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RELATIONSHIPS BETWEEN WATER QUALITY AND CORROSION OF PLUMBING MATERIALS IN BUILDINGS

VOLUME I. GALVANIZED STEEL AND COPPER PLUMBING SYSTEMS

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DISCLAIMER

Although the Information described in this article has been funded wholly or in part by the United States Environmental Protection Agency through assistance agreement number CR808566-02 to the Illinois State Water Survey, Department of Energy and Natural Resources and the Board of Trustees of the University of Illinois, it has not been subjected to the Agency's required peer and administrative review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water Systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxic Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the producta of that research and provides a vital communication link between the researcher and the user community.

Galvanized steel and copper plumbing materials have been used extensively in this country to distribute drinking water in . buildings. Corrosion of these materials within the distribution system may cause the drinking water to become contaminated by lead, zinc, and copper corrosion products. This publication presents the findings of a corrosion study of galvanized steel and copper materials exposed to public water supplies in Illinois. The relationships between water quality, corrosion rates, and metal concentrations are reported.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

A 3-year corrosion study was conducted on galvanized steel and copper piping materials installed in six public water supplies in Illinois. The water supplies were selected to represent the influence of water source, treatment processes, corrosion control programs, and water quality on the corrosivity of water. A comprehensive water sampling program was implemented to quantify the total metal concentrations found in both standing and running water samples. The major inorganic constituents in the water were determined to evaluate their contributions to the corrosivity of each water supply to copper or galvanized steel plumbing materials.

Corrosion rates were measured by a weight loss method using the ASTM (D2688 Method C) corrosion tester. Nineteen corrosion test sites were installed to investigate the effects of time and changes in water quality on the corrosivity. Corrosion data, metal concentrations, and water quality were incorporated into a data base from which multiple linear regression modeis were tested for significant data correlations.

Several significant findings were observed-. Most significant was the observation that chrome-plated brass faucets were making a large contribution to the lead, zinc, and copper concentrations found in drinking water. The experiments showed conclusively that brass sampling valves can be a considerable source of readily leachable lead and zinc when lead solder, lead pipes, and galvanized pipes are not present. Metal concentrations in water were significantly reduced with increased age of the plumbing installations. Extremely high metal concentrations were observed under stagnant water conditions in new plumbing installations, whereas reduced concentrations were observed in both running and standing water from older piping and fittings.

The lead, zinc, copper, iron, and manganese concentrations exceeded the MCL in 10.6 to 25.6$ of the standing samples and in 2.2% to 16.0% of the running samples collected during the study. Cadmium did not exceed the MCL in any sample. The metal concentrations generally decreased to equilibrium values within 6 months at most sites, but the zinc and copper concentrations increased during the last 12 months to concentrations much above the MCL in the most aggressive water supply.

The statistical association analysis was unsuccessful because of the exceedingly large number of variables encountered under the field conditions of the study. All six public water supplies experienced unanticipated upsets in water quality during the study. The simulated corrosion test loops were effectively used to monitor the corrosivity of the water with improved control of the running and standing periods of sampling.

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SECTION 1

INTRODUCTION

SCOPE AND OBJECTIVES

The principal objective of the corrosion study was to determine the influence of water quality on the corrosion rates of galvanized steel and copper pipe specimens installed in the potable water Systems of residences and large buildings. Six public water supplies in Illinois were selected for the study, representing both ground-water and surface water sources. Each water supply used various water treatment methods, which included lime-softening, ion exchange softening, polyphosphate, and Silicate programs.

Nineteen corrosion test sites were selected for the study and were located in different sections of the distribution system of each water supply. The corrosion rates for galvanized steel and copper specimens were determined by a weight loss method (ASTM D2688, Method C). Seven corrosion specimens were exposed for set intervals during the two years each site was in operation.

A second objective of the corrosion study was to monitor the trace metal concentrations contributed by galvanized steel and copper plumbing materials to the drinking water. Total zinc, copper, lead, iron, manganese, and cadmium concentrations were determined for both running and standing samples collected from taps in the buildings where corrosion test sites were located. Water samples were collected for a complete chemical analysis at 2-week intervals throughout the corrosion study.

On completion of the data collection phase of the corrosion study, the water quality, corrosion, and trace metal data were evaluated by statistical methods in an attempt to identify significant factors influencing the corrosivity of water. Laboratory studies were conducted to identify particulate and soluble corrosion products and to measure the contribution of brass valves to the total metal concentrations observed in drinking water.

BACKGROUND

Corrosion has been a long-standing and serious problem in public water supply distribution Systems. Hudson and Gilcreas[1] estimated in 1976 that nearly half of the 100 major U.S. cities distribute a corrosive water. The Potential health effects of corrosion led to federal regulations establishing maximum contaminant levels (MCL's) for certain metal concentrations in drinking water[2,3]. As stated in the regulations, water supplies should be noncorrosive to all plumbing materials. Though some researchers[4,5] have attempted to identify or predict waters that are corrosive, none have found a universally acceptable method for identifying a corrosive water that takes into consideration all piping materials and conditions of exposure. Some of the controversy over establishing the Secondary Drinking Water Regulations to the Safe Drinking Water Act was in defining noncorrosive water and acceptable methods for determining the corrosivity of water. Originally, the U.S. Environmental Protection Agency (USEPA) considered the use of the Langelier Index,[6,7] the Aggressive Index,[8] and the Ryznar Index[9] for predicting the corrosion tendencies of water. Because these calcium-carbonate-based indices were not reliable indicators for corrosivity, the USEPA decided to require more extensive monitoring of the materials of construction, water chemistry, and corrosion products in the public water supplies.

Two materials that have found widespread use in plumbing Systems are copper and galvanized steel pipe. Experience has shown that both materials offer good corrosion resistance to drinking water when the materials are properly selected and installed. However, many corrosion failures have been documented for copper[10,11] and galvanized steel[12,13] piping. The corrosion impact of these materials on water quality has not been adequately investigated. Brass valves, lead-based solders, bronze meters, or other fittings associated with copper and galvanized steel may also make a significant contribution to the soluble or particulate metal concentrations in drinking water.

The Illinois State Water Survey (ISWS) has been determining the corrosion rates for copper and galvanized steel in public water supplies for many years. The ASTM D2688 Method C (Standard Method for Measuring the Corrosivity of Water[14]) was developed by the ISWS in 1955 and has been used extensively in state facilities. The method has been a reliable indicator for corrosion and/or scale deposition and has been used primarilyto indicate the effectiveness of various water treatment programs. Attempts were made by the ISWS to correlate the mineral content of the water supplies with the observed corrosion rates for copper and galvanized steel. The correlations met with only limited success because several important chemical parameters were not determined or evaluated.

The project outlined in the previous section grew out of the common interest of the USEPA and the ISWS in (1) developing correlations between water chemistry and the corrosion rates of copper or galvanized steel, and (2) investigating the impact of these piping materials on water quality.

PROJECT DESIGN AND CONSTRAINTS

The design of a corrosion project is often determined by the theoretical concerns of the research scientist or by the practical concerns of the corrosion engineer or environmental scientist. Because the research scientist is searching for a better understanding of basic corrosion mechanisms, short-term studies are usually conducted in the laboratory where the corrosion environment can be closely controlled. The corrosion engineer or environmental scientist searches for Information on the corrosion of materials as it affects equipment life or water quality. Since laboratory research does not often translate well into actual field experiences, long-term field studies in real Systems are preferred by the corrosion engineer or environmental scientist.

This latter approach was used in this study to investigate corrosion Problems in actual plumbing Systems of buildings as influenced by the water quality of various Illinois water supplies. The corrosion rate for metals in public water supplies is usually low because the water source has been treated to reduce the corrosivity or because the corrosivity of the water source is naturally low. Therefore a 2-year study was considered the minimum time needed to obtain adequate and reliable corrosion measurements and to collect sufficient water chemistry data.

The planned interval corrosion test method of Wachter and Treseder[15] was considered the best procedure for evaluating the effect of time and the effect of the corrosivity of the water on the corrosion of metals. Corrosion specimens prepared according to ASTM D2688 Method C are easily adapted to the planned interval method of evaluation. Installing two of the ASTM corrosion test assemblies (each containing two corrosion specimens) at each test site, and replacing each of the specimens in turn with another specimen at 6-month intervals during the corrosion study would provide seven weight loss measurements, each representing a different time period during the study. The use of duplicate specimens was considered and would have provided useful Information, but the additional plumbing and handling costs prohibited their installation. Copper and galvanized steel were the two materials selected for testing, since they represented the major plumbing materials installed in buildings. Several solders, copper alloys, and steel were other materials considered for testing, but they were rejected because of increased project costs.

The complete water chemistries for many water supplies are required if significant correlations are to be found between the water quality Parameters and the corrosion rates of metals. Both inhibiting and aggressive influences of various constituents on the corrosivity of drinking water have been reported. The chemical constituents commonly cited as influencing the corrosivity of water are calcium, alkalinity, pH, carbon dioxide, sulfate, chloride, dissolved oxygen, silica, temperature, and dissolved solids.[4,5,6] Other constituents such as chlorine, organics, and polyphosphates are also suspected to influence the corrosivity of water. The interaction among these various influences can be observed only by determining the corrosivity of water in real distribution Systems.

The analytical program of the corrosion study was designed to determine all the major chemical constituents in addition to those known to influence the corrosivity of water. The metal concentrations were to be determined for running and standing water samples. The complete water chemistry of each water supply was considered essential for future data evaluation. Table 1 summarizes the laboratory analytical load for determining the essential constituents for each sampling site.

Considerable costs were associated with the sampling and analytical requirements for the corrosion study. These costs limited the number of corrosion test sites and the number of public water supplies selected for study.

TABLE 1. LAB0RAT0RY ANALYTICAL LOAD

Test Sites (no.)	Sampling frequency (no. per year)	Chemical Parameters (per sample)	Analytical determinations (2-year total)
19	24*	Zn, Cu, Pb, Fe, Mn	4560
19	6*	Cd	228
19	24	Zn, Cu, Pb, Fe, Mn	4560
19	6	Cd	228
19	24	K, Na, Ca, Mg	3648
12	24	total PO_4, poly PO_4	1152
12	24	NO_3, Cl, SO_4	1728
12	24	P & M alkalinity, TDS, SiO_2	2304
19	12	TOC	456
19	24	pH, free Cl_2, total Cl_2	2736
19	6	Dissolved oxygen	228

* Nonflowing samples

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SECTION 2

CONCLUSIONS

METHOD OF CORROSION MEASUREMENT

Corrosion measurements were determined by modified ASTM corrosion test assemblies that were installed in the actual plumbing Systems of buildings or were part of a simulated piping loop. The ASTM D2688 corrosion test assembly was reduced in size from 1 inch to 1/2 inch to conform with the nominal pipe dimensions encountered in household plumbing Systems. The smaller test assemblies were successful in simulating the actual surface conditions found in piping without undue distortion of flow. Visual inspection of corrosion specimens and associated piping in the test loop, after 2 years of exposure, showed that the interior surfaces were identical in appearance.

The simulated loops were designed to approximate the usage, water velocity, material exposure, and stagnation periods of water in household Systems, and provided reliable control of water flow and stagnation intervals during operation. Standing samples were collected at times convenient to sampling personnel and were not biased by uncontrolled usage or by leaking plumbing fixtures which occurred in household Systems. The use of test loops also circumvented service disruptions during installation and removal of corrosion specimens at the test sites. Since each test loop was identical in design, the piping materials and exposed surfaces were equivalent at each site employing the test loops. The use of both simulated test loops and household plumbing for the corrosion study provided a mix of old and new plumbing materials for comparison purposes.

The planned interval test method was successfully used in this study to evaluate the corrodibility of copper and galvanized steel and to evaluate the corrosivity of the water supply. A decrease in the corrodibility of both metals was observed which was attributed to the formation of surface films. In the less aggressive water supplies, the corrosion rates of the metals were very low and remained relatively constant.

The weight loss data for galvanized steel specimens were more erratic than similar data for copper specimens. This was attributed to the spotty nature of the surface film observed on galvanized steel, in contrast to the surface film on copper, which appeared uniform and continuous. The use of multiple corrosion specimens for each exposure period is recommended for future studies of galvanized steel corrosion. The minimum exposure period for a Single, reliable corrosion measurement in the selected water supplies was determined to be 12 months for copper and 18 months for galvanized steel.

VARIABILITY OF WATER QUALITY IN PUBLIC SUPPLIES

The water supplies selected for the study represented a diversity of treatment processes, water quality, and corrosion control programs. Ground-water and surface water sources were chosen to provide a broad range of mineral concentrations. The preliminary evaluation of these supplies indicated that the quality of the distribution water had remained consistent for several years prior to the study. However, significant variations in water chemistry were observed in samples collected biweekly over a 2-year period from each water supply.

The observed upsets in water quality were caused by equipment failures, modification of treatment programs, or routine operational procedures employed by the water supply. Both random and cyclic variations in water quality were observed. Surface water supplies experienced normal cyclic variations in quality each year due to seasonal changes.

Chemical constituents that varied significantly in one or more of the water supplies were chloride, sulfate, nitrate, alkalinity, pH, sodium, calcium, magnesium, chlorine, dissolved solids, inorganic phosphate, dissolved oxygen, and organic carbon. Some of these constituents (i.e., pH, alkalinity) are known to influence the corrosivity of water while the effects of some others are unknown. Although it was not evident in this study, the Variation in water chemistry may adversely influence the corrosivity of a water supply. Additional corrosion studies are required to identify and document the effect of many of the chemical constituents on the corrosion of metals in water.

Random or cyclic variations in water quality occured more frequently than anticipated. It was found that the frequency with which samples should be collected must be modified to detect excursions in water quality. The sampling frequency for routine monitoring of drinking water outlined by EPA guidelines is not adequate for this purpose. The effect of these excursions in water chemistry on the corrosivity of water requires further study.

EFFECT OF WATER QUALITY ON CORROSION RATES

Major fluctuations in water chemistry of short duration did not significantly change the corrosivity of the water supplies studied. Any effects due to a change in concentration of specific chemical constituents known to influence corrosion were apparently averaged out by the long-term corrosion tests.

A reduction in corrosivity was observed in one supply when a zinc polyphosphate corrosion inhibitor program was replaced during the study with a pH control program. A difference in corrosivity was observed within the distribution Systems of some supplies, although there was no evidence of a significant change in water chemistry. Water velocity was suspected to be responsible for the difference in copper corrosion in one instance.

Corrosion of galvanized steel increased at one location under stagnant water conditions, although copper corrosion was not influenced. Very low corrosion rates were observed for both metals during normal patterns of water usage.

The least aggressive water supply to copper materials was characterized by a low alkalinity and high pH, dissolved oxygen, chlorine, and nitrate content. Copper corrosion rates ranged from 0.4 to 0.2 mdd for 6-month and 24-month exposure intervals, respectively. The most aggressive water supply experienced copper corrosion rates from 3.6 to 1.4 mdd for the respective exposure intervals. The distinguishing water quality characteristics of this supply were very high concentrations of chloride, sulfate, and sodium.

The water supply least aggressive to galvanized steel was a lime-soda softened supply in which the Langelier Index was maintained near +0.4 with a moderate mineral content. Corrosion rates ranged from 0.6 to 0.9 mdd for all 7 specimens in this supply. The most aggressive water had corrosion rates ranging from 6.3 to 3.8 mdd for 6-month and 24-month exposure intervals, respectively.

EFFECTS OF CORROSION ON TRACE METAL CONCENTRATIONS

In all the samples collected during the study, iron concentrations exceeded the maximum contaminant level (MCL) in 25.6% of the standing samples and 16.0% of the running samples. Manganese concentrations were found to exceed the MCL in 14.5 and 11.6% of the standing and running samples, respectively. The naturally occurring iron or manganese content of the water source was found to be more significant than corrosion processes or water quality in influencing the total iron or manganese concentration. The presence of polyphosphate in the water supplies was observed to complex both iron and manganese, maintaining the concentrations above the MCL in some supplies.

Cadmium concentrations were found to be very low in all samples, both running and standing. Most samples were below the minimum detection limit of 0.3 µg/L for cadmium. The MCL for cadmium was not exceeded by any sample collected during the study, with the maximum observed value being 4.8 µg/L cadmium.

The zinc, copper, and lead concentrations of the water samples were found to be associated with corrosion in Systems containing either copper or galvanized steel plumbing materials, although multiple linear regression models were unable to identify any significant relationships between metal concentrations and the water quality.

The maximum contaminant level for lead was exceeded in 17.1$ of the standing samples and in 3.1$ of the running samples. The running samples exceeding the MCL for lead were collected from five copper plumbing Systems and from one galvanized plumbing system. The corrosion of lead-tin solder and the brass sampling valves was responsible for the lead content of samples.

Copper concentrations exceeded the MCL in 10.6% of the standing samples and 4.5% of the running samples, while zinc concentrations exceeded the MCL in 11.8% of the standing samples and 2.2? of the running samples.

The concentration of copper, zinc, and lead of both standing and running samples generally decreased over the 24-month sampling period and approached an apparent mean concentration plateau around which the metal concentrations fluctuated. Prior to reaching the concentration plateau, the metal content, from sample to sample, was observed to fluctuate over a wide concentration range characterized by concentration "spikes" attributed to particulate corrosion products. The overall distribution of the trace metal concentrations appeared to be approximately log-normal, rather than Gaussian.

At six selected sampling sites, the total metal concentrations in filtered and unfiltered samples were studied and little evidence of any particulate metal species in the water samples was found. Contribution by particulate species to high metal concentrations in samples from other test sites could not be ruled out.

A dependency of the trace metal concentrations in samples upon the length of time during which the plumbing materials were exposed to the water was observed. Samples from sites where plumbing materials had 15 years or more of exposure attained the concentration plateau very quickly, while samples from some newly installed plumbing Systems required several months to approach the concentration plateau.

In one water supply, the metal concentrations were observed to increase sharply during the latter stages of the study, after apparently attaining stable concentrations. Similar observations in the Seattle system were observed by Sharrett et al.,[1] although the possible metal contribution by sampling valves was not considered.

The total metal concentrations in samples were influenced by other factors, such as piping configurations prior to the sampling valve and rate of flushing prior to sample collection.

