

Case Study to Reduce Lead and Copper Corrosion Through Water Quality Optimization and Control of Nitrification

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This article presents a methodology to approach and optimize corrosion control in a distribution system following a logical sequence of data gathering, investigative work and additional water quality sampling, bench- or pilot-scale testing, and full-scale implementation and monitoring. This methodology is considered best practice, and the same structured method can be used for other water systems to optimize corrosion control and compliance with the Lead and Copper Rule (LCR) from 1991 and Lead and Copper Rule Revisions in 2021.

The utility's system for this case study, located in City of Cocoa, is supplied by one water treatment plant (WTP), which includes a groundwater treatment process, a surface water treatment process, and an aquifer storage and recovery (ASR) well system; finished water can be a blend of treated waters from these three sources. Chloramines are utilized as the secondary disinfectant in the system.

The groundwater source is characterized by high hardness and alkalinity, moderate levels of organics and other minerals, and low levels of dissolved metals. Production wells draw water from both the Intermediate and Upper Floridan

aquifers, with some distinct differences in water quality. The groundwater treatment process includes forced draft aeration for stripping hydrogen sulfide; softening in the solids contact clarifiers with the addition of lime, soda ash, and potato starch; and recarbonation with carbon dioxide and media filtration.

The surface water source is characterized by low hardness, alkalinity, and other minerals, and high levels of organics and color. The source water quality varies during the year, with less stormwater flow into the reservoir during the winter. The surface water treatment process includes clarification in lamella clarifiers, with the addition of ferric sulfate, liquid calcium hydroxide, and polymer, followed by ozonation and media filtration.

Water recovered from the ASR wells is very similar in terms of water quality to the finished water; however, native water from the aquifer blends with the finished water and the recovered water quality varies based on the ASR well and the recovery stage.

There are some distinct differences in the treated water chemistry of the three water sources, and therefore, finished water chemistry is dependent upon the blend ratio of these sources. Understanding the differences in water chemistry between source waters and varying blend ratios is important for forecasting finished water quality and pipe scale stability on water

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mains, as well as understanding the potential for increased corrosion rates and possible drinking water discoloration. In addition, high detention time and nitrification are known to be significant issues in certain portions of the system, especially during the warmer months of the year.

Background

Formerly, the final location to adjust pH in the groundwater treatment process was recarbonation upstream of the media filters. The optimal pH in the system to promote chloramine stability would create precipitation of calcium carbonate in the filters; therefore, the utility installed a new chemical feed system with liquid calcium hydroxide to adjust the pH of the filtered groundwater. In combination with the recarbonation process upstream of the filters it also mitigated the calcium carbonate

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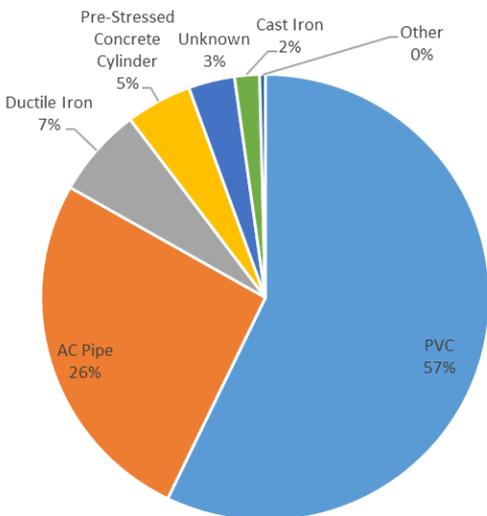


Figure 1. Percentage of total distribution system pipe length for various pipe materials.

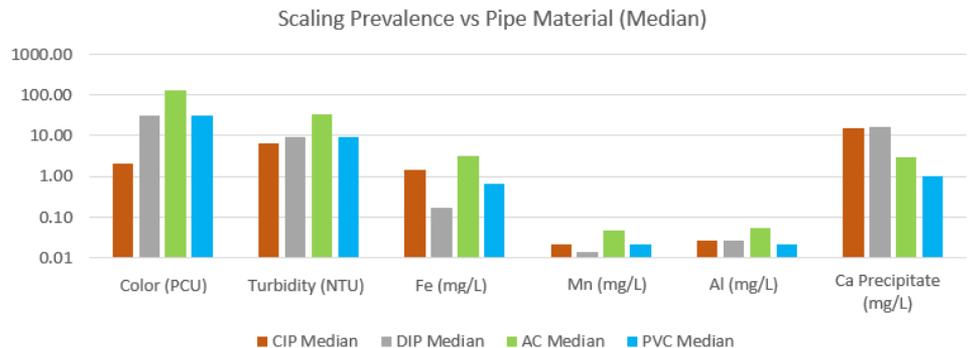


Figure 2. Median iron, manganese, and calcium concentrations (along with color and turbidity levels) found in each type of pipe material collected from high-velocity samples. Median is used to identify the prevalence of a measured parameter in the specific type of pipe. Note the Y-axis is in logarithmic format.

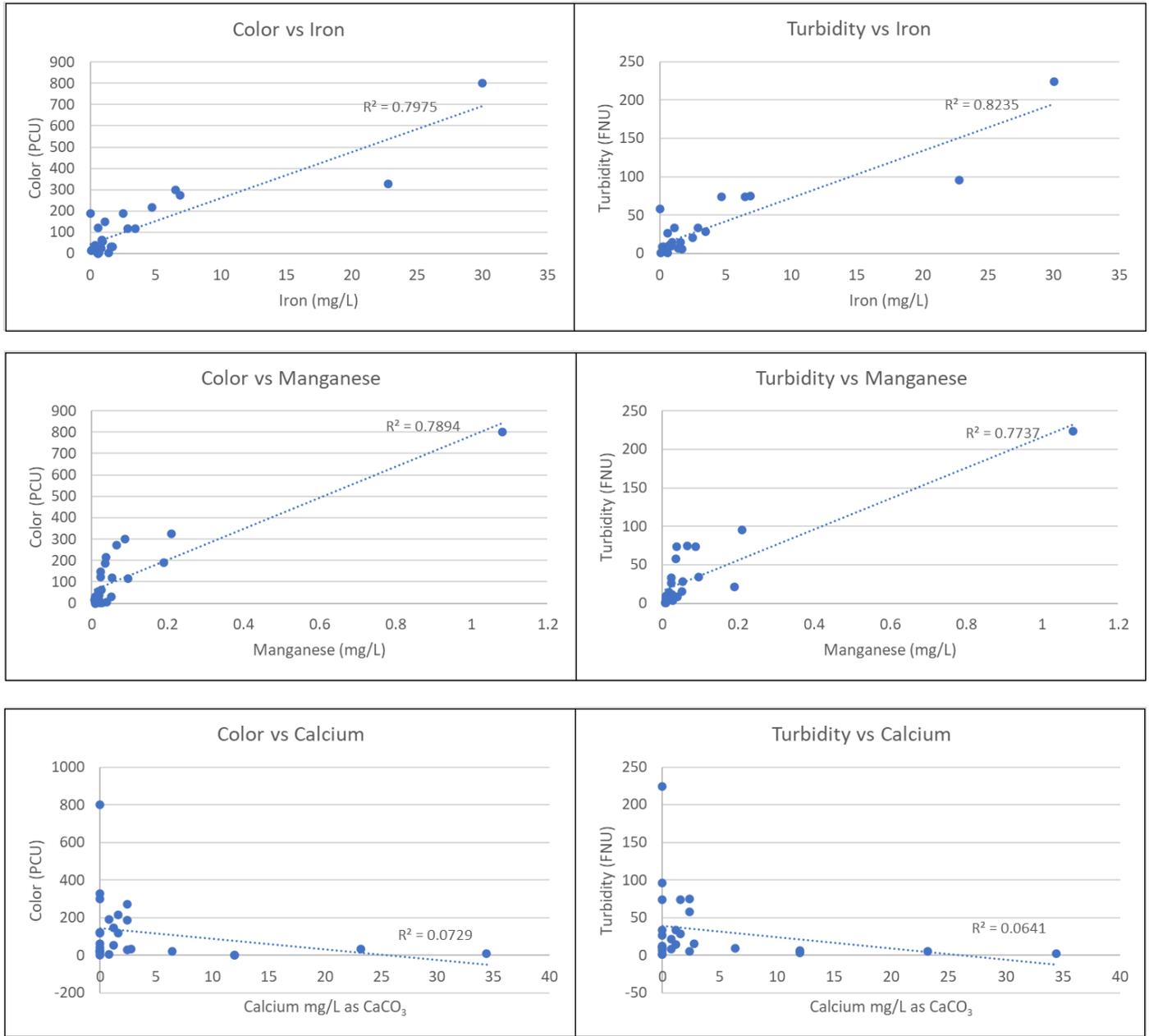


Figure 3. Correlation between iron, manganese, and calcium versus color and turbidity in the distribution system.

