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Lead, Copper, and Iron in University Tap Water

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The University of Southern Mississippi

Lead, Copper, and Iron in University Tap Water

by

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Abstract

This study observed concentrations of lead, copper, and iron in university tap water over an eight-week span during and between the summer and fall semesters. First draw and 30s flush samples were taken after overnight stagnation from the Honor House, College Hall, J. B. George Building, and International Center bathrooms and analyzed with an inductively-coupled plasma mass spectrometer (ICPMS). There was no obvious correlation between time in the semester and metal concentrations. Relative iron levels rose and fell at the same time in all buildings, but there was little correlation between buildings for lead and copper concentrations. The Honor House had the highest first draw lead levels, and College Hall had the highest copper levels in both first draw and 30s flush samples. All of the 30s flush samples had lower metal concentrations than the first draw samples. Lead and copper concentration variations between buildings indicates influence from building infrastructure, while the correlations in iron concentrations between buildings indicates a probable system-wide factor.

Keywords: Tap water, lead, copper, iron, university, University of Southern Mississippi,

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I would like to give my thesis advisor, Dr. Shiller, special thanks: I doubt many professors would even consider mentoring for an undergraduate thesis when they don’t even work at a campus with any undergraduate students.

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List of Abbreviations

μg	Micrograms
μL	Microliters
CH	College Hall
dL	Deciliter
HH	Honor House
IC	International Center
ICPMS	Inductively-coupled plasma mass spectrometer
JBG	J. B. George Builiding
ppb	Parts per billion
ppm	Parts per million
PVC	Poly vinyl chloride
USM	The University of Southern Mississippi

Chapter 1: Introduction

Potable water is essential to human life and health. In the United States, water is easily accessed by water systems that distribute water from a treatment facility to individual buildings via a system of pipes. While water treatment facilities generally eliminate biological contaminants in the water at the facility, contaminants of various classes can enter the water distribution system at points after the water has left the facility. Metal contaminants in particular can leech into water from pipes at any point. This has long been recognized as a human health problem: In the United States, the Environmental Protection Agency (EPA) regulates the water quality of these systems, including acceptable levels of certain metals (EPA, 2017).

Lead has been a historical problem, having once been a common material in water pipes themselves (WHO, 2011). Lead toxicity is cumulative, and primarily effects the nervous system (WHO, 2011). Pregnant women, fetuses, infants, and children under the age of 6 are the most susceptible (WHO, 2011). There is evidence of harmful effects even at very low levels of lead in the blood (WHO, 2011).

Copper is far less toxic than lead, but is still a potential hazard in drinking water, especially to infants fed formula reconstituted with tap water (WHO, 2004). The EPA mandates regular testing for it along with lead under the Lead and Copper Rule (EPA, 2017).

Iron is relatively nontoxic, and overdose would be difficult to achieve (WHO, 2003). Nevertheless, iron is a common irritant in water systems, encouraging the growth of iron bacteria in water systems, adding an unpalatable taste to water, and staining plumbing and laundry (WHO, 2003).

Many factors influencing metal leeching in water systems, including pH of the water, chemical additives, stagnation, and pipe composition, are well documented. However, the complex interactions between these factors can be difficult to elucidate experimentally. Case studies are therefore important for finding directions for future research.

While the effects of stagnation and water use on metal leeching are well studied, there is little research specifically on the water systems of university campuses, which often combine aging infrastructure and large fluctuations in on-campus population. The purpose of this study was to see if there was a correlation between the time in the semester and at-the-tap concentrations of lead, copper, and iron, as well as to observe the differences between metal concentrations between buildings and the effects of flushing for 30 seconds.

Chapter 2: Literature Review

Water quality is dependent on many factors in the water system, including pipe materials, water conditions (e.g., pH, hardness, and temperature), treatment, and biological factors such as microbial contamination. Corrosion from the pipes and fixtures interacting with water can form a solid scale, which can release contaminants into the water if disturbed by changing water conditions (Shi, 2007).

Flint, Michigan is an infamous example of how these factors can come together disastrously. The city had lead-containing plumbing, which became more corrosive when the city switched to a cheaper, and more acidic, water source (Torrice, 2016). The water system developed microbial contamination, and the chlorine used to treat the contamination combined with organic material to make toxic by-products (Torrice, 2016). Chloride, which makes lead more soluble in water systems, was used to coagulate organic material for removal. Common measures to contain lead corrosion (e.g., adjusting the pH of the water system and/or adding phosphates) were not taken (Torrice, 2016). These factors (water conditions, water treatment, pipe materials, and microbes,) came together to create water quality more akin to toxic waste than potable water. Lead levels rose to toxic levels city wide (Torrice, 2016).