STATISTICAL ASSOCIATION OF WATER QUALITY VARIABLES AND CORROSION RATES

The multiple linear regression modeis did not identify any significant relationships among the many independent water quality variables and the trace metal concentrations of water samples or the weight loss of corrosion specimens. The inadequacy of the modeis was attributed to four potential causes: (1) important variables of the water were not measured, (2) the independent water quality variables were not constant between sampling dates, (3) there were interactions between two or more variables that were not integrated into modeis, and (4) the variables needed to be transformed into other terms. The latter two causes are considered the most plausible and require further study.

There were too many relationships to examine and too much variability between sites and within sites for an uncontrolled field study to reach many definitive conclusions. No Single relationship was strong enough to rise above all the other variables to be identified. The study was important because it provides strong evidence that there are many more factors and interrelationships affecting corrosion rates than have been taken into account by a simple linear regression model.

No attempt was made in this study to evaluate the corrosion rate or trace metal leaching data within the framework of a solution chemical model. In order to do so, a complete chemical analysis of the standing samples would have been required and the stagnation time necessary to reach the solubility equilibrium would have had to be determined and adjusted accordingly.

CONTRIBUTION OF TRACE METALS BY SAMPLING VALVES

Field and laboratory studies were conducted to test the hypothesis that the chrome-plated brass sampling valves were making a significant contribution to the metal content of the water samples. A clear decrease in the concentration of lead, zinc, and copper occurred in successive samples taken from brass sampling valves at field sites, providing convincing evidence that the valves were contributing significantly to the metal content of samples. The field data also indicated that lead was not originating in the galvanized layer of the galvanized steel loop or from the lead-tin solder of the copper loop at these sites.

Contamination of samples by the brass valves decreased with time in a study at another site, but remained substantial after more than five months of testing. Substitution of a Polyethylene sampling valve for the brass sampling valve sharply reduced the lead and zinc concentrations in the samples, providing further evidence of contamination by the brass valve.

The effect of time on the trace metal content of water due to leaching within the valve body was investigated in the laboratory. Six identical brass faucets were filled to capacity with either deionized water or tap water and were drained after 2k hours' exposure to check the metal content of successive samples collected over a 14-day period. Leaching of cadmium was not significant; all concentrations were near the analytical detection limit. Iron concentrations decreased rapidly to the detection limit within five days. Copper concentrations decreased from approximately 10 mg/L Cu to 0.1 mg/L Cu for both deionized water and tap water. Zinc concentrations were above 10 mg/L Zn in the first sample and gradually decreased to 1 mg/L Zn in the last sample. Lead concentrations were extremely high in the deionized water samples, ranging from 100 mg/L Pb in the first sample to 1 mg/L in the last sample. Tap water samples were also above the MCL for lead, decreasing from approximately 1 mg/L Pb to 0.1 mg/L Pb in consecutive samples during the 14-day study.

ADDITIONAL LABORATORY STUDIES

A study on the effect of temperature and time on the hydrolysis of polyphosphate during sample storage revealed that the reversion rates to orthophosphate were influenced by unaccounted-for factors. For samples from water supply "E", the orthophosphate and acid hydrolyzable phosphate (AHP) concentrations did not change significantly whether stored for 45 days at room temperature or refrigerated. However, for water supply "D", both the orthophosphate and AHP fractions increased in concentration under the same storage conditions as those of supply "E". When samples from supply "D" were immediately preserved with sulfuric acid, the AHP concentrations were much greater than the AHP concentrations found in unpreserved samples. Due to some unknown influence, the AHP fraction was observed to increase in concentration although the concentration was not anticipated to change. Inorganic phosphate was the only form of phosphate assumed to be present in the samples.

The waterside surface deposits were removed from a few corrosion specimens exposed for two years in the water supplies and were examined by X-ray diffraction to identify specific Compounds. The most interesting Compounds found in the deposits were vaterite and orthophosphate Compounds of zinc and iron. The corrosion products associated with the corrosion of copper or galvanized materials (copper oxide, zinc oxide, and basic carbonates) were also identified in the deposits.

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SECTION 3

RECOMMENDATIONS

A summary of the recommendations and research needs developed from this study is listed for consideration in future investigations of similar nature.

1. The trace metal content of drinking water is strongly influenced by abnormalities in the sampling process; therefore, sampling protocols should be developed for the specific requirements of environmental health studies, corrosion studies, or water quality studies. The sampling valve materials, piping configurations, plumbing age, flushing volumes, flushing flow rates, and stagnation intervals must be considered in establishing the protocol for each type of study. Flow samples, collected from nonmetallic taps, are recommended for monitoring purposes in corrosion studies. If equilibrium chemical modeis are to be tested to determine if they can predict or simulate the cor—rosion or passivation behavior of the plumbing materials, complete water chemistry data must be obtained for standing samples, and tests should be made to ascertain the stagnation period actually required to reflect "equilibrium" solubility conditions.

2. The impact of brass, bronze, and other copper alloy plumbing materials on the trace metal content of drinking water should be given high priority in future studies. Chrome-plated brass faucets were found to be a major source of lead, copper, and zinc concentrations found in the public water supplies sampled. The factors influencing the trace metal content of drinking water contributed by these materials should be examined and identified.

   A testing protocol should be developed to determine the leaching potential of metals from faucets delivering water for human consumption, and the faucets should be tested prior to marketing. A certification and testing program was developed in Denmark[1] which may serve as a useful model.

3. The widespread application of various commercial polyphosphate chemicals to public water supplies should be critically examined. The benefits of polyphosphate usage have been well documented for sequestering iron and manganese, inhibiting mineral deposition, and Controlling tuberculation in distribution systems. However, the Potential health hazards from increased metal solubility and distribution system problems associated with the use of polyphosphate in public water supplies have not been adequately investigated. The ability of

polyphosphate to Sequester metals was found to be responsible for causing iron and manganese to exceed the MCL's in some samples and for increasing the content of other trace metals during this study. Polyphosphates may also increase biological activity, increase deposition of phosphate minerals, accelerate leaching of calcium from cement-lined and asbestos-cement pipe, and interfere with the formation of surface films in potable water. Silicates may also exhibit similar characteristics, particularly at high concentrations, and should also be studied. The studies should cover the identification of aqueous species contributed by the different treatment chemicals, their metal complexation and hydrolysis properties, and the temperature effects on the complex formation and ligand stability.

4. The effect of chlorine and chloramine content in drinking water on plumbing materials requires further investigation. Chlorination of public water supplies is practically a universal treatment process but varies widely in application and control practices in this country. The free residual chlorine concentration has been maintained as high as 5 mg/L in some Illinois water supplies. In two instances, the corrosion rate of copper increased and failure of copper tube occurred at free residual chlorine concentrations of 2 mg/L. Trace metal concentrations were not monitored; however, increased solubilization of copper by chlorine has been cited in the literature.2 Because chlorine is a very strong oxidizing agent, it can be expected to influence the formation or dissolution of corrosion products on metal surfaces.

5. Methods should be developed for preconditioning newly installed galvanized and copper plumbing Systems to minimize the potential health risks associated with the consumption of water containing excessive trace metal concentrations. The trace metal content of water samples from new Systems decreases with time of exposure; however, the metal content may remain at high levels for several months after installation. Pipe materials could be treated by the manufacturer. or after installation to form protective films on the surface. Metaphosphates, metasilicates, and nitrates, along with other chemicals, have been used for precoating galvanized steel materials in Australia[3] and France (M. Dreulle, Cie Royale Asturienne des Mines, personal communication, 1971).

6. Extensive studies are needed to identify the interrelationships and unknown factors which influence the corrosion rate and dissolution of metals in public water supplies. Field studies were inadequate for this purpose due to an excessive number of known variables, unknown or missing variables, lack of control of the variables, and interactions among the many variables. Future studies should be conducted under closely controlled laboratory conditions where a few selected variables are examined at one time. As the basic chemical relationships are established, a general model could be developed and extended to Systems of increasing complication.

7. A standard procedure should be adopted for determining and reporting corrosion measurements in public water supplies. The planned interval

test method, which compares the weight loSS of specimens over various time frames, is currently the best procedure for detecting significant changes in the corrosivity of potable water. Satisfactory weight loss measurements are obtained by the ASTM D2688 method; however, multiple corrosion specimens are recommended for each test interval. The method is adaptable to steel, galvanized steel, copper, solder, and brass materials in 1/2" to 2" nominal pipe dimensions.

Long-term exposure of corrosion specimens is required due to the low corrosivity of most water supplies. From six- to eighteen-month exposure of specimens is recommended depending on the material exposed and the corrosivity of the water supply. A Single weight loss measurement of corrosion rate assumes a linear relationship with time but may be satisfactory when only the corrodibility of the metal is of interest in a controlled environment.

8. An instantaneous corrosion rate measurement procedure capable of detecting short-term variations in the corrosivity of public water supplies should be developed. Commercially available instruments could be utilized, but suitable probes need to be developed which simulate the corrosion mechanisms occurring on the surface of a pipe. It is unlikely that a Single probe could be made sensitive to the multitude of variables present in water supplies and could reflect pitting or scale deposition, for example. Instantaneous corrosion rate values would be useful in providing immediate Information on the effects of changes in treatment or variations in water quality.

9. Further research is required to identify and quantify the minerals formed by corrosion or deposition on the surfaces of plumbing materials exposed to potable water. X-ray diffraction studies of the surface films would assist in understanding the basic corrosion mechanisms responsible for the film formation and also would assist in differentiating which water chemistry parameters are significant in the process of formation. This Information would be useful for designing water treatment programs which would enhance the development of protective surface films.

   Research is necessary to develop appropriate sampling and sample handling methodology for water-formed deposits, because dehydration and oxidation can readily transform solids prior to or during X-ray analysis. Correlation with the predictions made by chemical corrosion and water treatment modeis can be made only if the analyzed solids correspond to those that were formed and adhered to the pipe interior surface when covered by the water.

   Experience in this and other corrosion studies also indicates that the surface films are often mixtures of multiple solids and are poorly crystalline, microcrystalline, or amorphous. These properties make simple glass slide preparation techniques and manual pattern indexing and file searching of limited value in correctly identifying the Compounds. More emphasis is needed in this area, as well.

10. Further statistical analysis is recommended for the corrosion and analytical data presented in this report. Meaningful relationships between the chemical factors and the trace metal content of samples may have been obscured by the numerous variables evaluated by multiple linear regression analyses. The number of independent variables should be selectively reduced and when variables are interrelated, only one of the variables should be evaluated. In this study, the most common independent variables found in models predicting the metal concentrations in water samples were temperature, chlorine, pH, silica, and nitrate. To a lesser extent, chloride, sodium, potassium, sulfate, magnesium, and alkalinity appeared in some models. These parameters should be considered for continued modeling studies.

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SECTION 4

TREATMENT PROCESSES AND QUALITY OF SELECTED WATER SUPPLIES

CRITERIA EMPLOYED FOR SELECTING WATER SUPPLIES

The corrosion investigation was limited to public water supplies within the boundaries of the state of Illinois. This restriction was applied because of travel considerations. Frequent Visits were anticipated to each corrosion test site and were planned to coincide with other ISWS project activities within the state.

Approximately twenty public water supplies were evaluated as potential locations for the corrosion test sites. The selection process considered water source, treatment processes, water quality, and corrosion control programs, all factors which influence the corrosivity of public water supplies.

Abundant sources of water are found in Illinois, where in 1980, public water supplies withdrew 480,000,000 gpd (gallons per day) of ground water and 1,780,000,000 gpd of surface water for consumption.[1] The water supplies of Carbondale, IL and Springfield, IL were selected to be representative of typical surface water sources. A deep ground-water source was selected at the state correctional center near Dwight, IL, and shallow ground-water sources were selected at the Champaign, IL and Dwight, IL public water supplies.

The water quality of the distribution water for each supply was also examined and water supplies were selected which exhibited mineral concentrations typical of Illinois water supplies. The major chemical constituents considered for this purpose were pH, alkalinity, total dissolved solids, chloride, sulfate, calcium, chlorine residual, and dissolved oxygen. Because of the limited number of water supplies which could be studied, many constituents which influence the corrosivity of water were not employed as criteria in the selection process but were monitored throughout the corrosion study.

Common raw water treatment processes for Illinois supplies are lime softening, ion exchange softening, clarification, filtration, and aeration. chlorination and fluoridation are mandated treatment programs for all water supplies and may be the only treatment applied in the case of some ground-water sources. Treatment processes influence the corrosivity of water and were an important consideration for selecting specific water supplies.

Various treatment programs are also employed by Illinois water supplies to control corrosion in the distribution system.[2] Calcium-carbonate-based programs are prevalent for lime-softened water supplies and surface water supplies. Polyphosphate programs have been applied to both surface water and ground-water sources.[3] Silicate programs are often applied to Systems using ion exchange softening.[14] The effectiveness of the various corrosion control programs was studied and was the basis for selecting certain water supplies for the study.

Table 2 summarizes the criteria employed in selecting each water supply for the corrosion study and Table 3 summarizes the water quality of the selected supplies.

WATER SUPPLY "A", CARBONDALE, IL

The public water supply for the southern Illinois Community of Carbondale is a municipally owned utility serving approximately 65,000 customers. The source of water is a lake located eight miles from the city. The low alkalinity and low hardness characteristics of the surface water require only clarification, filtration, and chlorination to produce a water

TABLE 2. CRITERIA EMPLOYED FOR SELECTING WATER SUPPLIES

Criterion	Public water supply					
	"A"	"B"	"C"	"D"	"E"	"F"
Water source						
Surface water	X					X
Ground water (deep)			X			
Ground water (shallow)		X		X	X	
Water treatment processes						
Chlorination	X	X	X	X	X	X
Fluoridation	X	X	X	X	X	X
Clarification	X					X
Filtration	X	X			X	X
Aeration			X		X	
Lime softening		X				X
Ion exchange			X		X	
Corrosion control programs						
Calcium carbonate base		X				X
Polyphosphate	X			X		
Silicate			X		X	
pH	X	X	X		X	X

TABLE 3. RANGE OF WATER QUALITY PARAMETERS FOR SELECTED PUBLIC WATER SUPPLIES*

Parameter	Water Supply "A"	"B"	"C"	"D"	"E"	"F"
Sulfate (SO_4)	16-41	14-57	2-293	1-671	49-590	24-68
Chloride (Cl)	4-11	3-16	185-1032	36-235	52-323	17-35
Alkalinity (as $CaCO_3$)	31-68	82-128	215-336	253-397	266-369	25-60
Silica (SiO_2)	1-5	5-10	9-29	8-20	8-28	1-12
Nitrate (NO3)	0.2-3.0	0.1-0.5	0.1-6.2	0.1-11.0	0.3-13.5	2-34
Poly phosphate (PO_4)	0.0-0.6	0.0-0.1	0.0-0.1	0.4-8.9	0.0-3.8	0.0-0.6
Total inorganic phosphate (PO_4)	0.0-0.8	0.0-0.1	0.0-0.1	1.0-10.4	0.8-4.3	0.0-0.8
Free residual chloride (Cl_2)	0.1-2.6	0.1-1.8	0.1-2.5	0.2-2.1	0.1-0.6	0.1-3.0
Total residual chloride (Cl_2)	0.1-2.9	0.1-2.7	0.1-3.0	0.4-4.0	0.4-2.0	0.1-3.2
Total organic carbon (C)	3.6-10.5	1.1-8.2	1-13	4.8-27.5	5.3-16.6	1.7-4.8
Dissolved Oxygen (O_2)	1.5-13.2	1.0-7.0	6.8-10.6	0.6-5.4	0.4-8.9	5.0-13.0
Calcium (Ca)	9.8-24.5	9.8-14.5	1-77	32-129	8-24	13-35
Sodium (Na)	5-28	23-37	295-690	150-222	261-380	3-11
Potassium (K)	0.6-3.2	1.7-2.5	1.4-29.5	3.2-4.5	0.8-7.4	1.8-4.2
Magnesium (Mg)	1.0-5.3	9.8-11	0.9-56.0	20-55	4.0-10.4	5-20
Total dissolved solids	95-149	136-229	1181-1929	736-1270	830-1266	147-277
pH (Standard units)	6.0-10.0	8.1-9.1	7.3-9.4	7.3-8.2	7.6-8.7	9.0-10.4
Temperature (°C)	4-28	8-26	7-26	8-21	8-24	4-29

* Concentrations expressed as mg/L except for pH and temperacure

of acceptable quality for drinking. However, the finished water is still corrosive to galvanized steel, cast iron, and ductile iron materials in the distribution system. A corrosion control treatment program is therefore required in addition to the clarification and filtration treatment processes, to minimize "red" water problems.

The water treatment plant production averaged 3,800,000 gallons per day during the period from September 1, 1981 through June 30, 1983. During this time frame, the average chemical dosages were 7.3 mg/L lime, 2.0 mg/L poly-er, 34 mg/L alum, 7.5 mg/L chlorine, and 0.5 mg/L fluoride. Figure 1 is a line drawing indicating the locations where the chemicals were injected in the water treatment system.

Two corrosion control programs were employed during the aforementioned period. A proprietary fused phosphate-zinc glass product (0.7 mg/L) was injected into the filter effluent prior to the final chlorination point. The addition of this product was stopped on February 17, 1982 due to inadequate control of the "red" water. On February 22, 1982 liquid caustic soda treatment was begun to increase the distribution water pH to 8.5. The average caustic soda dosage was 19 mg/L (NaOH), although the dosage fluctuated daily with alum and chlorine dosage. The caustic soda was injected

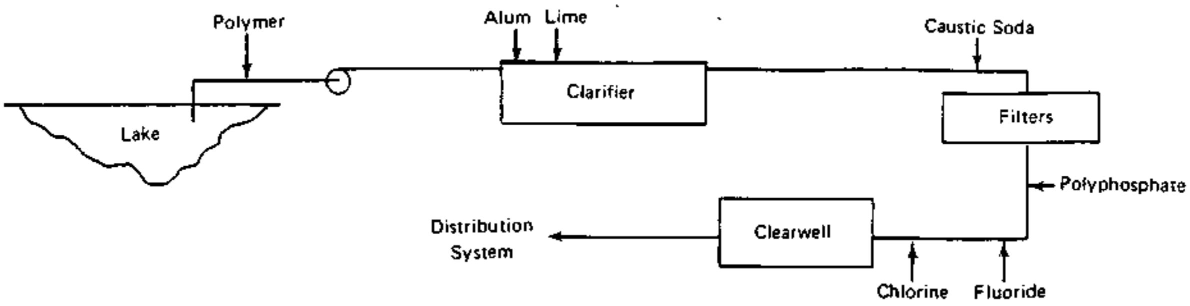

Figure 1. Water supply "A" treatment System.

prior to the filters during the study; however, the injection point has been changed to the filter effluent since the study was completed.