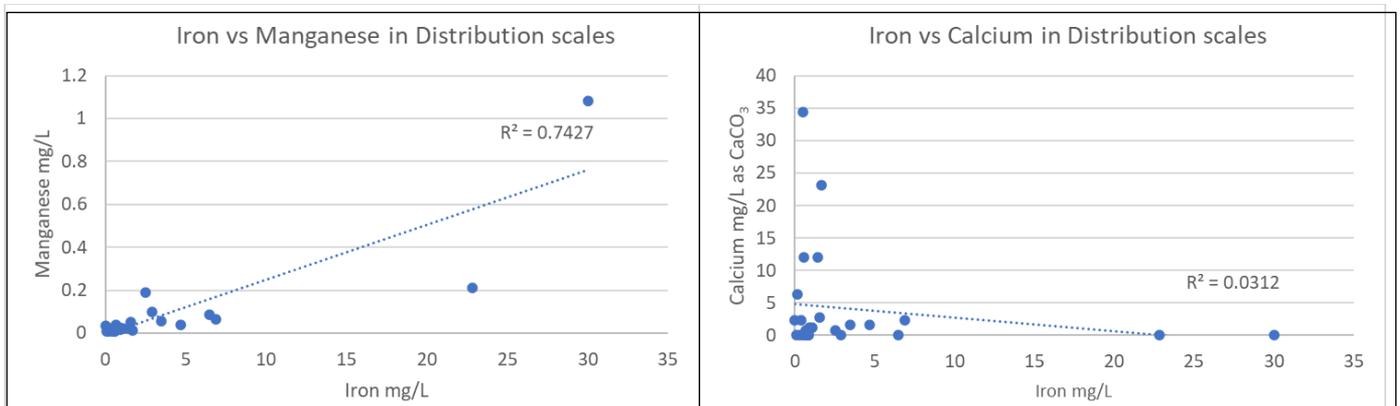


Figure 4. Correlation between iron and manganese concentrations and correlation between iron and calcium concentrations from high flow distribution system samples.

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precipitation in the groundwater filters and increased the alkalinity of the finished water. The increased total alkalinity increased the buffer intensity and thus aided in control of impacts of nitrification in the system.

During the potable water supply construction permitting process for the new liquid calcium hydroxide feed system, the change in finished water quality and impacts on corrosion control treatment and regulated water quality parameters (WQPs) were discussed with the Florida Department of Environmental Protection (FDEP). The utility and FDEP agreed that the utility would conduct additional sampling for a one-year period following implementation of the new chemical feed system. In addition, the utility would conduct an optimal corrosion control treatment (OCCT) analysis using the sampling results to determine new optimal WQPs.

The OCCT under the LCR requires that the utility select and implement the most effective corrosion control practice, while continuing to meet other regulatory and nonregulatory water quality requirements. The goal of OCCT is to reduce the concentrations of metals in the drinking water. Effective corrosion control requires understanding and management

of the common mechanisms that may cause metal release, such as changes to source water conditions, treatment practices, and distribution system operation and maintenance practices.

Historical Water Quality Data Collection and Analysis

Water quality data were collected from historical compliance sampling records and from the utility's electronic databases that store operational records. Data were collected on source water quality (both surface water and groundwater), treated water quality (both surface water and groundwater), ASR water quality, and distribution system water quality. Parameters of interest included alkalinity, calcium, magnesium, pH, temperature, chlorides, iron, manganese, sulfate, aluminum, sodium, fluoride, nitrate, phosphate, barium, aluminum, oxidation reduction potential (ORP), total dissolved solids (TDS), and conductivity. Collection of historical compliance sampling data included primary and secondary national drinking water standards sampling events, unregulated contaminant monitoring rule (UCMR) sampling events, LCR sampling events, and surface water iron sampling events. Operational data on historical chemical use at the WTP were also collected.

The data collected were used to define water quality for the various water sources (groundwater, surface water, and ASR water). The water quality data were then used in predictive water quality models to predict finished water quality for varying ratios of the different source waters.

Distribution System Assessment

An assessment of the system's water quality was conducted in August 2020 to identify the nature of the current scales on interior walls of the water mains and to develop a general evaluation of system water quality. The data collected, in combination with historical water quality data, were used to predict how pipe scales may react to changes in water quality resulting from changes in source water or treatment. This information was used as a basis for establishing recommended water quality ranges to minimize destabilization of existing pipe scales.

The utility serves potable water to more than 80,000 customer connections, or an estimated population of approximately 200,000, across a service area of more than 250 sq mi. The system is supplied from the utility's single WTP, which includes three water sources as described previously. Within the system, the utility operates one elevated storage tank and three booster stations consisting of ground storage tanks (GSTs), high-service pumps, and sodium hypochlorite storage and feed systems.

The distribution system contains more than 1,300 mi of pipeline. Data on the potable water system piping were obtained from the utility's geographic information system (GIS) database and included pipe material, pipe size, pipe length, and installation date. The system is predominantly comprised of polyvinyl chloride (PVC) and asbestos cement (AC) pipe. Ductile iron (DI) pipe, prestressed concrete cylinder pipe (PCCP), and cast iron (CI) pipe are also present in the system, while other pipe material types

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Table 1. Accumulated Metals Found at Locations With Highest Iron and Manganese Depositions

Location ID	#9	#19	#26	MCL ¹
Arsenic, µg/L	4.9	5.8	ND	10
Barium, µg/L	28.9	29.7	13.6	2000
Chromium, µg/L	3.1	6.6	ND	100
Copper, µg/L	17.3	4	3.7	1300 ²
Lead, µg/L	5.3	8.1	1.4	15 ²
Titanium, µg/L	9.5	5.9	2.2	NA

Notes: ¹MCL is measured at the POE and does not apply to distribution samples. ²Action level where 90 percent of samples must be below this value at a customer's tap after stagnating for at least 6 hours.

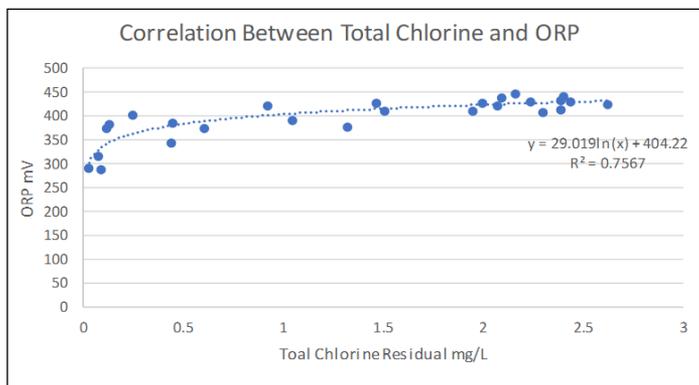


Figure 5. Correlation between oxygen reduction potential and total chlorine in the distribution system.

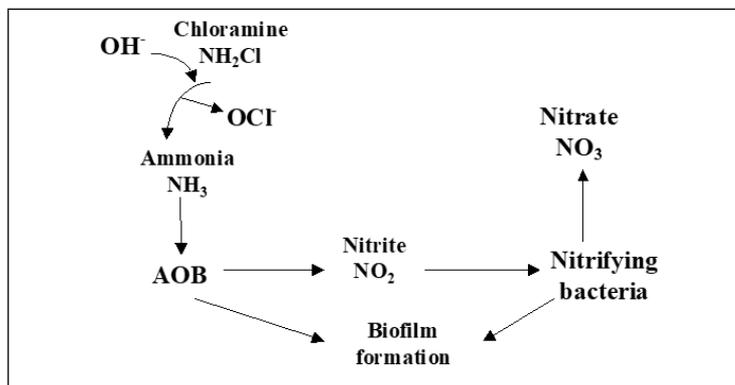


Figure 6. Nitrification cycle from the addition of chloramine.

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are limited. Figure 1 presents the percentage of each type of pipe material in the system by total length.

A calibrated distribution system hydraulic model that was previously developed was used to predict water age under different demand scenarios. Water quality in the system can vary with water age. Distribution system assessment sample locations were selected to provide a range of pipe materials, pipe ages, and water ages in the system. A wide variety of sample locations improves the likelihood of capturing the various scales and water quality conditions that may be present within the system. For example, different pipe materials can result in the formation of different scales within the system.

The 27 sample locations were identified, including 10 sample locations for PVC pipe, 10 for AC pipe, three for DI pipe, three for CI pipe, and one sample at the point of entry (POE) at the WTP. Selected sample locations targeted pipe diameters of 6 to 8 in. Large-diameter pipes were not sampled because of the inability to obtain samples by flushing at high flow velocities; therefore, no PCCP pipes were sampled because these pipes in the system are at least 24 in. in diameter.

Sample locations included some closer to the WTP, where the water age is low, and some

at the far ends of the system, including dead end pipes, where the water age is high. Sample locations covered the ends of the system in the north, south, and east. Some sample locations were intended to target older DI and CI pipes, while other locations targeted more-recently-installed PVC pipes.

The system assessment consisted of a series of water samples collected from fire hydrants during low- and high-velocity flushing of selected water mains. The hydrants were first flushed at a flow of 30 to 50 gal per minute (gpm) for a few minutes to remove sediment accumulation in the hydrant service line. After a few minutes of flushing, the low-velocity samples were collected under the 30- to 50-gpm flow condition. The low-velocity samples are generally indicative of water quality in the bulk water and can be used to identify the sensitivity of certain pipe scales.

After the low-velocity samples were collected, the hydrant valve was opened to increase the velocity in the water main; typical high-velocity flows ranged from 300 to 500 gpm. The goal of the high-velocity sampling was to purposely remove loose pipe scales to assess the composition of the scaled material and the potential for water discoloration from physical and chemical water quality changes in the system. It should be noted that these samples contained higher sediment and metal concentrations and

were not indicative of concentrations found in the bulk water flowing through the pipes at the normal, lower-flow velocities.

Samples collected under low flow conditions were analyzed for pH, temperature, ORP, total chlorine, color, turbidity, conductivity, free ammonia, and nitrite. Samples collected under high flow conditions were analyzed for color, manganese, iron, aluminum, turbidity, alkalinity, total calcium hardness, and dissolved calcium hardness. Select samples collected under high flow conditions were also analyzed for chloride and sulfate. Samples containing high levels of iron and manganese were also analyzed for natural source metals that could have accumulated on the pipes over decades, including mercury, antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, selenium, and titanium.