Lead

The Physiological Effects of Lead

Lead is a metal of particular note in human health: it is fairly common in the environment and has no threshold dose of effects. Children are at far more risk than adults: besides their significantly lower mass, children also absorb 4-5 times more of ingested lead than adults absorb (WHO, 2011). Disadvantaged children are at even more risk, as low iron, calcium, and phosphorus intake also increase lead absorption (WHO, 2011). This makes public policy and actions of the water system very important, as those most at risk often won’t have the resources to make changes on the individual level like replacing lead-containing pipes in a home.

Physiological effects of lead include behavioral/cognitive impairment, reproductive toxicity, genetic damage, and carcinogenicity. Acute lead toxicity occurs when adult blood lead levels are between 100-120 micrograms per deciliter (µg/dL) in adults and 80-100 µg/dL in children (WHO, 2011). Acute lead exposure leads to a laundry list of signs and symptoms. Behavioral and cognitive signs and symptoms include restlessness, irritability, a low attention span, hallucinations, memory loss, and dullness (apathy) (WHO, 2011). Physical symptoms include muscle tremors, kidney damage, abdominal cramps, headaches, and encephalopathy -brain damage (WHO, 2011).

Different signs and symptoms appear at lower (chronic) levels of blood lead. In adults, blood lead levels between 50-80 µg/dL initially cause irritability, tiredness, sleeplessness, headaches, gastrointestinal symptoms, and joint pain (WHO, 2011). One to two years of occupational exposure with blood lead levels of 40-60 µL leads to mood disturbances, lower scores on psychometric tests (used to measure mental ability), muscle weakness, gastrointestinal symptoms, and peripheral neuropathy (WHO, 2011). Anemia occurs at blood levels exceeding 50 µg/dL in adults and 40 µg/dL in children (WHO, 2011). Renal disease can occur in both adults and children at blood lead levels between 40-80 µg/dL, and hypertension increases with blood lead levels of 37 µL/dL (WHO, 2011). In 21-55-year-olds, blood lead levels between 7-37 µg/dL have a significant association to high blood pressure, and there is no evidence of a threshold dose (WHO, 2011). Lead levels between 12-120 µg/dL lead to reduced calcium metabolism in children with no evidence of a threshold dose (WHO, 2011). Lead can affect children's nervous systems at levels below 30 µg/dL (WHO, 2011).

Sources of Lead in the Water System

Lead can easily contaminate water systems, since it has natural sources and, more importantly, had many industrial applications (WHO, 2011). The most prominent source in water systems currently is lead leached from lead-containing water pipes, fittings, or solder (WHO, 2011). Lead piping was used extensively until it was banned in the 1960s, and continues to 'hide' in products like solder, which can leech enough lead to cause lead intoxication in children (WHO, 2011). The zinc coating of galvanized steel pipes, which are still in use but not as popular as in the past, can contribute considerable amounts of lead to tap water (Clark, 2015).

However, these sources are not equally problematic: lead leeching from fittings and solder decrease with time, while leeching from lead pipes does not (WHO, 2011). The sheer volume of lead sources makes the ideal lead concentration of 0 ppb in drinking water impossible (EPA, 2017). Therefore, EPA mandates an action level of 15 ppb in 10% or more of homes services for water systems (EPA, 2017). Water systems are required to test first draw water samples from at risk homes every 6 months, though the time period can be extended if the water system meets reduced monitoring criteria by having lead and copper below the action levels for certain periods of time (EPA, 2017). The number of samples required is based upon the number of people served by the water system, ranging from 100 samples from water systems serving over 1,000 people to 5 samples from water systems serving less than 100 people, but this can also be halved with reduced monitoring except in the case of water systems serving less than 100 people (EPA, 2017). The FDA, which oversees bottled water standards, places their limit significantly lower at 0.005 milligrams per milliliter (mg/L), or 5 parts per billion (ppb) (FDA, 2017).

Factors Influencing Lead Solubility

Lead tends to be more soluble in water that is soft (contains few dissolved minerals) and has acidic pH. Therefore, one way to deal with high lead in a water system is to raise the pH of the water to pH 8-9 (WHO, 2011).

