THE EFFECT OF CHLORINE ON CORROSION IN DRINKING WATER SYSTEMS

FINAL REPORT

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ABSTRACT

The concern of this study is whether the introduction of chlorine as required by the US EPA Groundwater Rule will push a water system that has not previously used chlorination for disinfection out of compliance with the US EPA Lead and Copper Rule. This will mostly affect small water utilities that do not chlorinate at this time.

A twelve-month pilot study using a series of pipe loops representing household plumbing materials was conducted to evaluate the effect of chlorine addition. Two test sites provided water with alkalinity 290 mg/L as CaCO3 and 140 mg/L as CaCO3. Orthophosphate addition was also tested at the high alkalinity water site to counteract the corrosion caused by chlorine. Sodium hydroxide was added at the low alkalinity water site to elevate the pH of the water and counteract the corrosion caused by chlorine at that site.

The results show that the higher alkalinity water has lower lead and iron levels but higher copper levels than the lower alkalinity water. Adding chlorine at a dosage of 0.2 mg/L as Cl₂ to drinking water will increase the corrosion of copper and iron in the system but may not adversely affect lead. In general, elevating the pH of the water to between 7.0 and 7.8 is beneficial in counteracting the corrosive effect of chlorinated water. Adding orthophosphate at a dosage of 1.0 mg/L as P and a pH of 7.0 or above will decrease corrosion of lead and iron in contact with chlorinated water. However, copper corrosion may increase in the long term.

THE EFFECT OF CHLORINE ON CORROSION IN DRINKING WATER SYSTEMS

BACKGROUND OF STUDY

This study on the effect of chlorine on corrosion in drinking water systems is funded by the Midwest Technology Assistance Center (MTAC). The organization provides technological assistance to small public water systems and water systems serving Native American communities. MTAC is described in its literature as "a collective effort of the University of Illinois and the Illinois State Water Survey in collaboration with the land grant universities of Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, Ohio, and Wisconsin. The mission of the Center is to provide small system administrators and operators with the information necessary to make informed decisions on planning, financing, and the selection and implementation of technological solutions to address their needs."

The Center issued a Request for Proposal in December 1998 for a study "to address corrosion control in small public water systems." Specifically, the study was to "evaluate the effect of chlorine on small distribution systems that have not previously used chlorination for disinfection."²

The impetus for this study comes from two Federal drinking water regulations that apply to small public water systems. The first regulation, The Lead and Copper Rule, was implemented in 1991.³ Small public water systems, which are defined as serving less than or equal to 3300 people, have been involved in sampling for lead and copper as prescribed by the Rule. At this time, the systems have either been shown to have optimal corrosion control or have implemented corrosion control techniques bringing them into compliance.

The concern is for the effect of the second regulation, The Groundwater Rule, which was proposed in November 1999. The final rule will be implemented in mid-2001.⁴ The Groundwater Rule will require all water systems to be reevaluated for disinfection needs. The majority of medium and large public water supplies already disinfect the water. A larger percentage of small public water supplies do not disinfect and will be most affected by this new regulation. Disinfection is most commonly achieved by introducing chlorine, an oxidant and a possible corrosive agent, into the water.

Will the introduction of chlorine as required by the Groundwater Rule push a water system out of compliance with the Lead and Copper Rule? Concerns with corrosion of other metals in the system arise as well as the possible corrosive effects of chlorine addition are studied.

The funding for this project was awarded jointly to Jae K. Park, Ph.D., professor of Civil and Environmental Engineering at the University of Wisconsin - Madison and to Abigail F. Cantor, P.E. of Process Research in Madison. Professor Park has a background in water chemistry and water treatment process design. Ms. Cantor has been a chemical engineering consultant in water treatment process design since 1980. She has designed and managed various corrosion control studies since 1992. A Masters Degree candidate from the Civil and Environmental Engineering Department at the University of Wisconsin - Madison, Prasit Vaiyavatjamai, is also on the project team. Mr. Vaiyavatjamai performed the weekly sampling of the apparatuses and analyzed the samples for various water quality parameters in this study. In addition, two statisticians were consulted on appropriate analysis of the data: Kevin Little, Ph.D. of Informing Ecological Design in Madison and Kevin Gross, a doctoral student in statistics at the University of Wisconsin—Madison, who worked under Little's supervision.

SCOPE OF STUDY

The scope of work for this study as discussed in the MTAC's request for proposal is:

- 1. Conduct a literature search of existing work relevant to this project.
- 2. Fully characterize the water quality information for each of the systems involved in the study.
- 3. Characterize the effects of the initiation of chlorination at the test sites.
- 4. Characterize the effects of introducing corrosion control techniques on the chlorinated water.
- 5. Communicate the results of the study:
 - a. Prepare an interim report six and twelve months after award of the contract.
 - b. Report on the project at a conference of the Midwest Center.
 - c. Develop Technical Briefs outlining the study findings for distribution through the National Drinking Water Clearinghouse and the Midwest Center.
 - d. Develop a consumer oriented informational product addressing these issues for distribution to systems experiencing or anticipating problems.

KNOWN EFFECTS OF CHLORINE IN DRINKING WATER SYSTEMS

In general, chlorine is considered to be a corrosive agent in water. Abatement of the corrosion is accomplished by increasing pH or by adding orthophosphate. However, there are many exceptions to this general understanding. The mechanisms of corrosion are influenced by a variety of environmental factors. Foremost, each metal in a drinking water system is affected by contact with chlorinated water in its own characteristic manner. Secondly, each constituent that comprises the water quality characteristics – carbonate, pH, dissolved oxygen, sulfate, and chloride, for example – exerts its own influence on corrosion. Finally, environmental conditions of the site or experiment – water temperature, surrounding air temperature, system pressure, flow rate, and piping configuration, for example – exert an influence on corrosion. Because of this, the technical literature often reports contradictory results. Nevertheless, each experiment contributes to the larger, complicated perspective that has so far evaded description.

In this experiment, comparative conditions were created to study the influence of chlorine. The fluctuations of environmental factors that could not be controlled were also recorded. The results are explained using the scrutiny of graphical and statistical methods and are then discussed in the light of previous research.

GOALS OF EXPERIMENT

The main goal of this experiment was to characterize the effect of chlorine on corrosion of three metals common to drinking water systems. To accomplish this, pipe loop apparatuses were constructed. Using water that had stagnated in contact with the pipe loops, the concentrations of metals that had leached into untreated water were compared to that in chlorinated water.

A secondary goal was to test if popular corrosion control chemicals can counteract the possible corrosive effects of chlorine. Metals concentrations from pipe loops with chlorinated water were compared to those from loops with chlorinated water plus a corrosion control chemical.

To take this study a step further, the influence of many factors – operating parameters and water quality parameters – on the outcome of such experiments was observed. Gathering this data during weekly sampling sessions and exploring its relationship to the test outcomes accomplished this.

DESIGN OF EXPERIMENT

Based on time and budgetary constraints as there are in any project, choices had to be made as to which factors could be isolated for study in one experiment. The first factors to be considered were water quality parameters. Past research has shown that alkalinity and its related parameter, dissolved inorganic carbonate, come to the forefront as water quality parameters that greatly influence the corrosivity of water.^{5,6} For that reason, two sites were chosen in this project that differed in these concentrations.

At each site, it was desired to test the corrosivity of the untreated water and compare it to the corrosivity of the same water with chlorine added at the required disinfection dosage.

Three metals representative of typical residential plumbing materials – lead, copper, and galvanized iron – were chosen as the apparatus materials of construction. Although lead piping has been banned in modern drinking water systems, some older systems remain in use. In addition, some older systems contain lead solder.

Finally, it was desired to demonstrate corrosion control techniques. Available corrosion control techniques include pH adjustment, alkalinity adjustment, and addition of corrosion inhibitors.⁵ For hard, alkaline water, pH and alkalinity adjustment is not an option because excessive precipitation of calcium carbonate can occur and diminish the hydraulic capacity of the pipes.⁵ Operators with this type of system water typically add a corrosion inhibitor.

Corrosion inhibitors create a passivating film on the pipe wall. This is a film that inhibits the electrochemical processes resulting in corrosion.⁵ One such corrosion inhibitor, silicate, has not been greatly researched. Plus, systems using silicate take a long time to come to a steady state where conclusions can be drawn about the chemical's effectiveness. Therefore, it was not chosen to study in this project.

Many water systems use a phosphate compound as a corrosion inhibitor. Blends of poly- and orthophosphates are commonly used. However, some studies have shown that polyphosphates can actually increase the leaching of pipe metal into the water under certain conditions.^{5,6,7,8,9,10} The conditions that this phenomenon occurs have not been identified by scientific means. Therefore, the use of polyphosphates for corrosion control is ambiguous and risky. They were not considered for this project.

Much success has been found with the use of orthophosphate as a corrosion control chemical for hard, alkaline water.^{7,11} An orthophosphate chemical was chosen to add into chlorinated water at the site with higher alkalinity. Potassium orthophosphate was selected because with its neutral pH, it would be a safer chemical to use than orthophosphoric acid at small water utilities where personnel and resources are scarce.

Orthophosphate has been found to be effective in lower alkalinity water also. However, in the interest of demonstrating a second corrosion control technique, pH adjustment using sodium hydroxide was chosen to add into chlorinated water at the site with lower alkalinity.

Table 1 summarizes the factors that were selected for study in this project.

Table 1. Summary of Experimental Design Factors

Pipe No.	Site	Chemical Treatment	Pipe Metal
1	High Alkalinity	Untreated Water	Lead
2	Site		Copper
3			Iron
4		Chlorinated Water	Lead
5			Copper
6			Iron
7		Chlorinated Water with Potassium	Lead
8		Phosphate Added for Corrosion Control	Copper
9		-	Iron
10	Lower	Untreated Water	Lead
11	Alkalinity Site		Copper
12			Iron
13		Chlorinated Water	Lead
14			Copper
15			Iron
16		Chlorinated Water with Sodium Hydroxide	Lead
17		Added for Corrosion Control	Copper
18			Iron

There were a total of eighteen pipes and conditions in this corrosion control study. The data from all pipes were compared with one another using nonparametric statistical procedures described in the literature.¹² More sophisticated statistical techniques were also used because shortcomings were found with the suggested method.

It should be noted that there are many factors in this type of experiment that cannot be controlled. For instance, the two sites differ in air temperature around the apparatuses and system static and dynamic pressures. There are also constituents in the water at the two sites that cannot be compared or held steady. For this reason, data on many additional factors were recorded beyond the primary experimental variables. Later, graphing techniques were applied to the data to observe a given factor's influence.

SITE SELECTION

As described above, the experimental design for this project called for two sites with different concentrations of alkalinity. With the help of the Wisconsin Rural Water Association and the Wisconsin Department of Natural Resources, two such sites were found within fifty miles of Madison. The Village Boards and the Water Utility Managers of the two sites were quite hospitable to the project.

