance and low cost led to its extensive use in construction, plumbing, as ballast in ships, in lead-acid batteries, bullets (due to its low melting point), solders, pewters, fusible alloys, white paints, leaded gasoline and radiation shielding (Triantafyllidou & Edwards, 2012). Compounds of lead are used in coloring agents, oxidants, candles, glass and semiconductors. Lead is also added to copper alloys such as brass and bronze. Lead is used in the automobile industry, in paints, ceramics and plastics as well. The sources of lead that contribute to human exposure are leaded gasoline, lead smelting in industries, coal combustion, lead-based paints, battery recycling, and in materials of concern with respect to drinking water such as lead containing pipes, lead-based solder in plumbing systems, and brass fixtures in premise plumbing (Cartier et al., 2008; Flora et al., 2012). Lead was and still is used in pipes carrying water and is also used to solder iron and copper pipes (Payne, 2008). Humans may also be exposed to lead via smoking (Wasserman, Liu, Pine & Graziano, 2001). Other uses of lead include cosmetics, hair dye, farm equipment, airplanes, shielding for x-ray machines, and in the manufacture of corrosion and acid resistant materials used in the building industry (Sanders et al., 2009).

2.1.3 Health Effects and Toxicity

Lead's toxicity was recognized in the late 19th century, and its usage has since been phased out of many applications (*Lead in Drinking Water,* 2011). It is a neurotoxin that accumulates in soft tissues and bones, damages the nervous systems and causes blood disorders (Triantafyllidou & Edwards, 2012). It has also been shown to have carcinogenic properties (Brown & Margolis, 2012; Steenland & Boffetta, 2000). It is stored in teeth and bones where it accumulates over time. Pregnant women, developing fetuses, infants and children are vulnerable populations. The human body cannot tell the difference between calcium and lead (*Lead in Schools and Selecting Leadfree Plumbing Products,* 2017). Whole blood lead levels (BLLs) are generally measured for biomonitoring of lead exposure, but lately bone lead measurement is proving to be a more robust method of measurement. Lead has a residence time of about 30 days in blood, and 10 years in bones (Payne, 2008). No safe blood lead level threshold has been identified for children (Brown & Margolis, 2012).

The toxicity of lead within the human body can be examined at 3 levels: biochemical, subclinical and clinical (Markowitz, 2000). Flora et al. (2012) describe the health effects of lead being caused by a mechanism known as oxidative stress which can result in disease manifestations such as cancer, cardiovascular diseases, brain damage, reproductive problems and other irreversible health effects. There are two types of toxicity or poisoning, acute and chronic. Chronic lead poisoning is characterized by persistent vomiting, encephalopathy, lethargy, delirium, convulsions and coma and is associated with three main types of symptoms: gastrointestinal, neuromuscular and neurological. Symptoms of acute lead poisoning are abdominal pain and vomiting, neurological signs such as pain, muscle weakness, and numbness, and gastrointestinal problems such as constipation, diarrhea and weight loss (Patrick, 2006).

In children, lead toxicity could result in permanent brain damage. BLLs of 10 µg/dL were considered acceptable (Lanphear et al., 2002). However, the Centres for Disease Control and Prevention (CDC) lowered the reference level to 5 µg/dL, at which level CDC recommends public health actions be initiated. Children in schools and child care centers may be exposed through water or food that has been prepared with contaminated water (*Lead in Schools and Selecting Lead-free Plumbing Products*, 2017). Moreover, maternal smoking during pregnancy has shown elevated risks of late child behavior problems (Wasserman et al., 2001). Reduced IQ and attention span, learning disabilities, poor classroom performance, hyperactivity, behavioral problems, impaired growth and hearing loss are some health effects observed in children (*Lead in Schools and Selecting Lead-free Plumbing Products,* 2017). However, most children with elevated BLLs are asymptomatic. The identification of children with lead exposure or poisoning can be determined through screening using a questionnaire and evidence from blood tests for Pb levels (Markowitz, 2000). The results strongly support their hypothesis that lead impairs children's IQ at low BLL, even below 10 µg/dL (Barn & Kosatsky, 2011; Needleman & Gatsonis, 1990). The potential for severe health effects in children is due to these reasons: 1) intake of lead per unit body weight is higher in children than in adults, 2) physiological uptake rates are higher in children, 3) children are more vulnerable to the effects of lead owing to their rapid developing systems. Elevated blood lead levels are more common and more of a problem among socially and economically deprived children, since poor families are more likely to be housed near industries or heavy traffic and are therefore more exposed to lead dust and the children are more nutritionally deprived (Tong, Schirnding & Prapamontol, 2000).

Lead not only harms the young and the occupationally-exposed, but also the older generations. Since older people have been alive longer, they may have had more potential exposures to lead and therefore higher blood and bone levels of lead (Vig & Hu, 2000). The degree of harm from lead exposure depends upon the duration of exposure, frequency of exposure, dose, and other individual risk factors (Bryant, 2004).

2.1.4 Significance of Lead in Drinking Water

Although lead exposure through tap water, air, food, dust and soil has considerably decreased since 1970, populations, especially children, are still sometimes exposed to high lead concentrations (Brown & Margolis, 2012). It is estimated that 14% to 20% of total U.S. lead exposure is from drinking water (Maas, Patch, Morgan & Pandolfo, 2005; Triantafyllidou et al., 2007). As many as 81 million homes may be at risk to potential lead exposure due to the presence of lead pipes and lead solder, and even new homes may be at risk due to the presence of brass or bronze plumbing (Triantafyllidou & Edwards, 2012). Lead leaches into drinking water through corrosion of plumbing materials that contain lead (Brown & Margolis, 2012). Lead contamination is rarely

present in finished water at a water treatment facility and is almost always the result of contact with plumbing components (Maas et al., 2005; Masters & Edwards, 2015). Lead in drinking water is especially of concern to children due to its impact on BLLs, with even low BLLs causing significant damage (Deshommes, Laroche, Nour, Cartier & Prévost, 2010). As water flows through or remains stagnant in pipes and other plumbing fixtures, it can get contaminated with lead through complex electrochemical, geochemical or hydraulic processes. Lead may flake off from distribution pipes, especially from soldered lead-tin joints, contributing to particulate lead levels in water. Particulate lead is usually defined as the fraction of lead retained on a 0.45 µm filter (Deshommes et al., 2010). Only the direct consumption of lead contaminated water is considered harmful, not its use for bathing or washing, as human skin does not absorb lead from water (Triantafyllidou & Edwards, 2012).