Lead can leech from deposits, especially iron deposits, left on pipes even after water conditions become less favorable for lead solubility (WHO, 2011). The obvious, albeit expensive and time consuming, solution is to replace lead-containing pipes. However, attempts to replace lead pipes are hindered by galvanic corrosion, in which placing copper and lead-containing pipes next to each other increases lead corrosion because of the resulting galvanic cell (Wang, 2012). This becomes a major problem when the water system replaces its pipes with copper ones, but the home and business owners that they supply don’t replace their lead-containing pipes (Wang, 2012). Phosphates are normally effective at controling lead corrosion, but not when there is galvanic corrosion (Cartier, 2012).

Chloride, a major component of the chemicals used extensively for water sanitation, can cause increased lead in tap water (WHO, 2011), as it can increase sulfate levels, though this decreases over time (Sun, 2017)

The city of Hattiesburg's last water quality report (City of Hattiesburg, 2017) reported lead levels of 0.002 parts per million (ppm) or 2 ppb (City of Hattiesburg, 2017). For scale, the EPA action level for the water system is 15 ppb (EPA, 2017), the FDA limit for bottled water is 5 ppb (FDA, 2017), and the ideal level of lead is 0 ppb (EPA, 2017).

Copper

The Physiological Effects of Copper

Copper is an essential nutrient, with a Recommended Dietary Allowance (RDA) of 340 to 900 µg/day depending on age (WHO, 2004). Most adults take in between 1 to 3 mg of dietary copper per day, with 0.1-1 mg of copper coming from tap water (WHO, 2004). However, drinking water from a distribution system with copper materials can greatly increase copper intake (WHO, 2004). This is of greatest concern to infants fed tap water reconstituted formula (WHO, 2004).

The adult lethal exposure for copper is between 4-400 mg/kg (WHO, 2004). Large doses of copper lead to acute renal failure, gastrointestinal bleed, hematuria (red blood cells in the urine), intervascular hemolysis (destruction of red blood cells), methemoglobinemia (the presence of methemoglobin, an oxidized and nonfunctional form of hemoglobin, in the blood), and hepatocellular (liver cell) toxicity (WHO, 2004). Lower doses lead to symptoms similar to food poisoning- nausea, vomiting, diarrhea, and headache generally 15 minutes to an hour after exposure (WHO, 2004). The lowest known copper concentration to cause this is 4 mg/liter (WHO, 2004).

Sources of Copper in the Water System

Low levels of copper are naturally present in water. However, copper is used extensively commercially and is currently a choice metal for water pipes (WHO, 2004).

Factors Influencing Copper Solubility

Acidic pH or a combination of basic pH and high-carbonate water increase dissolved cooper (as compared to particulate copper in a corrosion scale) concentration (WHO, 2004). Sodium orthophosphate is a common corrosion inhibitor for copper: phosphate ions decrease the solubility of copper and increase the resistance to pitting of the surface layer of pipes (Yohai, 2011). Phosphates are effective copper corrosion inhibiters even in the presence the common sanitizing chlorine compound sodium hypochlorite (Yohai, 2013).

Hattiesburg’s last water quality report indicated copper concentrations of 0.2 ppm (City of Hattiesburg, 2017), or 200 ppb. The EPA action level for copper is an order of magnitude larger at 1.3 ppm, or 1300 ppm (EPA, 2017).

Iron

The lowest known lethal dose of iron is 40 mg/kg body weight, and the average lethal dose is between 200-250 mg/kg body weight (WHO, 2003). However, while relatively nontoxic, iron causes several problems in water systems. For one thing, the corrosion of iron pipes encourages the growth of ‘iron bacteria,’ which can be detrimental to a water system (WHO, 2003). Iron can also cause an unpleasant taste and stain laundry when present in high enough concentrations (WHO, 2003). Some of these issues have been an ongoing problem in Downtown Hattiesburg, where the University of Southern Mississippi is located (Burns, 2017).

Sources of Iron in the Water System

Iron is a common water pipe material, and iron salts are used in water treatment (WHO, 2003). Iron is also used as a construction material, a pigment for paints and plastics, and as a treatment for iron deficiency (WHO, 2003).

Plastic Pipes: Not a Perfect Solution

Looking at the detrimental effects of metals, one may wonder why all metal pipes are not replaced with plastic alternatives. Plastic pipes leech chemicals the same way that metal pipes do, and we often know less about these chemicals than the corrosion products from the metal pipes that have been in use for decades (Kelley, 2014). In fact, polyvinyl chloride (PVC) pipes leech lead compounds (WHO, 2011; Zhang, 2015). Therefore, plastic pipes are not a solution to water contamination, but rather a new aspect of it.