Distribution System Assessment Results

The utility's distribution system contained a light to moderate coating of calcium-based scales in pipes closer to the WTP; pipes located further out in the system had a light to nonexistent coating of calcium scales. Iron was found throughout the system, with moderate concentrations in the middle of the system and significant concentrations in the system's further reaches. Iron deposits were most prevalent in older mains. Significant concentrations of manganese were found in areas with high concentrations of iron scales.

The CI pipes are the oldest pipes and had pockets of the highest concentrations of iron and manganese, as would be expected for this material. Metal deposition was more prevalent in the AC pipe, most likely because the pipes are old. This was identified by the median concentration of each metal broken down by pipe material, as shown in Figure 2.

Calcium concentrations in the distribution system samples did not correlate well with color and turbidity, and therefore, calcium scales

Figure 7. Nitrite concentrations versus total chlorine residuals in the distribution system.

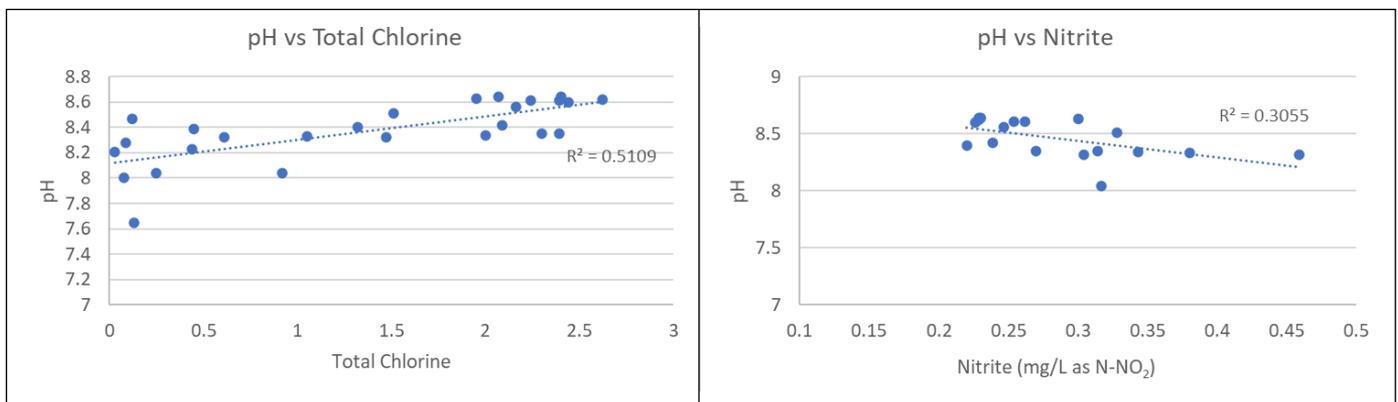
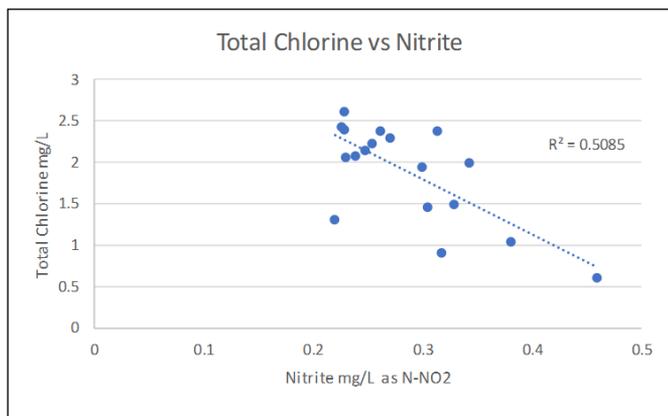


Figure 8. A correlation exists between nitrification and pH. As total chlorine residuals decrease and nitrite concentrations increase, the pH is depressed.

are unlikely to be the cause of discolored water events. Iron and manganese concentrations correlated well with color and turbidity, meaning that discolored water events are likely to be related to iron and/or manganese release and are most likely to occur in the cast iron and asbestos cement pipes because they had the most accumulated deposition. Figure 3 presents individual correlations between iron, manganese, and calcium versus color and turbidity.

Iron in the water can originate from the source water, but contributions can also come from iron-based water mains. Manganese in the water typically originates from the source water. Based on historic source water data, several of the utility's wells contain iron and manganese concentrations above the secondary maximum contaminant level (MCL) of 0.3 mg/L and 0.05 mg/L, respectively; however, data from the POE in 2018 show iron and manganese concentrations well below the secondary MCL and also below the concentration of distribution accumulation of 0.15 mg/L and 0.020 mg/L, respectively.

Iron-based scales can adsorb and accumulate manganese from source waters or from byproducts of treatment chemicals, such as ferric sulfate. Thus, a correlation is expected to exist if both metals have been present in the distribution system for some time. A linear correlation exists between iron and manganese concentrations in the distribution system pipe scales, as illustrated in Figure 4. The figure also verifies that there is no relationship between iron and calcium in the pipe scales.

The results indicate that manganese has adsorbed onto the iron scales in the system. It's likely to have occurred over decades, starting with the unlined CI pipe, where manganese adsorbed onto existing iron pipe scales. The relationship also exists in the AC pipe, which is the second oldest pipe in the distribution system; however, original AC pipe lining is cement and contains no iron. Iron deposition on these pipes must have originated from the source water and accumulated over many years. Iron deposits were greatest further out in the distribution system, indicating that lower water velocity may also play a role in accumulation in addition to pipe age.

Iron and manganese can also accumulate other heavy metals, such as arsenic and lead, if they exist in low concentrations in the source water. Like iron and manganese, over the years these metals can accumulate to concentrations above the MCL in iron- and manganese-based pipe scales. Based on the results of a study conducted by the Water Research Foundation (Friedman et al., 2016), iron has an affinity to adsorb arsenic, while manganese may adsorb lead. This would infer that pipe scales containing iron and manganese could contain arsenic and lead, and possibly some other heavy metals.

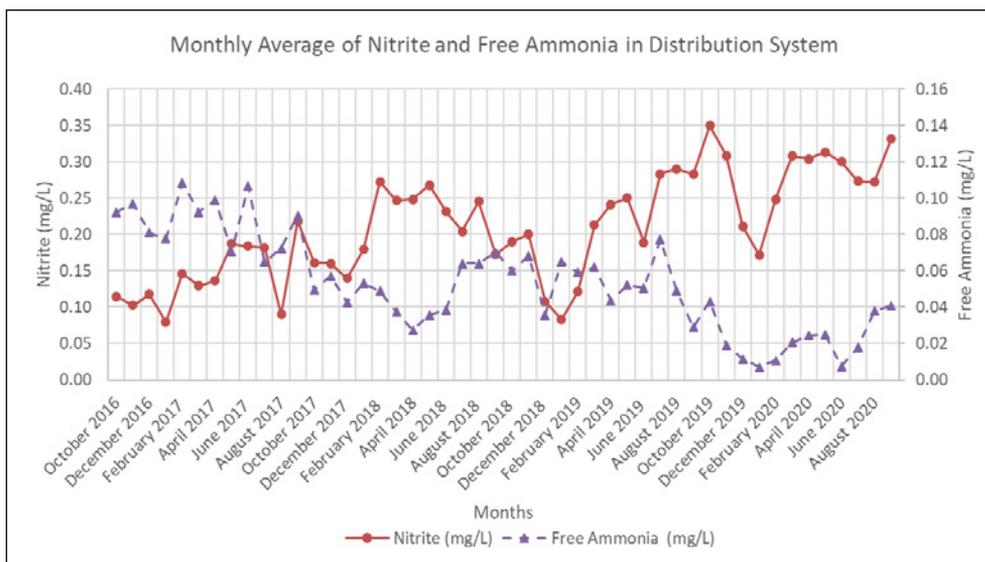


Figure 9. Monthly average of nitrite and free ammonia in the distribution system.

Table 2. Average Water Quality Entering the Distribution System Between 2015 and 2018

	Average Historic Treated Water Quality	Average Treated Groundwater Water Quality After Calcium Hydroxide System	Average Treated Surface Water Quality	Predicted Blended 70% Groundwater 30% Surface Water	Predicted Blended 50% Groundwater 50% Surface Water
TDS, mg/L	379	379	100	295	240
Calcium (Total), mg/L	33.0	33.0	43.0	36.0	37.9
Total Alkalinity, mg/L as CaCO ₃	33	41	21	35	31
pH	9.10	9.00	9.20	9.05	9.00
Water Temperature, C	23	23	23	23	23
Chloride, mg/L	112	120	28	92	74
Sulfate, mg/L	107	107	26	83	80
Magnesium, mg/L	7.0	7.0	5.0	6.4	4.7
Corrosion Indices					
DIC, mg/L as C	7.1	9.2	4.5	7.8	7.0
Aggressive Index (AI)	12.5	12.5	12.5	12.5	12.4
Langelier Saturation Index (LSI)	0.61	0.60	0.68	0.63	0.58
Calcium Carbonate Precipitation Potential, mg/L as CaCO ₃ (CCPP)	5.4	4.4	3.7	4.3	3.4
Buffer Intensity	0.136	0.123	0.101	0.116	0.095
Alk/(Cl ⁻ + SO ₄ ²⁻) (Larsons Ratio)	0.1	0.1	0.3	0.2	0.2
Copper II, mg/L at Field Temp	0.01	0.01	0.01	0.01	0.01
Lead II, mg/L at Field Temp	0.09	0.106	0.084	0.100	0.1
Chloride-to-Sulfate Mass Ratio (CSMR)	1.05	1.12	1.08	1.12	0.92

Release of iron and manganese can not only cause discolored water complaints, but can also co-release other metals at concentrations higher than their respective regulatory entry point levels in customer taps that are close to the scale release event.