2.1.5 Factors Affecting Lead Concentrations

Increased velocity, hot temperatures, soft water, aged piping and acidity can increase leaching of lead in drinking water (Bryant, 2004). Water chemistry conditions such as a high chloride to sulfate mass ratio (CSMR) is also associated with galvanic corrosion and other factors such as pH, alkalinity, carbon dioxide and oxygen also have an impact on the corrosivity of water (Cartier et al., 2013; Isaac et al., 1997; Tam & Elefsiniotis, 2009). Plumbing components such as solder, fluxes, pipes, pipe fittings and sediments are potential sources of lead in drinking water. Corrosion control measures for water leaving the water treatment plant, such as pH/alkalinity control or addition of corrosion inhibitors, are used to limit the amount of lead leaching from plumbing materials. Buildings that were constructed in the 1930s more often had lead piping and the use of lead solder was common before 1986. Therefore, the risk of increased lead levels is greater for these older buildings. Apart from age, the type of plumbing material can affect levels

and variability of lead concentrations (Masters, Parks, Atassi & Edwards, 2016). The presence or absence of lead service lines (LSLs), including the length of the LSL influences lead concentrations (Cartier et al., 2011). Several studies have identified partial replacement of a LSL to be more harmful than a full LSL replacement, due to galvanic corrosion when replaced with copper piping (Cartier et al., 2013; Del Toral, Porter & Schock, 2013). Partial LSL replacement refers to the replacement of only the part of the LSL that is not on the homeowner's property.

Sampling protocols/methods also influence measured lead concentrations as described in the Sampling Methods section of this report. In a study conducted by Del Toral et al. (2013), seasonal variability was found to occur, with lead concentrations higher in Sept/Oct than in Mar/Apr or June. Seasonal variation may occur due to multiple contributing factors from the source water through premise plumbing, including factors such as water temperature, water chemistry variation, and fluctuations in water usage based on season. Del Toral et al. also describe the necessity of consistent flow to deliver corrosion inhibitor effectively and correlates an increased inhibitor dose with reduced lead release. The duration of stagnation of water in plumbing lines as well as the number of joints in a pipe could also potentially produce variability in lead concentrations (Schock, 1990). The only way to know if lead is present in water is to analyze water samples for lead.

2.1.6 Regulations

One of the first initiatives taken in the US to control lead levels in drinking water was the Federal Lead Ban which fell under the Safe Drinking Water Act (SDWA) and was passed in 1986 (Maas et al., 2005). The amendments banned the use of solders and flux containing >0.2% lead as opposed to the 40-50% lead used earlier, and additionally regulated the use of lead in brass to <8% by

weight. The National Sanitation Foundation and American National Standards Institute (NSF/ANSI) 61 is a standard that certifies the safety of endpoint devices and limits the mass of Pb that can be released by an endpoint device to 11 µg (Cartier et al., 2012). The use of new pure lead pipes in home plumbing systems was eliminated in 1986 as was the case with leaded solder, but many lead pipes are still present in old homes and in public distribution systems (Triantafyllidou et al., 2007). Prior to the 1986 regulation, lead in drinking water was regulated only through the 1975 National Interim Primary Drinking Water Regulations, which was inadequate because these regulations mandated monitoring at a distributions system's entrance point rather than at the consumer's tap.

In 1988, the Lead Contamination Control Act (LCCA), established under the federal Safe Drinking Water Act, was implemented to provide guidance to schools in monitoring levels of lead in water used for drinking and food preparation and for which the EPA published guidelines for sampling and monitoring (Maas et al., 2005). All schools and EEC facilities were covered under the LCCA and the Act also targeted the recall of drinking water coolers with lead lined tanks and included a publication of a list of water coolers that were not "lead free". The 1988 LCCA defines "lead free" as no more than 8% lead for components that come in contact with water and no more than 0.2% lead for solder, flux, or storage tank interior that comes in contact with water. The 1988 LCCA recommended an action level (AL) for lead of 20 ppb at the point of use in a 250 mL sample, and both first draw and flush samples were required to be collected. 'The 3Ts for Reducing Lead in Drinking Water in Schools and Child Care Facilities' is a manual that was produced subsequent to the LCCA of 1988. The revised October 2018 version mentions no acceptable level for lead in drinking water, and the manual instead directs schools to achieve the lowest levels of lead possible,

preferably non-detectable (*3Ts for Reducing Lead in Drinking Water in Schools and Child Care Facilities,* 2018; Burlingame et al., 2018).

Because lead contamination is largely due to contamination from the service line and/or building plumbing, the EPA promulgated the Lead and Copper Rule (LCR) in 1991. According to the LCR, if more than 10% of samples collected from a specified number of households have lead concentrations that exceed an Action Level (AL) of 15 ppb or copper concentrations that exceed an Action Level of 1.3 ppm, the system is required to take a number of actions for corrosion control. The LCR applies to homes and other buildings served by a public water system (PWS) and aims to assess the effectiveness of corrosion control treatment adopted by these PWSs. PWSs are required to sample sites that are presumed to have the highest risk of lead release (Del Toral et al., 2013). The LCR recommends corrosion control optimization, lead service line replacement and public education as part of efforts that can be taken to minimize exposure to lead and copper contamination (Maas et al., 2005). The US EPA has also set a health effects based maximum contaminant level goal (MCLG) of zero for lead at the tap. This MCLG is not enforceable but is the lead level that is desired as it is the level for which there is no known or expected health risk (Triantafyllidou & Edwards, 2012). The federal Reduction of Lead in Drinking Water Act of 2011 further decreased the amount of lead in pipes, pipe fittings, plumbing fittings and fixtures to a weighted average of 0.25 percent (Maas et al., 2005).

Although children are more at risk to the ill effects of lead in drinking water, there are no federal laws requiring testing in schools and childcare facilities, except for schools and childcare facilities that own/operate their own public water supply and are thus regulated under the Safe Drinking Water Act (SDWA) and must comply with the LCR.

2.2 Copper

2.2.1 Chemical Properties

Copper is a chemical element with the symbol Cu and atomic number 29, occurring in stable isotopes 63 Cu and 65 Cu with abundances of 69.15% and 30.85% respectively. Copper metal is soft, malleable and ductile, with high electrical and thermal conductivity. It is a reddish metal occurring naturally in rock, soil, water and sediment. It is a rather ubiquitously found metal that may be present in natural drinking water sources in generally low concentrations on the order of micrograms per liter. The metal may sometimes be found in rather high concentrations in waste waters. However, copper is generally not present in water that leaves a drinking water treatment facility (Masters & Edwards, 2015). Copper, although generally corrosion-resistant, can be corroded by certain water quality conditions. Corrosion leads to copper contamination in drinking water and copper levels can vary due to various factors in the distribution system and premise plumbing. Copper pipe corrosion is a major cause for concern, potentially causing leaks, failures and subsequent financial costs. Soluble copper is found to occur more commonly than particulate copper, and copper concentrations in stagnant water are much higher than in flowing water (Dietrich et al., 2004). The mechanism of copper corrosion is complex and the interactions between pipe surfaces, chemical factors, and microbial growth play roles in the corrosion of copper, including pitting corrosion (Dietrich et al., 2004).

2.2.2 Uses of Copper

Copper being abundantly available and low in cost, is a very useful and versatile metal. Copper's properties of high electrical and thermal conductivity make it an appropriate metal to be used for wiring in electrical equipment. Many coins are made of copper alloys and copper can be found in gun metals as well as in cookware and cooking utensils. Copper is commonly used in distribution system piping and home plumbing as it is considered safe and long-lasting (Lytle & Schock, 2008). Copper is used to produce alloys such as brass and bronze and these metals are used in plumbing components as well. Copper is also sustainable as it can be recycled or repurposed.