The site with hard, alkaline water was the Village of Dane (population 620) located twenty miles northwest of Madison. The project apparatus drew water from their distribution system that is a mixture of water from two wells. The utility does not chlorinate or fluoridate the water.

The site with softer, less alkaline water is the Village of Lone Rock (population 630) located fifty miles west of Madison. The distribution system is composed of two wells, but the project apparatus drew water from Well No. 2 only. The pump for Well No. 2 is set to turn on every evening at 10:00 PM and run for about two hours until the water tower is filled. The apparatus was set to turn on at 10:15 PM and run for one hour ensuring that water only flowed through the apparatus when the well pump was running. The utility does not chlorinate but does fluoridate the water. The apparatus was tapped into the well pump discharge line upstream from the fluoride addition.

Table 2 lists the average water quality characteristics at the two sites.

Table 2. Average Water Quality Characteristics at the Two Sites

Analysis	Units	Dane, Wisconsin	Lone Rock, Wisconsin
рН	S.U.	7.4	7.8
Temperature	Degrees C	14	14
Residual Chlorine	mg/L as Cl2	0	0
Total Phosphorus	mg/L as P	0	0
Dissolved Oxygen	mg/L	11	6
Total Dissolved Solids (TDS)	mg/L	470	210
Calcium	mg/L as Ca	80	40
Magnesium	mg/L as Mg	40	20
Alkalinity	mg/L as CaCO3	290	140
Chloride	mg/L /L	60	9
Sulfates	mg/L /L	30	15
Manganese	μg/L	1	3
Lead	μg/L	1	1
Copper	μg/L	2	1
Iron	μg/L	5	2

DESIGN, INSTALLATION, AND STARTUP OF APPARATUS

The apparatuses were designed similar to the AWWARF Pipe Loop Model.⁵ The AWWARF model is intended to simulate the plumbing of a residence.

One difference between the AWWARF model and this project's apparatuses is that the AWWARF model is designed for loops that can hold a liter of sample. This project used loops that

held a little more than 250 mL of sample. The smaller loops are more economical and take up less space in this situation where nine loops are installed at each site.

Other differences with the AWWARF model involve the operating parameters of flow, pressure, and stagnation time. Because of site constraints, the flow in this project was 1.0 gpm per loop and 60 gallons per loop per day. The static pressure was 60 to 90 psig and the dynamic pressure was 15 to 45 psig. The flow and dynamic pressure values reached the lower end of the range that is seen in residential plumbing. There was also great variability of pressures throughout the experiment.

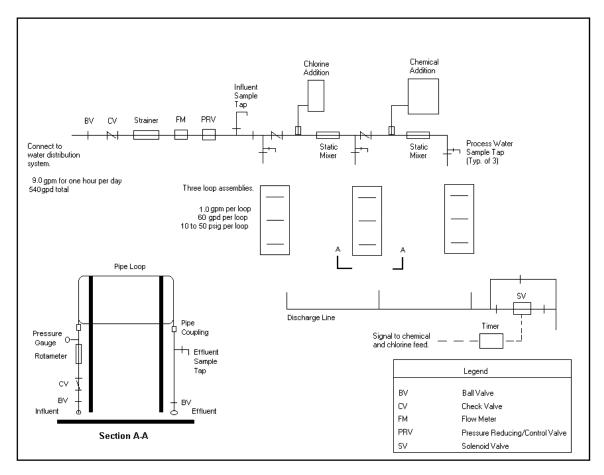
Because the apparatus at the Lone Rock site could not operate unless the well pump was running, the experiment was restricted to operating only once for an hour a day. This implies that the water stagnation time in this project is 23 hours. Typically, a pipe loop would be operated over a number of on and off periods throughout the day as is seen in a residence. The time that the water sits in the metal pipe loops affects the concentration of metal that is leached from the pipe into the water. Past studies have shown that the metals concentration in pipe loops can increase to a maximum and then fall over time.¹³ Special stagnation studies were run in the present experiment to capture this effect.

The apparatus at the Village of Dane was installed in a heated maintenance building and garage. The building's three-quarter inch galvanized iron water line running across the ceiling was teed off to supply water to the apparatus. The waste from the apparatus ran a short distance across the floor to a floor drain.

The apparatus at the Village of Lone Rock was installed in the Well No. 2 pump house. The apparatus was tapped into an existing three-quarter inch copper pipe that in turn was tapped into the discharge line from the well pump. The waste from the apparatus was piped to a floor drain with at least a two-inch air gap.

A schematic of the apparatuses is shown in Figure 1. Photos of the apparatuses installed at the two sites are shown in Appendix A.

Figure 1. Schematic of Apparatus



Three safeguards were installed to totally separate the public water supply from the processed water in the apparatuses:

- 1. A backflow preventer was located immediately after the tap to the public water supply.
- 2. A series of check valves throughout the apparatus also prevented backflow.
- 3. All chemical feed pumps included anti-siphon devices.

Installation and startup activities occurred as follows:

- 1. August 17, 1999 Installation at Village of Dane
- 2. August 24, 1999 Installation at Village of Lone Rock
- 3. August 26, 1999 Startup of both apparatuses
- 4. September 7, 1999 First sampling at Village of Dane
- 5. September 9, 1999 First sampling at Village of Lone Rock
- 6. September 14, 1999 Second sampling at both sites; began routine weekly sampling of both sites on Tuesdays.

SELECTION OF CHEMICALS

For the chlorinated water in the experiment, a chlorine residual of 0.2 mg/L was achieved. This dosage was based on the requirements of the U.S. Environmental Protection Agency's Proposed Groundwater Rule.¹⁴ The chlorine used was in the form of sodium hypochlorite with 12.5% available chlorine and a density of 10 lb/gal. The chemical was purchased from a local swimming pool supply store.

For corrosion control at the Village of Dane site, a dosage of orthophosphate of 1.0 mg phosphorus (P)/L was achieved based on optimum dosages discussed in the literature. The orthophosphate used was in the form of potassium orthophosphate with 27% total phosphate and a density of 12.7 lb/gal. The Carus Chemical Company donated the potassium orthophosphate.

For corrosion control at the Village of Lone Rock site, 50% sodium hydroxide was diluted with deionized water and fed into Lone Rock's water in the apparatus until the pH was adjusted from about 7.7 to 8.2. This was the largest pH adjustment that could be made before calcium carbonate began to precipitate into the apparatus. The Carus Chemical Company also donated the sodium hydroxide.

EXPERIMENTAL METHOD

Table 3 describes the sample taps on each apparatus.

Table 3. Sample Taps per Site

Sample Tap Number	Description		
1	Influent water to the apparatus		
2	Raw process water to the first pipe loop group		
3	Chlorinated process water to the second pipe loop group		
4	Treated chlorinated process water to the third pipe loop group At Dane, orthophosphate was added. At Lone Rock, sodium hydroxide was added.		
5	Lead loop using raw process water		
6	Copper loop using raw process water		
7	Iron loop using raw process water		
8	Lead loop using chlorinated process water		
9	Copper loop using chlorinated process water		
10	Iron loop using chlorinated process water		
11	Lead loop using treated chlorinated process water		
12	Copper loop using treated chlorinated process water		
13	Iron loop using treated chlorinated process water		

Samples taken from the sample taps during the study fulfilled one of three goals:

1. Document influent water quality

- 2. Document operational parameters and achieve process control
- 3. Document the loop effluent metals concentrations

The analyses performed on samples from each sample tap are shown in Table 4.

Table 4. Analyses Performed on Samples From Each Tap

Legend: X – samples were taken weekly; *X – samples were taken quarterly

Analysis	Sample Tap Number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
рН	X	X	X	X	X	X	X	X	X	X	X	X	X
Temperature	X	X	X	X	X	X	X	X	X	X	X	X	X
Residual Chlorine	*X	X	X	X									
Total Phosphorus	*X	X	X	X									
Dissolved Oxygen	*X												
TDS	*X	*X	*X	*X									
Calcium	*X												
Magnesium	*X												
Alkalinity	X	X	X	X									
Chloride	*X												
Sulfates	*X												
Manganese	*X												
Lead	X				X			X			X		
Copper	X					X			X			X	
Iron	X						X			X			X

The following describes the procedure of obtaining samples from the apparatuses:

- 1. The apparatuses should be off and sitting stagnant for 22 to 23 hours.
- 2. Record the flow meter reading. Check that 540 gpd (72.2 cfd) has been obtained daily since the last sampling event.
- 3. Record the pressure gauge reading from each loop for static pressure.
- 4. Calibrate the pH meter with pH buffer 7.0 and 10.0
- 5. Obtain a 200 mL sample from each pipe loop effluent sample tap using the appropriately labeled bottle.
- 6. Acidify the sample with 50% Nitric Acid. Put a cap on each sample bottle securely.
- 7. Obtain a 50 mL sample from each pipe loop effluent sample tap in a clean, dry beaker.
- 8. Record the temperature and measure and record the pH for each beaker.

- 9. At Lone Rock, record the pressure gauge reading for static pressure while Well Pump No. 2 is operating. (Well Pump No. 2 operates a few minutes before the apparatus turns on.)
- 10. Wait for the apparatus system to turn on by the set timer.
- 11. Set out three beakers and thermometers.
- 12. Rinse the thermometer and beaker with the water to be sampled.
- 13. *Draw a sample and record temperature and pH for the first process water sample tap. Repeat steps 12 and 13 for the other two process-water sample taps. At the Lone Rock site, NaOH flow is adjusted, if necessary, and pH is rerun. It will be reported in "comments" section on the sampling sheet if changes are made.
- 14. *Run a chlorine residual test by following the instructions in the Hach kit at each of the three process-water sample taps. Record the reading. Adjust the chlorine flow, if necessary, and rerun test. Note in "comments."
- 15. *Obtain one orthophosphate sample and one alkalinity sample from each of the process water sample taps. Cap bottles securely and keep samples in a cooler on ice.
- 16. Every three months, take a sample at each process water sample tap for Total Dissolved Solids (TDS).
- 17. Record rotameter and pressure gauge (dynamic pressure) readings at all loops. Note: rotameters are read at the marking covered by the largest diameter of the float.
- 18. If flow meter and/or rotameters and pressure gauges are not at the proper settings, adjust flow and pressure as was done in startup. Record any comments and adjustments made to the system.
- 19. Take a metals sample from the influent sample tap. Acidify and cap the bottle securely.
- 20. Take an alkalinity sample from the influent sample tap. Place bottle in a cooler on ice.
- 21. Measure pH and temperature from an influent sample tap sample.
- 22. Every three months, extra samples will be taken at the influent sample tap for TDS, chloride, sulfate, and orthophosphate.
- 23. Every three months, also analyze the influent sample tap water for chlorine residual and dissolved oxygen.
- 24. Record chemical feed storage tank level. Determine if the supply needs replenishing.
- 25. Upon returning to the lab. Store samples in the refrigerator. Clean all equipment to prepare for the next sampling event.
- 26. Analyze for orthophosphate and alkalinity. Enter all data into the database.
- 27. Perform other analyses per <u>Standard Methods</u>. ¹⁶ Perform quality control analysis for each analyte. Enter all data into database.