Three samples collected during the assessment that contained high concentrations

of iron and manganese were sent to a certified laboratory for heavy metal analysis. Table 1 shows the detected metals and their respective concentrations. Two of the samples contained arsenic concentrations at 5 and 6 µg/L, which is half of the MCL (at the POE), and lead concentrations between 5 and 8 µg/L, which is

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also almost half of the lead action level (from 90 percent of stagnated samples collected at customer taps).

The ORP identifies the level of oxidation capacity applied by a body of water, which can have a major influence on pipe scale formation in the distribution system. The ORP was measured in the system during the field sampling of the distribution assessment. Distribution systems containing chloramine typically have an ORP ranging from 250 to 500 millivolts (mV), where

the lower end of the spectrum is chloraminated groundwater or water with higher water age, and the higher end is preozonated surface water with chloramine and lower water age. During the assessment, water leaving the WTP was a blend of approximately 70 percent treated groundwater and 30 percent surface water, with no water supply from the ASR wells.

In distribution systems that have free chlorine, there is a distinct correlation where higher free chlorine residuals have higher ORP values. This correlation may not be as distinct

in chloraminated systems, but it was visible in the system from samples collected during the system assessment (Figure 5). The ORP levels ranged from 290 to 449 mV, with an average of 398 mV. These values are typical of blended chloraminated groundwater and surface water systems. For those samples where ORP was measured, total chlorine residuals ranged from 0.03 to 2.62 mg/L with an average residual of 1.37 mg/L.

Nitrification can occur in systems that add chloramine as a secondary disinfectant or systems that have natural ammonia in the source water. When chloramine is produced at the WTP, free ammonia can enter into the system. The breakdown of chloramine in the distribution system can also contribute to free ammonia, which is a primary source of food for ammonia-oxidizing bacteria (AOB). The AOB are ubiquitous in distribution systems and will convert ammonia to nitrite, which in turn becomes food for nitrogen-oxidizing bacteria (NOB). To be simplistic, this creates a symbiosis community that will continue to grow and break down chloramine, utilizing the ammonia to spark what's called the nitrification cycle (Figure 6). Under full nitrification, chloramine disinfectant can decay rapidly, leaving very little disinfectant downstream and causing pH levels to decrease in low buffered water.

Nitrification parameters were also measured during the distribution system assessment, as nitrification can have an impact on pipe corrosion and scale stability, mostly because the process can depress pH. Nitrification was prevalent throughout the system and nitrite concentrations collected in the system that are greater than 0.05 mg/L typically indicate

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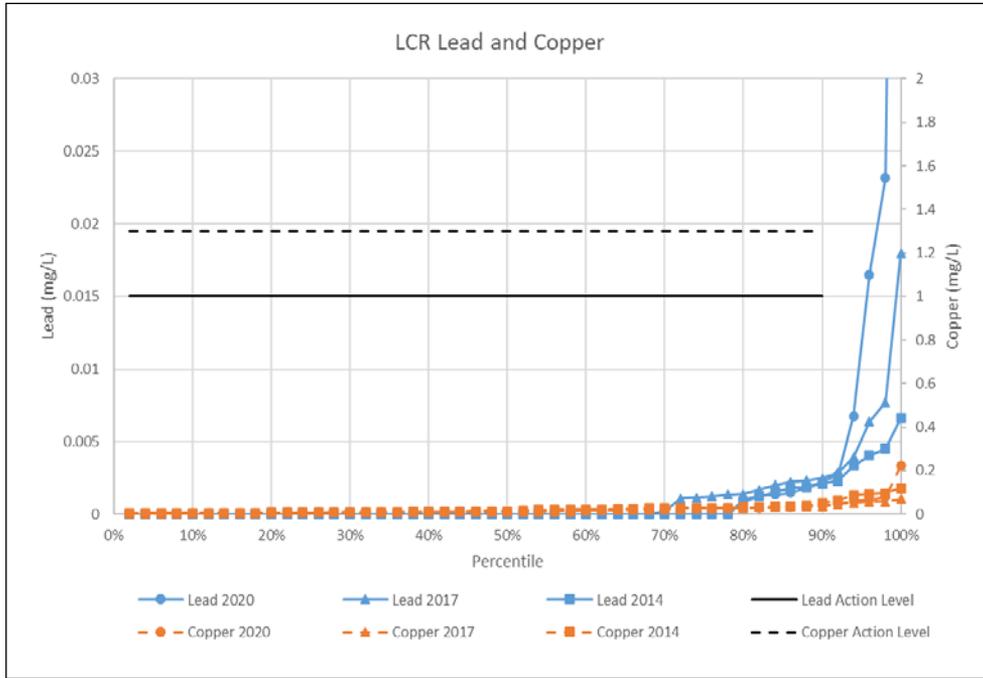


Figure 10. Lead and copper results from Lead and Copper Rule monitoring events expressed as a percentile.

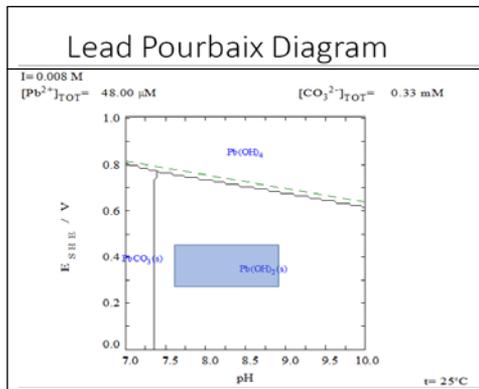


Figure 11. Pourbaix diagram showing that the current lead species is predicted to be lead (II) hydroxide (shown in blue). This compound is rarely formed in water distribution systems and is most likely hydrocerussite, a combination of lead carbonate and lead (II) hydroxide.

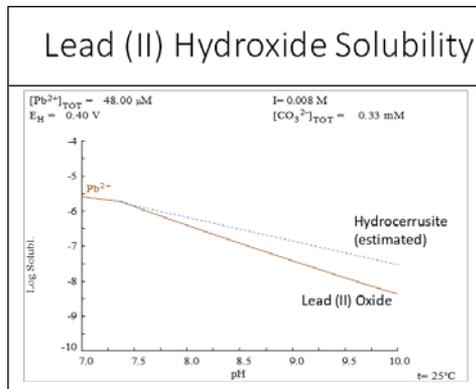


Figure 12. Lead (II) hydroxide solubility chart. The dashed line is the estimated solubility of hydrocerussite. In general, as pH increases, the solubility of lead decreases.

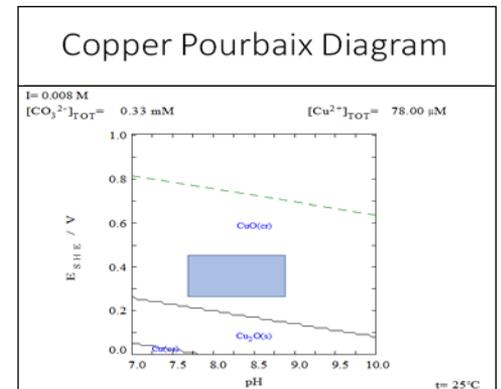


Figure 13. Pourbaix diagram showing that the current copper species is predicted to be cupric oxide, shown in blue.

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localized nitrification in the pipe. Average nitrite concentrations found in the system during the assessment was 0.238 mg/L. Higher nitrite concentrations correlated well with lower total chlorine residuals (Figure 7).

Higher total chlorine residuals correlated well with higher pH levels. Higher nitrite concentrations did not correlate as well with pH compared to pH and total chlorine (Figure 8), but still correlated, indicating that nitrification and biological activity have an impact on internal pipe scale corrosion and scale stability. During the distribution assessment, the pH leaving the WTP was 8.8 and ranged between 7.65 and 8.64 in the distribution system, with an average of 8.4. As would be expected, the distribution system assessment results indicated that higher water age was associated with higher nitrite concentrations, lower total chlorine residuals, and lower pH values.

The evidence of nitrification observed in the distribution system assessment was supported by the collected historical data. Figure 9 shows the monthly average nitrite concentrations and the monthly average free ammonia concentrations in the distribution system over the past four years. The monthly data points are derived from the average of 150 samples collected from 75 locations in the system each month. During this time, monthly average nitrite concentrations have increased, while monthly average free ammonia concentrations have decreased due to the increased breakdown of monochloramine from microbiological activity and oxidation of nitrite. Increases in nitrite concentrations and decreases in free ammonia concentrations are typical indicators that nitrification has been increasing in the distribution system. Sample data also showed a clear relationship between nitrite concentrations and total chlorine concentrations, similar to what is shown in Figure 7.

Water Quality Evaluation

Distribution system water quality data were collected to better understand current conditions. The data collected in the distribution system assessment were combined with the collected historical data and used to predict how pipe scales may react to changes in water quality resulting from changes in source water or treatment. For example, increased use of the surface water source, which has lower dissolved inorganic carbon (DIC) compared to the groundwater source, can impact corrosion and the stability of existing pipe scales. Water quality data were input into WaterPro, a water quality modelling software, to calculate water quality indices, such as the Langelier Saturation Index (LSI) and buffer intensity. Geochemical models were used to predict the theoretical speciation of lead, copper, iron, and manganese based on the water quality observed in the distribution system.