The unforeseen change in the corrosion control program contributed to a dramatic change in pH and polyphosphate concentrations and subtle changes in sodium and calcium concentrations during the corrosion study.

WATER SUPPLY "B", CHAMPAIGN-URBANA, IL

The public water supply for the central Illinois Community of Champaign-Urbana is a privately owned utility serving approximately 95,000 consumers. The source of water is a sand aad gravel aquifer located 150-300 feet below the surface. Eighteen wells are in operation which pump water from two well fields to two water treatment plants at separate locations in the Community. The treatment plants combine to produce 14-16 mgd of lime-softened water. The plant effluents are of equivalent quality and discharge into a common distribution system. The general water quality of the untreated and the treated water is shown in Table 4.

A split stream lime-softening process is employed to reduce the hardness, alkalinity, and iron concentrations of the source (Figure 2). Lime, liquid sodium Silicate, and ferric sulfate are applied to an upflow solids contact clarifier at a dosage rate of 200-300 mg/L, 7-10 mg/L, and 5 mg/L, respectively. Approximately 30$ of the raw water bypasses the clarifier and is mixed with the clarifier effluent. Sulfuric acid, chlorine, and fluoride are added prior to filtration.

Breakpoint chlorination is practiced during the spring, summer, and fall months each year to control ammonia-metabolizing bacteria which have caused water quality problems in the past. A breakpoint chlorination program is practiced for 30 days with 12-15 mg/L of chlorine applied. The chlorine dosage is then reduced to 3-4 mg/L for 30 days. During breakpoint chlorination periods, sulfuric acid dosage is reduced from 35-40 mg/L to 15-20 mg/L. The chlorination program caused cyclic variations in chloride, sulfate, and free chlorine concentrations during the study.

TABLE 4. QUALITY OF WATER SUPPLY "B"

Parameter	Untreated water	Treated water[#]
Iron (Fe)	1.2	<0.1
Calcium (Ca)	59.8	12.0
Magnesium (Mg)	28.8	10.0
Sodium (Na)	35.0	39.0
Silica (SiO_2)	15.4	5.9
Fluoride (F)	0.3	1.1
Chloride (Cl)	2.0	4.9
Nitrate (NO_3)	5.3	<0.1
Sulfate (SO_4)	7.0	45.0
Alkalinity (as $CaCO_3$)	328.0	100.0
Hardness (as $CaCO_3$)	268.0	60.0
Total dissolved solids	347.0	190.0

[*] ISWS Lab. No. 150853, composite of five wells; concentrations expressed as mg/L

[#] IEPA Lab. No. B28823; concentrations expressed as mg/L

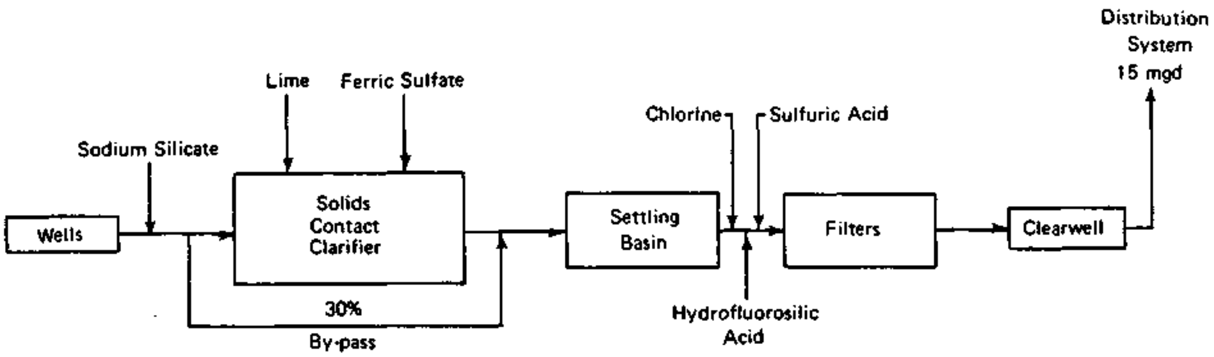

Figure 2. Water supply "B" treatment System.

WATER SUPPLY "C", DWIGHT CORRECTIONAL CENTER

The Dwight Correctional Center (DCC) is a State of Illinois facility serving approximately 500 female residents in central Illinois. The public water supply for DCC pumps water from two deep wells (1200 feet) which are highly mineralized and have high hydrogen sulfide and iron concentrations. Well No. 2 is slightly less mineralized than Well No. 1 and is the well pumped on a daily basis. Well No. 1 is operated only during repairs to Well No. 2 or when backup capacity is needed. Average pumpage is 72,000 gallons per day.

The ground water is aerated and chlorinated to remove iron and hydrogen sulfide. It then flows by gravity into a clear well where the iron is allowed to settle. The water is then pumped from the clear well through water softeners to reduce the hardness in the distribution system, which is controlled by blending approximately 25% hard water into the softener effluent. A flow diagram and chemical injection locations are shown in Figure 3.

The high dissolved solids, high dissolved oxygen, and low hardness of the distribution water were anticipated to increase the corrosivity of water supply "C".

Liquid sodium Silicate is applied to provide an 8-11 mg/L (as SiO_2) silica increase to inhibit corrosion. Caustic soda is also applied to increase the distribution water pH to 8.3 to further reduce the corrosion of the system. Chemicals are automatically proportioned and injected into the distribution system after softening.

The chemical analyses of the ground water and distribution water observed for water supply "C" during the corrosion study are shown in Table 5. Unscheduled outages of Well No. 1 occurred on two occasions which drastically altered the water quality. A significant change in chloride, sulfate, and sodium concentrations was experienced due to use of Well No. 2 during the outages.

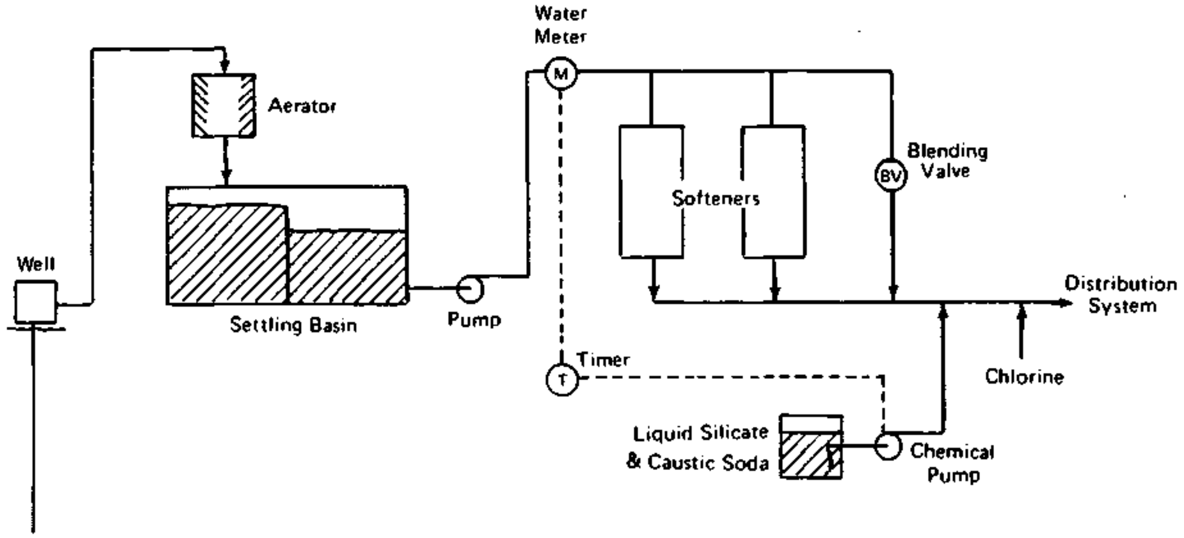

Figure 3. Water supply "C" treatment system.

TABLE 5. QUALITY OF WATER SUPPLY "C"

Parameter	Well no. 1*	Well no. 2#	Distribution$^{\Delta}$
Iron (Fe)	0.5	2.9	0.2
Calcium (Ca)	95.4	58.0	19.0
Magnesium (Mg)	54.6	31.0	10.4
Sodium (Na)	547.0	320.0	410.0
Silica (SiO_2)	16.6	6.7	19.0
Fluoride (F)	--	1.3	1.3
Chloride (Cl)	0	358.0	357.0
Sulfate (SO_4)	980.0	221.0	217.0
Alkalinity (as $CaCO_3$)	240.0	288.0	268.0
Hardness (as $CaCO_3$)	462.0	295.0	88.0
TDS	1790.0	1250.0	1270.0

* ISWS Lab. No. 217018, April 19, 1982; concentrations expressed as mg/L

\# IEPA Lab. No. B034063, Jan. 27, 1982; concentrations expressed as mg/L

$^{\Delta}$ IEPA Lab. No. B034059, Jan. 27, 1982; concentrations expressed as mg/L

WATER SUPPLY "D", DWIGHT, IL

The municipally owned public water supply serving Dwight, Illinois (population 4200) operates five wells to obtain water from a sand and gravel aquifer at a depth of 130-140 feet below the surface. The wells are located close together in the center of the Community. Well No. 1 is the oldest operating well and has been in use since 1891. Well No. 2 and Well No. 3 have been abandoned and filled. Wells No. 4, 5, 6, and 7 were added as the demand for water increased. Well No. 7 is the newest and was placed in operation in late 1980.

The wells are operated 4-6 hours a day on a 3-day rotation schedule with Wells No. 1 , 4, and 5 operating as a unit on the first day of the schedule, Well No. 6 operating on the second day, and Well No. 7 operating on the third day. The average daily pumping rate for the wells from November 1981 through October 1983 was 434,000 gpd. During this two-year period, the percentage of the total water withdrawn by the various wells was as follows: Wells No. 1, 4, & 5 (36%), Well No. 6 (30%), and Well No. 7 (34%).

To meet public health regulations, chlorine gas and fluosilicic acid are also applied to the well discharge before it enters the distribution system. Twenty-nine finished water samples were submitted to the Illinois EPA laboratory for analyses between January 1981 and May 1983, indicating an average fluoride concentration of 0.92 mg/L.

Because of the high iron content of the well water and lack of iron removal equipment, sodium hexametaphosphate, 4.3 mg/L (as $(NaPO_3)_6$) is applied at each well head to Sequester the ferrous iron and reduce the tuberculation in the cast-iron mains (Figure 4). The water plant operator reported that the polyphosphate addition has been successful in removing tuberculation in the distribution mains and in minimizing iron staining Problems in the Community.

Although the wells are similar in location and depth, the water quality of the wells is significantly different. The general water characteristics of each well are shown in Table 6.

The calcium, magnesium, sulfate, chloride, and total dissolved solids concentrations from the wells vary sufficiently to cause the Dwight distribution water quality to cycle between extremes in concentration for several Parameters.

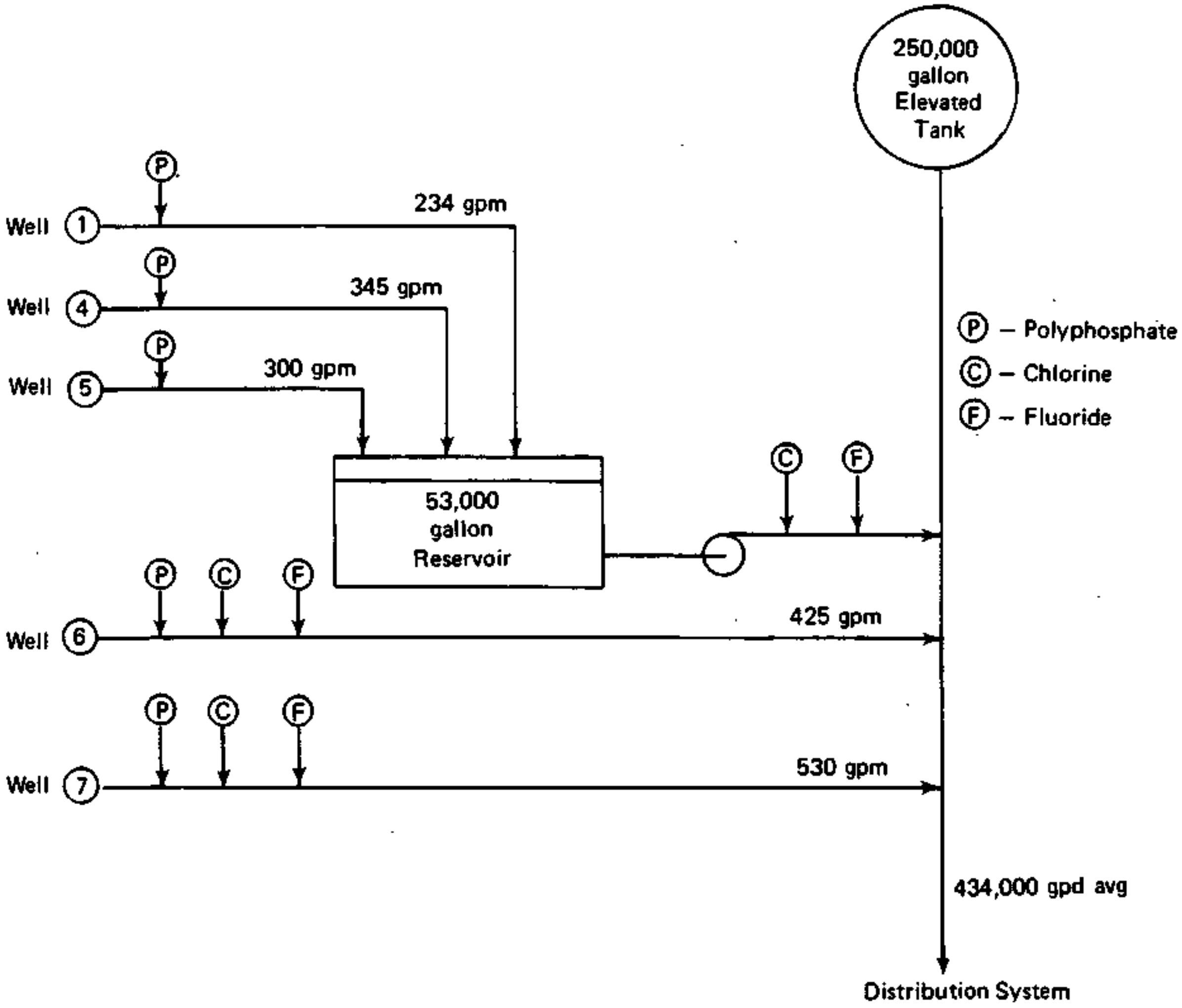

Figure 4. Water supply "D" treatment System.

TABLE 6. QUALITY 0F WATER SUPPLY "D"*

Parameter	Well no. 1	4	5	6	7
	1/5/82	1/5/82	3/7/83	1/5/82	3/1/84
Calcium (Ca)	119	142	135	63	35
Magnesium (Mg)	48.3	56.2	52	30.6	23
Sodium (Na)	172	177	171	191	207
Boron (B)	1.3	1.3	1.4	1.2	1.5
Ammonium (NH_4)	3.7	4.0	3.7	3.6	3.9
Potassium (K)	5.1	5.2	4.6	4.6	4.9
Alkalinity (as $CaCO_3$)	300	270	261	353	382
Sulfate (SO_4)	500	620	612	210	20
Chloride (Cl)	37	40	28	86	185
Silica (SiO_2)	11	12	11	8.8	7.5
Fluoride (F)	0.54	0.50	0.44	0.67	0.72
Nitrate (NO_3)	<0.4	<0.4	<0.4	<0.4	<0.4
Residue (TDS)	1077	1219	1178	833	715
pH (units)	7.6	7.4	7.9	7.9	8.4
Iron (Fe)	2.60	4.4	2.3	.28	0.49
Manganese (Mn)	0.26	0.39	0.32	.07	0.28

* Illinois Environmental Protection Agency Chemical Analysis Reports, chemical concentrations expressed as mg/L

WATER SUPPLY "E", WM. FOX DEVELOPMENTAL CENTER

The William Fox Developmental Center is a State of Illinois Institution located in the Community of Dwight, Illinois, serving approximately 200 mentally handicapped children. The Developmental Center obtains water from the distribution System of the Dwight public water supply (water supply "D"). However, additional treatment is applied to reduce the corrosivity and to reduce the hardness concentration of Fox Developmental Center distribution water. The Illinois EPA considers the Fox Developmental Center a public water supply separate from the Dwight city public water supply.