Notes:

- 1. *Because of the pulsating chemical feed pumps, process water samples are to be obtained in an 80 mL beaker rinsed with that tap's water. The beaker is filled to the 80 mL line in 60 seconds.
- 2. Sample bottles are to be cleaned and prepared as follows:
 - Step 1: Clean inside and outside of the sampling bottle with 20% ACS-grade Nitric Acid for 2 days.
 - Step 2: Fill the sampling bottle with 1% Trace Metal grade Nitric Acid, leave the acid in the bottle until used.
 - Step 3: Put the sampling bottle in the plastic zip bags.
 - Step 4: At site, dump the 1% Trace Metal grade Nitric Acid in the prepared container and immediately fill the metals samples into the bottle.
- 3. Table 5 displays the analytical methods used in this project.

Table 5. Analytical Methods Used in this Project From Standard Methods 16

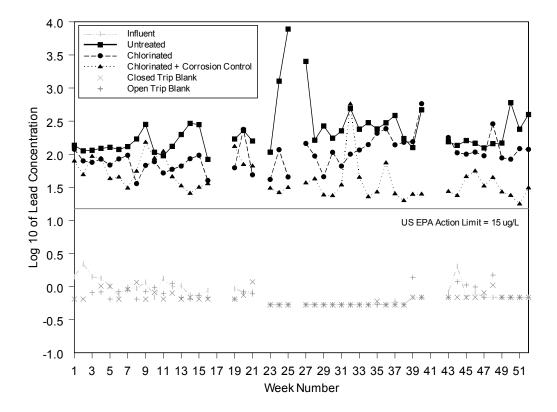
Analyte	Method
Alkalinity, Total	Titration Method 2320-B
Calcium	EDTA Titrimetric Method 3500-Ca D
Chloride	Ion Chromatography 4110
Chlorine, Residual	Hach Kit (Cat No. 46700-00)
Copper	Atomic Absorption (Frame Method) 3113-B
Iron	Atomic Absorption (Frame Method) 3113-B
Lead	Atomic Absorption (Graphite Furnace Method)
Magnesium	EDTA Titrimetric Method 2340-C & 3500-Ca D
Oxygen, Dissolved	Azide Modification 4500-O C
рН	pH meter
Phosphate, Ortho	Ascorbic Acid Method 4500-P
Solids, Total Dissolved	Gravimetric 2540-C
Sulfates	Ion Chromatography 4110
Temperature	Thermometer

RESULTS

The corrosivity of water cannot be quantified. However, relative corrosivity can be depicted by graphical means where the concentration of metal that leaches from a pipe wall into water of specific characteristics is plotted versus time. Metal concentrations for water having other characteristics are plotted on the same graph for comparison. In addition, the lead and copper concentrations from the pipe loops can be compared to the health Action Limit concentrations of 15 μ g/L of lead or 1300 μ g/L of copper set by the US EPA. For iron, the US EPA has set a Secondary Limit of 300 μ g/L above which aesthetic problems such as staining of sinks and laundry occurs, but consumer health is not affected. These features are presented in Figures 2 to 7 and are described below. The base 10 logarithm of the metals' concentration is shown on the graphs for easier viewing.

Lead. Figure 2 compares the corrosivity of untreated water on lead pipes versus chlorinated water versus chlorinated water with orthophosphate using the high hardness, high alkalinity water of the Village of Dane. The data for the influent water before contact with the lead pipes show that no lead was originally in the water. The data for the open and closed trip blanks show that the water samples were not contaminated by lead from other sources. The lead in the three types of water under study comes solely from the waters' contact with the lead pipes. The US EPA Action Limit appears in the figure as a horizontal line. Lead concentrations above this line are of a health concern. It can be seen that lead in all three water types were over the Action Limit, but the water with phosphate added dropped to the Action Limit by the end of a year of operation. The corrosivity of the chlorinated water, in general, appeared surprisingly to be lower than or equal to that of untreated water. The addition of phosphate lowered the corrosivity even further.

Figure 2. Dane, Wisconsin: Lead Pipe Loops



In a similar manner, Figure 3 compares the corrosivity of untreated water on lead pipes versus chlorinated water versus chlorinated water with pH elevation using the softer, lower alkalinity water of the Village of Lone Rock. Here, the chlorinated water also reduced the corrosivity in comparison to untreated water. Elevation of pH did not appear to add further benefit. The lead levels did not drop down as low as the Action Limit in this scenario.

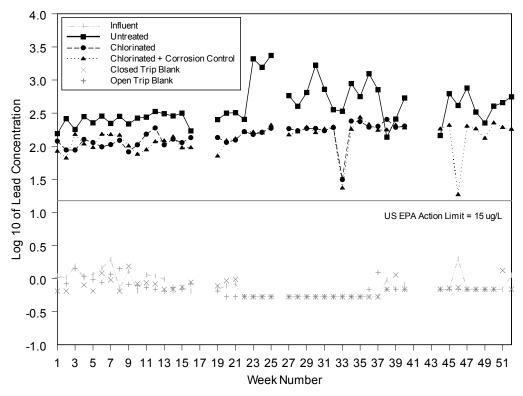


Figure 3. Lone Rock, Wisconsin: Lead Pipe Loops

In contrast to these results, past research has found that water containing oxidants such as dissolved oxygen and free chlorine is the most corrosive to lead.¹⁸ In that research, static leaching tests were performed on lead coupons and copper/lead solder coupons with low alkalinity waters (31 to 103 mg/L as CaCO3). These tests compared the effects of free chlorine at a concentration of 1.9 mg/L versus combined chlorine. No comparison was made to untreated water. Water with free chlorine had higher concentrations of lead than water with combined chlorine. In addition, a significant benefit to increasing the pH of the water in order to lower the lead levels was shown. In agreement with the present experiment, water with the higher alkalinity showed lower concentrations of lead. Finally, phosphate was added in various doses using various commercial products. Lower lead levels were achieved in all cases after phosphate was added.

It is possible that the effect of free chlorine varies with its concentration. The present experiment used 0.2 mg/L free chlorine versus ten times that amount in Lin's experiment. Also, the effect of pH elevation may be more evident in water of lower alkalinity and initial pH than Lone Rock's water.

Another research project is difficult to compare but interesting in the trends that were uncovered.¹⁹ In that project, electrochemical activity was measured in a special recycled-flow cell constructed of copper and lead solder coated pipe in contact with water of low alkalinity. Water at both pH 7 and 9 had similar rates of passivation. When the pH was 6 and 5, the passivation was greatly reduced. An additional experiment in the project, looked at the effect of free chlorine. The chlorine residual was increased in increments of 0 to 1 mg/L and then 1 to 3 mg/L. At each increment, galvanic currents peaked greatly but this dissipated almost immediately and the current

returned to pre-chlorine addition levels. The researcher concluded that chlorine residuals are of little importance to the galvanic corrosion process. Finally, orthophosphate at a dosage of 0.33 mg/L as phosphorous was found to substantially reduce the galvanic current at pH 7. For water of lower pH, the orthophosphate did not have any apparent effect. It was also noted that if the pH of the water dropped below 7, the benefits from a previously formed orthophosphate film were destroyed.

Copper. Figure 4 represents the results from the copper loops at Dane. In general, the three water types produced copper concentrations below the Action Limit. Chlorine appeared to increase the corrosivity of water in contact with copper. The addition of the phosphate further increased the corrosivity by the end of a year of operation, whereas it was hoped that it would counteract the effect of the chlorine.

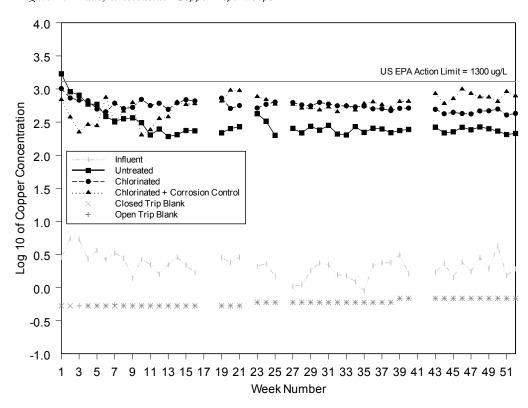


Figure 4. Dane, Wisconsin: Copper Pipe Loops

Figure 5 displays the results from the copper loops at Lone Rock. By the end of a year of operation, chlorine had slightly elevated the corrosivity of the water. The increase of pH intended to counteract the effect of the chlorine had instead increased the corrosivity even more.

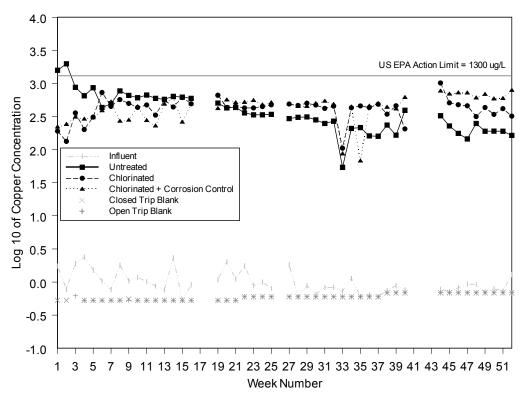


Figure 5. Lone Rock: Copper Pipe Loops

The effect of chlorine addition on copper corrosion in soft drinking waters has been addressed by Sprague and Edwards.²⁰ Their literature survey found that "chlorine has been observed to both increase and decrease the corrosion of copper in drinking water pipes." They cited studies where free chlorine concentrations were found to increase the dissolution of copper especially at lower pH. They also cited studies where the free chlorine decreased the corrosion rate of copper at a high pH of 9.3. They then noted that the experiments described in the literature were short in duration and may not be representative of the phenomena occurring in a distribution system over a long period of time. Sprague and Edwards' own project ran for six months exposing copper tubing to chlorinated water at 0.7 mg/L and 2.0 mg/L as free chlorine. It was found that copper corrosion did not increase in the chlorinated water at pH 7.0 in comparison to unchlorinated water. It did significantly increase at pH 9.5.

Another experiment found that free chlorine is primarily responsible for the corrosion of copper in chlorinated drinking water systems.²¹ Dissolved oxygen, in comparison, plays a relatively minor role. The corrosivity of chlorinated water is enhanced by low pH because of the greater oxidizing strength of hypochlorous acid (favored at low pH) over that of hypochlorite ion. The researchers conclude that free chlorine levels should be maintained no higher than 2 mg/L and the pH of the water maintained between 7 and 8 in order to minimize copper corrosion.

Comparing the previous two experiments with the present one, there is an implication that the benefits of pH adjustment may be optimized between pH 7 and 8. In chlorinated water with pH below 7 or above 8, there appears to be a greater corrosive action against copper.