Treated groundwater is the utility's primary source of finished water; however, the utility began increasing the use of the surface water source in recent years. During the distribution system assessment, the treated surface water contributed approximately 30 percent of the total finished water flow, but it can contribute up to 50 percent. In addition, the utility has ASR wells that can provide as much as 30 percent of the flow.

Table 2 shows the average historic treated water quality entering the distribution system between 2015 and 2018; average treated groundwater quality after the installation of the calcium hydroxide system; average treated surface water quality; and a predicted blend of treated 70 percent groundwater, 30 percent surface water, and a 50 percent blend of each. Corrosion indices were calculated using the WaterPro model. These data represent "historic"

data that can help identify the original pipe scales on the water mains in the distribution system before the addition of the calcium hydroxide system to the groundwater treatment process.

With respect to corrosion indices, the water blends are similar; however, the buffer intensity in the treated surface water is lower compared to the treated groundwater. This could cause wider pH swings in the distribution system unless additional alkalinity is added to the blended water, especially if the use of the surface water source is increased.

The water recovered from the ASR wells is similar to the historic treated water, but the chloride concentrations increase in the water recovered from ASR wells when they are operated for consecutive days. Based on historic treated water quality data, the average chloride concentration is 112 mg/L when the ASR wells are operating, which is not significantly different from historic averages when they are not operating. Over run times of several weeks, chloride concentrations could increase in the treated water.

There have been case studies that reported increases in customer red water complaints (iron release) when chloride concentrations increased greater than 50 mg/L (on average) leaving the POE, and this scenario could occur if chloride concentrations increase to approximately 160 mg/L leaving the WTP. In addition, if sulfate concentrations do not increase as chloride concentrations increase, then the chlorine-to-sulfate mass ratio (CSMR) will also increase, causing the potential for higher lead concentrations at customer taps.

With respect to predicting pipe scale and metal deposition speciation, the differences in water quality between the blended water and groundwater (with and without calcium hydroxide) are marginal. The key water quality

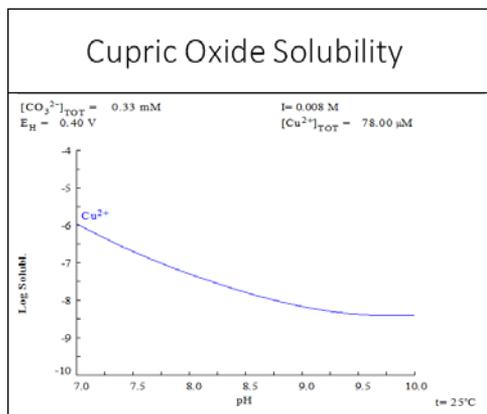


Figure 14. Cupric oxide solubility chart. In general, as pH increases, the solubility of copper decreases.

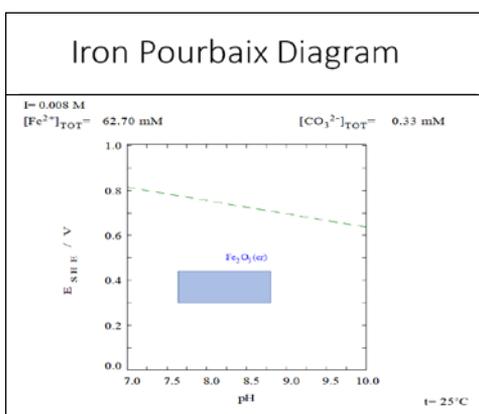


Figure 15. Iron Pourbaix diagram showing ferric oxide as the only species predicted to be found in the distribution system.

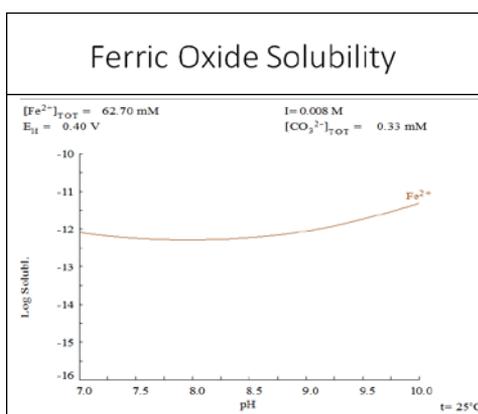


Figure 16. Ferric oxide solubility chart. A pH of 7.9 is the optimal pH for ferric oxide solubility.

parameters from blended water containing 30 percent surface water were used in the geochemical models, which generate Pourbaix diagrams that are useful in identifying the primary metal species that would theoretically form on the pipe wall.

Understanding the current species can help predict how a pipe scale may react with a change in water quality or treatment in the future. In addition, the diagrams can predict if the metal speciation will change, and any changes in metal species in many instances can create periods of pipe scale destabilization. The data from the Pourbaix diagrams can then be used to create solubility charts of the identified metal species based on key water quality parameter changes.

In addition to DIC, other key water quality parameters that can have an impact on pipe scale speciation and solubility are pH, alkalinity, calcium, and ORP (total chlorine residuals).

Historic lead and copper data can help assess the impacts that changes in source water quality and treatment can have on pipe scales in the distribution system mains and customers' premise plumbing. Lead in the water distribution system can be found within lead solder in the premise plumbing from homes built before the lead ban in the 1980s and within some fixtures. The LCR compliance samples were analyzed from the past three sampling events.

Figure 10 presents lead and copper results from LCR monitoring events expressed as a percentile. With regard to lead, concentrations slightly increased from 2014 to 2017 and remained similar in 2020, while copper concentrations remained similar and extremely low during all three sample events.

Lead corrosion is primarily affected by pH, alkalinity, DIC, and ORP, but can also be impacted by a change in CSMR. The ORP is primarily dependent on the type of disinfectant used and the disinfectant residual; in this instance, the type of disinfectant was chloramine in the presence of groundwater or a groundwater/surface water blend. Total chlorine residual concentrations ranged between 0.03 and 2.62 mg/L in the distribution system during the distribution assessment. The ORP range was 290 to 449 mV, with an average of 389 mV. The pH range was between 7.65 and 8.64, with an average of 8.37.

Pourbaix diagrams and solubility curves were developed using the SPANA geochemical model. Figure 11 shows a Pourbaix diagram for theoretical lead speciation based on the water quality observed in the distribution system. The blue box represents the water quality range expected with groundwater only and blended ground/surface water in all areas of the distribution system. According to Figure 11, the

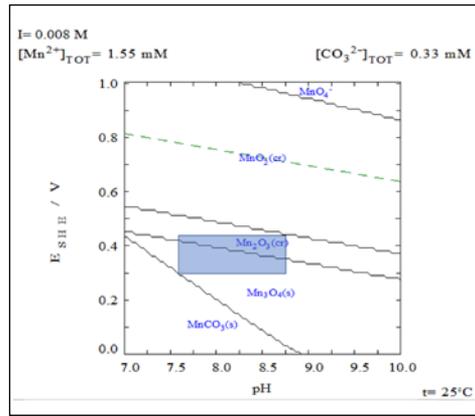


Figure 17. Manganese Pourbaix diagram showing both hausmannite and manganese (III) oxide as the dominant species in the distribution system. Hausmannite is more likely to form in areas of lower chlorine residuals and is not as stable as manganese (III) oxide.

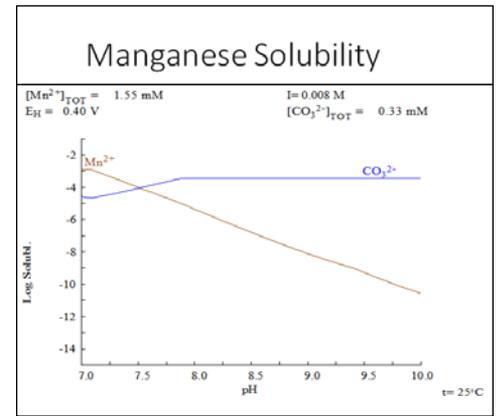


Figure 18. Manganese solubility chart. As pH increases, manganese solubility will decrease.

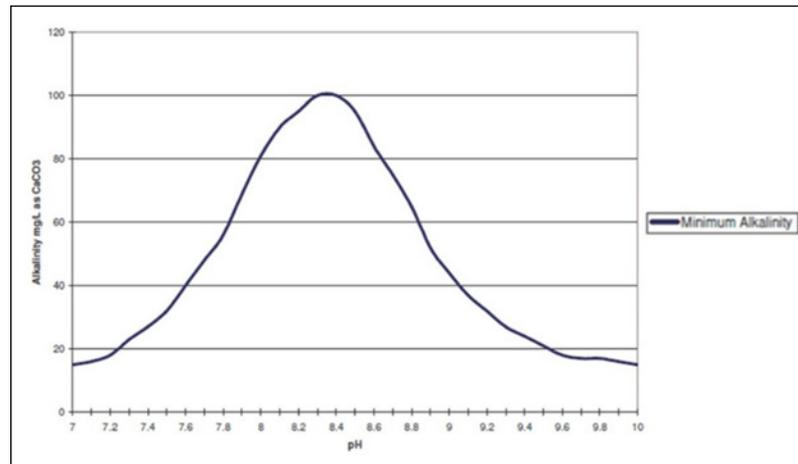


Figure 19. Buffer intensity. Points above the minimum alkalinity line indicate an adequate alkalinity and pH combination to maintain a stable pH in the distribution system.

current lead compound is predicted to be lead (II) hydroxide ($Pb[OH]_2$) in the entire distribution system; however, this compound is rare to form in reality and is more likely a combination of lead carbonate and lead hydroxide known as hydrocerussite ($PbCO_3 \cdot 2Pb[OH]_2$). Figure 12 shows the solubility of lead (II) hydroxide and hydrocerussite (pH below 7.5). These models are only theoretical models and cannot develop a solubility curve for hydrocerussite; however, the dashed line on Figure 12 is an estimated solubility curve.