2.2.3 Health Effects

Copper is an essential micronutrient and an intake of about 900 µg/day is recommended by the National Center for Biotechnology Information (NCBI) for adult men and women, with an upper limit of 10 mg/day. The WHO guidelines state that concentrations more than 5 mg/L can impart color to water and could cause a bitter taste. Copper, although being an essential nutrient for humans, can have harmful effects on human health when present at high concentrations. Acute copper exposure can cause nausea, cramping, vomiting, and irritation of the stomach. Information from direct consumption of copper salts indicate that acute toxemia or death could occur from amounts greater than 1 g Cu (*Copper in Drinking Water,* 2000). A handful of studies where consumption and concentration were not controlled indicate that copper could be a potential source for gastrointestinal (GI) illness. Controlled studies with subjects drinking copper-containing test water found a dose-response relationship with higher copper levels (>10 mg/L) producing more GI effects. Few studies have investigated the long-term effects of excess copper intake, and also the effects of copper exposure on children (Barn et al., 2014).

2.2.4 Aesthetics and Guidelines

With regard to aesthetics, copper contamination of drinking water may attribute a metallic, acidic, astringent, salty or bitter taste to water, depending on individual taste (Dietrich et al., 2004). Research on the odor properties of copper is sparse and no citations concerning metallic odors in water have been found.

Especially for copper in drinking water, the effect of water quality on corrosion and corrosion on water quality must be paid attention to. Copper corrosion in conjunction with health, aesthetic and microbial effects needs to be studied further. The Canadian drinking water guideline recommends a maximum copper concentration of 1 mg/L and is an aesthetic objective based on taste, staining of laundry and plumbing fixtures (Barn et al., 2014).

The US EPA developed a health-based action level of 1.3 mg/L for copper in drinking water. The LCR based Action Level for copper is the same as the Maximum Contaminant Level Goal (MCLG) (Murphy, 1993). The US EPA had also established a secondary aesthetic-based maximum contaminant level of 1.0 mg/L for copper in 1979, because a metallic or bitter taste in water can develop above this level.

2.2.5 Factors Affecting Copper Concentrations

Water which is soft and is low in alkalinity has been found to cause higher copper corrosion byproduct release. Soluble copper is found to occur more commonly than particulate copper. The release of soluble copper was found to increase with lower pH and lower temperatures as well. Lower levels of free chlorine were found to increase copper release at a higher pH (Boulay $\&$ Edwards, 2001). Temperature, chlorine, alkalinity (DIC), phosphate, dissolved oxygen, natural organic matter (NOM) and microbial extracellular-polymeric substances (EPS) are the most commonly cited factors known to influence copper concentrations in water (Boulay & Edwards, 2001; Tam & Elefsiniotis, 2009; Isaac et al., 1997). Metallic copper is not inert and can experience uniform and non-uniform or pitting corrosion. Uniform corrosion refers to the

corrosion of the metal evenly across the surface, causing relatively uniform corrosion deposits on the pipe surface. Uniform corrosion may occur with low pH and high alkalinity (Broo, Berghult & Hedburg, 1997). Pitting or localized corrosion occurs at isolated points along the metal surface possibly leading to pipe breaks and leakages, and factors such as microbial activity, material imperfections, stray currents, soldering flux, carbonaceous manufacturing residues on the pipe surface, and other factors may be responsible. Localized copper corrosion may be subcategorized into three types based on water chemistry and physical features: cold water, hot water and soft water. Soft water copper pits are wide and shallow and may be caused by water having low conductivity, low alkalinity and relatively high pH, and sulfate and chloride are associated with pitting as well. The most common failure mechanism observed for copper pipes is the breakdown of the thin, protective cuprous oxide film that coats the copper surface that may be a result of chemical or mechanical causes (Broo et al., 2007; Lytle & Schock, 2008).

Copper concentrations vary due to an interaction of factors such as corrosion of pipes, variation in chemical factors (pH, hardness, dissolved oxygen, dissolved inorganic carbon, oxidizing and complexing agents), stagnation time in pipes, and microbial growth (Dietrich et al., 2004).

2.3 Incidences of Elevated Lead and Copper Levels

The most notorious incidence of elevated lead levels is the Flint, Michigan water crisis that started in 2014 (Rosen et al., 2017). Due to economic reasons, the town decided to switch its water source from the Detroit Water and Sewer Department to the Flint River and reopened the Flint water treatment plant. Soon after the switch, residents began noticing that the tap water looked bad and that children were developing skin conditions. Obvious signs of corrosive water and complaints continued into 2015, but it was only in 2016 that the city was declared to be in a

state of emergency (Rosen et al., 2017). Flint river water had not been properly treated with corrosion inhibitors or pH control to limit lead leaching from the aging pipes and lead goosenecks. Between 6,000 and 12,000 children were exposed to extremely high levels of lead. In Flint, the percentage of children below 5 years of age with BLL above 5 µg/dL rose from a baseline of 2.4% in 2013, to 4.9% after 2015, and for children between 1-5 ages from 4% at baseline to 10.6%. The corrosive water resulted in lasting damage to the water distribution system, prolonging the crisis even more. The Flint water crisis also saw a spike in Legionnaire's disease caused by the bacterium *Legionella pneumophilia.* Water temperature, pH and watermetal content are known influencing factors for the growth of *Legionella* in water and biofilm in the water distribution system. It has been put forth that the high corrosivity may have depleted the free chlorine residual in the water distribution systems, thus increasing the growth of biofilm and microorganisms which in turn resulted in an increase in *Legionella* (Rosen et al., 2017).

Children are more susceptible to the health effects of lead and therefore drinking water from school buildings could be a significant source of lead exposure for children (Bryant, 2004). Instances of blood lead poisoning in children in Greenville, N.C., were belatedly attributed to high concentrations of particulate lead found in water, one year later (Triantafyllidou et al., 2007). About 25% of residential water sampled in 2004 in Greenville had lead levels exceeding the US EPA action level of 15 ppb for lead (Massey & Steele, 2012). Lead particles were found to be trapped in the aerator screens in the houses of lead-poisoned children, that mostly originated from solder or lead-corrosion by-products (Triantafyllidou, Lambrinidou & Edwards, 2009). In Durham, N.C., several homes saw high water lead levels starting in 2006. The switch from alum to ferric chloride for coagulation interfered with the anti-corrosion treatment in place and caused lead to leach from pipes (Rosen et al., 2017). Another treatment change incident

occurred in Washington DC between 2001 and 2004 and only after a year had passed, did investigators consider tap water to be the source of elevated blood lead levels in children (Triantafyllidou et al., 2007). DC switched its disinfection treatment method from free chlorine to chloramine to decrease levels of disinfection by-products, but the disinfectant change caused lead levels to spike, probably because the stable lead oxide phase changed from Pb (IV) to more soluble Pb (II) (Schock, Scheckel, DeSantis & Gerke, 2005). Pb (IV) has a strong oxidative potential, forming a practically insoluble product $PbO₂$ (s) on the inner surfaces of lead pipes when free chlorine residual is maintained. Studies show that monochloramine is a weaker oxidant, therefore not resulting in the formation of $PbO₂$ (Lin & Valentine, 2009). Chloramines can attack brass and cause lead leaching and may also adversely affect galvanic connections between lead pipe or lead solder to copper pipe, again causing lead to leach. DC residents were not informed about the extent of contamination and were not clearly instructed on simple steps that could be taken to minimize exposure (Edwards & Dudi, 2004; Triantafyllidou et al., 2009). Both the Greenville and Washington D.C cases are examples of how the standard US EPA sampling protocol may miss human exposure to particulate lead, as Pb and Pb oxide particles are generally missed during routine sample collection (Triantafyllidou et al., 2007).