The benefit of adding orthophosphate to decrease the corrosion of copper has been ambiguous in previous experiments as well as the present one.⁷ Studies have shown that copper corrosion is greatly influenced by environmental factors -- pH, temperature, and bicarbonate concentration, as well as concentrations of dissolved oxygen, chloride, nitrate, sulfate, and chlorine residual.^{22,23,24} A recent project discussion acknowledged that orthophosphate addition speeds compliance with the drinking water Action Limit for copper in new copper piping at low pH. However, at higher pH levels and over long periods of time, the presence of orthophosphate may stabilize higher copper levels than would naturally evolve.²⁵ This seems to agree with the present results.

Iron. Figure 6 shows the results from the iron loops at Dane. Here, chlorine increased the corrosivity of water in contact with iron. The addition of orthophosphate brought the metals concentrations back down to the level of the untreated water.

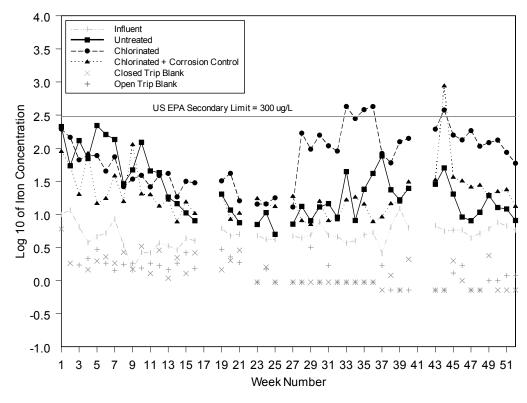


Figure 6. Dane, Wisconsin: Iron Pipe Loops

Figure 7 shows the results from the iron loops at Lone Rock. Here, chlorine greatly increased the corrosivity of water in contact with iron. Elevating the pH brought the metals concentrations back down to the level of the untreated water.

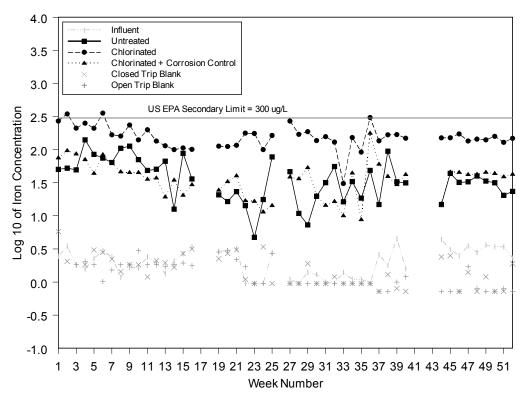


Figure 7. Lone Rock, Wisconsin: Iron Pipe Loops

A previous study where deionized water (water with extremely low alkalinity and hardness) kept at a pH of 7.0 in contact with iron pipe showed that a 4 mg/L free chlorine residual was much more corrosive than an equivalent amount of monochloramine residual as a disinfectant.²⁶ No comparison was made to untreated water.

The previous research also pointed out that there is a complex circle of events where free chlorine may cause corrosion and corrosion by-product buildup on the pipe wall. This, in turn, may provide an environment on the pipe wall for biofilm growth. It has been found in iron pipes that the corrosion by-products consume the free chlorine before it can penetrate the biofilm to destroy the microorganisms.²⁶ With the reduced efficiency of the free chlorine as a disinfectant, higher doses of free chlorine might be used which would, in turn, might increase corrosion.

To break the circle, LeChevallier, et. al. found that implementing corrosion control techniques increased the efficiency of the free chlorine as a disinfectant.²⁶ The researchers were most impressed with the addition of a polyphosphate blend for corrosion control. Using this chemical, they held the corrosion to a very low rate and found a biofilm inactivation of 2.0 log reduction of viable plate counts versus less than 0.5 for the same chlorinated water without polyphosphate addition.

Other researchers do not like the idea of adding phosphorus in any form to a water system. Phosphorus addition was observed to consistently stimulate microbial counts.²⁷ There are other nutrients found in water systems such as nitrogen, carbon, iron, and nitrate. However, phosphorus proved to be the limiting factor for microbial growth in a number of experiments.

If a disinfectant is not added to the water, there exists a possibility of the growth of microorganisms in the system. Depending on the microbial species, the nutrients available, and the water chemistry, the microbes can greatly affect both pH and alkalinity.²⁸ With a change in pH and alkalinity comes a change in the corrosive state of the water. Thus, the presence of microorganisms can cause increased corrosion in a water system. The remedy to this calls for the addition of a disinfectant. In this case, corrosion will be reduced by the addition of chlorine. The previous research projects concerning iron point to a very delicate balance of pH, free chlorine levels, and possible phosphate levels to control corrosion while effectively controlling microorganism growth in the water system.

Tables 6 to 8 summarize conclusions that can be made by inspection of Figures 2 to 7. These are not final conclusions, however. The characteristics of the stagnation curves must be taken into account. In addition, an attempt must be made to show the significance of these observations using statistical methods. Nevertheless, it is important to study the figures and note the following:

Table 6. Tentative Conclusions for the Corrosivity of Water on Lead

Lead Pipe Loops		
Issue	Dane (High Alkalinity)	Lone Rock (Lower Alkalinity)
Corrosivity of the untreated water with respect to lead	Corrosive (over the action limit)	Corrosive (over the action limit)
Effect of adding chlorine	Lowers the lead slightly	Lowers the lead levels
Effect of corrosion control chemicals added to the chlorinated water	Adding orthophosphate lowers the lead greatly in the long term	Increasing pH does not add further benefit
Background "noise" as shown in the influent sample and two trip blanks	Insignificant	Insignificant

Table 7. Tentative Conclusions for the Corrosivity of Water on Copper

Copper Pipe Loops		
Issue	Dane	Lone Rock
	(High Alkalinity)	(Lower Alkalinity)
Corrosivity of the untreated	Not over the action limit	Not over the action limit
water with respect to copper		
Effect of adding chlorine	Water is more corrosive than	Water is not different than
	untreated water but still not	untreated water at first, but
	over the action limit	later on, copper is elevated
Effect of corrosion control	Adding orthophosphate	Increasing pH increases the

chemicals added to the	increases the copper levels	copper levels further
chlorinated water	further	
Background "noise"	Insignificant	Insignificant

Table 8. Tentative Conclusions for the Corrosivity of Water on Iron

Iron Pipe Loops		
Issue	Dane (High Alkalinity)	Lone Rock (Lower Alkalinity)
Corrosivity of the untreated water with respect to iron	Not over the secondary limit	Not over the secondary limit
Effect of adding chlorine	Chlorine has no effect at first but elevates the iron later on	Chlorine elevates the iron levels
Effect of corrosion control chemicals added to the chlorinated water	Adding orthophosphate is effective in counteracting the influence of chlorine	Increasing pH is effective in counteracting the influence of chlorine
Background "noise" as shown in the influent sample and two trip blanks	Insignificant	Insignificant

As stated previously, the above data and conclusions must be tempered by information gleaned from stagnation curves.¹³ Stagnation curves are measures of metals concentrations and oxidants (dissolved oxygen, chlorine residual) over various times that the water is in contact with the pipe loop metal. The curves show that maximum metals concentrations can occur sooner or later than expected. This critical information may not be captured during routine sampling and conclusions may be different. It should be noted that stagnation curves could change with pipe age. The curves developed in this study are applicable to the loop conditions around weeks 41 to 45. In addition to metals concentrations, chlorine residual and dissolved oxygen data were also obtained as well as pH and temperature.

Figures 8 to 11 show the decrease of the oxidants, chlorine and dissolved oxygen, over time. The free chlorine appears to be depleted before the first sampling period of three hours in all cases but the Dane lead loops. Dissolved oxygen levels drop slightly over time.

Figures 12 and 13 show the fluctuation of pH in the loops' water over time. The pH makes a dramatic dip in all loops at Dane. The pH stays relatively steady in Lone Rock.

Stagnation curves for lead, copper, and iron at the two sites are shown in Figures 14 to 19. In some cases, a maximum metal concentration was reached before 23 hours of stagnation time. This means that the true corrosive effect of the water was not measured during routine sampling. However, the relative positions of the untreated, chlorinated, and chlorinated/corrosion control chemical addition data curves on the graph remained the same. Therefore, previous conclusions concerning relative corrosivity were unchanged. There was one exception as shown in the stagnation curves for the lead loops at Dane in Figure 14. Here, chlorinated water exhibits higher lead levels than the untreated water. After six hours of stagnation, however, these lead levels approach each other.