The water is delivered to the Fox Developmental Center through a cast-iron main, which is transformed into a copper main as it enters the water treatment building (Figure 5). The water flows under city water pressure (60 psig) to an aerator to oxidize ferrous iron and flows by gravity into an open 5000-gallon storage tank. A calcium hypochlorite solution is injected into the storage tank to provide the chlorine residuals in the distribution system required by the Illinois EPA. The chlorine addition is controlled by a water meter and timer to proportionally apply chlorine based on water consumption. A booster pump transfers the water from the

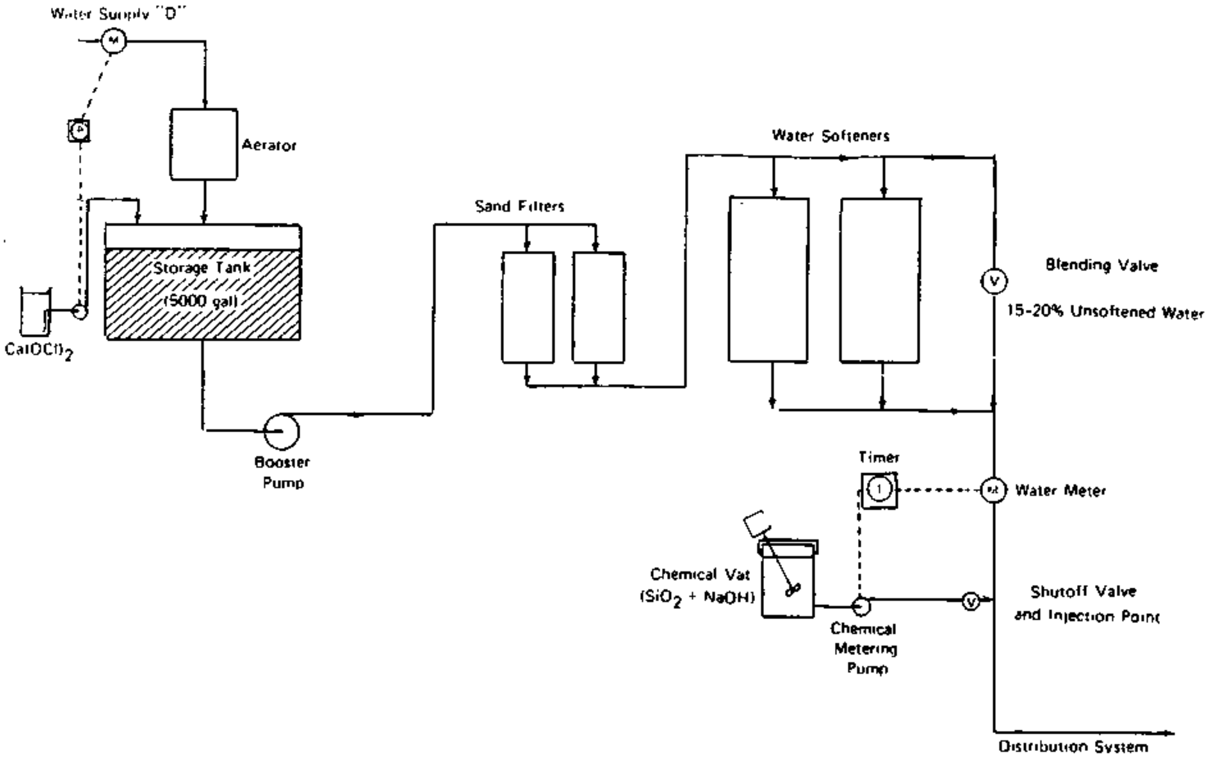

Figure 5. Water supply "E" treatment system.

storage tank through two pressure sand filters to remove particulate iron and then through two water softeners to reduce the hardness content. A hard water bypass valve is adjusted to blend 15-20% hard water into the softener effluent. The total hardness concentration is maintained between 60-90 mg/L (as $CaCO_3$) in the distribution system by adjusting the blending valve. A solution of liquid sodium Silicate (28.8% SiO_2) and caustic soda is proportionally applied to the blended plant effluent to provide an 8 mg/L (SiO_2) increase, and to increase the pH to approximately 8.2 in the distribution system.

The average daily water usage at the Fox Developmental Center is 30,700 gpd. The average chemical dosage during the corrosion study was 2.4 lb. of liquid sodium Silicate and 0.5 lb. of caustic soda per 10,000 gallon of water treated.

WATER SUPPLY "F", SPRINGFIELD, IL

The public water supply for the central Illinois Community of Springfield is municipally owned, serving approximately 115,000 consumers. The primary source of water is an impounded reservoir constructed in 1934. When needed, water is pumped from the Sangamon River into the reservoir to maintain the water level.

The water treatment plant produces between 15,000,000 to 22,000,000 gallons per day and has a nominal capacity of 40,000,000 gallons per day. Coagulation and softening occur in Spaulding upflow units installed in 1936. A schematic of the water treatment plant is shown in Figure 6. Pretreatment consists of activated carbon, chlorine, potassium permanganate, and an iron coagulant. Lime and ferrous sulfate are added to the mixing basin of the Spaulding precipitator. Hydrofluosilicic acid and carbon dioxide are added to the water stream prior to the filters. Prior to July 1982, sterilization was accomplished by use of ammonia and chlorine addition to provide a 1 .0 mg/L combined chlorine residual. Due to system contamination problems, the ammonia addition was stopped in July and the chlorine dosage was increased to produce a 2.0-5.0 mg/L free residual chlorine in the distribution system.

After the distribution system contamination problem was corrected, the water plant reduced the free residual chlorine concentration and plans to return to the combined chlorine residual program employed prior to the contamination.

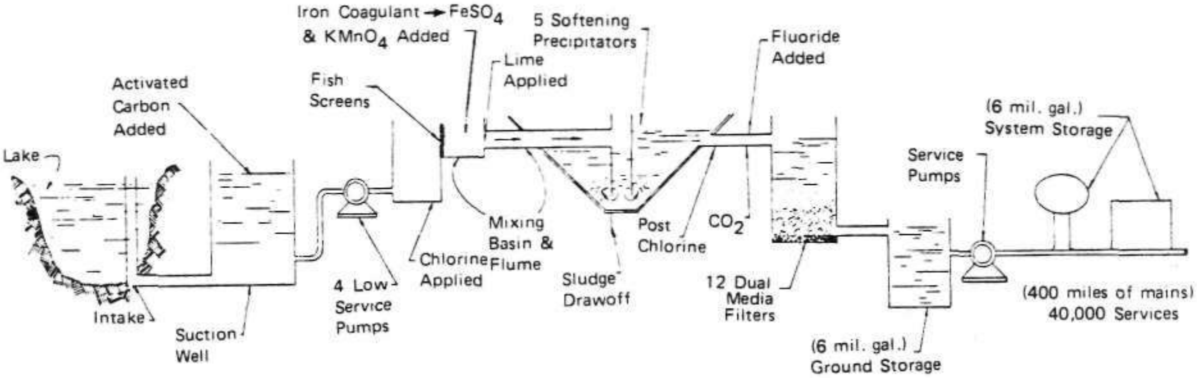

Figure 6. Water supply "F" treatment system.

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SECTION 5

CORROSION TESTING PROGRAM AND PROCEDURES

ASTM D2688 CORROSION TESTERS

The corrosion test assemblies and corrosion specimens employed in the study were prepared according to ASTM D2688 Method C procedures.[1] A notable difference was in sizing the test assembly and specimens, which were reduced for installation in 1/2-inch nominal pipe size plumbing, typical for galvanized steel or copper tube installed in homes.

All of the galvanized steel pipe, copper tube, and fittings were purchased at a local plumbing supply house. The corrosion test assemblies and specimens were constructed from these materials by ISWS machine shop personnel to conform to the reduced dimensions shown in Figure 7.

After careful inspection of the piping materials, two twenty-foot lengths of schedule 80 galvanized steel pipe and two twenty-foot lengths of type L copper tube were selected for specimen stock material. From this material, specimens were machined in a lathe to an outside diameter of 0.625 inch and to 4.00 inches in length. The specimens were stamped with an I.D. number and degreased with trichloroethylene.

One galvanized steel specimen was randomly selected from. every ten prepared specimens to evaluate the thickness of the zinc coating. ASTM A90, Standard Method for Weight of Coating on Zinc-Coated (Galvanized) Iron or Steel Articles,[2] was employed for this evaluation. Table 7 is a summary of the weight of zinc (oz/ft^2) found for the selected specimens. The average weight of the zinc coating was observed to be 3.56 oz/ft^2 which exceeds the ASTM A53 minimum coating weight of 2.0 oz/ft^2.

SIMULATED CORROSION TEST LOOP DESIGN

The ASTM corrosion testers were either installed in the plumbing Systems of a home or building or were part of a simulated test loop shown in Figure 8.

The test loop was designed to simulate actual household water usage under very controlled conditions. Water velocity, water usage, pipe surface exposure, and water standing time were easily established by the use of the simulated test loops. The test loops also provided valuable information on

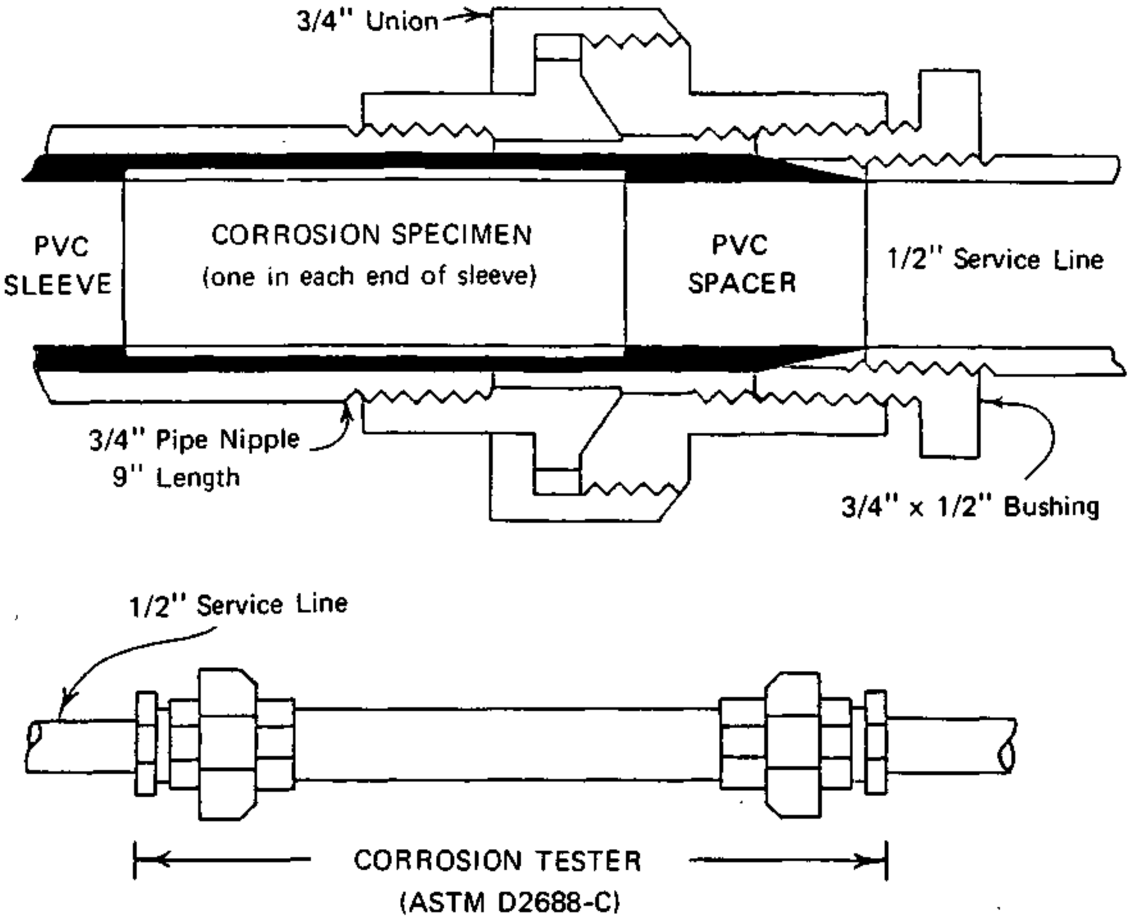

Figure 7. Cross section of specimen, spacer, sleeve, and union of assembled corrosion tester.

TABLE 7. ZINC COATING ON INTERIOR SURFACE OF GALVANIZED STEEL SPECIMENS*

Specimen no.	Surface area (in^2)	Total zinc (g)	Coating weight (oz/ft^3)
G066	6.86	4.179	3.09
G068	6.86	5.376	3.98
G063	6.86	5.016	3.71
G058	6.86	4.475	3.31
G013	6.86	4.331	3.21
G047	6.86	4.478	3.32
G060	6.86	5.773	4.27

* Prepared from 1/2-inch Schedule 80 galvanized steel pipe, 0.546 in. I.D.

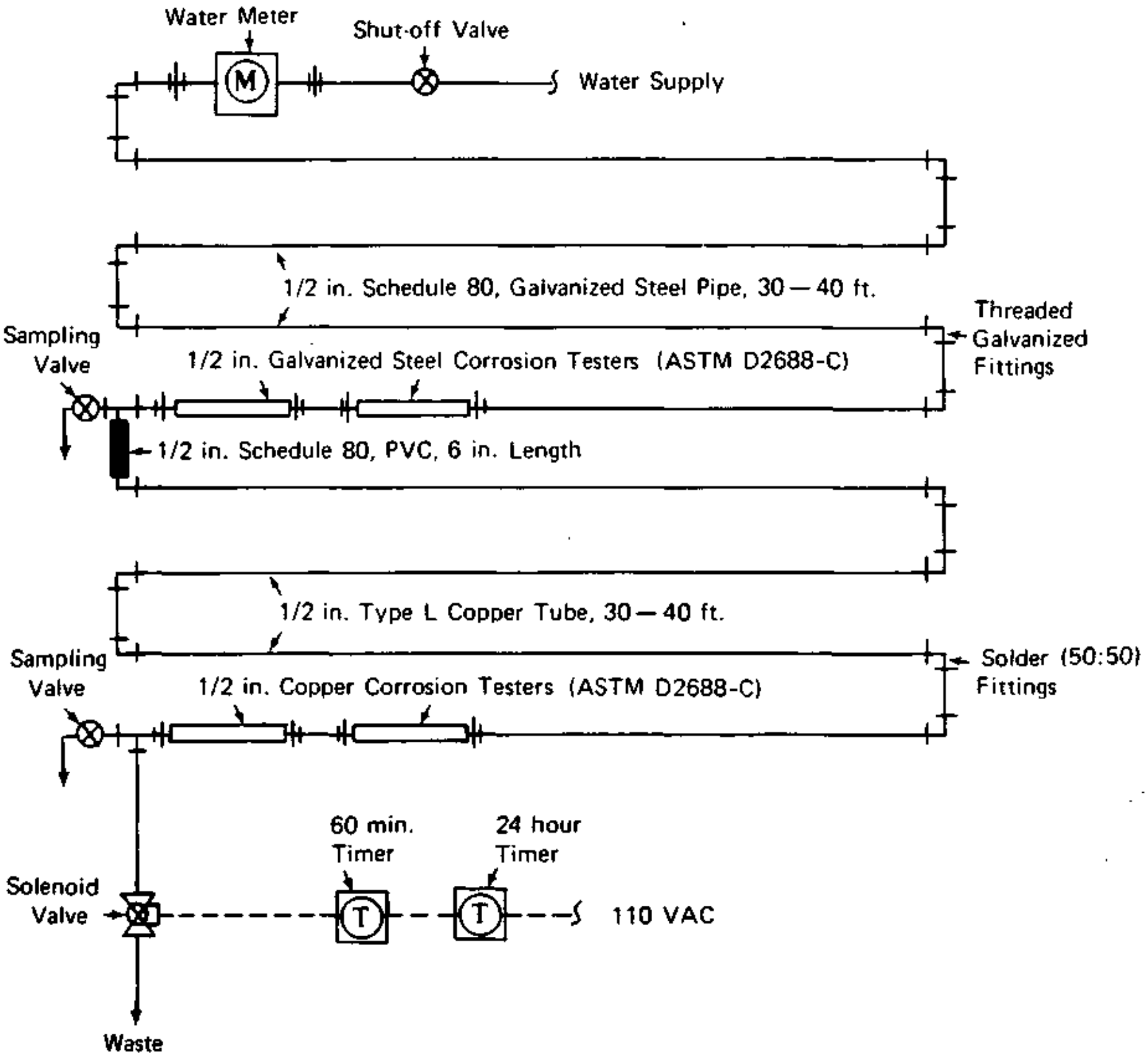

Figure 8. Simulated corrosion test loop.

the impact of new plumbing Systems on water quality, which is not observed when testing is done in existing buildings.

The test loop consisted of two sections of piping. One section was assembled using 30-40 feet of schedule 80 galvanized steel pipe and threaded galvanized steel fittings. The second section was assembled using 30-40 feet of type L copper tubing, solder fittings, and 50:50 lead-tin solder. The two sections were electrically isolated by a 6-inch polyvinyl chloride (PVC) pipe nipple. In all instances where the simulated corrosion test loops were installed, the galvanized steel section was placed ahead of the copper tube section in the flow stream to reduce any chance of copper plating effects on the galvanized steel.

Water flow through the test loop was monitored by a positive displacement cold water meter. Water usage was regulated by an electrically operated solenoid valve controlled by the two timers shown in Figure 8. The 24-hour timer was set to allow the 60-minute timer to operate for 16 hours each day. The 60-minute timer was then adjusted to open the solenoid valve every hour for 5-10 minutes. Final adjustment of the flow rate was accomplished by use of the shut-off valve.

In the loop there was a period of eight hours of constant exposure to standing water, which could be regulated to end at a convenient time for sample collection.

CORROSI0N TEST SITE INSTALLATIONS

When a long-term corrosion study is undertaken, consideration must be given to unforeseen events which could cause the loss of data from any one testing site. The chance for this occurring increases when corrosion tests are conducted in the field as compared to controlled laboratory investigations. To reduce the risk of data loss, corrosion test sites were located where skilled personnel were readily available for the long-term sampling, testing, and maintenance requirements at each site. Therefore, a prerequisite was established that personnel at each testing site have experience in determining pH and chlorine residuals. Corrosion test sites were located where ISWS staff, licensed water plant operators, or environmental science students were available and the sites were easily accessible to these personnel.

The water quality of public water supplies has been observed to change within the distribution system.[3] Corrosion tests at one location in a water supply may not be indicative of corrosion rates at another location. Because of this concern, corrosion test sites were installed at two locations in four of the water supplies studied. A site was located at the water treatment plant and another site was located at some distance away in the distribution system.

Originally the corrosion study considered one test site for each water supply. In order to investigate the impact of two piping materials at two separate locations in the distribution System, the number of test sites had to be increased from two to four in some of the water supplies. The number of test sites were limited to nineteen: ten copper and nine galvanized steel systems. Water usage and test site locations are summarized in Table 8. A brief description of each test site follows.