2.3.1 School Case Studies

A few studies in schools across the US are discussed here. In the case of school water systems, stagnation and outlet design are two key factors that influence lead contamination in drinking water (Barn & Kosatsky, 2011).

A study of drinking water samples from 292 school buildings in Philadelphia in the year 2000 showed that about 46.5% of schools had mean lead levels greater than 20 ppb for primary

samples, and 22% of school buildings had flush samples exceeding 20 ppb (Bryant, 2004; Massey & Steele, 2012). Primary or first draw samples were collected before any water was used following overnight stagnation. Flush samples, taken after allowing the water to run for 30 seconds, were collected only for those fixtures that had lead levels that exceeded 20 ppb for the initial first draw sample.

Another extensive study was launched in Seattle public schools in 2004 following parental inquiries. The sampling procedure included collection of two 250 mL samples: a first draw following 15-18 hours of stagnation and a flush sample after 30 seconds of flushing. Results showed that about 19% of first draw samples and about 3% of flushed samples exceeded 20 μ g/L of lead. A follow-up study was conducted to assess the variability of lead from drinking water taps after the implementation of a lead remediation program. The remediation program proved to be successful and greatly lowered lead levels in school drinking water (Boyd, Piersen, Kirmeyer & English, 2008).

The Los Angeles Unified School District conducted sampling at its schools in 2008-2009 after a local news investigation and parental inquiries. 6% of first draw samples and 1% of flush samples contained excessive lead (Triantafyllidou, Le, Gallagher & Edwards, 2014).

Although studies and information on lead contamination in rural and suburban areas in the US are few, a couple of examples are listed here. One study reported extreme lead levels in a rural school in Utah in 1996, including a 670 ppb level at a classroom tap and 840 ppb at a drinking water fountain (Massey & Steele, 2012). Another study was implemented in primary and preschools in five suburban and rural schools in south central Kansas to analyze lead content in

drinking water. The results indicated that about 32.1% of samples had detectable lead levels and about 3.6% exceeded 20 ppb (Massey & Steele, 2012).

Burlingame et al., (2018) published summaries of experiences of school water sampling for lead in Chicago, Portland, Cincinnati and Philadelphia and reported that were many technical challenges faced in sampling and in the responses to sample results. There was confusion between the LCR and LCCA sampling protocols and this in turn caused confusion for the public, the media and various other stakeholders.

2.4 Distribution Systems and Premise Plumbing

2.4.1 Distribution Systems

The materials used in distribution systems and premise plumbing along with the chemical characteristics of the water significantly impact the levels of lead and copper in drinking water delivered to consumers. The distribution system is a key source of unwanted water loss, aesthetics and health problems influenced by chemical, biological and economic factors (Dietrich et al, 2004). AWWA defines the distribution system as "including all water utility components for the distribution of finished or potable water by means of gravity storage feed or pumps though distribution pumping networks to customers or other users, including distribution equalizing storage" (*Drinking Water Distribution Systems: Assessing and Reducing Risks*, 2006). Distribution systems generally consist of pipes, pumps, valves, storage tanks, reservoirs, meters, fittings and other plumbing parts. Materials generally used are cast iron, ductile iron, pre-stressed concrete, poly vinyl chloride (PVC), reinforced plastic, lead, copper, brass and steel. The components of a distribution system that are relatively more significant for lead and copper corrosion are lead pipes, lead service lines (LSLs), lead goosenecks, copper piping, lead solder,

and lead joints in water mains. Longer lead pipes can increase contact time of the water with lead. Service lines are pipes that carry water from the distributing main to the property being served. Around 6.1 million LSLs are estimated to be present in the United States (Deshommes, Gagnon, Andrews & Prévost, 2018). Lead goosenecks are curved pieces of piping that allow for a flexible connection between rigid pipes, usually from the distribution main to the building inlet or meter. An example of a lead gooseneck is shown in Figure 1. Service lines and goosenecks may also be considered to be a part of the premise plumbing rather than the main distribution system. Temperature, pH and other changes to water conditions within the distribution system, can cause variations in lead and copper levels.

Figure 1. Lead gooseneck Source: https://goo.gl/images/kwbAe7

2.4.2 Premise Plumbing

Premise plumbing refers to the internal plumbing within a building that distributes water to the point of use. Typical plumbing sources of lead within a property are represented in Figure 2. The diameters of pipes in premise plumbing are relatively smaller than in the distribution system, with greater surface to volume ratio, meaning that more water is in direct contact with plumbing

(Barn & Kosatsky, 2011). Many plumbing lines are made of a combination of materials, such as lead service lines with copper piping within the building, or copper sections that are connected by lead/tin solder. Galvanic coupling of different pipe materials and parts can cause corrosion. Stagnation of water for a long duration in plumbing within a building can cause changes in pH, chlorine residual, dissolved oxygen level, temperature, hardness and alkalinity, and these changes can cause variability in lead concentrations (Schock, 1990). Studies have also found that even in the absence of lead pipes or solder, as is the case in relatively newer plumbing systems, significant amounts of lead can result from contact with brass fittings (Schock, 1990). End-use plumbing fittings are often made of brass which is an alloy of lead with other elements such as copper or zinc.

Figure 2. Sources of lead in drinking water within a property

Source: https://goo.gl/images/jCPRzM

2.5 Sampling Methods

Sampling protocols used in different countries, including the USA, differ in numerous ways including in stagnation duration, number of samples required to be collected, sample volumes, and treatment of samples (Cartier et al., 2011). The volume of water drawn for a sample can potentially affect lead levels in the water sample (Schock, 1990). Different sampling protocols may produce different lead and copper concentrations and different forms of lead.

LCR- based sampling is the US regulatory compliance sampling protocol. Based on the LCR, PWSs are required to use a first draw (FD) sampling protocol to collect water samples for lead and copper analyses. Samples are generally collected from single-family homes with LSLs and a typical sample consists of a 1-liter volume collected after at least a 6-hour stagnation period (Cartier et al., 2011). Del Toral et al., (2013) lists two variations of the LCR based sampling protocol; the first defined as the normal household usage (NHU) first-draw sample where water is used in a normal fashion before it is let to sit stagnant for at least 6 hours before collecting a sample, and the second known as the pre-flushing (PF) first-draw sampling where water is run for a specified amount of time before the stagnation period and subsequent sample collection. Instructions on water-use during the stagnation period vary in the U.S. where restrictions by PWSs may be imposed on water-use from taps to be sampled only or on water-use in the entire household. It is difficult to ensure strict adherence to sampling protocols, and more so when residents collect the samples. Moreover, other factors such as flow rates, hydraulic flow characteristics, diverse premise plumbing materials and configurations, influence lead concentrations in a sample (Del Toral et al., 2013).