This Study

The overall objectives of this study were to a) observe USM campus tap water concentrations of lead, copper, and iron over time to see if there are changes potentially due to differences in stagnation due to changes in water use between semesters, b) observe any differences in metal concentrations between buildings of different ages and location, and c) observe differences between first draw and 30s flush water samples in these buildings. Water use is a known influence on the concentration of corrosion products (metals) in tap water, so an increase in water use from an increase in student population could affect the concentration of lead, copper, and iron in university tap water. Old pipes are known to increase the risk of lead release, and new pipes are known to increase the risk of copper release, so building age would be expected to correlate with higher lead or copper concentrations. The reduction in corrosion product concentrations from flushing the water pipes is established enough to be an EPA recommendation for temporary management of lead and copper, so we expect the 30s flush samples to have lower concentrations of lead, copper, and iron.

Chapter 3: Methodology

Water samples were collected from first floor women's or unisex bathroom sinks in the Honor House, JB George Building, International Center, and College Hall for eight consecutive weeks starting on July 29th. Building locations are shown in Figure 1. Samples were taken between 5:00 am and 7:30 am so that no water use could have occurred after the buildings were locked the night before. These buildings were chosen for their varying ages, varying locations on campus, and ease of access. Acid-washed bottles (250 mL) were used to collect first draw and 30s flush samples after overnight stagnation. The acid washed bottles were Nalgene high density polyethylene prepared by soaking for at least 8 hours in hot 1.2 M hydrochloric acid (reagent grade) then thoroughly rinsing with ultrapure distilled deionized water. Water samples were immediately placed in individual plastic zip bags, then placed in another plastic zip bag for storage and transport.

pH readings were taken using a Oakton 150 or SymPHony pH meter after the samples were taken in each location.

The samples were taken to the laboratory and acidified to pH less than 2 using ultrapure hydrochloric acid (Seastar). The trace metals in the samples were analyzed using a double-focusing ICPMS (ThermoFisher Element XR) using a low-flow (100 µL/min) self-aspirating nebulizer (Elemental Scientific) and Teflon spray chamber. Samples were slightly diluted due to the addition of ultrapure dilute nitric acid (Seastar) with added internal standards (High Purity Standards.) Calibrations were done using standards made in 0.16 M nitric acid. Sample preparation was done in a laminar flow clean bench.

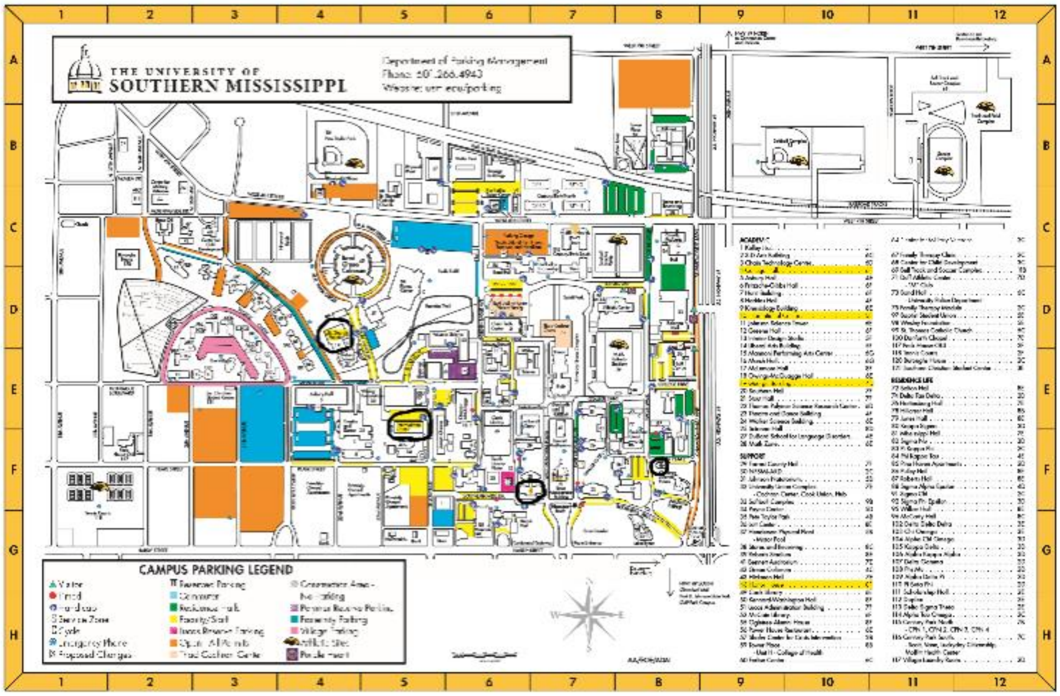

Figure 1: Map of The University of Southern Mississippi (The University of Southern Mississippi, n.d)

Chapter 4: Results

Metal concentrations and pH of water were not clearly correlated over time or between buildings (Figures 2-8). Only iron showed a correlation between buildings: iron concentrations tended to either increase or decrease in all the buildings at the same time (Figures 5 and 6). All of the 30s flush samples had lower metal concentrations than the first draw samples taken on the same day from the same building (Figures 3-8). Many buildings saw metal concentrations dip on 8/26/17 (Figures 3-8).