Sites 301 and 302

Two corrosion test sites were installed in the water treatment building of water supply "A" (Figure 9). The copper test site (301) and the galvanized steel test site (302) were located in the existing plumbing system supplying two restrooms. Each restroom contained one sink and one toilet. The facilities were primarily used by laboratory and operations personnel between 7:00 a.m. and 5:00 p.m. A night operator occasionally used the

TABLE 8. WATER USAGE AT TEST SITES

Site no.	Water supply	Plumbing materials	Service	Avg. usage rate (gpd)*
301	A	Copper	Restroom, showers	229
302	A	Galv. steel	Restroom, showers	229
303	A	Copper	Kitchen, bathroom	99
304	A	Galv. steel	Kitchen, bathroom	158
305	3	Copper	Simulated	201
306	B	Galv. steel	Simulated	201
307	B	Copper	Total household	405
308	C	Copper	Simulated	341
309	C	Galv. steel	Simulated	341
310	C	Copper	Simulated	375
311	C	Galv. steel	Simulated	375
312	E	Copper	Clothes washer	97
313	E	Galv. steel	Pots & pans washer	29
314	D	Copper	Simulated	167
315	D	Galv. steel	Simulated	167
316	F	Copper	Simulated	220
317	F	Galv. steel	Simulated	220
318	F	Copper	Simulated	191
319	F	Galv. steel	Simulated	191

* Two-year period of corrosion study

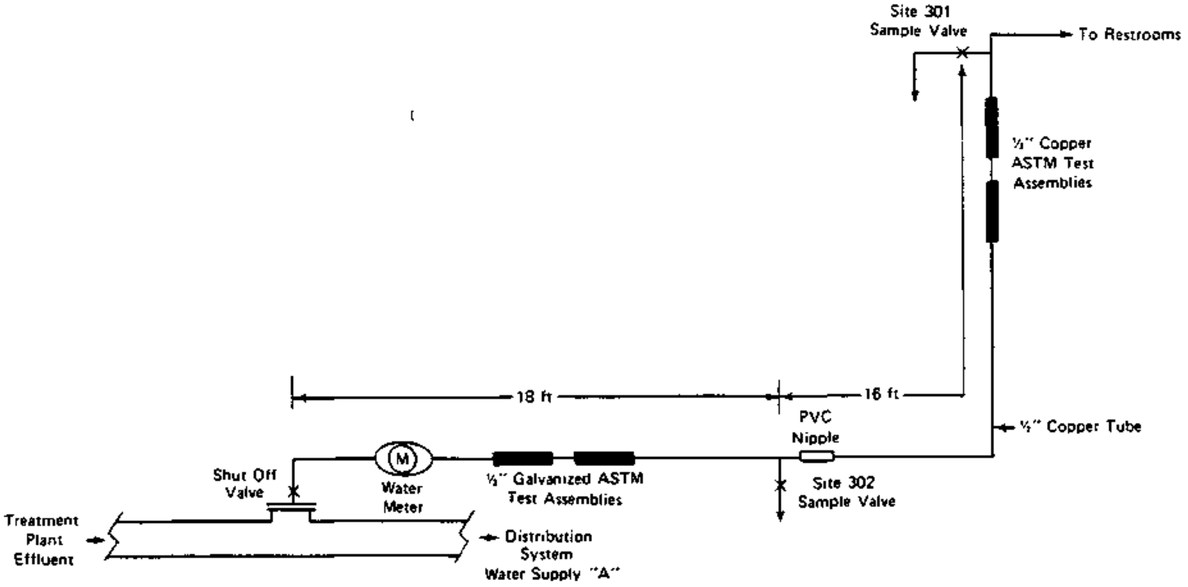

Figure 9. Corrosion test sites 301 and 302.

facilities. Average daily water usage for sites 301 and 302 during the study was 229 gal. per day.

The galvanized steel test assemblies were installed in a horizontal 1/2-inch galvanized steel Service line prior to the 1/2-inch type L copper tubing servicing the restrooms. The copper test assemblies were installed in the vertical section of the copper service line. Sixteen feet of copper tubing preceded the chrome-plated sample valve at site 301, and 18 feet of galvanized steel pipe preceded the chrome-plated sample valve at site 302. The water meter and water usage was common to both sites. Water samples were collected and tested by the water plant laboratory personnel.

Sites 303 and 304

Two adjacent houses, a mile distant from the water treatment plant in water supply "A", were selected for the installation of corrosion test assemblies (Figure 10). Site 303 was a typical one-story house with copper plumbing. Site 304 was a typical two-story house with galvanized steel plumbing.

The houses were used as offices for university personnel; therefore, water usage was confined to office hours, 7:30 a.m. to 5:30 p.m., Monday through Friday. Water usage was restricted to hot or cold water needs in kitchens or bathrooms, as no laundry facilities were installed in either house. The average daily water consumption at site 303 and site 304 was 99 gal. per day and 158 gal. per day, respectively.

Samples were collected from a chrome-plated faucet at the kitchen sink. Approximately 30 feet of 1/2-inch piping preceded each sample valve, not including the service line from the distribution water main. Students in an environmental science program collected the samples and conducted the tests under the supervision of a senior environmental engineer.

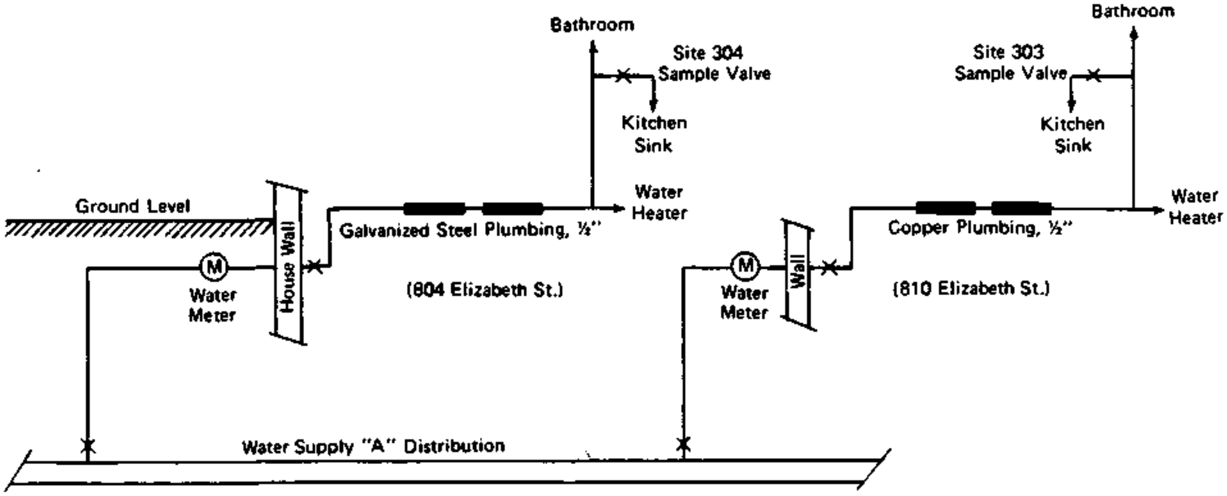

Figure 10. Corrosion test sites 303 and 304,

Sites 305 and 306

A simulated corrosion test loop (see previous section) was located in water supply "B" and installed in the basement of the Water Resources Building housing the Illinois State Water Survey (Figure 11). The location was selected as a control site where ISWS personnel would be available to collect all water samples and make field tests. The site was easily accessible for investigating phenomena arising during the study.

Site 306, the galvanized steel section of loop, was preceded by 65 feet of existing 1/2-inch schedule 40 galvanized steel pipe. Site 305, copper section of loop, was separated from the galvanized section by a PVC pipe nipple. Each section of the loop was 30 feet in length prior to the respective sampling valves.

Water usage was controlled by a timer-regulated solenoid valve and averaged 201 gallons per day during the corrosion study.

Site 307

Corrosion test assemblies were installed in the existing copper plumbing of a two-bathroom tri-level home located in water supply "B" (Figure 12). The home was built in the late 1950's and is located approximately 3-1/2 miles distant from sites 305 and 306. Site 307 was supplied water from the west treatment plant, while sites 305 and 306 were supplied water from the east treatment plant, of water supply "B".

Approximately 25 feet of 3/4-inch copper tubing preceded the water meter and test assemblies, followed by an additional 25 feet of 1/2-inch copper tube preceding the chrome-plated sampling valve located at the kitchen sink. The corrosion specimens were exposed to the total water use of four adults residing in the house. The water consumption averaged 405 gallons per day during the corrosion study.

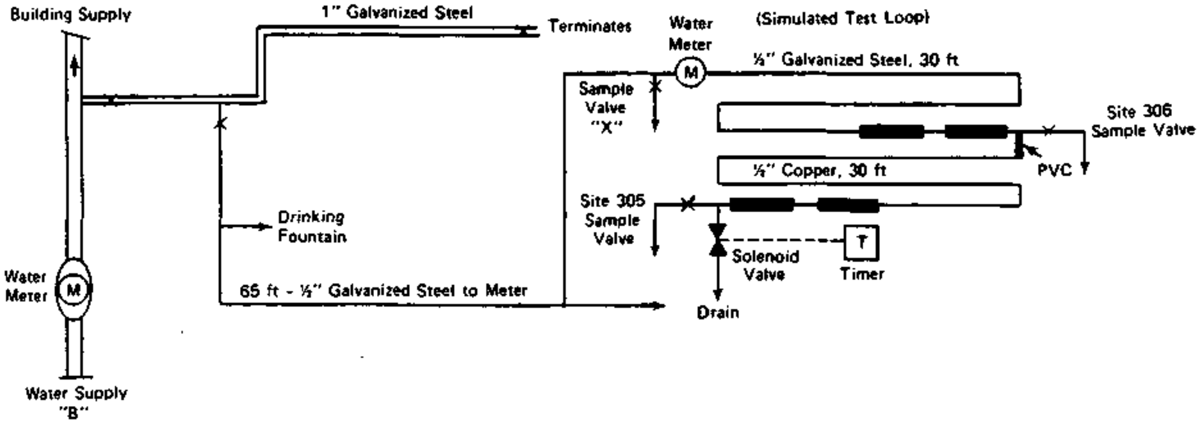

Figure 11. Corrosion test sites 305 and 306.

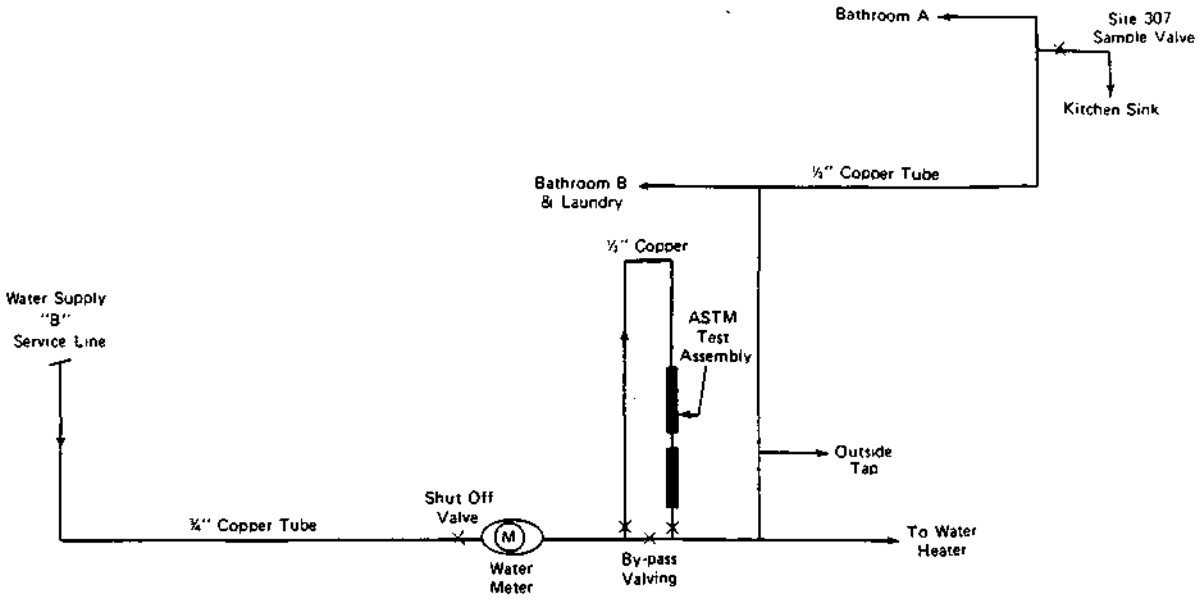

Figure 12. Corrosion test site 307.

The senior author collected all water samples and made all field tests at site 307.

Sites 308 and 309

A simulated corrosion test loop was located in water supply "C" at the water treatment building (Figure 13). Originally the two sites were to employ unsoftened and untreated water directly from a well supplying water to the treatment plant. Plumbing complications and space restrictions during the installation of the test loops caused partially softened and treated water to be employed except during periods where the water softeners were out of service.

The galvanized steel section (site 309) was connected directly to galvanized steel piping immediately following the water softeners. The copper section (site 308) of the test loop followed the galvanized steel section and was separated by a 6-inch length of PVC pipe. Both sections contained 35 feet of 1/2-inch piping. Water usage was controlled by the timer-solenoid valve arrangement described in the previous section. The water usage averaged 341 gallons per day during the corrosion study.

Water samples were collected and field tests were made by the water plant operator, who has been licensed to operate both the water and the sewage treatment plant for the state facility.

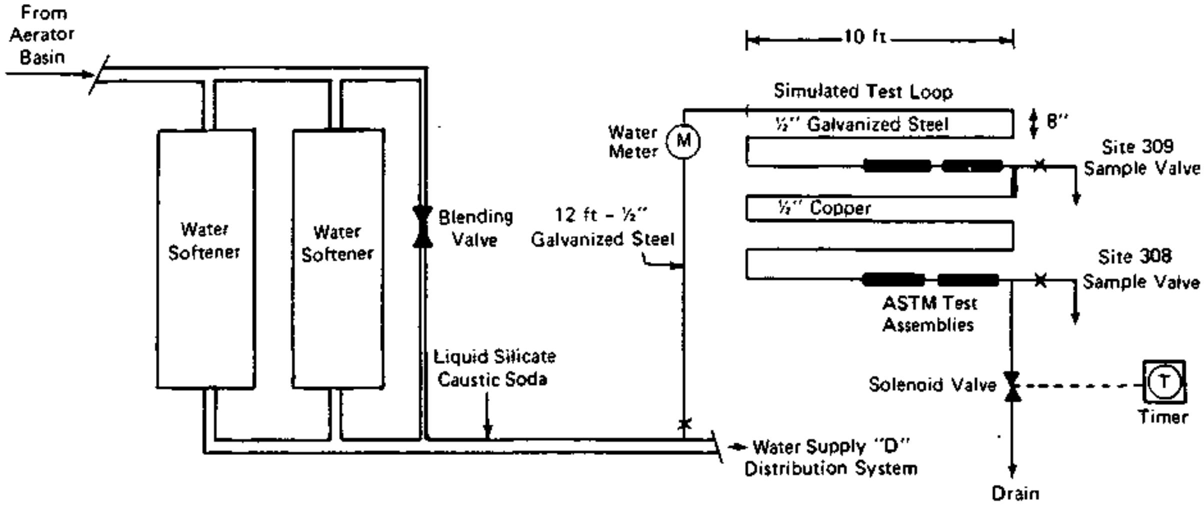

Figure 13. Corrosion test sites 308 and 309.

Sites 310 and 311

A second simulated corrosion test loop was also located in water supply "C" and was installed in the maintenance building of the correctional facility (Figure 14). The test loop was directly connected to galvanized steel piping servicing the vehicle wash area which operated eight hours per day. The water from the distribution system was considered equilibrated at this location.

The service line consisted of approximately 75 feet of 3/4-inch galvanized steel pipe. Each section of the simulated corrosion test loop, galvanized steel (site 311) and copper (site 310), contained 35 feet of 1/2-inch pipe.

Water usage controlled by the timer-solenoid valve arrangement averaged 375 gallons per day during the study. Samples were collected and field tests were made by the same water plant operator responsible for sites 308 and 309.

Sites 312 and 313

The corrosion test sites were located in water supply "E" and were installed in the existing plumbing of a State building housing 200 mentally handicapped children (Figure 15). Two galvanized steel corrosion test assemblies (site 313) were installed in a 40-foot section of 1/2-inch schedule 40 galvanized steel line servicing a kitchen sink that was used primarily for washing pots and pans. An existing chrome-plated valve at the sink was employed for sampling purposes. Usage of water at site 313 was confined to the period between 7:00 a.m. and 5:00 p.m. daily and averaged 29

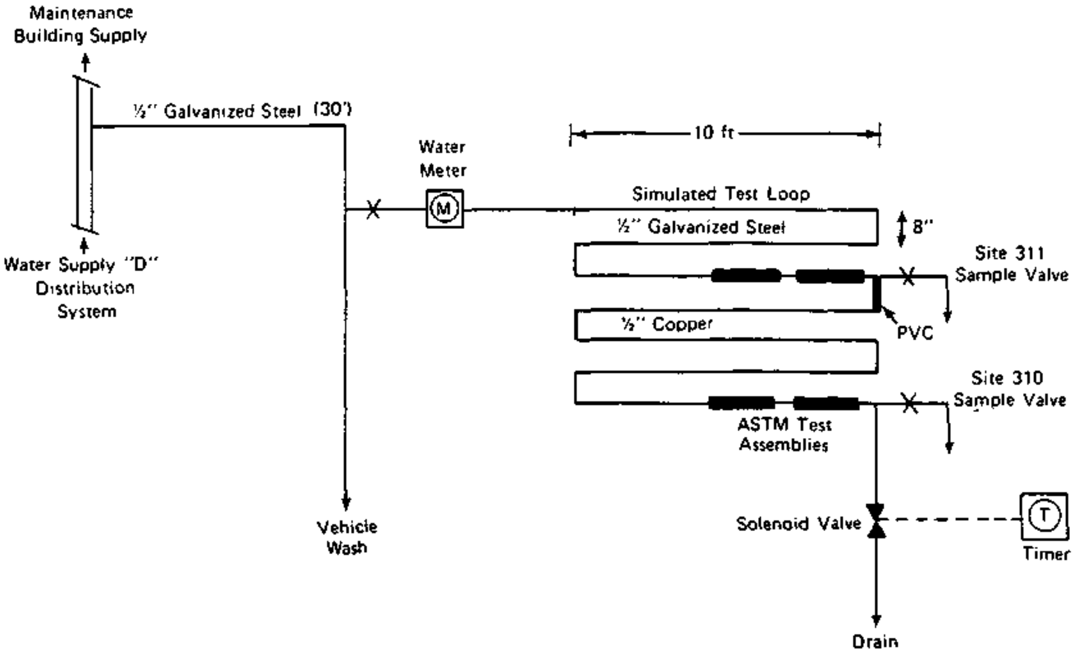

Figure 14. Corrosion test sites 310 and 311.