The Chicago Department of Water Management (CDWM) conducted an LCR compliant study to determine lead concentrations in homes in Chicago, Illinois that had LSL connections. Residents were asked to complete a plumbing profile identifying the kitchen tap and meter or internal shutoff valve, and describe the internal plumbing, including any recent plumbing work. One-liter high density polyethylene (HDPE) wide-mouth (5.5 cm, 2.2 in) sample bottles were used and residents were instructed not to remove aerators prior to sampling and not to collect samples after point-of-use or point-of-entry treatment devices. Residents were instructed to collect samples from cold water taps only by opening the tap slowly until fully open, to mimic realistic field conditions with the most aggressive high flow conditions. Additional to the first-draw sample, 45 second flushed samples were also collected. Samples were also visually inspected for particulate matter at the laboratories (Del Toral et al., 2013). The study found that both variants of the first-draw sampling protocol severely underestimated peak lead levels and the NHU firstdraw variant yielded higher results overall than the PF first-draw sampling protocol. However, the 90th percentile values for each of the successive sequential liter samples were up to four times higher than Chicago's average 90th percentile value using first draw samples, indicating that sequential sampling represented peak lead levels more effectively. Del Toral et al. stress the importance of sample-site selection, sampling protocol and other site conditions for evaluating the amount of lead corrosion and release. However, in general, the LCR based first-draw sampling method detects many lead sources and tracks corrosion control effectiveness, although it does not readily translate to typical human exposure (Cartier et al., 2011).

van den Hoven & Slaats, (2006) describe a method of proportional composite sampling which is more useful as a research tool, as it gives better estimates of human exposure to lead from drinking water. Random daytime sampling (RDT), without any prior preset stagnation time could also provide fairly reasonable estimates of average lead concentrations at the tap but is more effective for a larger number of samples taken, and with samples collected as the first liter from the tap (Cartier et al., 2011). RDT is used as the regulatory treatment assessment in the UK (Schock, Tully & Calahan, 2016). Fixed stagnation time is used as a regulatory sampling protocol in Ontario, Canada with a 2.5-minute flush prior to a 30-minute stagnation time (30MS) and the first two liters collected as the sample. Regulation mandates a $90th$ percentile Action Level of 10 µg/L that may be revised to 5 µg/L (Schock et al., 2016). Another possible method involves sequential or profile sampling with a defined stagnation time and 10-20 samples collected, each with a defined volume (Schock et al., 2016).

Schock at al. (2016) list a number of other possible options for lead sampling, one of which is a composite proportional sampling protocol for exposure assessment by monitoring normal water use patterns. A device that collects 5% of the volume of every draw from the tap is used for one week. Another method, particle simulation sampling, recommends just a 5-minute stagnation period followed by collecting the first liter at the maximum flow rate, opening and closing the tap five times and then filling the rest of the bottle at normal flow rate. A second liter is collected at normal flow followed by a third liter that is collected in a similar fashion to the first sample. Service line or second draw sampling is used as a US regulatory method for lead source assessment with a six-hour stagnation followed by the volume between the tap and the LSL being flushed and then collecting the first liter. This method requires knowledge of the length of plumbing. The last method described by Schock et al. (2016) is the 3T's sampling for schools. Schools are instructed to let water stagnate overnight and a first draw (FD) 250 mL sample is collected from all taps and fountains, followed by a second 250 mL sample after a 30 second flush period if the first sample exceeds 20 ppb of lead. The 2018 revised version of the '3Ts for

Reducing Lead in Drinking Water in Schools and Childcare Facilities' does not indicate any lead concentration that is acceptable for samples from schools (*3Ts for Reducing Lead in Drinking Water in Schools and Childcare Facilities,* 2018). These various methods described of course have different regulatory compliance requirements, varying between countries.

2.6 Summary

The key takeaways from the literature review are as follows: (1) Lead and copper present in drinking water is of significant importance, as can be seen from the number of recent incidences across the US, and can cause adverse health effects depending on frequency and dose of exposure; (2) Distribution systems, water quality, and premise plumbing play a role in understanding the pathways, sources and concentrations of lead and copper in drinking water at the tap; (3) Various sampling protocols can be implemented depending on the purpose, resulting in different lead and copper concentrations.

3. METHODS

This chapter describes the "Assistance Program for Lead in School Drinking Water" by the Massachusetts Department of Environmental Protection (MassDEP) and the sampling protocol followed to collect drinking water samples from schools for analysis of lead and copper concentrations.

3.1 The MassDEP Assistance Program

The Massachusetts Department of Environmental Protection (MassDEP) has long provided guidance and advice to schools in implementing components of the LCCA. In April 2016, the Commonwealth of Massachusetts launched a cooperative program called the "Assistance Program for Lead in School Drinking Water" to help Massachusetts public K-12 schools and early education and childcare (EECs) facilities voluntarily test for lead and copper in drinking water. The program is of importance because it targets populations vulnerable to the ill effects of lead in drinking water. Moreover, schools are facilities that have intermittent water use patterns and are thus more likely to have elevated lead concentrations in their drinking water. The assistance program, which began in May 2016, has been funded by the Massachusetts Clean Water Trust and managed by MassDEP. MassDEP contracted with the University of Massachusetts, Amherst to implement significant components of the Program and the laboratory of the Massachusetts Water Resources Authority (MWRA) was also extensively involved. The technical assistance largely included helping public schools and childcare facilities to establish a sampling program, providing lab analysis for samples taken at all points of drinking water consumption and water taps for food preparation, and assisting with identification of fixtures with lead and copper concentrations greater than the Action Level defined by the LCR. The

Program follows the US EPA technical guidelines found in the document called "3Ts for Reducing Lead in Drinking Water in Schools and Childcare Facilities", with the 2018 revised 3Ts defined as "A Training, Testing and Taking Action Approach". The details of the Program are further elaborated below.

The program was conducted in two phases; Phase I between May 2016 and March 2017, and Phase II between August 2017 and December 2018. Phase I included about 170 systems and 818 school buildings participating, and with 40 systems and 174 buildings in Phase II. A total of 210 systems, 992 buildings and 68,000 samples were collected. The program components include:

- DEP LCCA Program
- Forms and information materials
- Application by the school system
- Informational meeting with the community
- Sample Plan/Fixture Map
- Web-based LCCA Program Management Tool
- Sampling
- Laboratory Analysis
- Reporting of lab results to DEP and schools
- Follow-up steps

The Sample Plan with a map of the fixture locations in the school identifies all locations where students and staff may consume drinking water from or where water is used for preparation of food. A unique, sequential code is used to label these locations. Each school system is also assigned a unique code that can be used to provide and access information on the online LCCA Program Management Tool. The Tool contains all documents and information related to each school sampled, such as Sample Plans, Chains of Custody (CoCs), and lab results. Samples collected were sent to state certified commercial laboratories and subsequent results were electronically sent to MassDEP and uploaded on the Tool as well. The results were sent to schools soon after laboratory analyses were completed, along with DEP contacts, information links and template letters for parents, and the results were made public approximately two weeks later.