Hydrocerussite is not as stable as lead (II) hydroxide and is more likely to leach higher concentrations of lead into the water. Based on these data, it's expected that higher lead concentrations at the tap would be found where the pH in the distribution system is lower. This means that nitrification has an impact on corrosion solubility as it's the main cause for pH depression in the system and minimizing nitrification can reduce pH depression. According to Figure 12, lead levels could be

reduced by as much as 37 percent (estimated) if the pH were increased from 8.3 to 8.7 on average throughout the entire distribution system.

Increases in CSMR above a value of 0.6 have caused an increase in lead release in some systems. Historically, The CSMR was 1.1 and remains the same for groundwater treated with calcium hydroxide and for the groundwater/surface water blend leaving the WTP. As previously mentioned, the ASR wells increase chloride concentrations over time of operation, but recent data from December 2019 to January 2020 show little change in chloride concentrations leaving the WTP when the ASR wells are blended with groundwater.

The CSMR calculated from the distribution system during the assessment had slightly higher values than historic entry-point ratios, ranging between 1.2 and 1.3. These values indicate that a slight increase in lead release could potentially occur, but most likely would be insignificant with regard to the 90th percentile value (under

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the LCR). If the surface water treatment process were to switch coagulants from ferric sulfate to a chloride-based coagulant, such as ferric chloride, the CSMR could increase enough to cause noticeable lead release.

Copper can be found in customers' premise plumbing inside the home and in some service lines copper corrosion is affected primarily by pH, DIC, ORP, and chlorides. Copper speciation is primarily dependent upon pH and DIC. Figure 13 is a Pourbaix diagram that indicates cupric oxide as the expected copper species in customers' homes.

Similar to most copper species, cupric oxide solubility will decrease as the pH increases and the DIC decreases. Figure 14 shows the solubility of cupric oxide. Although copper concentrations (collected from LCR sampling events) are well below the action level, according to the WaterPro model, copper II concentrations can decrease by as much as 64 percent if the pH were to remain 8.7 throughout the entire distribution system. The solubility curve generated by the geochemical models (Figure 14) indicates a lower cupric oxide solubility at a pH of 8.7 compared to a pH of 8.4.

Increase in copper solubility has also been associated with increases in chloride

concentrations. With respect to copper corrosion, chloride concentrations in the blended groundwater/surface water are lower than groundwater concentrations and should not have an impact on copper solubility when switching between the two sources, but copper solubility could increase when the ASR wells are operating and if chloride concentrations increase by as much as 50 mg/L when leaving the WTP.

The distribution system contains a small percentage (2 percent) of CI pipe, which typically was not manufactured with a protective lining. There is a larger percentage of DI pipe (7 percent), but this type of pipe typically contains a mortar lining. The majority of pipe is PVC and AC, with AC pipe being older. From the assessment, there are portions of the distribution system that contain moderate to significant iron deposition. The AC pipe contains a higher deposition compared to PVC, mostly because it's older pipe. This deposition could have come from upstream CI pipe, but most likely has come from the treated source water that has accumulated over several decades. Iron deposition was significant near the ends of the system.

With regard to water quality parameters, iron is primarily affected by pH, ORP, DIC, and chloride. The Larson's Ratio (LR) is the ratio of concentration of alkalinity in moles to the sum of chloride and sulfate concentrations in moles in a water sample. The LR is used to qualify the water's aggressiveness to iron pipe scales and the LR values less than 5 are typically aggressive to iron. Based on the WaterPro model, the average LR in the distribution system was 0.1, which is considered extremely aggressive to exposed iron scales, such as cast iron pipes and galvanized pipe, where the zinc coating has worn away. With these values, considerable tuberculation would be expected; however, this effect has most likely been dampened by the calcium layer found in most areas containing CI mains.

Changes to water quality can cause discolored water complaints in areas with significant and moderate accumulation of iron. Figure 15 presents an iron Pourbaix diagram, which indicates that the iron species in the distribution system is ferric oxide. This compound is commonly found in water

distribution systems. The ferric oxide solubility is slightly dependent on pH (Figure 16), with the lowest (most optimal) solubility occurring around pH 7.9. The average pH for all locations that had significant iron deposition was 8.3. If the pH were to stabilize and increase from an average of 8.3 to 8.7, according to the solubility chart (Figure 16), iron solubility would increase by approximately 37 percent. This could potentially be enough to cause an increase in discolored water complaints in areas where iron deposition is significant. It should be noted that areas with significant iron deposition at the ends of the distribution system do not have the calcium layer that is on the CI pipes; therefore, there would be no calcium layer to help dampen iron release.

Similar to copper, an increase in chloride concentrations can impact iron release, but the blended water has a lower concentration of chloride compared to the groundwater and is therefore not expected to have an impact on iron scales and deposits. Like for copper, chloride concentrations should be monitored at the POE when the ASR wells are in operation. Concentrations nearing 160 mg/L could cause noticeable iron release that could cause widespread discolored water complaints.

Manganese was found in low concentrations throughout most of the system, but moderate to significant concentrations were found on CI pipe in the older section of the system and on some of the AC pipe. Although manganese concentrations were lower than iron concentrations, manganese can cause the same type of discolored water event at concentrations two and a half times lower than iron concentrations.

Based on the Pourbaix diagram in Figure 17, manganese can primarily exist as two species: manganese (III) oxide (Mn_2O_3) and hausmannite (Mn_3O_4). Manganese (III) oxide is more likely to form in areas with higher chloramine residuals. The average pH and ORP in areas with moderate to significant manganese deposition was 8.2 mV and 363 mV, respectively, indicating that hausmannite dominates these areas. Hausmannite is not as stable as manganese (III) oxide and is much more susceptible to causing discolored water complaints. Reducing nitrification will most likely increase pH and chlorine residuals (ORP), which will then most likely form manganese (III) oxide in the areas of concern. As shown in Figure 18, increasing pH from an average of 8.3 to 8.7 can reduce manganese solubility by as much as 96 percent.

The average calcium carbonate precipitation potential (CCPP) in these areas was -0.1 mg/L as calcium carbonate ($CaCO_3$), indicating that there is little to no calcium coating in these areas; therefore, no "dampening" effect exists in these areas to further reduce manganese release.

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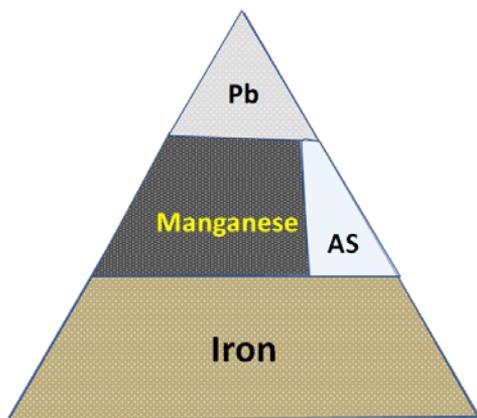


Figure 20. A simplified diagram of what pipe scales may look like in older portions of the distribution system that contain both iron and manganese.

Table 3. Optimal Water Quality Parameters

Location	WQP (units)	Previous OWQP Value	New OWQP Value
POE	pH	8.5 – 9.5	8.5 – 9.5
	Alkalinity (mg/L as $CaCO_3$)	30 - 50	Minimum of 30*
Distribution System	pH	Minimum of 7.0	7.5 – 9.5
	Alkalinity (mg/L as $CaCO_3$)	20 - 50	Minimum of 20*

*Alkalinity greater than 70 mg/L as $CaCO_3$ should be avoided to prevent calcium carbonate precipitation potential above 10 mg/L as $CaCO_3$.

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Calcium deposition was highest in distribution system locations closest to the WTP with moderate scale formation; further out, calcium scales were minimal to nonexistent. A logical explanation would be, as pH is depressed from nitrification, the potential to precipitate calcium decreases. The CCPP is a calculation that can predict localized calcium precipitation potential based on key water quality parameters. The CCPPs were calculated using the WaterPro model. The average CCPP leaving the WTP with groundwater only and blended groundwater/surface water was 4.4 mg/L and 4.3 mg/L as CaCO₃, respectively. The median for the distribution CCPPs was 0.5 mg/L as CaCO₃, with a maximum CCPP of 6.2 mg/L as CaCO₃.

The CCPP values between 1 and 4 mg/L as CaCO₃ will form a light microscopic layer over several years, while values between 5 and 10 mg/L as CaCO₃ will cause a light noticeable scale to form. The CCPP values greater than 10 mg/L as CaCO₃ can cause a thicker calcium layer that can create friction and pipe-clogging issues. These theoretical values were in line with the true values obtained from the distribution system, which had a median of 3 mg/L as CaCO₃.

The AC and DI pipes contain a cement lining that is primarily made from calcium; positive CCPP values between 1 and 10 mg/L are beneficial in protecting these linings. The aggressive index (AI) is used to determine the water's aggressiveness to cement lining. Values greater than or equal to 12 indicate that the water is nonaggressive to the lining. The median AI was 11.4, with a range between 11.1 and 12.5. Values between 11.5 and 12 are considered slightly aggressive to the cement lining; values between 11 and 11.5 are considered moderately aggressive. The more-moderately aggressive

values were found in the further sections of the distribution system, which is primarily PVC pipe and has no lining. Some AC pipe exists in these areas, which would indicate that the calcium layer on the pipe wall is slowly dissolving. Stabilizing the pH to 8.7 throughout most of the distribution system will reduce the slow dissolving of the cement lining layer and further protect the life of the pipe.