Two first draw samples from the Honors House approached the EPA’s action level for lead (15 ppb; EPA, 2017), but none reached the action level (Figure 2). The rest of the first draw samples were below 5 ppb, and all of the 30s flush samples were below 1.5 ppb (Figures 3-8).

Only one sample had levels of iron below that which is potentially detectible by taste or 50 ppb, and several samples had iron levels over those at which staining of laundry and plumbing can occur, or 300 ppb.

All of the water samples had copper levels several orders of magnitude below the action level 1300 ppb. College Hall had copper concentrations well above the other buildings in both first draw and 30s flush samples (Figures 7 and 8).

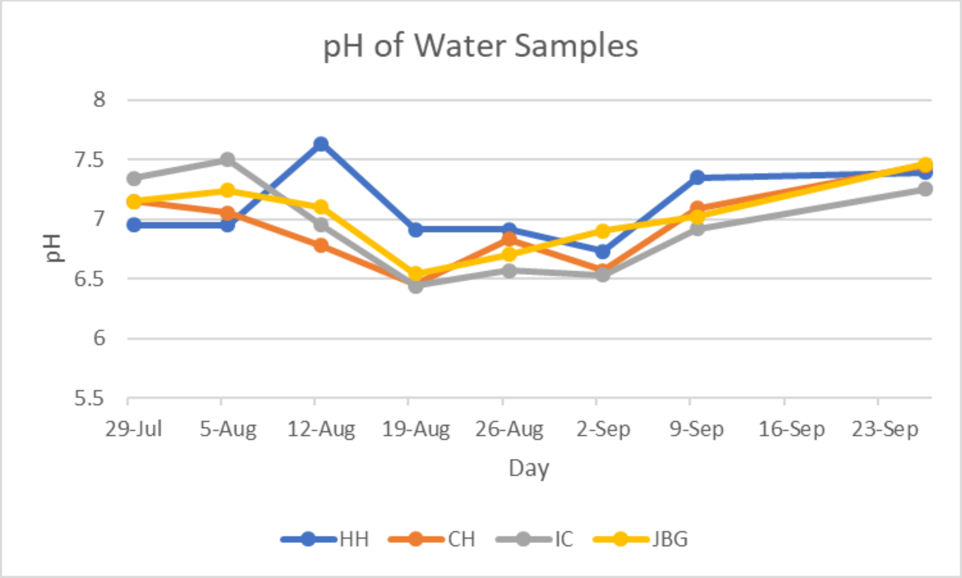

Figure 2: pH of water samples. HH is the Honor House, CH is College Hall, IC is the International Center, and JBG is the J. B. George Building.

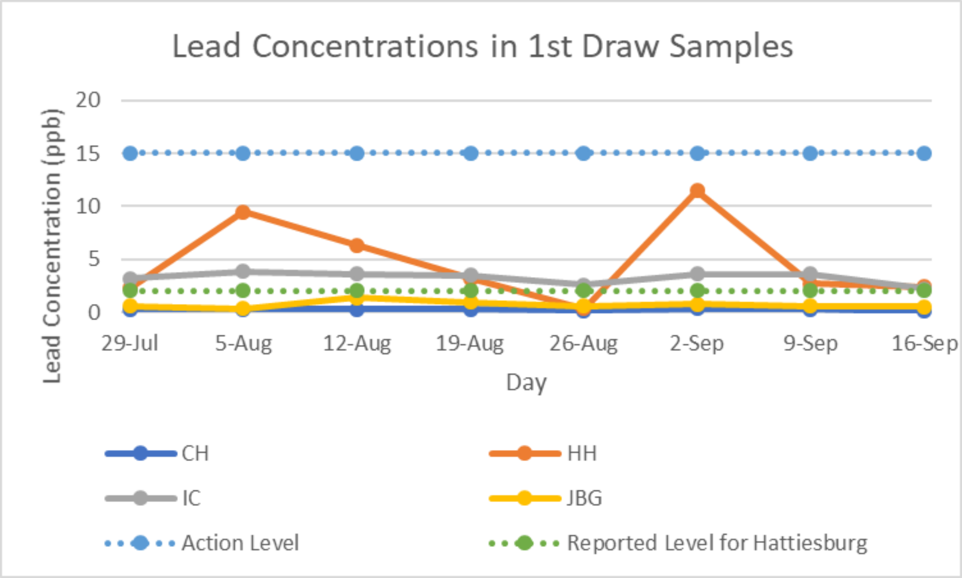

Figure 3: Lead concentrations in 1st draw water samples.