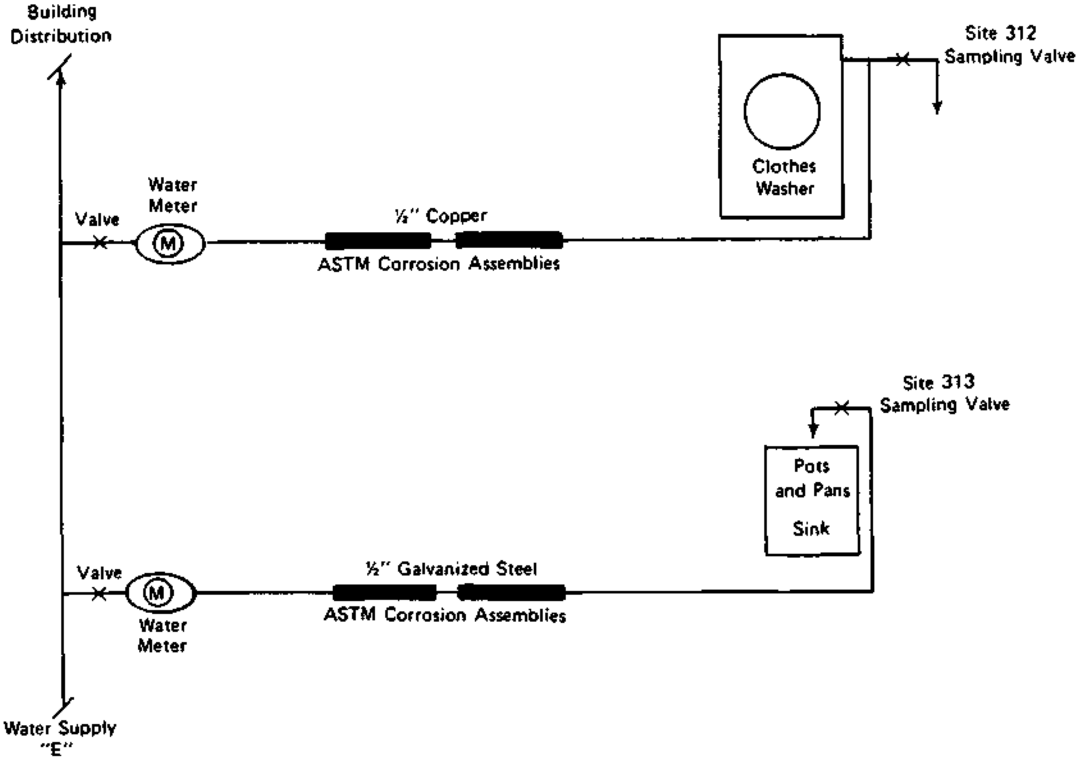

Figure 15. Corrosion test sites 312 and 313.

gallons per day, the lowest usage rate of any site observed during the corrosion study.

At site 312, two copper corrosion test assemblies were installed in a 15-foot section of 1/2-inch type L copper piping servicing an institutional clothes washer. A new chrome-plated valve was installed prior to the clothes washer for sampling purposes. Water usage was confined to daytime hours between 7:00 a.m. and 5:00 p.m. and averaged 97 gallons per day during the study.

Water samples were collected and field tests were made at both sites by the licensed water plant operator on the staff of the state facility.

Sites 314 and 315

A simulated corrosion test loop was located in a water treatment building in water supply "D". The simulated test loop at this location was vertically oriented due to wall space limitations. Figure 16 is a schematic of the piping associated with sites 314 (copper) and 315 (galvanized steel).

Water usage was controlled by the timer-solenoid valve arrangement employed in all simulated test loops and averaged 167 gallons per day during the corrosion study. Water samples were collected and field tests were made by the same individual responsible for sites 312 and 313.

Sites 316 and 317

A simulated corrosion test loop was installed at the water treatment plant of water supply "F" (Figure 17). The test loop was connected to a 4-inch cast-iron line supplying wash water to the filters. Forty-six feet

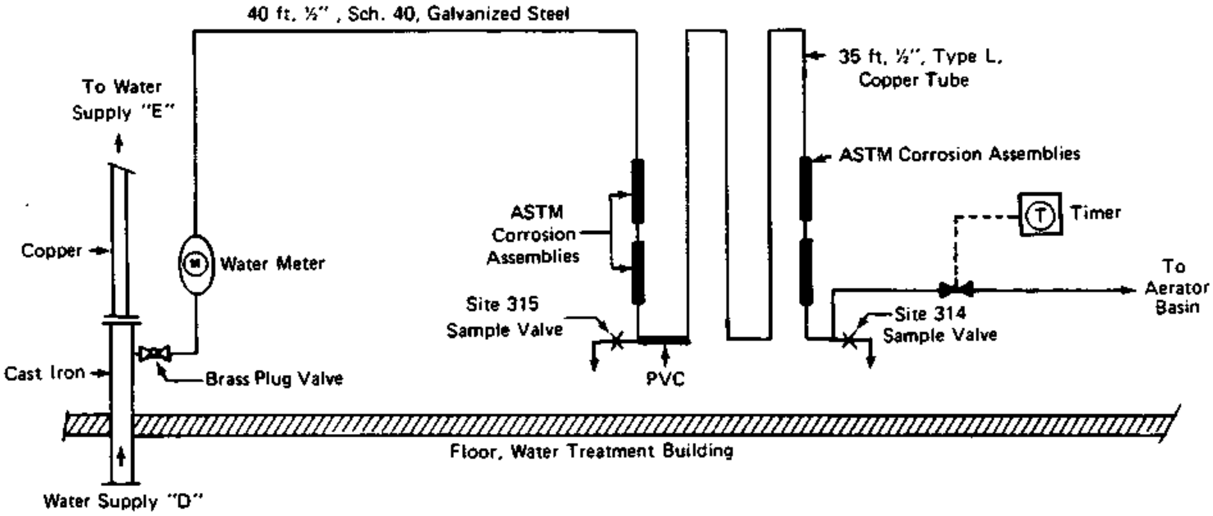

Figure 16. Corrosion test sites 314 and 315.

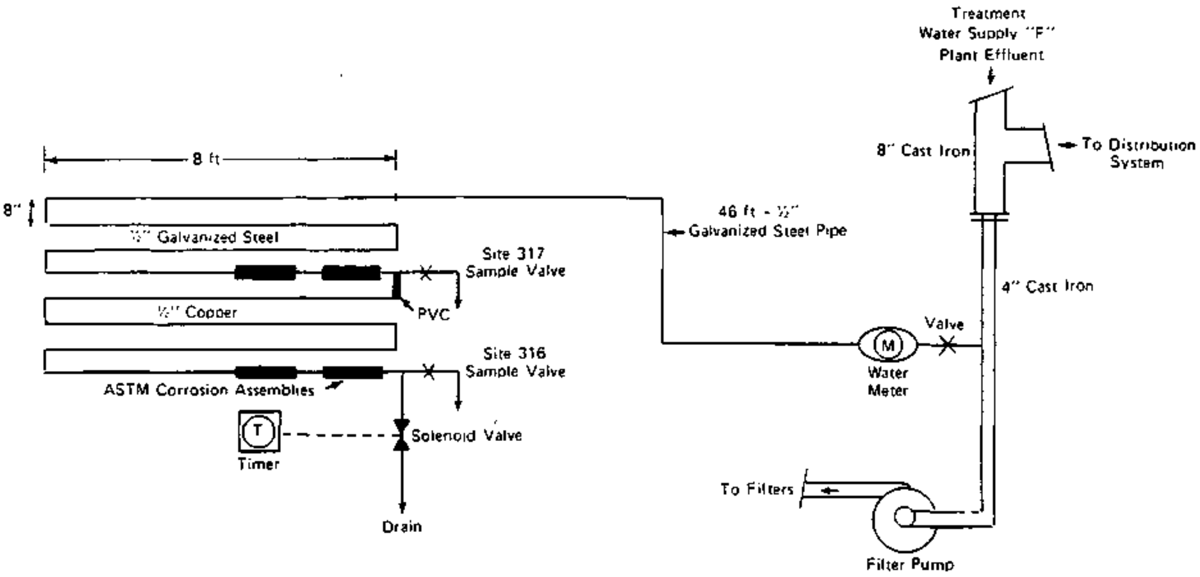

Figure 17. Corrosion test sites 316 and 317.

of 1/2-inch schedule 40 galvanized steel pipe was installed between the test loop and cast-iron service line. The galvanized steel section (site 317) and the copper section (site 316) of the test loop were constructed from 34 feet of 1/2-inch piping per section.

The water usage was controlled by the timer - solenoid valve arrangement; however, during the first two months of operation the timer mechanism failed to operate. Three sets of water samples were collected by water plant personnel during this period when the flow was restricted to the flushing of water during the collection of samples. Because of timer failure, the original set of corrosion specimens were removed and a new set of specimens were installed. The corrosion study was reinitiated with ISWS field staff responsible for testing and collecting of samples. Water usage averaged 220 gpd after the timer was repaired.

Sites 318 and 319

A second simulated corrosion test loop was located in water supply "F" approximately two miles distant from sites 316 and 317. The test loop was installed in a building of a state mental facility and was connected to a service line supplying water to a closed recirculating heating system (Figure 18). The connection was near the main water supply line and water meter servicing the facility.

Water samples were tested and collected by building engineers who proved to be reliable and conscientious in following sampling procedures throughout the study. Water usage averaged 191 gpd at sites 318 (copper) and 319 (galvanized steel).

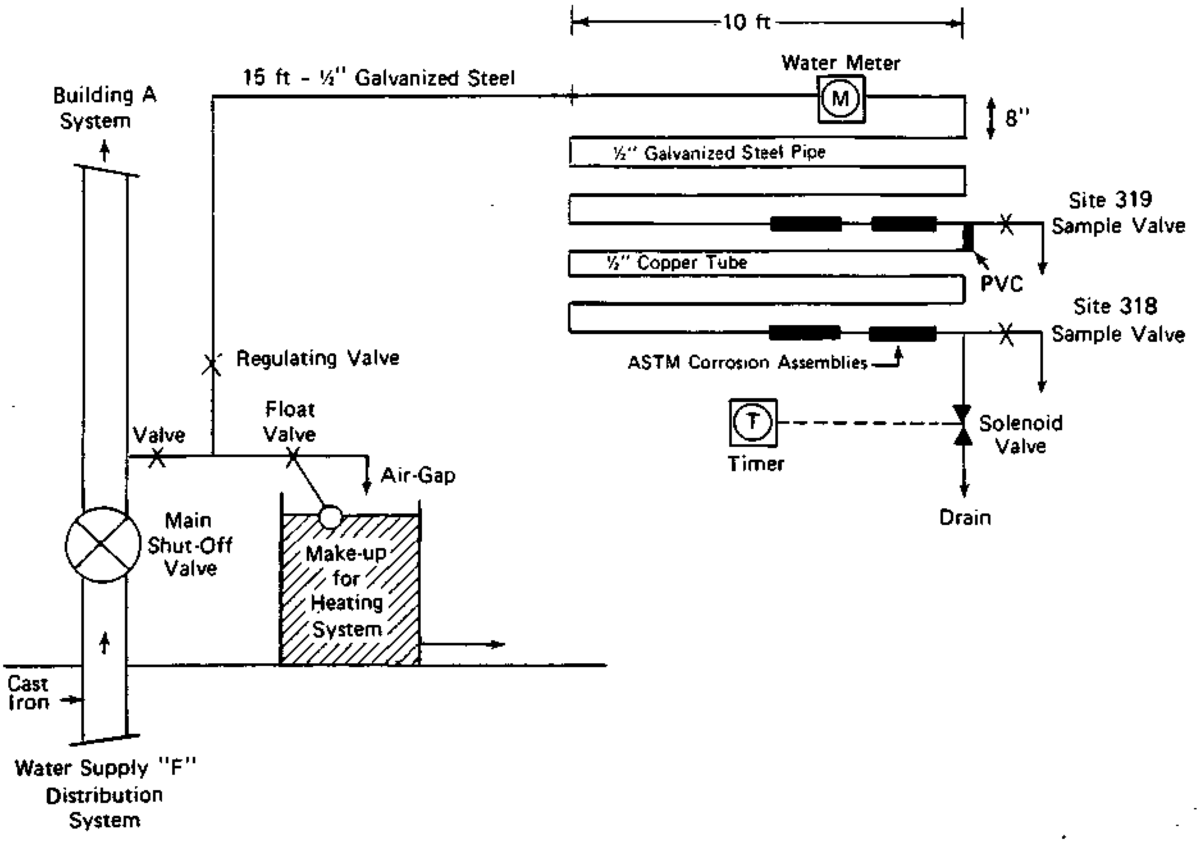

Figure 18. Corrosion test sites 318 and 319.

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2. ASTM Standards on Hot-Dip Galvanized Coatings, Specification A90:32 (1967).

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SECTION 6

FIELD METHODS FOR COLLECTING, HANDLING, AND TESTING OF SAMPLES

SAMPLE COLLECTION PROCEDURES

Standard sampling procedures were established prior to commencing the corrosion study. The procedures were needed to guarantee uniformity and control for the collection, testing, and handling of water samples. USEPA-approved methods for sampling water were followed when applicable. All responsible personnel were provided written Instructions and were given a personal demonstration of the correct sampling techniques by ISWS field personnel (Appendix D).

Chlorine test kits, pH meters, and thermometers were provided at all corrosion test sites. Chlorine reagents, pH buffers, sample bottles, shipping cartons, and ice packs were also supplied as needed. ISWS personnel visited each Site at six-week intervals to insure that proper testing and sampling procedures were being followed.

Where corrosion test sites were located in homes or buildings, water samples were collected from the cold water tap during early morning hours prior to morning water demands. This required that samples be taken between 5:00 a.m. and 7:00 a.m. The simulated corrosion test loops were regulated to allow samples to be taken at convenient times for sampling personnel with absolute control of running and standing intervals. Water samples were taken from the galvanized steel section of the simulated test loop prior to sampling the copper section to preserve standing conditions in the copper section.

At all corrosion test sites, water samples were collected from a chrome-plated brass faucet or service tap. Screen filters were removed from the faucets prior to sampling. The first 50-100 mL of water was collected from the tap for a temperature measurement of the standing sample. The next 125 mL of water drawn from the tap was collected in a 125-mL Polyethylene bottle containing acid for use in determining the metal concentrations of the standing water in the test loop.

The sampling valve was then opened to allow approximately 1/2 gpm of water to flow to waste until the water temperature appeared stable and representative of the distribution water (usually a 4-5 min. interval). The temperature of the running sample was recorded and a second 125 mL of water was collected in a Polyethylene bottle containing acid for use in determining the metal concentrations of the running water. The remaining two

Polyethylene sample bottles, 125-mL and 500-mL, and a glass vial for TOC analyses were filled with the running water from the tap.

The sample bottles were capped and labelled by date, time, site number, and sample number. Chlorine and pH measurements were made on the running water after the samples had been collected. The pH value, chlorine concentrations, temperatures, and meter reading were then recorded on a prepared form for enclosure with the sample bottles.

SAMPLE PRESERVATION AND HANDLING PROCEDURES

The chemical concentrations of the constituents in the drinking water which could not be reliably preserved during shipment of the samples to the analytical laboratory were determined at each corrosion test site. This was considered essential for pH measurements, since reliable pH values were necessary for meaningful evaluation of the data. Dissolved oxygen, free chlorine residual, and total chlorine residual concentrations were also made at the test site because sample preservation methods were not available for these constituents.

The 125-mL water samples collected for running and standing metal concentrations were preserved by addition of 2.5 mL of 1:1 HNO_3 prepared from AA grade nitric acid. The 125-mL water sample collected for total phosphate analyses was preserved with 1.0 mL of concentrated reagent grade sulfuric acid. The sulfuric-acid-preserved sample was also used when nitrate concentrations were rechecked in the laboratory.

Styrofoam insulated cartons were used to ship water samples to the laboratory. Two ice packs were placed in each carton with the five water samples prior to shipment. Water samples from corrosion test sites 301, 302, 303, 304, 308, 309, 310, 311, 318, and 319 were shipped by one-day express • delivery Services. Samples from the remaining test sites were delivered directly to the laboratory by sampling personnel. The water samples were refrigerated until time of shipment if delays were experienced.

Upon receipt of the water samples in the laboratory, the alkalinity, silica, orthophosphate, polyphosphate, TOC, and total dissolved solids concentrations were determined. Early in the study, laboratory personnel were observed delaying analyses until a minimum number of samples were available. Water samples for trace metal determinations were allowed to accumulate in the lab for trace metal determinations since the samples were acid-preserved. The trace metal concentrations were found to be stable in these samples after a year in storage.

FIELD TEST METHODS

Free available chlorine residual, total (free and combined) chlorine residual, pH, and dissolved oxygen concentrations were determined at each test site when water samples were collected. The field test methods for these constituents are briefly described in the following sections.

Chlorine Residuals

Precise measurements of chlorine residuals were not considered as essential as employing a simple, but reasonably accurate chlorine procedure which could be easily and uniformly applied by field personnel. A field test kit method meeting these criteria (LaMotte Chemical, DPD Chlorine Test Kit, Model LP-26) was selected for use during the corrosion study. Free and total chlorine residuals were determined using the test kit based on the DPD (diethyl-p-phenylene diamine) method developed by Palin.[1] DPD reagents were stable when supplied in tablet form and sealed in foil packets. The color comparator used color standards representing 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, and 3.0 mg/L Cl_2. The sample Instructions for determining free chlorine and total chlorine residuals using the test kit are described in Appendix D.

pH

Reasonably accurate pH measurements were required for the corrosion study since pH is a major influence on the corrosivity of water. Color comparator test kits for pH measurement were not considered sufficiently accurate. The electrometric method[2] using a glass electrode for determining pH was selected for use at all corrosion test sites. Where pH meters were not available to sampling personnel, a pH meter and pH buffers were provided. ISWS field staff checked the pH meter calibration and electrode response every six weeks. Glass and/or reference electrodes were replaced when electrode response was unsatisfactory. Commercial pH 7.0 and pH 9.0 buffer solutions (±0.01 pH unit) were used for standardizing the pH meters.