3.2 Sampling Protocol

The sampling protocol largely followed the USEPA 3Ts document which was created subsequent to the LCCA of 1988. The sampling protocol requires an 8-18-hour stagnation period with no pre-flushing. The stagnation period attempts to replicate typical overnight stagnation durations as well as enabling collection of samples of water that have been in contact with premise plumbing. Stagnation generally occurred overnight, with samples from schools being collected Tuesday through Saturday in the early mornings before school sessions began and before any water was used. If there are multiple floors in a building, it is recommended to start from the bottom floor and work upwards. Samples were collected as a 250 mL first draw (or primary) stagnation sample with medium/normal flow rate, and another 250 mL flush sample being collected after a 30 second water flush immediately following the first draw sample collection. Wide-mouthed, 250 mL volume, translucent, plastic bottles were used to collect the water samples. First draw samples typically represent the water volume in a fixture (5 to 200 mL) along with the closest attached piping and also represents water that might be used at the start of the day or after infrequent use. Without a fixture, a 250 mL sample might represent the water volume in about 5 feet of $\frac{1}{2}$ inch copper piping or about 2.5 feet of $\frac{3}{4}$ inch copper piping.

Flush samples were collected for most locations, contrary to the 3Ts guidance which recommends collecting a flush sample only if the lead concentrations in first draw samples exceeded ALs. For some sample locations with multiple adjacent taps, only one flush sample was collected as this sample represents further interior piping that is common to adjacent fixtures; the 30 second flush period might represent the water volume in about 20-100 feet of ½ inch piping, or 10-50 feet of ¾ inch piping.

Samples were delivered within 14 days to the laboratory for analysis. At the laboratories, samples were typically acidified and pH lowered to \leq 2.0 with the addition of 0.15% nitric acid (trace metal grade is recommended) at room temperature. A minimum of 16 hours holding time is recommended before testing samples for lead and copper levels. Unfiltered, acidified samples are typically analyzed for total lead and copper using inductively coupled plasma/mass spectrometry (ICP-MS) with a low method detection limit; graphite furnace atomic adsorption (AA) is also utilized by some laboratories (Triantafyllidou et al., 2007).

4. RESULTS AND DISCUSSION

The samples collected from school buildings were sent to state-certified laboratories for determination of lead and copper concentrations. The lead and copper concentration results were received and extracted into Excel files by MassDEP. During Phase I of the assistance program, MassDEP sent the Excel file results directly to the school systems. In Phase II, the Excel files generated by MassDEP were received by UMass and an R script was used to generate a report format that was useful to schools, parents and the public. R Studio, Tableau and Excel software were used to analyze the results. The schematic representation below in Figure 3 outlines the Assistance Program from start to finish.

Figure 3. Schematic Representation of the MassDEP Assistance Program

4.1 R-Program Generated Report Format

The laboratory results obtained for every school were reported electronically to MassDEP. MassDEP or UMass then emailed the results to each school system, along with DEP contacts, information links and template letters for parents. DEP also transferred the results to the online LCCA Program Management Tool. DEP posted the results publicly on their website approximately 2 weeks after sending the results to the school. Figure 4 is an example of a Phase II results file sent to schools following the laboratory analysis. The report states the location, name of the school and facility type, school code, sample date and sampler name, the laboratory that performed the analysis, the analytical method used, method detection limit (MDL) of the instrument used to perform the analysis, the units of concentration used, and the Action Levels for lead and copper. A table describing the fixture types and abbreviations used, and concentration data for first draw and flush samples is included. Results marked as 'Non-Detects' (ND) are samples that had a concentration below the laboratory MDL. Results marked as 'Not Sampled' are generally flush samples that were not collected because of the common feed plumbing with the adjacent fixture. Results that exceed the respective Action Levels for lead and copper are highlighted in red text. The report also summarizes the total number of action level exceedances separately for lead and copper and for first draw and flush samples.

Figure 4. Example of portion of a results file generated using an R-script

The data have been organized and analyzed from a school building perspective and from an all samples perspective.

4.2 School Building Analysis

The results in this section are analyzed from a school building perspective. 170 school systems and 818 school buildings participated in Phase I of the assistance program, and about 40 systems and 174 buildings were sampled in Phase II. A total of 210 systems, 992 buildings and 37885 sample locations were tested, and 68,000 samples were collected. The number of buildings in a school system ranged from 1 to 76. An average of 40 locations were sampled per facility, with as few as only 1 location being sampled in a building to a maximum of 234 locations in a building. Approximately 432 buildings, or 44% of the total school buildings sampled, had at least one fixture exceeding the 15 ppb Action Level (AL) for lead (Pb), and about 91 buildings or 9% of total buildings had at least one sample that exceeded the 1.3 ppm AL for copper (Cu). 287 buildings or 29% of total buildings had one or more samples that exceeded the Action Level for both Pb and Cu, and an approximately equal percentage of schools, 28%, had no Action Level

exceedances. Figure 5 represents these percentages.

Figure 5. Results-school building basis

4.2.1 Examples of school buildings

The lead and copper concentrations for each location for three example school buildings are shown below.

Example School 1: The concentrations measured at example school 1 for each fixture location are represented in Figure 6 and Figure 7 for lead and copper, respectively. The school was constructed in 2003 and 85 locations were sampled. This example shows a school facility with locations for which both lead and copper concentrations exceeded the respective ALs. Lead concentrations were as high as 40 ppb and the highest copper concentration observed was approximately 2 ppm. The average concentrations observed for lead for first draw and flush samples were 12.5 ppb and 3.2 ppb respectively. Average concentrations for copper for both first draw and flush samples were about 0.6 ppm. A much larger impact of the 30 second flush period

on decreasing metal concentrations was observed for lead as compared to copper for the same locations.

Figure 6. Example school 1: lead first draw and flush concentrations

Figure 7. Example school 1: copper first draw and flush concentrations

Example School 2: Concentrations by fixture location for example school 2 are represented in Figure 8 and Figure 9 for lead and copper, respectively. This school was constructed in the year 1955 and 75 locations were sampled. In this example, no concentrations greater than the ALs were observed for either lead or copper. The maximum concentration for lead was about 7 ppb and maximum concentrations for copper were about 0.4 ppm. The average concentrations observed for lead for first draw and flush samples were 2.43 ppb and 1.92 ppb respectively. Average concentration for copper first draw and flush samples were about 0.16 ppm and 0.12 ppm respectively. Blanks appearing at some locations may be either due to the results being recorded as NDs or due to the reason that flush samples were not collected in the case of locations sharing common piping.