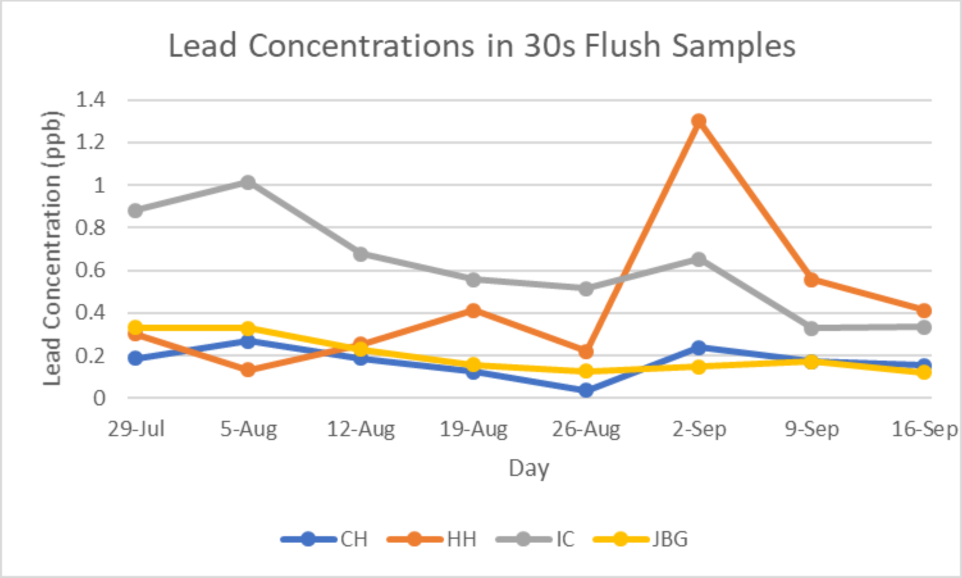

Figure 4: Lead concentrations in 30s flush water samples. Note the change in scale.

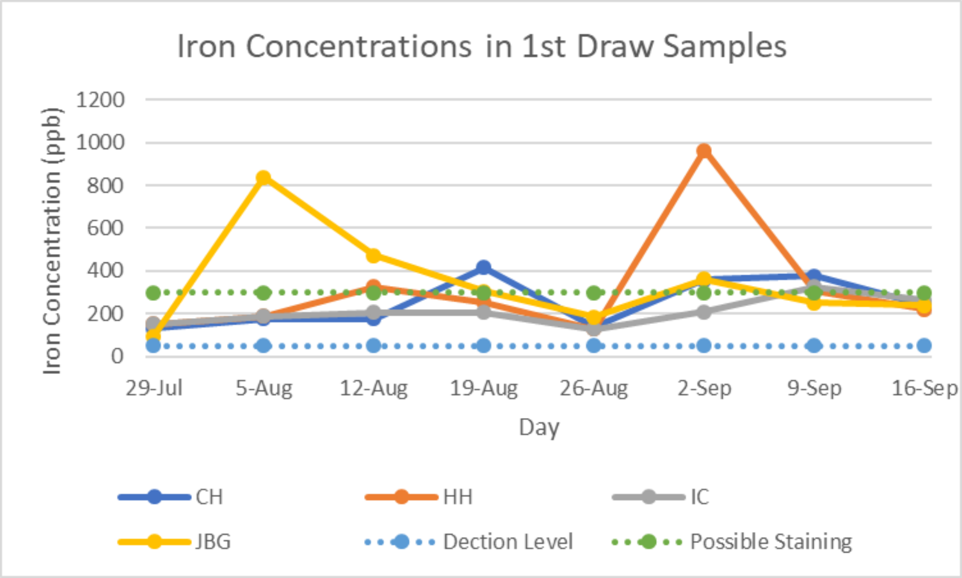

Figure 5: Iron concentrations in 1st draw samples.