Figure 8. Dane Stagnation Curve – Chlorine Residual

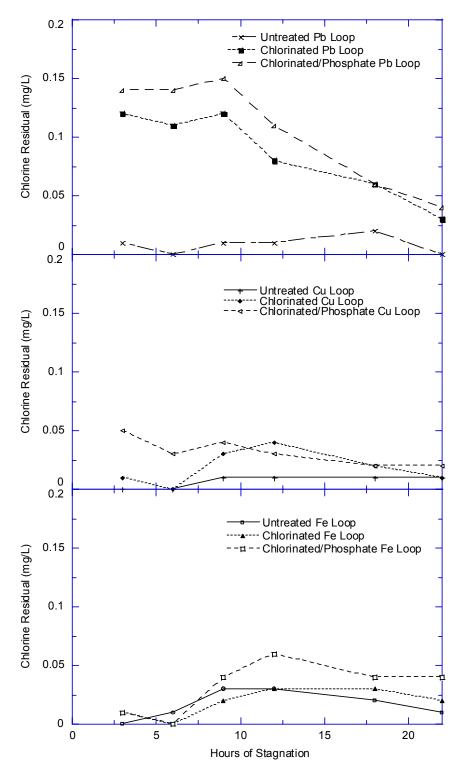


Figure 9. Lone Rock Stagnation Curve - Chlorine Residual

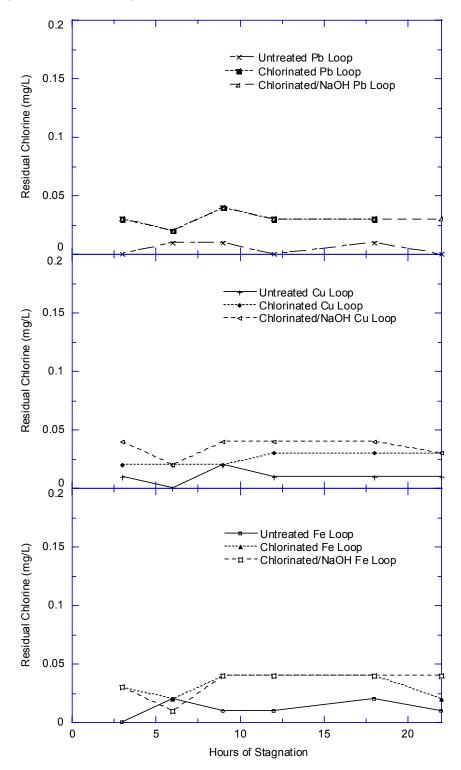


Figure 10. Dane Stagnation Curve - Dissolved Oxygen

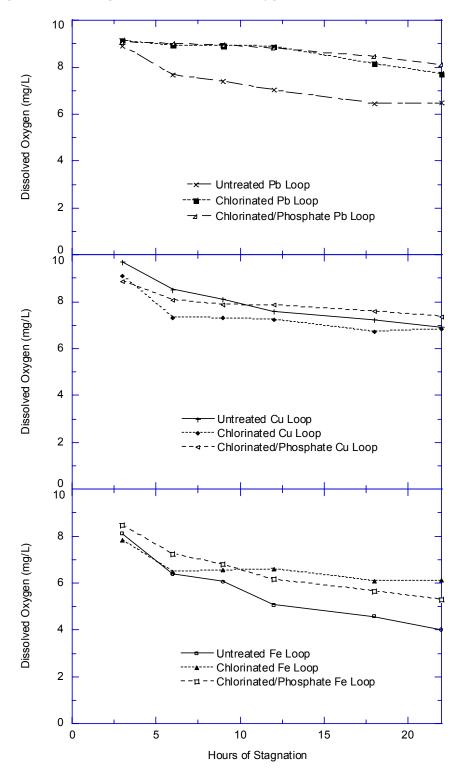


Figure 11. Lone Rock Stagnation Curve – Dissolved Oxygen

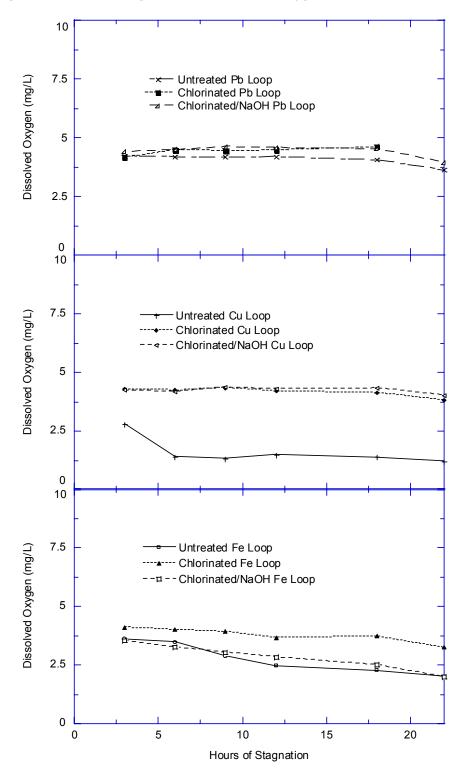


Figure 12. Dane Stagnation Curve -- pH

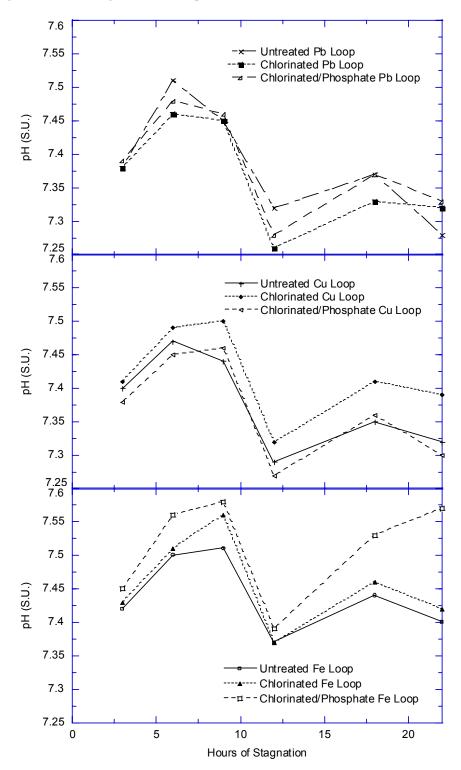


Figure 13. Lone Rock Stagnation Curve -- pH

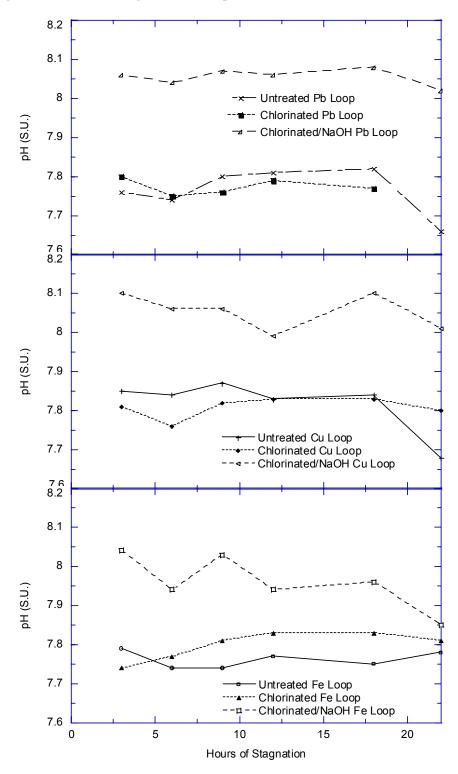


Figure 14. Dane Stagnation Curve -- Lead

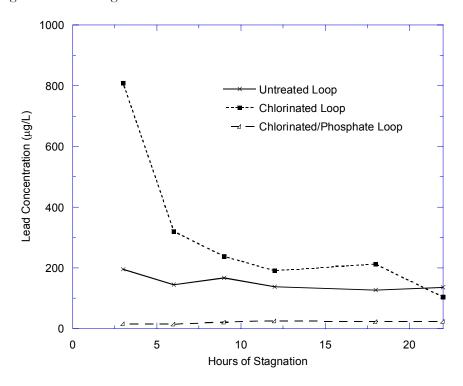


Figure 15. Lone Rock Stagnation Curve -- Lead

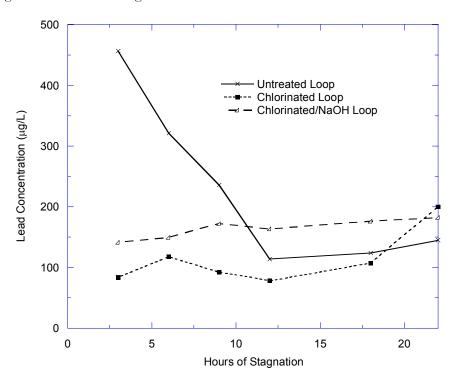


Figure 16. Dane Stagnation Curve -- Copper

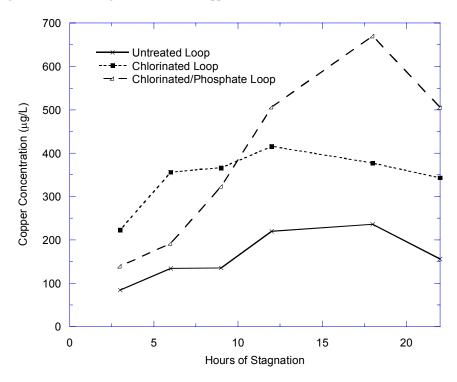


Figure 17. Lone Rock Stagnation Curve -- Copper

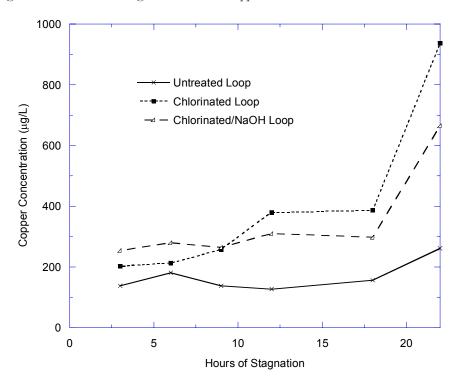


Figure 18. Dane Stagnation Curve -- Iron

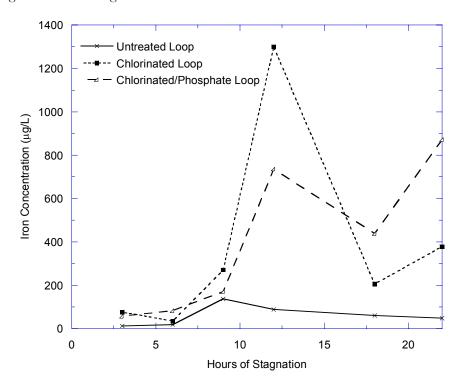
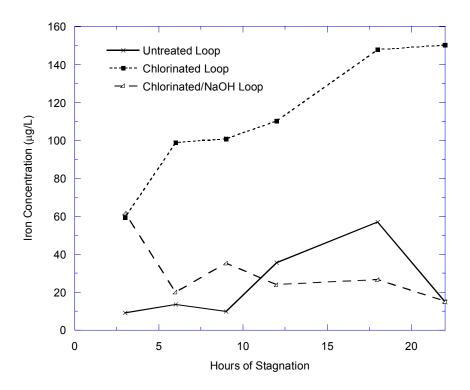


Figure 19. Lone Rock Stagnation Curve -- Iron



STATISTICAL ANALYSIS

DETERMINING THE EFFECTIVENESS OF TREATMENTS

Pipe loop data cannot be approximated by a normal distribution. Associated normal distribution methods are, therefore, not valid. The US EPA recommends Wilcoxon nonparametric methods for analysis. However, the Wilcoxon methods assume that the samples are obtained randomly. Random sampling implies that the variables that generate the observed values are statistically independent. For data taken in time order, as in this study, correlations over time must be considered and statistical independence cannot be assumed. When the random sampling hypothesis is inappropriate, erroneous results can occur. To work around this problem, the US EPA recommends only data from pipe loops that have achieved a steady state should be used with the Wilcoxon methods. However, most studies cannot be conducted long enough to reach a steady state; in many cases, it is difficult to prove that steady state has been reached; and some metals, such as copper, can take years to approach a steady state. Therefore, the statisticians involved in this project elected first to study the entire data record and summarize the outcomes of the tests with linear models that could account for correlation between observations taken over time. The results of the linear model were also compared to the results of the Wilcoxon test using the last twelve weeks of data chosen to represent steady state conditions.

For the linear model, the data was transformed by taking logarithms to stabilize variances. Then, six linear models were developed – one for each metal at each site. The form of each model is:

Log(y) = intercept +
$$\beta_1$$
Week + β_2 TrtCl + β_3 TrtPlus + β_4 (Week x TrtCl) + β_5 (Week x TrtPlus) + error

where:

Week = the week number of the experiment that the data was taken; represents the influence of time

TrtCl, TrtPlus = indicator variables to represent the different treatments for each pipe loop; the variables are assigned the following values:

Treatment	Value of "TrtCl"	Value of "TrtPlus"
Control	0	0
Chlorine	1	0
Chlorine + Corrosion Control	1	1

Week x TrtCl, Week x TrtPlus = represents the influence of time on the treatment scenario

The beta letters represent the coefficients in the equation. If β_2 or β_3 is calculated as negative, the metal concentration is reduced by treatment. If β_1 , β_4 , or β_5 is negative, the metal concentration drops over time. Table 9 lists the interpretation for the linear regression coefficients.

The error term was modeled by a first order autoregression. This means that the departure from the linear model at week W is related in a simple way to the departure from the linear model at week W-1: error at Week W = ϕ *error at Week (W-1) + a random shock where the random shock is statistically independent of the errors. In each of the models fitted, the estimated value of ϕ was

positive. The same linear model was also fitted assuming the value of ϕ is zero, which corresponds to the assumption that the errors are statistically independent. The two methods were compared to understand the effect on coefficients of the different error structures.