Buffer intensity is the natural ability of the water to maintain a stable pH throughout the distribution system, and water's natural pH stability is influenced by both pH and alkalinity. As the buffer intensity decreases, changes in pH can be more easily influenced by factors such as biological activity and metal scales in the distribution system. Large swings in pH can cause an increase in corrosion rates of all metal scales. Water's natural buffer intensity is lowest between a pH of 8.2 and 8.4; in this range, a high concentration of alkalinity is required to maintain adequate pH stability.

In general, a buffer intensity greater than 0.1 millimolar per pH unit (mM/pH) will typically result in a stable pH in the distribution system (American Water Works Association [AWWA] *Manual M58, Internal Corrosion Control in Water Distribution Systems*). Figure 19 illustrates an acceptable pH and alkalinity combination to maintain a buffer intensity value of 0.1 mM/pH. The pH and alkalinity combinations that are above the minimum alkalinity line in the graph are considered adequate to maintain a stable distribution system pH.

The average buffer intensity value leaving the WTP with groundwater only since 2015 was 0.12 mM/pH at a pH of 9 and an alkalinity of 33 mg/L as CaCO₃. When blended with 30 percent surface water the predicted buffer intensity remained the same at 0.12 mM/pH. These values are right at the minimal level to maintain pH stability. During the assessment,

the water leaving the WTP had a pH of 8.8 and an alkalinity of 37 mg/L as CaCO₃, which calculates to a buffer intensity of 0.088 mM/pH. This allowed nitrifying bacteria to depress the pH to as low as 7.6. If the blended water were to increase to 50 percent surface water, the predicted buffer intensity would decrease to 0.10, which could be a concern in areas where nitrification is occurring.

Due to the elevated nitrification activity in the distribution system, it's recommended to maintain a buffer intensity greater than 0.15. This can be accomplished by adding additional alkalinity in the water leaving the WTP using existing soda ash, carbon dioxide, and calcium hydroxide feed systems. At a pH of 9, obtaining an alkalinity of 50 mg/L will accomplish a buffer intensity of 0.15 mM/pH in both the treated groundwater and blended groundwater containing 30 percent surface water. Under this combination, pH depression should lessen; however, the CCPP will increase from 4 to 7 mg/L as CaCO₃, meaning the calcium layer would be slightly thicker, but should not cause friction or clogging issues. If the percent surface water were to increase to 50 percent, then the soda ash, carbon dioxide, and calcium hydroxide doses will also need to increase to achieve a finished water alkalinity of 50 mg/L.

Another option to reduce the impact of nitrification is to conduct an annual temporary switch to free chlorine in the distribution system. Switching to free chlorine (turning off the ammonia) for approximately three weeks should reduce nitrification and pH depression. This would then only require a buffer intensity of 0.12 mM/pH, which would be similar to the water quality currently leaving the WTP. Increasing chloramine residuals at booster stations could also reduce nitrification, provided that chloramine residuals remain consistently above 2 mg/L throughout the entire distribution system.

The utility occasionally receives discolored water complaints. Based on the distribution assessment data, most noticeable discolored water events are the result of the simultaneous release of iron and manganese. In areas where manganese is nonexistent (newer portions of the distribution system) iron release can cause "light" discolored water events. During these releases, some arsenic and lead that accumulated on these metals from adsorption may also release.

Figure 20 shows a simplified diagram of a pipe scale containing both iron and manganese. Iron has the ability to adsorb both manganese and arsenic, while manganese can further adsorb additional lead. In this situation, iron is considered the most sensitive metal, meaning that if iron were to release, it would



Figure 21. Lead and copper results from Lead and Copper Rule monitoring events expressed as a percentile.

simultaneously release all the other metals that have coprecipitated on the pipe, including arsenic and lead if they exist within the pipe scale. This can happen in both the distribution mains and customers' premise plumbing.

Optimal Corrosion Control Treatment

The primary chemical treatment strategies commonly used by utilities to achieve corrosion control are pH adjustment, alkalinity (DIC) adjustment, and application of corrosion inhibitors, such as orthophosphates. The goal of these strategies is to form and maintain an insoluble, uniform, nonporous barrier layer between the drinking water and the pipe material to prevent or limit corrosion. Adjustment of pH and/or alkalinity achieves corrosion control by reducing the solubility of most pipe materials and the compounds that create a protective barrier along the pipe wall (for example, lead precipitates like hydrocerussite). In other words, the goal of pH and alkalinity adjustment is to create water quality conditions conducive to a stable pipe scale that will not leach metals into the drinking water.

Optimizing finished water quality to minimize lead and copper release in the drinking water is the primary focus because they are regulated metals, but iron and manganese must also be considered because they most likely have additional lead and arsenic within their scales that have been adsorbed and accumulated over time.

One of the primary concerns was the large decrease in pH by more than 1 pH unit (from 8.8 to 7.7) observed in the far reaches of the utility's distribution system. A pH variance of this magnitude makes it difficult to control pipe and scale corrosion. The buffer intensity in the distribution system is right at, or at times slightly below, the recommended minimum value of 0.1 mM/pH.

The depression in pH correlated well with other indicators of nitrification, which is the common cause of pH suppression in low-buffered waters. This becomes a cyclic process because as nitrification causes pH depression, it also causes monochloramine to become less stable and break down easier, releasing more free ammonia as food for the AOB. These AOB produce nitrite, which is food for the NOB. These NOB produce nitrate and hydrogen ion, which cause further acidification and a pH reduction in the drinking water.

Based on the WaterPro model used to simulate water quality conditions in the distribution system, increasing the alkalinity to 50 mg/L as CaCO₃ at a pH of 9 will form a calculated buffer intensity of 0.15 mM/pH, which

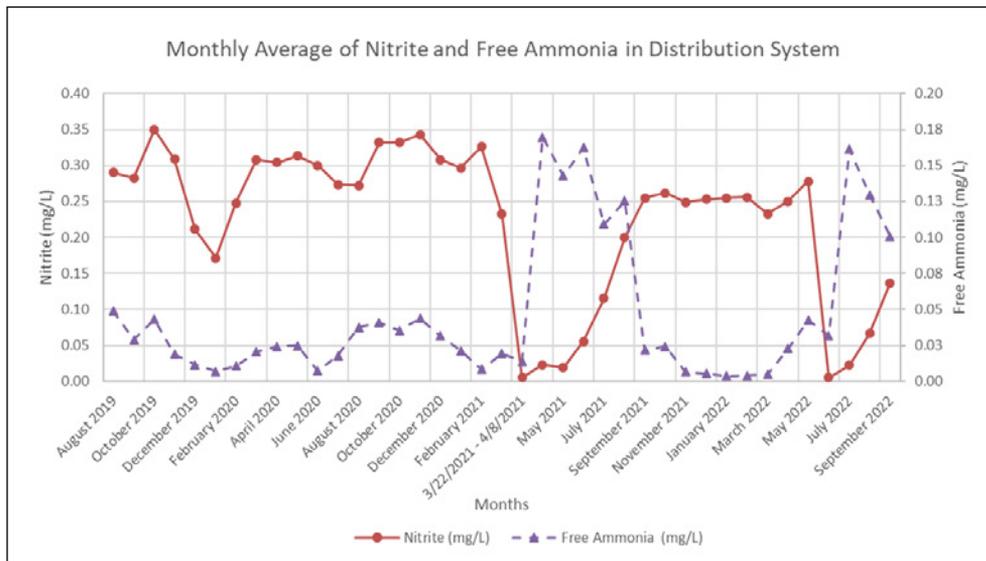


Figure 22. Monthly average of nitrite and free ammonia in the distribution system.

would provide additional resistance to a pH change from nitrification. If pH values were to stabilize where the minimum pH was 8.3 and the average pH was near 8.7 in the system, it should further decrease lead and copper solubility (release) into the tap water from customers' homes, while possibly increasing the stability of monochloramine, thus reducing nitrification. This will also further stabilize manganese, making it more difficult to release on its own in the distribution system.

The weakest link is iron scale and deposits. If the pH were to stabilize and increase from an average of 8.3 to 8.7, iron solubility would increase by approximately 37 percent based on the geochemical model. This could potentially be enough to cause an increase in discolored water complaints in areas where iron deposition is significant and a calcium layer is nonexistent, and areas with elevated manganese deposition. As the iron releases, it will also release the manganese that has adsorbed to it, along with other heavy metals that have coprecipitated. To minimize scale release, it's recommended to physically remove the iron in the locations that have significant iron scales and deposition by either swabbing the pipe walls or using unidirectional flushing (UDF) methods.

Controlling nitrification in the distribution system will improve pH and alkalinity, thus reducing the corrosion of lead, copper, and manganese. Reducing lead and copper corrosion will also improve LCR compliance sampling results. Reducing manganese corrosion will decrease discolored water complaints and additional release of lead into the bulk water; therefore, an additional recommendation to improve corrosion control is to reduce nitrification in areas with high

water age by increasing the monochloramine residual.

The utility plans to modify the booster stations to include ammonium sulfate storage and feed systems, in addition to existing sodium hypochlorite storage and feed systems to boost monochloramine residual further out in the system. Maintaining monochloramine residuals consistently above 2 mg/L throughout the system would help control nitrification, increase pH and alkalinity, and reduce corrosion.

In addition to monochloramine booster stations, the utility was recommended to perform a free chlorine burn where the secondary disinfectant is switched to free chlorine for several consecutive weeks. Annual free chlorine burns are common in potable water distribution systems using monochloramine as the secondary disinfectant. Based on the historic and current levels of nitrification parameters, such as nitrite, pH, and monochloramine residual in the distribution system, the utility should perform at least a one-time free chlorine burn.