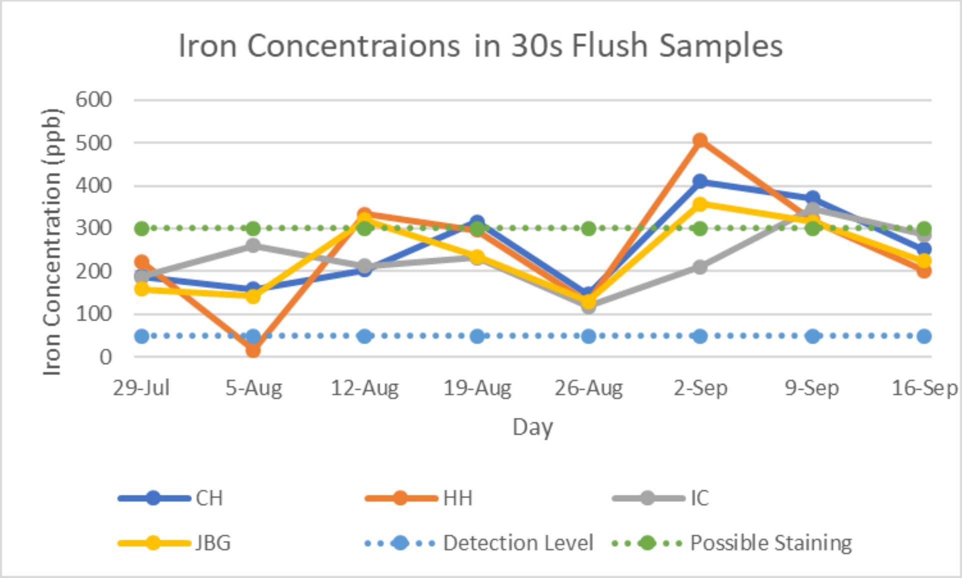

Figure 6: Iron concentrations in 30s flush samples. Note the change in scale.

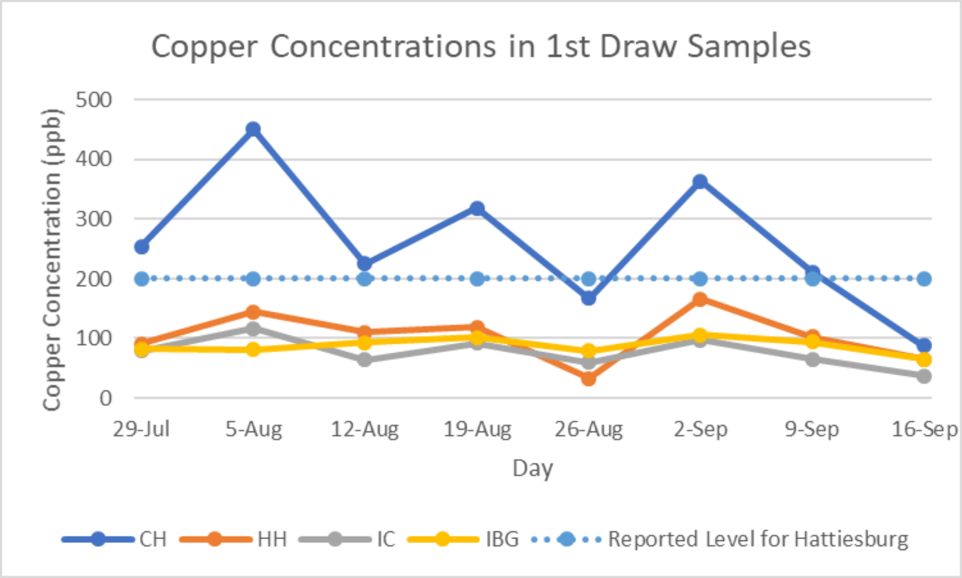

Figure 7: Copper concentrations in 1st draw samples. Action level (1300 ppb) not shown due to scale.