Figure 8. Example school 2: lead first draw and flush concentrations

Figure 9. Example school 2: copper first draw and flush concentrations

Example School 3: Concentrations by fixture location for example school 3 for the 62 locations sampled are presented in Figure 10 and Figure 11 for lead and copper, respectively. This school is an example of a facility with a large number of results recorded as NDs for lead, and very low concentration levels for copper. The year of construction is unknown. The average concentrations observed for lead for first draw and flush samples were 0.25 ppb and 0.02 ppb respectively. Average concentration for copper first draw and flush samples were about 0.07 ppm and 0.067 ppm respectively. The MDLs set by the laboratory conducting the analyses for this particular school were 0.001 ppm and 0.003 ppm for lead and copper, respectively. The highest lead concentration was 5 ppb and copper concentrations do not exceed 0.2 ppm.

Figure 10. Example school 3: lead first draw and flush concentrations. (Locations with no bars had non-detectable lead levels)

Figure 11. Example school 3: copper first draw and flush concentrations

From these example schools, it can be seen that a wide range of results may be possible between school buildings and within a school building. Very low lead can be achieved, and this is probably due to the lack of lead in plumbing. Flushing is also seen to be very effective for short term decrease in lead.

4.3 All Samples Analysis

An average of 69 samples per facility were collected from the average of 40 locations per facility. 57% of the total samples collected were first draw samples, and 43% were flush samples. Flush samples were not always collected for all fixture types. This typically occurred for multiple adjacent fixtures fed by a common supply line, such as a classroom sink that had a cold water bubbler fixture and a cold water faucet, or a hallway drinking water source that had two bubblers (higher and lower distance off the floor) or had a bottle fill station with one or two bubbler fixtures. The minimum and maximum number of samples collected per facility were 2 and 431, respectively, over both phases of the Assistance Program. The lead concentration in schools ranged from non-detects (concentration too low to be detected) to 42 mg/L, and copper concentrations varied from non-detects to as high as 164 mg/L. Detection levels ranged from 0.0005 to 0.001 ppm for Pb and from 0.0002 to 0.005 ppm for Cu.

The distribution of lead concentrations in samples is shown in Figure 12, as percent in range and percent cumulative frequency, separately for first draw (P) and flush (F) samples. Approximately 10.4% of lead first draw (P) samples exceeded 15 ppb, 26% exceeded 5 ppb, and 58% of samples exceeded 1 ppb. Amongst flush samples, about 2% of samples exceeded 15 ppb, about 6.8% exceeded 5 ppb and 31% exceeded 1 ppb. The significant impact of 30 second flushing on decreasing lead levels is shown by the data.

Figure 12. Results- sample basis: lead concentration distribution

A similar plot in Figure 13 presents distributions of copper concentrations, separately for first draw (P) and flush (F) samples. Approximately 3.3% of first draw samples and less than 2% of flush samples exceeded the Action Level of 1.3 ppm for copper. In comparison to lead, a lower impact of flushing on decreasing copper concentrations was found. This could be attributed to the fact that copper piping is present throughout the plumbing system leading to water chemistry and corrosion control issues that may raise copper levels in drinking water, and to the fact that stagnation causes less of an increase in copper as compared to lead.

Figure 13. Results- sample basis: copper concentration distribution

4.4 Fixture Types and Fixture-based Results

Table 1 below shows the twelve different types of fixtures sampled and their respective percentages of the approximately 38,000 sample locations tested. Classroom faucets, drinking water bubblers and water cooler units constituted the greatest number of fixture types sampled and were also the most common types of fixtures observed in schools.

Table 1. Fixture types and percent of sample locations

Figure 14 shows the percent exceedances of Pb and Cu Action Levels on a fixture basis. Kitchen Kettles and Kitchen Kettle hot had the highest percentage of first draw and flush samples exceeding the Pb AL, although the number of samples from these fixture types constitute a small fraction of the total samples. As for copper, the fixture types Home Economics Room- Cold and Kitchen Kettle- Hot had the highest percentages of first draw samples exceeding the Cu AL. The Service Connector fixture type also shows high percentage exceedances, however very few buildings were sampled for service connectors. Amongst classroom faucets, which have the highest percentage of total samples, about 14.6% of first draw samples exceeded the Pb AL.

Figure 14. Results-fixture basis: lead and copper AL exceedances

Figure 15 shows percentage distributions of concentrations based on fixture type with ranges of > 1 to 5 ppb, > 5 to 15 ppb, and > 15 ppb for lead samples for both first draw and flush samples.

Decreased concentration levels in flush samples versus first draw samples can be observed for every fixture type across all concentration ranges, except for water coolers where the first draw and flush samples remain at almost similar concentrations (this is expected as water coolers have a significant storage volume that is probably not all discharged during the 30 second flush). Not shown in Figure 14 is the fact that the percentage of samples with less than 1 ppb lead increased from 42% for first draw samples to 69% for flush samples.

Figure 15. Results-fixture basis: lead concentration distribution

A similar plot for copper with ranges of > 0.1 to 0.5 ppm, > 0.5 ppm to 1.3 ppm and > 1.3 ppm, for both first draw and flush samples is represented below in Figure 16. First draw and flush samples in this case too remain at almost similar concentrations for water coolers.

Figure 16. Results-fixture basis: copper concentration distribution

4.5 Influence of Building Age

Information on building age was obtained for approximately 800 schools out of the total sampled. The oldest school was built in 1878 and the newest in 2018. The majority of schools were constructed between 1950 and 1980, except for a boom in 1900, as can be observed in Figure 17 below. The year of construction of the building indicates the likely age of premise plumbing within the building as well.

Figure 17. Schools and Year of Construction

Figure 18 shows the fraction of AL exceedances for lead first draw and flush samples versus the age of the building from which samples were collected. A decrease in exceedance percentage is seen for the newer schools since the year 1990, possibly reflecting the implementation of lead materials control following the regulations in the 1980s and the LCR. In the case of copper, there is no clear impact of building age on percentage of samples exceeding Action Levels, as seen in Figure 19.

Figure 18. Results-fraction of lead AL exceedances

Figure 19. Results- fraction of copper AL exceedances

4.6 Remedial Actions

MassDEP recommends shutting off taps or discontinuing consumption from fixtures that have high concentrations of lead or copper, i.e., results exceeding the Action Levels. Signs must be posted on problem fixtures, warning against their use. The local Public Water Supplier or MassDEP Drinking Water Program can be contacted for assistance in dealing with problem fixtures. An important step in taking remedial action is to determine the source of contamination. Generally, exceedances in first draw samples indicate issues with the fixture itself and exceedances in flush samples might indicate that interior plumbing in general may be the source of the metal. Additionally, details about the plumbing profile are required to determine volumes associated with plumbing components and accordingly to devise a sample plan to determine the exact plumbing parts that may require replacement. It is also advisable to draw cold water only from taps, as hot water increases the chances of reactivity of water with plumbing materials. Point-of-use (POU) filters may be installed at individual water outlets. POUs differ from pointof-entry (POE) filters, which are installed at the water entry source into the building and are ineffective in controlling lead and copper contamination. Filters containing activated carbon and other media can remove dissolved lead in drinking water. Appropriate certified filters must be installed, maintained and routinely replaced for point of use treatment to be effective. Filters that are tested and certified as meeting NSF/ANSI Standard 53 are effective in preventing lead exposure. An alternative source of water, such as bottled water, may also be provided in schools until other remedial measures are taken to decrease lead and copper levels. Follow-up sampling plans and analyses need to be performed after replacement of plumbing components to assess the change in concentration levels.