The time frame of the free chlorine burn would be approximately four to six weeks and is dependent on the free chlorine concentrations observed in the distribution system. The goal of the burn is to observe stable free chlorine residuals throughout the system.

The recommended OCCT strategy for the utility is summarized:

- ◆ Maintain a buffer intensity of 0.15 mM/pH at the POE by targeting a monthly average finished water alkalinity of 45 to 55 mg/L as CaCO₃ to minimize the impacts that nitrification has on pH depression.
- If nitrification is controlled through booster chloramination and free chlorine

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burns, then the buffer intensity may be lowered to current levels of 0.12 mM/pH by targeting a monthly average finished water alkalinity of 35 to 45 mg/L as CaCO₃ (approximately 10 mg/L reduction in alkalinity).

- ◆ Maintain a target pH of 8.9 to 9.1 at the POE and stabilize pH levels in the distribution system to further reduce lead, copper, and manganese corrosion in customers' plumbing and the distribution mains.
- ◆ Reduce iron and manganese concentrations in the system by physical means, such as UDF or swabbing in areas with moderate to significant iron and manganese concentrations, to minimize discolored water complaints. Iron solubility is expected to increase with the recommended water

quality changes, which could potentially cause an increase in discolored water complaints. The UDF will reduce the negative impacts of the higher pH and alkalinity values, as discussed previously.

- ◆ Reduce nitrification by installing ammonium sulfate storage and feed systems at the distribution system booster stations to increase monochloramine residual levels in the distribution system.
- ◆ Conduct at least a one-time free chlorine burn of the distribution system for an extended time (four to six weeks), with possible repeat chlorine burns in the future.
- ◆ Monitor the water quality in the system routinely to proactively identify areas of concern. The utility currently monitors key nitrification water quality parameters. The utility should develop process control charts

that automatically analyze the data and provide routine analysis and visualization of the water quality conditions at sample stations to help utility staff manage distribution water quality and optimize flushing.

The utility's corrosion control strategy prior to this study was to maintain pH and alkalinity within optimal water quality parameter (OWQP) ranges approved by FDEP. The OWQP ranges were approved by FDEP because the utility has been operating within these conditions and it has been shown to be an effective strategy for control of lead and copper concentrations in the drinking water based on historical LCR sampling. The lead and copper compliance sampling conducted by the utility during the first year of operation of the calcium hydroxide system (while this study was being conducted), were well below the 90th percentile MCL, as shown in Figure 10. Based on the distribution assessment and water quality evaluation performed, the utility can continue to utilize pH and alkalinity adjustment (following the recommendations described herein) to adequately control corrosion in its distribution system without the need for a corrosion inhibitor.

There are no anticipated changes in finished water quality that would require a change in the corrosion control strategy. Table 3 presents the utility's OWQP prior to this study and the new OWQPs recommended in this study, which were subsequently approved by FDEP.

Implementation of Recommendations

Since completing this study in early 2021, the utility was able to implement some, but not all, of the recommendations identified. Following the completion of the study, the utility was able to increase the finished water alkalinity at the POE to the recommended range of 45 to 55 mg/L as CaCO₃ using a combination of its existing soda ash, carbon dioxide, and calcium hydroxide feed systems. The utility also raised the finished water pH consistently, from 8.9 to 9.1 at the POE, as recommended.

Figure 21 presents lead and copper results from LCR monitoring events expressed as a percentile. Sampling events from 2021 and 2022 were conducted after implementation of some of the recommendations. The 90th percentile lead and copper values continue to remain well below the MCL. The maximum lead and copper concentrations observed during sampling events have decreased in 2021 and 2022, compared to 2020 and 2017 and prior to implementation of the recommendations.

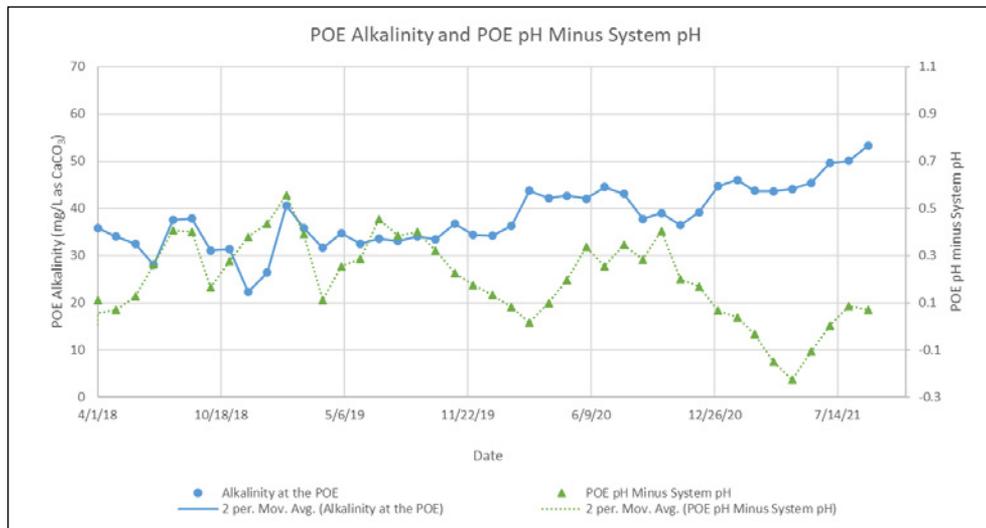


Figure 23. Monthly average alkalinity at the point of entry and the monthly average pH at the point of entry minus the monthly average pH in the distribution system.

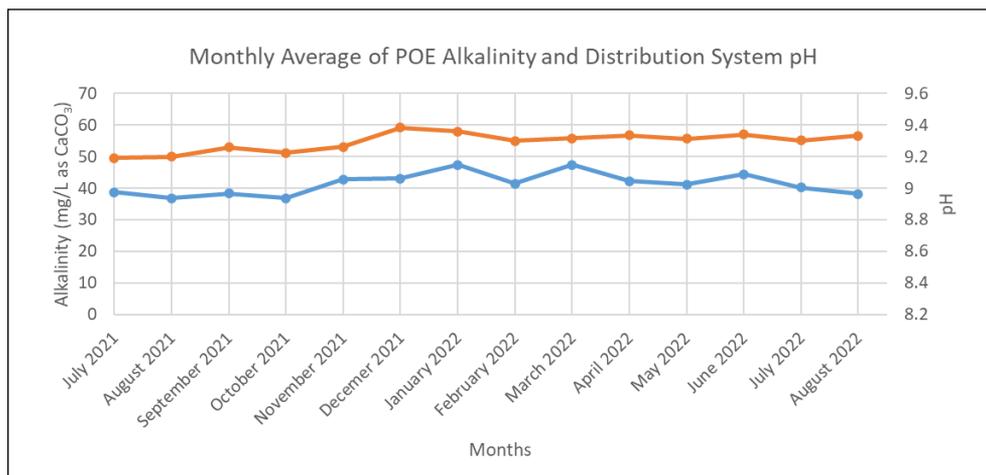


Figure 24. Monthly average alkalinity at the point of entry and the monthly average pH in the distribution system.

The utility has conducted annual four-week free chlorine burns over the last two years, which have successfully achieved stable free chlorine residuals in the distribution system. The free chlorine burns significantly reduced nitrification activity in the distribution system, but nitrification activity slowly returned to the system over time. Figure 22 presents the monthly average nitrite concentrations and the monthly average free ammonia concentrations measured in the distribution system. The monthly average data are derived from the average of 150 samples collected from 75 locations in the system each month.

As shown, the nitrite levels in the distribution system dropped to near zero during the free chlorine burns, but then slowly returned. There was a relatively high concentration of free ammonia following the free chlorine burns, partly because the chlorine feed pumps at one remote pump station were not operational. This is evidence that nitrification activity was diminished and was not consuming the free ammonia in the system; however, over time the nitrification returned and was able to begin consuming the

free ammonia present in the system, and thus, free ammonia concentrations decreased.

Figure 23 presents the monthly average alkalinity at the POE and the monthly average pH at the POE minus the monthly average pH in the distribution system. The alkalinity at the POE and the pH at the POE are measured three times per day and the monthly average values are derived from the average of the approximately 90 samples collected each month. The monthly average pH in the system is derived from the average of 150 samples collected from 75 locations in the system each month.

As shown, the difference between the POE pH and the system pH was reduced when the alkalinity at the POE increased. In other words, the increased buffer intensity improved the ability of the treated water to resist pH depression caused by nitrification activity, and therefore, the decrease in system pH was mitigated. As previously discussed, decreases in pH increase the solubility of metals like lead, copper, and manganese; therefore, the implemented recommendations improve the ability to control corrosion in the system by reducing the impact of nitrification activity on metal release.

The utility has continued to maintain finished water alkalinity at the POE to the recommended range of 45 to 55 mg/L as CaCO_3 and the pH in the distribution system has remained stable, even with the presence of nitrification activity. Figure 24 presents the monthly average alkalinity at the POE and the monthly average pH in the distribution system.

The utility plans to implement UDF or swabbing to reduce iron and manganese concentrations in the distribution system in areas with moderate to significant deposition, but has not implemented these strategies to date. The utility has not received any discolored water complaints, indicating that significant iron release has not been prevalent in the system, even with the slightly increased pH.

The utility also plans to implement ammonium sulfate storage and feed systems at the booster stations to better control nitrification in the further reaches of the distribution system. Even with annual free chlorine burns, it's apparent that the chloramine booster stations are necessary to control nitrification in the system for the long term. ◊