The Splus 2000 statistical software's function, "general linear regression" was used to fit the models. Table 10 shows the results of the analysis. In each of the six cases, the full model was fitted and then terms were dropped that were not significant at the 0.05 level. If a Week x treatment interaction was significant, the treatment term was retained. The numbers in parentheses are the standard errors of the coefficients.

Table 9. Interpretation of Linear Regression Coefficients

Intercept	If no other coefficients are statistically
	significant, then there is no treatment effect.
β_1	Trend in the data over time
β_2	The effect of chlorine treatment on metal
·	concentration
β_3	The incremental effect of corrosion treatment,
, -	beyond chlorine treatment
β_4	Week x treatment interaction: An allowance for
·	change in effect of chlorine treatment over time
β_5	Week x treatment interaction: An allowance for
, -	change in incremental effect of corrosion
	treatment over time.

Table 10. Linear Regression Analysis on the Complete Data Set

Location	Response	Intercept	Week	TrtCl	TrtPlus	Week x	Week x	Lack of
Dane	Lagland	2.187	0.0065	-0.368	0.0157	TrtCl	TrtPlus -0.0142	Fit?
Dane	Log Lead std. error	(0.106)	(0.0031)	(0.096)	(0.171)		(0.0053)	
	significant?	Yes	Yes	Yes	No	No	Yes	
Lone		2.451	0.0056	-0.447	110	100	1 68	
Rock	Log Lead							
	std. error	(0.062)	(0.0017)	(0.053)				
	significant?	Yes	Yes	Yes	No	No	No	
Dane	Log Copper	2.667	-0.0070	0.267	-0.301		0.0120	The model does not fit the first third of the series well.
	std. error	(0.075)	(0.0021)	(0.070)	(0.120)		(0.0037)	
	significant?	Yes	Yes	Yes	Yes	No	Yes	
Lone	Log	2.962	-0.0157	-0.441		0.0195		
Rock	Copper							
	std. error	(0.066)	(0.0022)	(0.080)		(0.0027)		
	significant?	Yes	Yes	Yes	No	Yes	No	
Dane	Log Iron	1.787	-0.0163	0.0049	-0.544	.0191		The model can't bend around the step changes apparent in the time plots.
	std. error	(0.235)	(0.0076)	(0.301)	(0.173)	(0.009)		
	significant?	Yes	Yes	No	Yes	Yes	No	
Lone Rock	Log Iron	1.659	-0.0049	0.657	-0.648			
	std. error	(0.0716)	(0.0019)	(0.072)	(0.072)			
	significant?	Yes	Yes	Yes	Yes	No	No	

Tables 11 to 13 verbalize the meaning of the linear regression analyses.

Table 11. Linear Regression Conclusions for the Corrosivity of Water on Lead

Lead Pipe Loops		
Issue	Dane (High Alkalinity)	Lone Rock (Lower Alkalinity)
General trend of the data over time	Lead increases over time	Lead increases over time
Effect of adding chlorine	Chlorine decreases the lead	Chlorine decreases the lead
Effect of corrosion control chemicals added to the chlorinated water	Over time, orthophosphate decreases the lead	Increasing pH has no added benefit in decreasing lead

Table 12. Linear Regression Conclusions for the Corrosivity of Water on Copper

Copper Pipe Loops			
Issue	Dane (High Alkalinity)	Lone Rock (Lower Alkalinity)	
General trend of data over time	Copper decreases over time	Copper decreases over time	
Effect of adding chlorine	Chlorine increases the copper.	Over time, chlorine increases the copper	
Effect of corrosion control chemicals added to the chlorinated water	Over time, orthophosphate increases the copper	Increasing pH has no added benefit in decreasing copper	

Table 13. Linear Regression Conclusions for the Corrosivity of Water on Iron

Iron Pipe Loops			
Issue	Dane (High Alkalinity)	Lone Rock (Lower Alkalinity)	
General trend of data over time	Iron decreases over time	Iron decreases over time	
Effect of adding chlorine	Over time, chlorine increases the iron	Chlorine increases the iron	
Effect of corrosion control chemicals added to the chlorinated water	Orthophosphate decreases the iron	Increasing pH decreases the iron	

For comparison, the last twelve weeks of data were analyzed by the Wilcoxon signed rank test using the Splus 2000 statistical program. Table 14 shows the results of this analysis. First, the signed rank statistic is shown. Then the p-value is stated. The difference between two treatments is significant at a 0.05 level if the p-value is less than or equal to 0.05.

Table 14. Wilcoxon Signed Rank Analysis on the Last Twelve Weeks of Data

Location	Response: Concentration	Untreated vs. Chlorinated	Untreated vs. Chlorine and	Chlorinated vs. Chlorine and
	Difference	Chiorinated	Corrosion Control	Corrosion Control
Dane	Lead signed rank	12	()	0
Dane	p-value	(0.0674)	(0.001)	(0.001)
	significant?	No	Yes	Yes
Lone Rock	Lead signed rank	2	1	25
	p-value	(0.0015)	(0.0039)	(0.3013)
	significant?	Yes	Yes	No
Dane	Copper signed rank	66	66	66
	p-value	(0.001)	(0.001)	(0.001)
	significant?	Yes	Yes	Yes
Lone Rock	Copper signed rank	52	55	54
	p-value	(0.0098)	(0.002)	(0.0039)
	significant?	Yes	Yes	Yes
Dane	Iron signed rank	66	66	1
	p-value	(0.001)	(0.001)	(0.002)
	significant?	Yes	Yes	Yes
Lone Rock	Iron signed rank	55	55	0
	p-value	(0.002)	(0.002)	(0.002)
	significant?	Yes	Yes	Yes

The linear model described earlier was fitted to the same portion of the data used for the Wilcoxon tests. While the results from the linear models substantially match the results from the Wilcoxon tests, in three of the six cases, a time trend can be detected in the data, which casts doubt on the Wilcoxon assumption of independent observations from a single distribution.

Allowing for autocorrelation among the errors produces only slight changes in the numerical estimates of the parameters. Except for the copper concentrations at Lone Rock, the statistical models identified the same parameters as statistically significant, regardless of the error structure. For the copper concentrations at Lone Rock, the assumption of independence leads to a significant "Week x TrtPlus" term. The copper concentration at Lone Rock is one of the three models that shows a statistically significant time trend, so we are getting additional information that there may be time-dependent structure for the copper series at Lone Rock in the last period of sampling.

Table 15 summarizes the results of the two data analysis methods.

Table 15. Comparison of Wilcoxon Results and Linear Regression

Location	Response: Concentration Difference	Analysis Method	Untreated vs. Chlorinated	Untreated vs. Chlorine and Corrosion Control	Chlorinated vs. Chlorine and Corrosion Control
Dane	Lead	Wilcoxon	No (p=.0674)	Yes (0.001)	Yes (0.001)
		Regression *	Yes (neg)	Yes (neg)	Yes (neg)
Lone Rock	Lead	Wilcoxon	Yes (p=0.0015)	Yes (p=0.0039)	No (p=.0.3013)
		Regression	Yes (neg)	Can't distinguish from effects of chlorine alone	No
Dane	Copper	Wilcoxon	Yes (p=0.001)	Yes (p=0.001)	Yes (p=0.001)
		Regression	Yes (pos)	Yes (pos)	Yes (pos)
Lone Rock	Copper	Wilcoxon	Yes (p= 0.0098)	Yes (p=0.002)	Yes (p=0.0039)
		Regression *	Yes (pos)	Yes (pos)	Yes (pos)
Dane	Iron	Wilcoxon	Yes (0.001)	Yes (0.001)	Yes (0.002)
		Regression *	Yes (pos)	Yes (pos)	Yes (neg)
Lone Rock	Iron	Wilcoxon	Yes (0.002)	Yes (0.002)	Yes (0.002)
		Regression	Yes (pos)	Can't distinguish as the effect of corrosion additive is about equal and opposite to effect of chlorine additive	Yes (neg)

^{*}The regression model detects a time effect.

In this study, conclusions from application of Wilcoxon method to the last portion of the data match the conclusions from the linear regressions. The Wilcoxon method has the advantage of simplicity in application and in summarizing the presence or absence of treatment effects. Nevertheless, as stated before, the Wilcoxon method can mislead when samples are not obtained randomly. Steady state, used to signal statistical independence and so validate the Wilcoxon test, may not occur during a test period. Also, the Wilcoxon test by itself does not provide an estimate of the effects. The linear regression, on the other hand, provides estimates of the treatment effects and accommodates time effects both in terms of the model and the error structure. By analyzing model residuals, it can be seen where the linear model does not fit well and the physical meaning of the lack

^{**} pos, neg = sign of parameter in the linear model

of fit can be reflected upon. In addition, closeness to steady state can be ascertained by the linear regression method. The closer the coefficient for "Week" and also the interaction coefficients involving time are to zero, the closer the process is showing itself to be to steady state.

STUDYING THE INFLUENCE OF OTHER FACTORS

A second goal in analyzing the data was to view the influence of various water quality and operating parameters on the results of the study. Many such factors cannot be controlled in on-site pipe loop studies, as they should be in a more rigorous scientific experiment. The variation of these factors over the duration of the experiment is shown in Appendix B.

The influence of various factors was determined qualitatively by graphical means. Conclusions are listed in Tables 16 to 18.

Table 16. Effects of Various Parameters on the Results from Lead Pipe Loops

Parameter	Parameters Confounded With	Clear Patterns in the Data
Loop tap pH	Location; Treatment	The elevated pH loops at Lone Rock have the highest pH.
Loop tap temperature		There is a spike in temperature around Week 22 at the Dane untreated water loop that coincides with a spike in lead levels. No other patterns are seen.
Dynamic Pressure	Location; Treatment	Increasing pressure correlates with increased lead, but this may be misleading. Pressure decreased along the apparatus, so effects would be greatly confounded with treatment.
Loop Water Flow	Location; Treatment	The chlorinated water at Lone Rock has the highest flow and the lowest lead, but this is greatly confounded with treatment.
Static Pressure	Location	There is a slight suggestion that higher static pressure produces lower lead.
Alkalinity	Location	Dane has higher alkalinity and lower lead concentrations
Phosphorous		Ignoring the loop at Dane where phosphorous was added, there is a slight suggestion of higher phosphorous concentrations correlating with lower lead levels. However, the low phosphorous measurements may just be within the variability of the analytical method.
Process tap Temperature	Location; Treatment	Except for the Week 22 spike at Dane, there is no pattern
Process tap pH	Location; Treatment	No apparent relationship with lead.
Process tap Chlorine	Location; Treatment	

Table 17. Effects of Various Parameters on the Results from Copper Pipe Loops

Parameter	Parameters Confounded With	Clear Patterns in the Data
Loop tap pH	_	A slight suggestion that when pH goes up, copper concentration goes down.
Loop tap temperature	_	No pattern
Dynamic Pressure		Maybe a small negative relationship, but not if you discard the Dane loop with orthophosphate added where the lowest pressures and the highest copper occurred.
Loop Water Flow		No pattern.
Static Pressure		No pattern.
Alkalinity	Location	Dane copper concentrations are slightly higher.
Phosphorous		Ignoring the loop at Dane where phosphorous was added, no pattern is apparent.
Process tap Temperature		No pattern.
Process tap pH		A few data points with extreme copper levels suggest very slightly that high pH levels produce lower copper levels.
Process tap Chlorine	Treatment	No pattern otherwise.