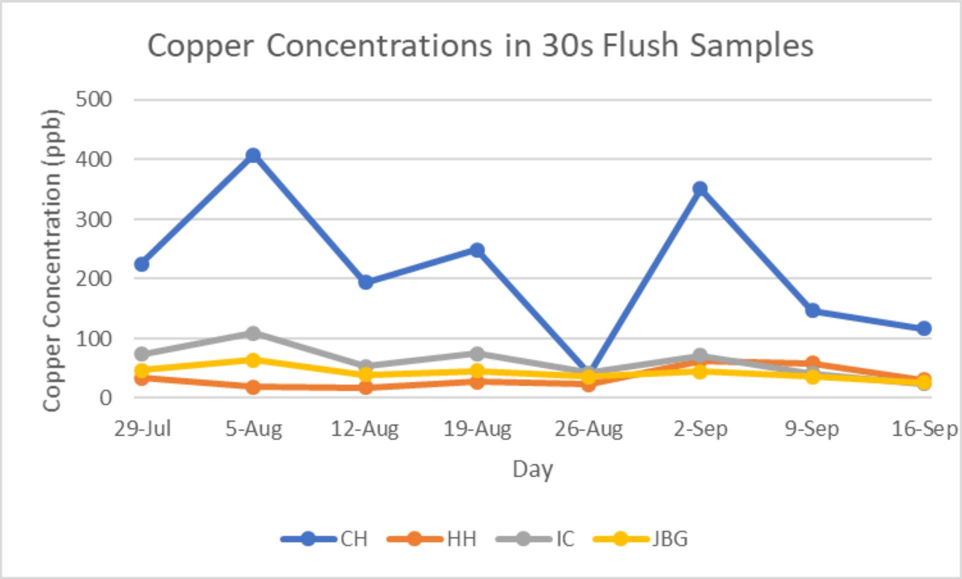

Figure 8: Copper concentrations in 30s flush samples.

Chapter 5: Discussion

Each building had its own ‘profile’ of relative lead and copper concentrations, which fluctuated independently of the other buildings. This could suggest a large influence from the plumbing of the buildings rather than the water system. All of the buildings had ductile iron pipes (Crenshaw, C., Physical Plant Director. 2017, June 13. Personal interview), so pipe material was not a factor.

The Honor House had the highest levels of lead, which is unsurprising considering its age as one of the original buildings on campus (The University of Southern Mississippi, n.d). Its pipes were replaced in 1990 (Crenshaw, C., Physical Plant Director. 2017, June 13. Personal interview), but being in one of the oldest sections on campus might have allowed for a larger buildup of lead scale, especially since it had 1-inch pipes. This could explain why there were two spikes of higher lead concentrations, rather than a consistent level of lead.

While built in 1921, College Hall was renovated in 2013 (Arnold, 2013), and its pipes replaced in 2011 (Crenshaw, C., Physical Plant Director. 2017, June 13. Personal interview), which may contribute to its relatively high copper concentration, as copper release is highest from new pipes then decreases over time. College Hall also has the biggest pipes (6-inch) (Crenshaw, C., Physical Plant Director. 2017, June 13. Personal interview), which could explain why it had low lead and iron levels compared to the other buildings.

The G. B George Building, known as the Speech, Reading and Special Education Building prior to its renaming in 2012, was built in 1976 (The University of Southern

Mississippi, 2016). Its pipes were installed in 1974 (Crenshaw, C., Physical Plant Director. 2017, June 13. Personal interview), but its lead profile was the second lowest. It and the International Center have 4-inch pipes (Crenshaw, C., Physical Plant Director. 2017, June 13. Personal interview), which may be a factor.

The International Center was constructed in 2004 (The University of Southern Mississippi, n.d.). and its pipes were installed in 2001 (Crenshaw, C., Physical Plant Director. 2017, June 13. Personal interview). Therefore, it is not at high lead risk from old construction nor at high copper risk from new construction. Its lead, copper, and iron levels were middling compared to the other buildings, which makes sense with its age and pipe size.

The Honor House and J. B. George Building had large spikes in first draw iron concentration, but iron concentration otherwise remained similar between buildings. This could reflect a more upstream factor, especially since concentrations changed between sampling periods. This is not unexpected, as much of downtown Hattiesburg has had problems with iron (Burns, 2017).

There was no clear linear correlation between time of the year and metal concentration. There may be a dip in some metal concentrations around August 26. There is no obvious explanation for this: the presumed peak on-campus population would be the week that classes started, the week of August 16. The pH for the buildings was neither at their peak nor their lowest, either.

The 30 sec flush samples all had appreciably lower metal concentrations than the corresponding 1st draw samples. This is expected, considering that flushing water before use is an EPA recommendation for suspected metal contamination from plumbing (EPA, 2017).

Chapter 6: Conclusion

While there was little evidence to support a major seasonal change in lead, copper, and iron concentration on this university campus, this study did show the potential of the campus for future studies regarding tap water quality, especially between buildings of different ages in the same water system. Studies focusing on old, renovated buildings may also find the University of Southern Mississippi campus a useful location for study.

The four buildings showed distinctly different concentrations of metals, despite their relatively close geography, which indicates differences in the buildings themselves that could be investigated. One major question is what is the relative contribution of age, pipe size, and location on tap water metal levels. However, after over a hundred years of operation, some information on university infrastructure is difficult if not impossible to access.

The decreased metal concentrations in the 30 sec flush samples clearly demonstrate the rationale for the EPA recommendation for flushing water before use.

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