5. SUMMARY AND CONCLUSIONS

5.1 Summary

Between June 2016 and November 2018, water samples from a total of 210 school systems, encompassing 992 buildings and 37885 sample locations, were collected for lead and copper analysis; of the total of 68,000 samples collected, 57 % were first draw samples collected after 8-18 hours of stagnation and 43 % were 30 second flush samples. About 44% of school buildings had one or more samples exceeding the lead AL and 9% of school buildings had one or more samples exceeding the copper AL. 29% of buildings had one or more samples exceeding both lead and copper ALs. 10.4% of lead first draw samples exceeded 15 ppb and about 58% exceeded 1 ppb. The highest lead and copper concentrations observed were 42 mg/L and 164 mg/L respectively. Flushing was found to have a higher impact in decreasing lead concentrations as compared to the impact on copper concentrations. Of the twelve different types of fixtures tested, classroom faucets, drinking water bubblers and water coolers were the most commonly sampled. Kitchen Kettles were found to have the highest percentages of first draw and flush samples exceeding the AL. A decrease in lead concentration levels is seen in schools constructed later than the year 1990, possibly indicating the implementation of lead materials control following the regulations in the 1980s and the LCR.

5.2 Conclusions & Broader Considerations

Flushing of plumbing components before use or consumption of water may serve as a temporary measure to decrease exposure to lead and copper. Flushing decreases both lead and copper exposure as it purges contaminated water that has remained stagnant in premise plumbing and draws out water that has had less contact time with internal plumbing. About 10.4% of first draw samples exceeded the AL for lead, whereas only about 2% of flush samples exceed the lead AL.

In the case of copper, about 3.3% of first draw samples exceeded the copper AL, and less than 2% of flush samples exceeded the copper AL. The analysis results show that flushing had a substantial impact in decreasing lead and copper levels, much more so for lead than copper. The drawbacks of flushing are that it is time-consuming, wastes water and may not be as effective without knowledge of flushing durations required. A one-time morning flush may not prevent exposure all day long. Stagnation time also has an impact on copper concentrations, as can be seen from the decrease in samples exceeding the copper AL, from 3.3% to less than 2% for first draw and flush samples respectively. A more long-term, permanent solution is the removal of all lead or copper from drinking water system components. However, this is expensive and challenging, as detailed information regarding plumbing components such as premise plumbing and the presence of lead service lines and lead pipes is required. Apart from the distribution system and building plumbing materials, source water needs to be treated to minimize corrosion of materials that may contain lead or copper. This approach can be very effective for soluble copper control and is very important for soluble lead control but often cannot decrease lead levels to below a detectable level, the desired health based goal. Optimum corrosion control may include control of water pH, alkalinity, and chloride to sulfate mass ratio among other water chemistry parameters. Optimal corrosion control treatment may also be implemented through the addition of phosphates such as orthophosphates. Corrosion inhibitors work by forming a coating on metals and providing a protective barrier between water and pipes. However, changes in water treatment or disinfection practices can severely affect lead corrosion control.

Analysis of the influence of building or plumbing age on lead and copper concentrations is affected by the fact that insufficient data were obtained to clearly correlate the two. In many cases, different parts of the school buildings were built at different times, with renovations and plumbing replacements being made frequently over the years.

An interesting perspective of analysis would be to study the effect of water quality on lead and copper concentrations in school drinking water. Water quality parameters such as pH, alkalinity, chloride to sulfate mass ratio and the addition of corrosion inhibitors are known influencing factors. Such water quality data were not obtained for this particular study. In this case, distribution systems would also have to be analyzed in detail to characterize the effect of water quality on plumbing materials in place and its subsequent effect on water quality at the tap.

Drinking water fountains and water coolers, two of the most commonly seen fixture types in schools, are also fixtures that are more likely to be used intermittently, with prolonged stagnation periods. Drinking water fountains may also contain more soldered joints and narrower piping than traditional taps, adding to the risk of increased lead exposure. Bubbler heads may be replaced with low-lead brass bubblers and new end-use plastic lined connectors, valves and fittings are some options for replacement parts.

Apart from the inherent variability in lead release from plumbing materials, factors that may have caused variability in sample concentrations include tap flow-rates, as high flow-rates and hydraulic disturbances cause detachment of lead and copper from pipe scales resulting in higher particulate lead concentrations. Low flow rates or pre-flushing before sampling may reduce variability in lead concentrations but with the risk of underestimating lead exposure. Possibly a range of flow conditions might help assess exposure concentrations more effectively, particularly particulate lead concentrations. Achieving consistent sampling flow rates across all fixtures sampled is challenging with the number of schools sampled, variations in fixture types, and

different samplers. Another possible cause for concern could be the presence of aerators while sampling. Particles can get lodged in an aerator and could thus influence lead concentrations in samples. Although advisable to not remove aerators while sampling, this may pose a difficulty in identifying the true source of contamination. To sufficiently characterize lead and copper contamination within the premise plumbing of a building, a larger number of samples may need to be collected in sequence, in combination with a range of flow conditions.

The standard US protocols and regulations may not be enough to truly quantify exposure to lead. Particulate lead that may detach from plumbing does not undergo complete dissolution with the standard preservation protocol and up to 80% of lead present in water could be missed (S Triantafyllidou, Lambrinidou, & Edwards, 2009). The standard acidification procedure followed helps preserve soluble lead but may not be as effective for particulate lead. Particulate lead was not measured and even if turbidity readings are taken, they are likely to be inaccurate as particles may settle down and attach to the plasticware used to sample. Particulate lead may become bioavailable when ingested into the human system, and therefore is important that it is taken into account while estimating exposure to lead.

Meeting the LCR does not necessarily mean protection from lead and copper exposure at the tap. The revised 3Ts document that provides tools and recommendations for voluntary lead testing across schools and childcare facilities, recommends that schools should aim for the lowest lead level possible and that there is no safe level for lead in drinking water.

5.3 Future Perspectives

A follow-up study following remediation at all schools sampled during Phase I and Phase II of the MassDEP Assistance Program, would be useful in assessing the success of remedial

measures taken. Schools and child care centers are of particular importance in quantifying lead and copper exposure, not only due to the vulnerable population involved, but also because of the long stagnation durations and intermittent water use typical of these institutions. Other factors such as water quality and distribution system conditions can be taken into consideration for future studies.

There is increasing need for better public health studies to refer to the MassDEP Assistance Program. Other states and countries need to incorporate policies specific to schools and early education centers. The Flint water crisis also brought to light the importance of decision-making by government bodies in ensuring safe water supply to the public. The human element in environmental and water policies play an equally important role as the policies. For lead monitoring programs in schools to be effective, municipalities, schools and parents have to be better involved, aware and pro-active.

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