Portable battery-operated pH meters were employed at all test sites except sites 301 and 302 where a line-operated pH meter was available near the sampling point. After calibration of the pH meter, grab samples of the running water were taken in succession until a stable pH reading was obtained. pH and temperature values were reported for every water sample submitted to the laboratory except when a pH meter was not functioning properly.

Dissolved Oxygen

ISWS field staff determined the dissolved oxygen concentrations of the running water samples at six-week intervals. The azide modification of the Winkler method3 was adapted to a portable field kit for this purpose. A 300-mL volume of the running sample was collected through rubber tubing and trapped in a narrow-mouth glass-stoppered B0D bottle. Reagents were added to the bottle, mixed, and a 203-mL aliquot was titrated with standard thiosulfate as outlined in the procedure. Dissolved oxygen concentrations were reported to the nearest 0.1 mg/L.

Temperature

General purpose mercury-in-glass thermometers were used for determining the temperatures of the running and standing water samples collected at each test site. A bulk purchase of thermometers was made prior to the corrosion study and the accuracy of the thermometers was checked with the ice point and boiling point of water. Thermometers more than 1°C in error were discarded.

The temperature range of the thermometers was -20°C to +110°C with a 1°C resolution. The temperature was determined by immersing the thermometer to the 76-mm mark in the water sample. Temperature values were reported to the nearest 0.5°C.

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2. Standard Methods for the Examination of Water and Wastewater, 14th Edition. APHA-AWWA-WPCF, Part 422B (1975).

3. Standard Methods for the Examination of Water and Wastewater, 14th Edition. APHA-AWWA-WPCF, Part 424 (1975).

SECTION 7

LABORATORY ANALYTICAL METHODS

TRACE METAL AND MAJOR CATION DETERMINATIONS

Trace metal (Fe, Zn, Mn, Cu, Pb, Cd) and major cation (Ca, Mg, Na, K) determinations were performed by the Analytical Chemistry Unit of the State Water Survey on a contract basis. They were performed by either conventional flame atomic absorption spectroscopy (AAS) or by flameless graphite furnace atomic absorption spectroscopy (GFAAS).

A Perkin-Elmer model 380 AA spectrophotometer was used for the flame atomic absorption analyses when the concentrations were high enough to permit its use. The instrument was calibrated using the built-in procedure, which employed a blank and two standards to define the analytical curve and provide a basis for direct concentration readout. Additional check standards were inserted in the runs to monitor linearity of response. Samples with concentrations beyond the linear working range were diluted. A releasing agent consisting of a 1% lanthanum solution (in HCl) was used for calcium and magnesium determinations. An ionization suppressant consisting of a 1% cesium chloride solution was employed in the sodium and potassium determinations.

An Instrumentation Laboratory model 151 AA spectrophotometer with a model 655 graphite furnace and model 254 (FASTAC) automatic sampler was used for the bulk of the flameless AA analyses. Late in the project, an IL Video 22 AA spectrophotometer supplanted the model 151. Concentrations were calculated from calibration curves of peak heights versus standard concentrations. The Cd determinations utilized deuterium arc background correction. No matrix modifiers were used for any of these metals.

All of the metal analyses were done on solutions preserved with 2.5 mL of 50% v/v ultrapure nitric acid in the 125-mL sample bottle. The amount of time that elapsed before analysis was variable, but was within the latest EPA recommended guideline of six months.[1]

MAJOR ANION DETERMINATIONS

Sulfate, nitrate and chloride were determined using a Dionex model 12 Ion Chromatograph with an autosampler and a conductivity detector. Samples were unpreserved and filtered through a 0.45-um pore-size cellulose acetate membrane, using a glass vacuum filtration apparatus. Originally, concentrations were determined from calibration curves based on peak heights measured from a chart recorder output. Later, a locally developed software system on an Apple II Computer was used to record peak heights and calculate calibration data. The extreme range of concentration of sulfate and chloride caused many problems of peak overlap. Also, large dilutions were necessary to bring the sample concentrations down to the normal operating range of this instrument, which was normally one appropriate for rainwater analysis.

Most of the IC analyses were performed within the 28-day suggested holding limit for sulfate and chloride. However, few analyses were done within the 48-hour limit suggested for nitrate. A major problem encountered was that by the time the analytical results were returned to project personnel, the suggested holding times were usually greatly exceeded. The chloride levels were probably still stable, but repeat determinations of nitrate performed on the unpreserved samples indicated that the nitrate concentrations in many of those samples were unstable. The relatively poor precision of all sulfate methods attempted did not enable any firm conclusions to be drawn concerning sulfate stability in the samples.

Manual spectrophotometric methods were used to determine the concentrations of orthophosphate and of "total inorganic phosphate." The absorbances after color development were measured on either a Perkin-Elmer Lambda 3 or Beckman model DBG spectrophotometer in almost all cases. A Beckman DU spectrophotometer was employed for the remaining samples.

Unpreserved 0.45-µm filtered samples were used for orthophosphate determinations. The "total inorganic phosphate" analyses, actually "acid hydrolyzable phosphate" analyses, were done on samples preserved in the field with 1.0 mL analytical reagent grade sulfuric acid. The analytical method used most closely corresponds to that described by Robertson[2] and ASTM procedures.3

Considerable problems were encountered in getting orthophosphate analyses performed in a short time after sample receipt. The problem is critical, because at one time or another during the project, inorganic polyphosphate treatment chemicals were used at sites 301, 302, 303, 304, 312, 313, 314 and 315. Polyphosphates hydrolyze upon standing, Converting to the orthophosphate form. Thus, although the total inorganic phosphate concentrations should remain stable, the orthophosphate fraction will continually develop a high bias over time.

The error introduced by delayed analyses was investigated in a special study reported in a later section. After approximately November 14, 1983, additional efforts were made to speed orthophosphate analyses, and samples were kept refrigerated at 4°C until analyzed to slow hydrolysis. An examination of the analytical and collection records revealed that delays of two to four weeks were typical, and sometimes reached eight weeks. The orthophosphate levels reported for all sites containing polyphosphates, except perhaps 312 and 313, must be considered to be significantly in error with a variable positive bias.

MISCELLANEOUS ANALYSES

Silica analyses were originally performed using an undocumented molybdenum blue procedure, similar in many respects to that recommended by ASTM.[4] During June and July of 1983, the Performance of the method was evaluated in detail using USGS Standard Reference Water Samples and commercially prepared stock standard solutions. The method had been previously found to be very time sensitive, so that only a small number of samples could be run per analysis batch. Further, the Performance was found to be somewhat inconsistent in the hands of our analysts, normally yielding high bias. Therefore, from July 12, 1983 onwards, all silica analyses were done using the manual ascorbic acid reduction/molybdenum blue procedure of the U.S. Geological Survey.[5]

Total alkalinity titrations were initially performed on the filtered, unpreserved samples by titrating with standardized 0.02 N sulfuric acid to an endpoint of pH 4.50. In late January 1983, the alkalinity method was changed to a Gran plot titration with 0.02 N HCl titrant, as described by Kramer.[6] This change not only reduced the time required for each analysis, but greatly improved the accuracy of the determinations. Titration equivalence points were computed by a Hewlett-Packard HP-34C calculator program.

The total dissolved solids (TDS) analyses were done by evaporating a 100 mL aliquot of filtered unpreserved sample to dryness on a steam bath in preweighed glass dishes, and finally drying completely at 105°C in an oven. The samples were cooled to room temperature in a desiccator and were then weighed in a 4-place (0.1 mg) mechanical or electronic analytical balance.

Total Organic Carbon analyses were performed along the procedural lines given by Barcelona[7] for the nonvolatile fraction (NVOC). The instrument used was an Oceanographic International Model 524 T0C Analyzer, with direct injection module, purging and glass ampule scaling units, and an infrared detector. Calibrations were calculated relative to potassium hydrogen phthalate standards.

Analytical rechecks of chloride values were done with silver nitrate titrations using first an adsorption indicator endpoint (Standard Methods, 408A),[8] and later a Potentiometric endpoint sensed by a double junction reference electrode (Corning 476067) and Ag_2S membrane electrode (Orion 94-16) pair. The Potentiometrie titrations were done in the presence of 1 mL concentrated HNO_3, which served to limit silver ion adsorption, and an ionic medium buffer. Titrations were carried out to a set potential endpoint, determined at the start of the analytical session by averaging observed potential readings from replicate titrations of chloride standard solutions.

Sulfate repeat determinations were done using barium Perchlorate titration with Thorin indicator, following methods of Haartz et al.,[9] Cook and Miles[10] and USGS.[5]

Nitrate rechecks were done on both unpreserved and sulfuric acid preserved samples by the chromotropic acid spectrophotometric method.[7]

The acid-preserved samples yielded the most consistent results in comparison with the original analyses, although significantly different concentrations from the ion chromatograph values were found for many samples.

QUALITY CONTROL PROCEDURES

Periodically, trace metal reference standards were received from the USEPA. These glass ampule sets were turned directly over to the Analytical Chemistry Laboratory Unit for analysis, and the results were sent directly to the USEPA project officer. We are aware of no problems that were indicated in these quality control checks.

Relatively late in the project, Standard Reference Water Samples for both trace metals and mineral constituents were obtained from the U.S. Geological Survey. These samples were immediately applied to use as internal QC samples in our analytical runs, and were further used as "blind" unknowns, submitted along with other project samples. Additional USEPA Environmental Monitoring and Support Laboratory quality assurance sample ampules were obtained and prepared to evaluate residual chlorine, filterable residue, mineral, trace metal and nutrient analyses. The blind unknowns indicated the expected analytical accuracy for all constituents (except orthophosphate and free chlorine residual) to be on the order of ±5-10% relative. Every tenth sample received was split and submitted as duplicate samples to monitor the adequacy of the precision of the analyses.

Analytical data were periodically reviewed by the principal investigators, and questionable data were flagged for additional scrutiny, based on previous behavior of the water Systems under investigation. When the Computer data base was completed, an interface program was developed to pass all of the analytical data through a modified version of the WATSPEC aqueous chemical equilibria program. In addition to Computing ion balance errors after considering the aqueous chemical speciation in the samples, incompatibilities between pH and alkalinity were tested. Samples failing the ion balance test by more than ±10% were reanalyzed for appropriate anionic or cationic constituents. Samples with incompatible pH and alkalinity values and samples with major chemical parameters not analyzed were deleted from the data base in their entirety. Figure 19 shows the final distribution of ion balance errors.

A total of 890 samples were collected during the course of the study. Of these, 35 (4%) samples were reanalyzed by at least one method for chloride, sulfate and nitrate, before ion balances were performed. Following the ion balance computations, 38 samples were reanalyzed for the same three constituents. Fifteen samples were reanalyzed for TDS, seven for alkalinity, and seven for total inorganic phosphate. Records are not readily available for the number of major metals reanalyzed, but the analytical Problems were largely confined to the anionic constituents. Most samples having metal concentrations in excess of the MCL were reanalyzed, as a matter of course. Approximately 100 additional samples were reanalyzed for zinc, copper, and/or lead.

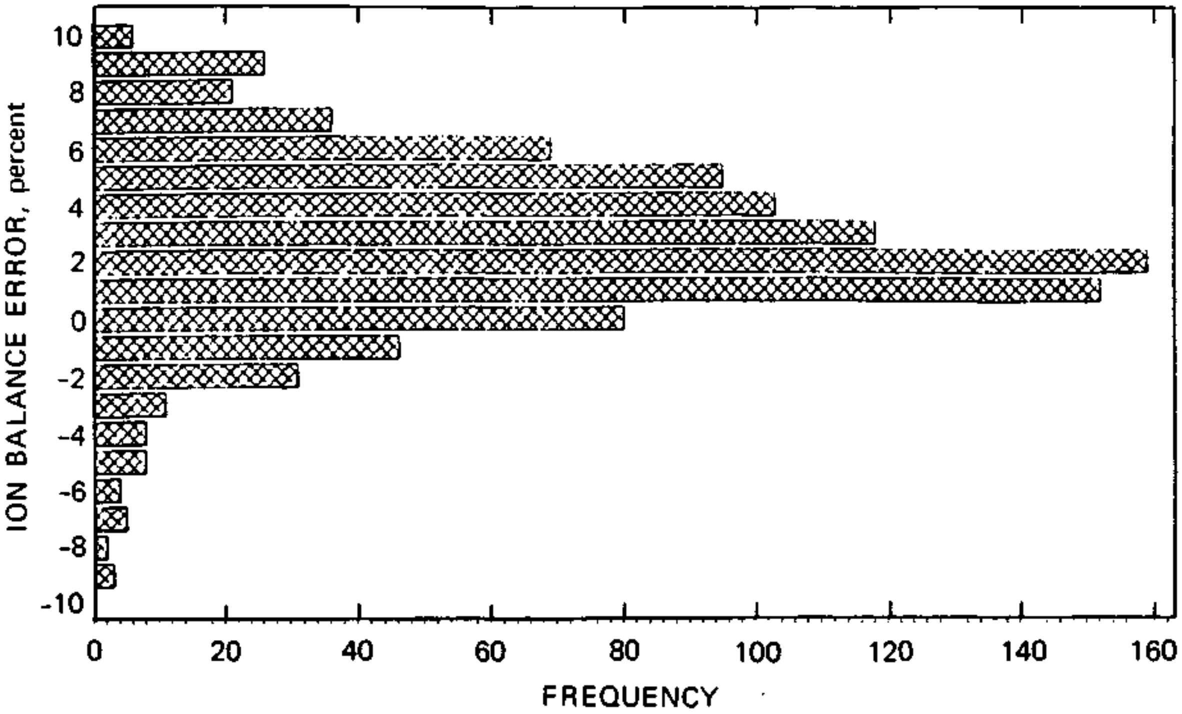

Figure 19. Distribution frequency of ion balance errors.

STUDY OF THE REVERSION OF POLYPHOSPHATE TO ORTHOPHOSPHATE

In order to ascertain whether or not significant bias was introduced into the orthophosphate and hydrolyzable phosphate determinations by the long waiting times before sample analysis, a laboratory study was initiated in November 1983. A total of eighteen 500-mL samples were taken at both site 312/313 and site 314/315 on November 14. An acid-preserved sample was also taken at each location. The samples were immediately refrigerated and returned to the laboratory for analysis within two hours of collection.

At the laboratory, half of the samples from each site were separated and were kept refrigerated at 4°C in a cold room until analyzed. The other half were maintained at the ambient laboratory temperature: 20-25°C.

The first day (T = 0), triplicate aliquots were taken from the acid-preserved and unpreserved samples from each site, and analyses were performed for orthophosphate and acid hydrolyzable phosphate. The results are summarized in Table 9. The behavior of the polyphosphate at site 314/315 is already considerably different from its behavior farther along in the same system (site 312/313). While at site 312/313 the acid hydrolyzable phosphate (AHP) is the same in the acid-preserved and nonpreserved portions, a considerable difference is apparent for those fractions at site 314/315.

TABLE 9. FIRST-DAY ANALYTICAL DATA FOR THE PHOSPHATE REVERSION STUDY (mg PO_4/L)

Site	Aliquot	Acid-preserved		Unpreserved	
		Ortho-PO_4	AH-PO_4	Ortho-PO_4	AH-PO_4
312/313	1	--	2.67	1.70	2.61
	2	--	2.59	1.64	2.61
	3	--	2.67	1.70	2.59
314/315	1	--	6.43	0.33	2.00
	2	--	6.48	0.25	1.97
	3	--	6.48	0.30	1.97

Refrigerated and room temperature unpreserved samples were then analyzed in triplicate after 1, 2, 3, 7, 14, 21, 28, and 44 days. The data are plotted in Figures 20 through 23, with the error bars indicating plus or minus one standard deviation. As can be seen in Figures 20 and 21, the orthophosphate and AHP concentrations remained essentially identical throughout the test period, although some very slow reversion might be indicated after approximately 20 days (not statistically significant at the 95* level).

At site 314/315, the polyphosphate behavior is considerably different. Rapid reversion of polyphosphate to orthophosphate is evident in Figure 22. Refrigeration slowed the reversion rate considerably, but the concentration of orthophosphate still doubled within seven days. Interestingly, the AHP fraction also increased tremendously in the first week. One explanation for the observation could be the presence of an "organic" phosphate fraction, which might have been formed by reaction of the inorganic polyphosphate treatment chemical with naturally occurring organic material. This form may have been rapidly hydrolyzed upon acid addition, invalidating the implicit assumption that the total phosphate in the sample was simply the sum of the orthophosphate plus the polyphosphate from the treatment chemicals. It is not at all clear, however, why the immediate addition of sulfuric acid upon collection results in higher AHP values.

The differences between the refrigerated and nonrefrigerated samples from Site 314/315 were significant at the 95% level (t-test). Similarly, the differences between the AHP function and the orthophosphate were also significant. Figures 24 and 25 show the behavior of reference standards analyzed in conjunction with the sample stability test. They did not vary at the 95% confidence level, indicating that the analytical procedures remained in control throughout the study.