Table 18. Effects of Various Parameters on the Results from Iron Pipe Loops

Parameter	Parameters Confounded With	Clear Patterns in the Data
Loop tap pH	Location; Treatment	After removing the effects of Treatment and Location, data suggests that increasing pH decrease the iron levels.
Loop tap temperature	_	Weaker pattern than with process water temperature but relationship is evident in the pattern of temperature at Dane
Dynamic Pressure	Treatment	Maybe looks like higher dynamic pressure creates lower iron levels, but this is hard to disentangle from the treatment effects.
Loop Water Flow		No pattern.
Static Pressure		No pattern.
Alkalinity	Location	Dane samples have higher alkalinity and lower iron levels.
Phosphorous		Dane samples with orthophosphate added have high phosphorous and lower iron, but no other patterns are discernable.
Process tap Temperature	Location; Treatment	After removing the effects of location and treatment, increasing the temperature increases the iron levels.
Process tap pH	Location; Treatment	No pattern otherwise.
Process tap Chlorine	Location; Treatment	No pattern otherwise.

To summarize Tables 16 to 18, the operating and water quality parameters do not appear to greatly influence the outcomes of the tests. Most of these parameters suggest that the site location (higher alkalinity water versus lower alkalinity water) and the treatment (untreated versus chlorinated versus chlorinated with corrosion control chemicals) are the main influences as was hoped in the experimental design. The higher alkalinity site at Dane has lower lead and iron levels but higher copper levels than the lower alkalinity site at Lone Rock. High pH levels show lower copper and iron levels, but no influence on lead levels. Temperature does not affect the lead and copper levels much, but does greatly affect the iron levels. Outcomes appear to be independent of pressures and flows.

CONCLUSIONS

An increase in corrosion can be expected when free chlorine is introduced for disinfection into a drinking water system. Iron appears to be the most affected by free chlorine addition, followed by copper, followed by lead, which may or may not experience increased corrosion. This increase may not necessarily push the water characteristics over Action Limits for lead or copper or over standards for other metals.

Elevating the pH of the water is beneficial in counteracting the corrosive effect of chlorinated water on iron.

In very low alkalinity and low pH water, elevating the pH may be beneficial in alleviating lead corrosion as well. The low alkalinity groundwater used in this experiment with its pH and alkalinity higher than typical surface waters did not show decreased lead corrosion.

Also, in low alkalinity and low pH water, elevating the pH to between 7 and 8 may be beneficial in alleviating copper corrosion. Copper corrosion may be increased if the pH of the chlorinated water is taken above 8 in the chlorinated water.

Adding orthophosphate will decrease corrosion of lead and iron in contact with chlorinated water. However, copper corrosion may reach an increased level in the long term.

RECOMMENDATIONS

Should elevated levels of metals become a problem after chlorine addition, a first step in counteracting the increased corrosion should be to elevate the pH of the water, but great care must be taken. A pH above about 7.8 to 8.0 greatly diminishes the effectiveness of chlorine as a disinfectant.³⁰ A pH below 7 creates water of high corrosivity.^{5,6} In water with high alkalinity and high hardness, an increase in pH may cause excessive precipitation of calcium carbonate with associated hydraulic problems in the piping system. It has been suggested that the calcium carbonate precipitation potential (CCPP) be within the range of 3 to 10 mg/L.³¹ Therefore, if the water characteristics allow an increased pH with a CCPP in the proper range, then elevate the pH between 7 and 7.8.

If one or more metals in the drinking water system continue to show increased corrosion levels or if pH elevation is not practical in the first place, add orthophosphate to the chlorinated water. Note that the pH of the water should be at a minimum of 7 before orthophosphate is added. Past research has established an effective dosage of orthophosphate to be at 1 mg/L as P initially, later reducing to a maintenance dose of 0.33 mg/L as $P.^{6,11,15}$ The operator must also be aware that phosphate addition to drinking water may cause conflicts with the phosphorous discharge limits at the wastewater treatment plant and with phosphorous levels allowable for runoff into nearby lakes and streams. Also be aware that with orthophosphate addition, copper corrosion in the system may increase. The increase can be tolerated if copper levels do not rise above 1300 μ g/L in residences.

Proper monitoring is essential to proper corrosion control. Chemicals should not be added to a system without appropriate feedback as to their effectiveness. However, several problems to monitoring exist.

The monitoring prescribed by the Lead and Copper Rule is flawed. The emphasis is on selecting older buildings with lead or lead solder in the plumbing systems for sampling. Newer homes with

copper plumbing are overlooked, sometimes causing a false sense of security about copper levels in the system.⁷ Other materials of construction, such as iron, are neglected.

An established and effective monitoring method is to use pipe loops similar to the ones used in this project. A loop of each metal of interest can be connected at one or more locations in the water distribution system. Routine samples taken from the pipe loops will describe the corrosive trends in the system and chemicals can be adjusted accordingly. The advantages of this method are that the conditions under which samples are taken can be better controlled than in a private residence and the operator does not have to depend on the good will of consumers to obtain samples. The disadvantage of this system is that a small water utility does not have the resources and personnel to attend to the apparatuses.

Other methods of monitoring have not yet been established as presenting a clear picture of corrosion for various metals in a system. Research is proceeding in this direction.

Until conclusions are established on new effective and economical corrosion monitoring techniques, water utility operators who do not use pipe loops for monitoring should obtain additional samples from buildings in their distribution system. Samples must certainly be obtained according to the Lead and Copper Rule. Those samples can be used in the utility's internal evaluation for corrosion of lead. Newer homes with copper plumbing systems should also be selected and sampled in the same manner. That data should be used for the utility's internal evaluation for corrosion of copper. Other materials of concern in plumbing systems, such as iron, should also be sampled by proper selection of buildings or residences and by obtaining these extra samples. Samples obtained for internal evaluation of corrosion can be from public buildings or businesses as well as residences. Careful sampling can be achieved by paying attention to the following details:

- Select the appropriate buildings close to the utility water source and also at the extreme ends of the distribution system
- Verify the materials of construction in the buildings selected for sampling
- Verify that the water being sampled has not been softened or treated by any other means at the sample site.
- Verify that no water flowed through the building's plumbing system for the prescribed stagnation time of a first-draw sample.
- Be consistent in the stagnation time of each sample.
- After obtaining the first-draw sample for metals, gather other information such as the temperature and pH of the stagnated water, the temperature and pH of the flowing water, the orthophosphate concentration of the flowing water (if using any phosphate product), the total phosphate concentration of the flowing water (if using a polyphosphate product), and the chlorine residual of the flowing water.
- Plot all information on graphs versus time. Note changes to corrosion control treatments or other system changes on the graphs.

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APPENDIX A

Pictures of Project Sites



Pipe loop apparatus at the Village of Dane Maintenance Building



Side view of the pipe loop apparatus at the Village of Dane. Along the back wall are chemical tanks and pumps for sodium hypochlorite and potassium orthophosphate. The timer which controls the drain line solenoid valve and the chemical pump electrical outlet is the rectangle on the back wall.



Prasit Vaiyavatjamai measuring pH of samples at the Village of Dane site.

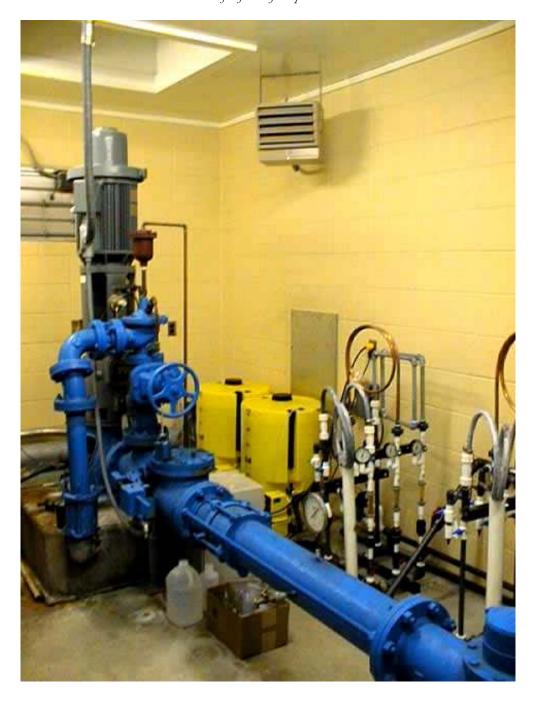


A close-up picture of the lead, copper, and galvanized iron pipe loops.



Pipe loop apparatus at the Village of Lone Rock Well No. 2 pump house. The loop racks extend along the side wall of the pump house. In the back corner are chemical tanks and pumps for sodium hydroxide and sodium hypochlorite.

Another view of the pipe loop apparatus at the Village of Lone Rock. Well Pump No. 2 and discharge piping are in the forefront of the picture.

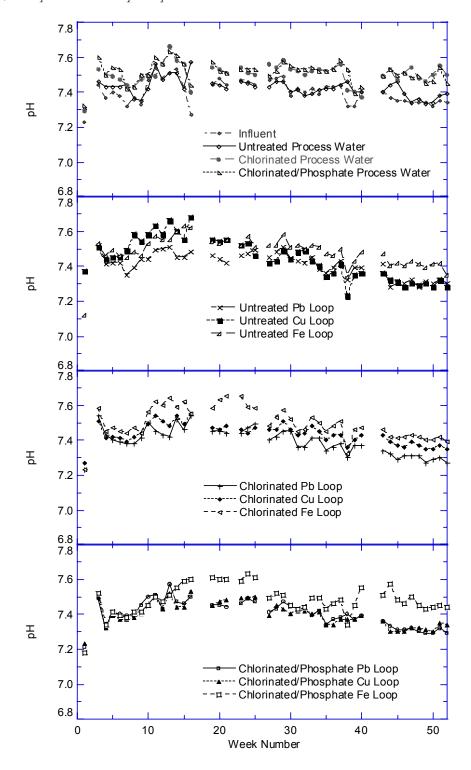


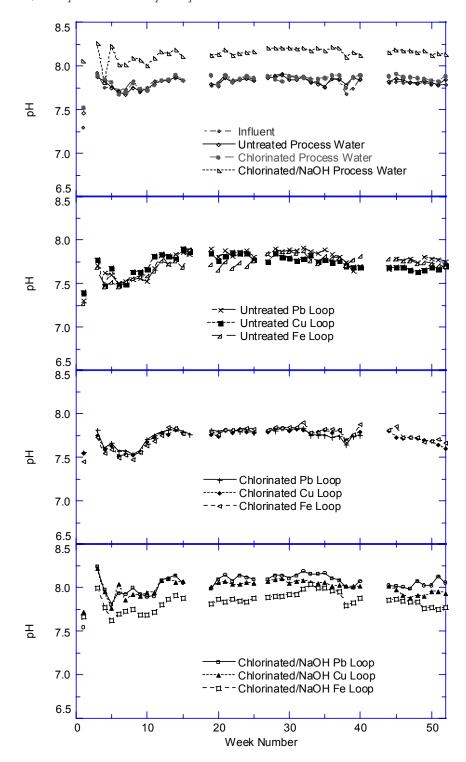
A close up view of a pipe loop rack at the Village of Lone Rock. The pipe above the floor drain discharges the apparatus' water. The rectangular box on the wall is the controlling timer. (The water on the floor comes from a dehumidifier in the left hand corner of the picture.)



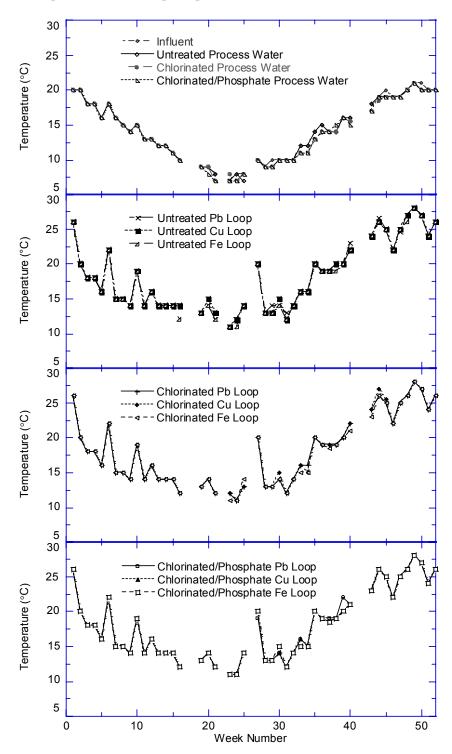
APPENDIX B

Graphs of Operating Parameters

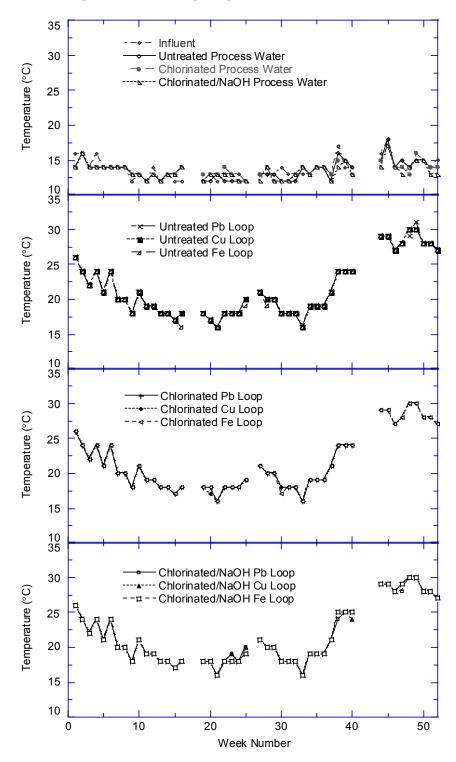


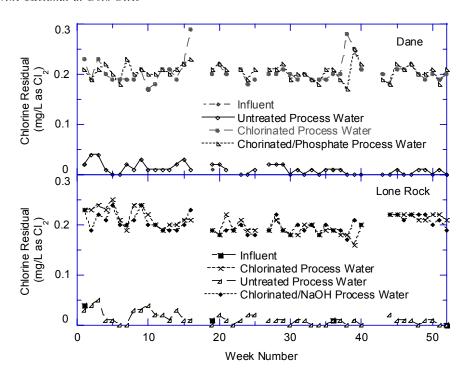


Dane, WI: Temperature At All Sample Taps

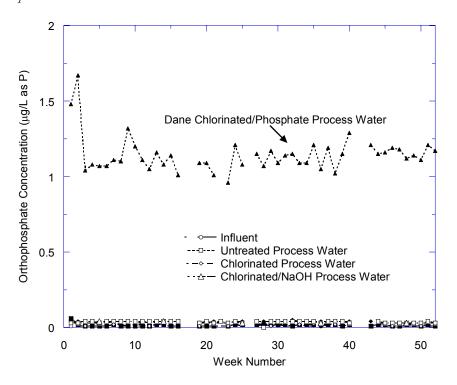


Lone Rock, WI: Temperature At All Sample Taps

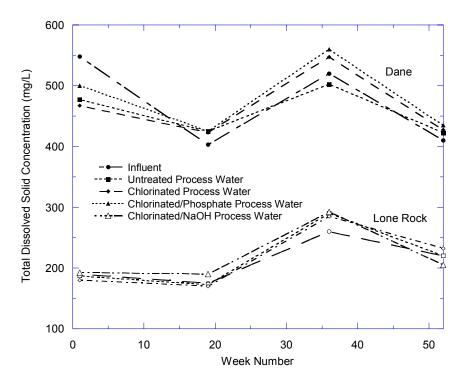




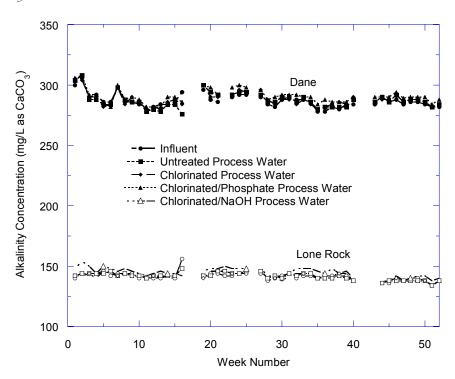
Orthophosphate at Both Sites



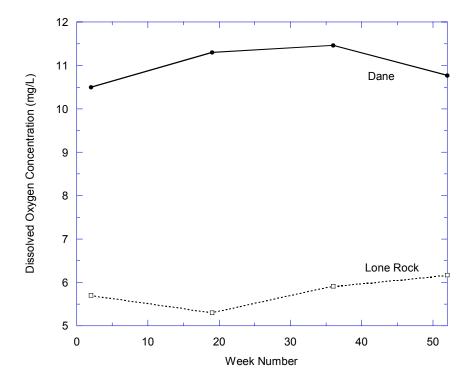
Total Dissolved Solids at Both Sites



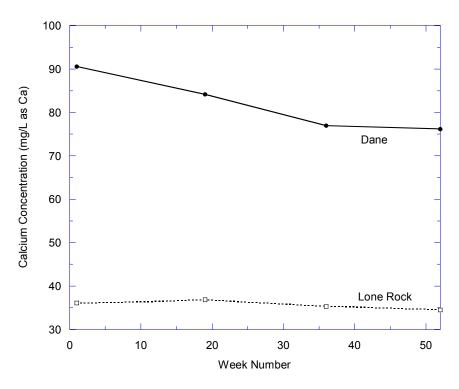
Alkalinity at Both Sites



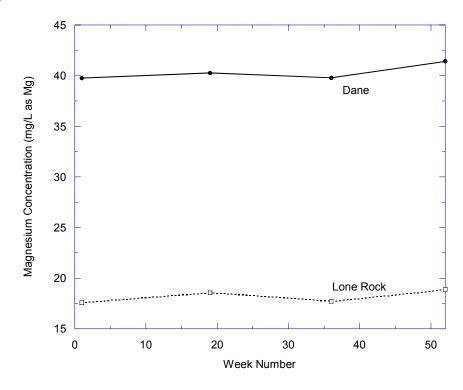
Dissolved Oxygen at Both Sites



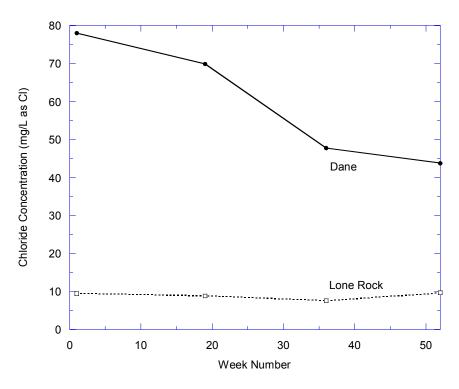
Calcium at Both Sites



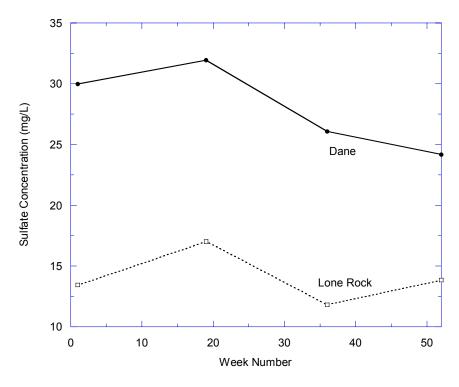
Magnesium at Both Sites



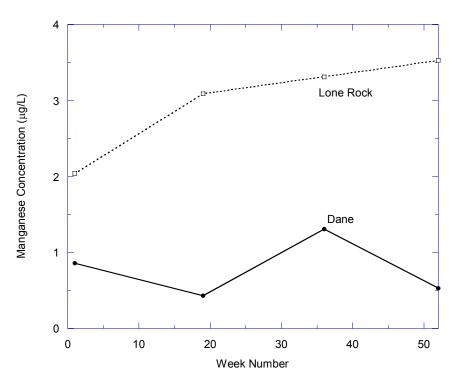
Chloride at Both Sites

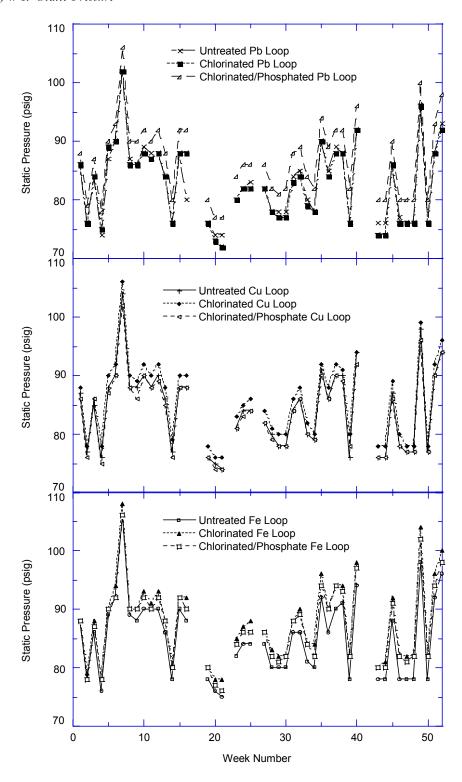


Sulfate at Both Sites



Manganese at Both Sites





Lone Rock, WI: Static Pressure Before Well Pump No. 2 Turns On