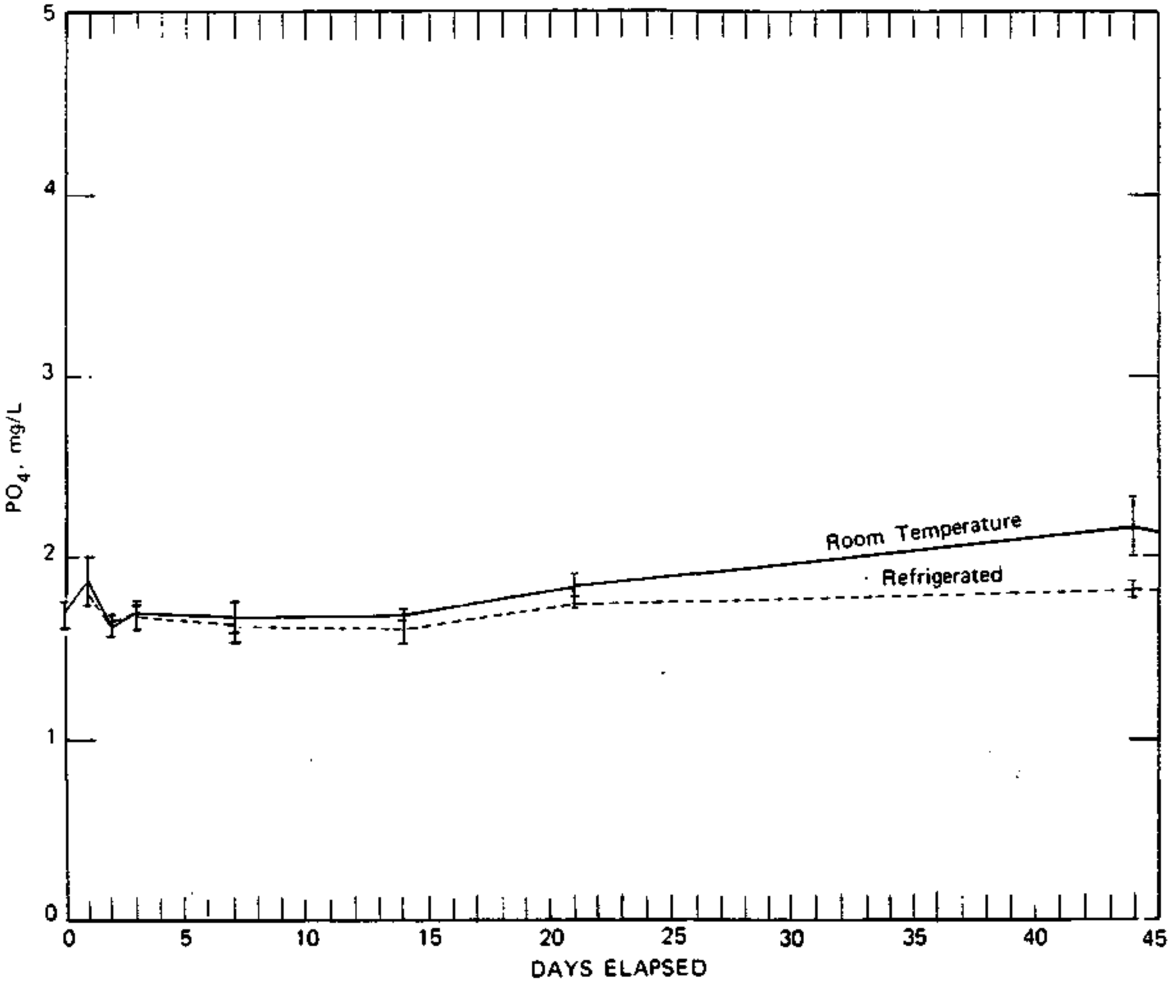

Figure 20. The effect of refrigeration and time on the orthophosphate concentration in samples from sites 312/313 Error bars represent ±1 standard deviation.

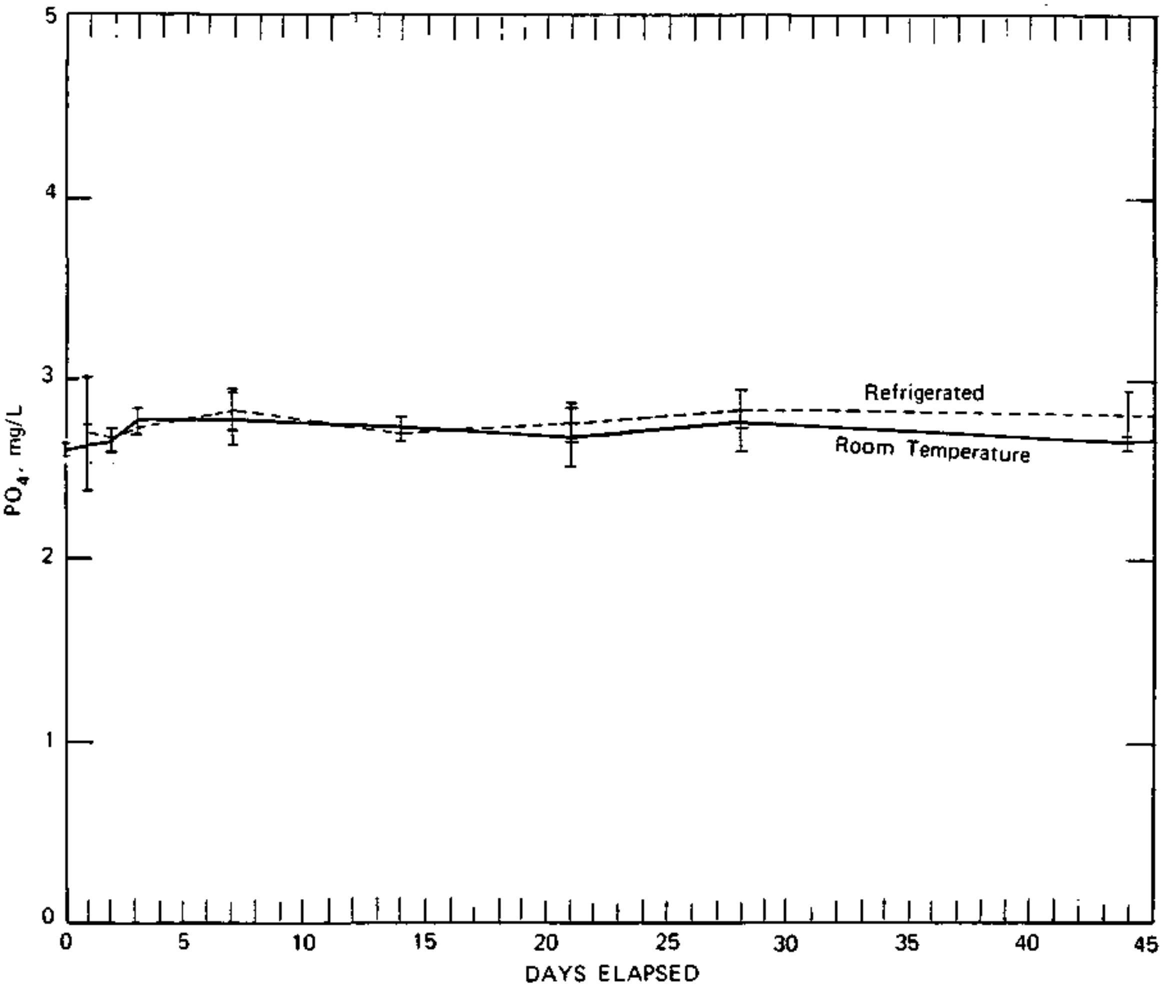

Figure 21. The effect of refrigeration and time on the acid hydrolyzable phosphate concentration in samples from sites 312/313. Error bars represent ±1 standard deviation.

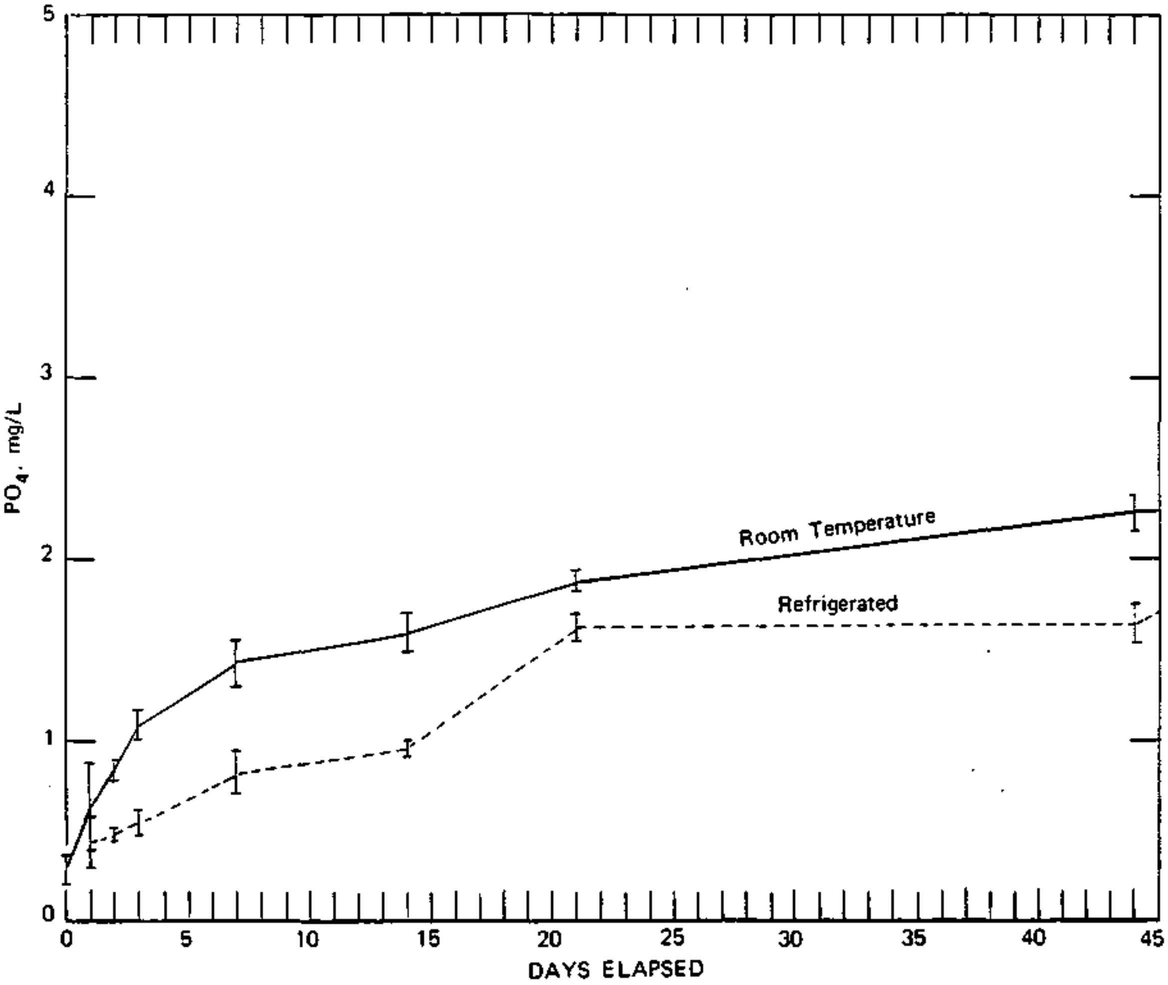

Figure 22. The effect of refrigeration and time on the orthophosphate concentration in samples from sites 314/315. Error bars represent ±1 standard deviation.

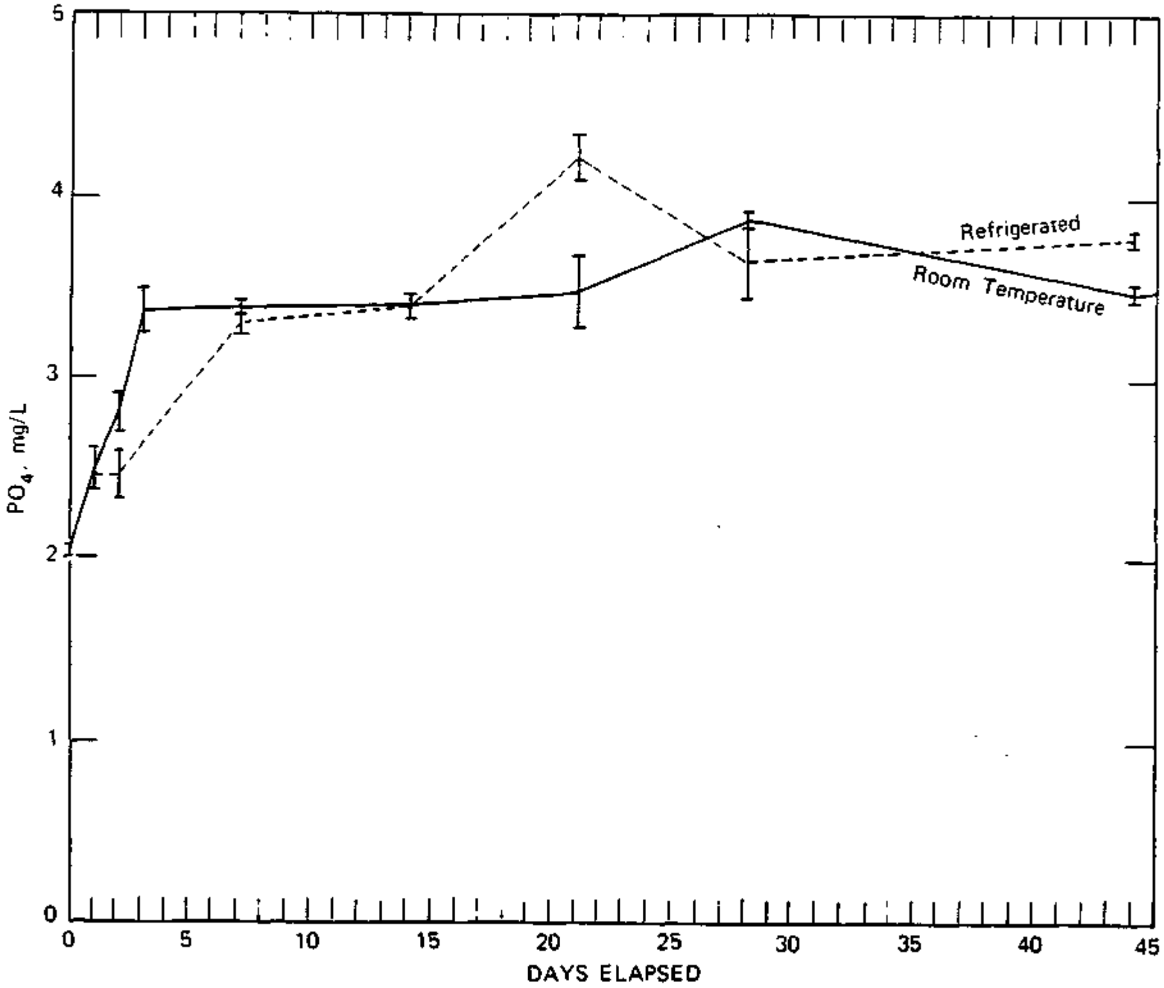

Figure 23. The effect of refrigeration and time on the acid hydrolyzable phosphate concentration in samples from sites 314/315. Error bars represent ±1 standard deviation.

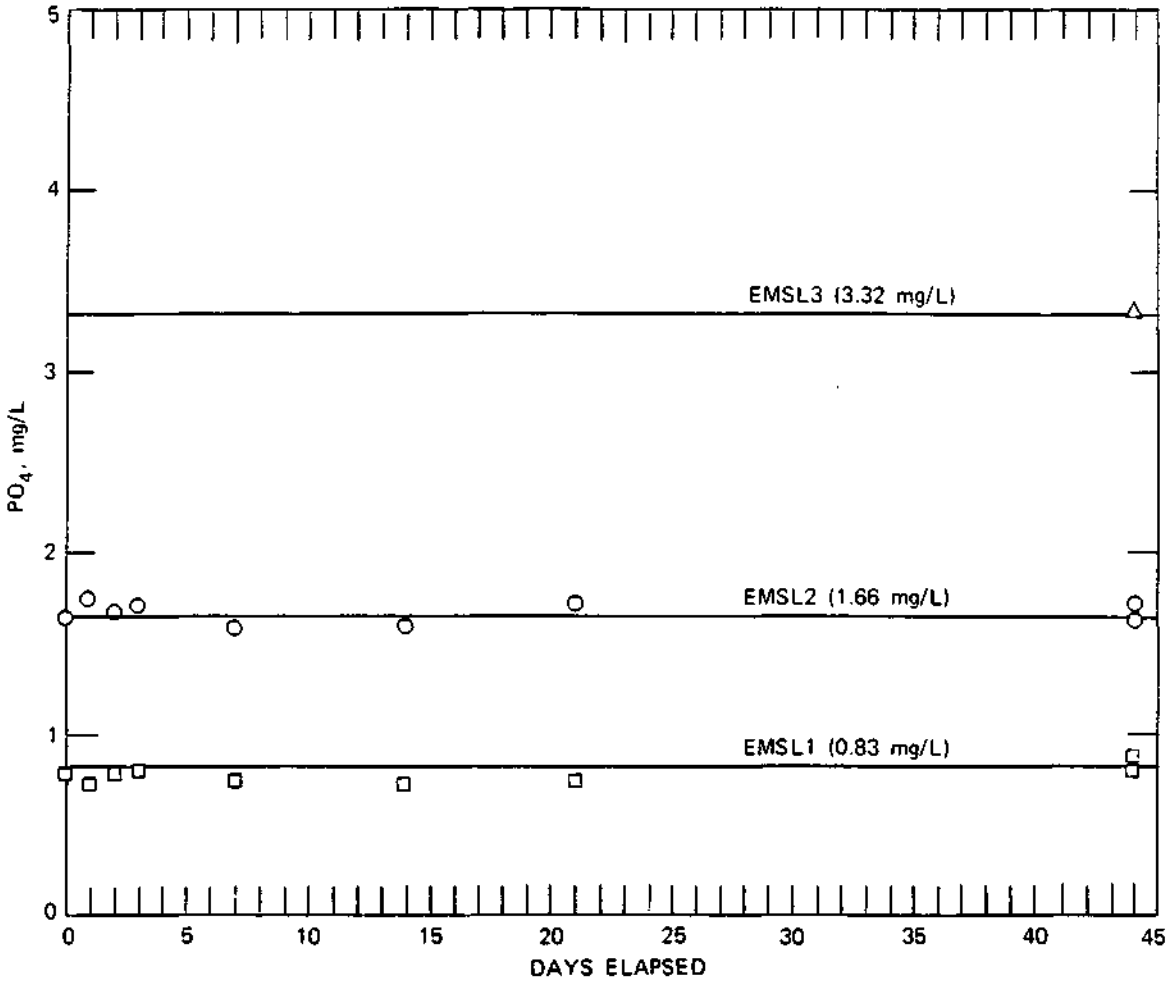

Figure 24. Analyses of USEPA quality control standards for orthophosphate to verify analytical Performance during the stability study.

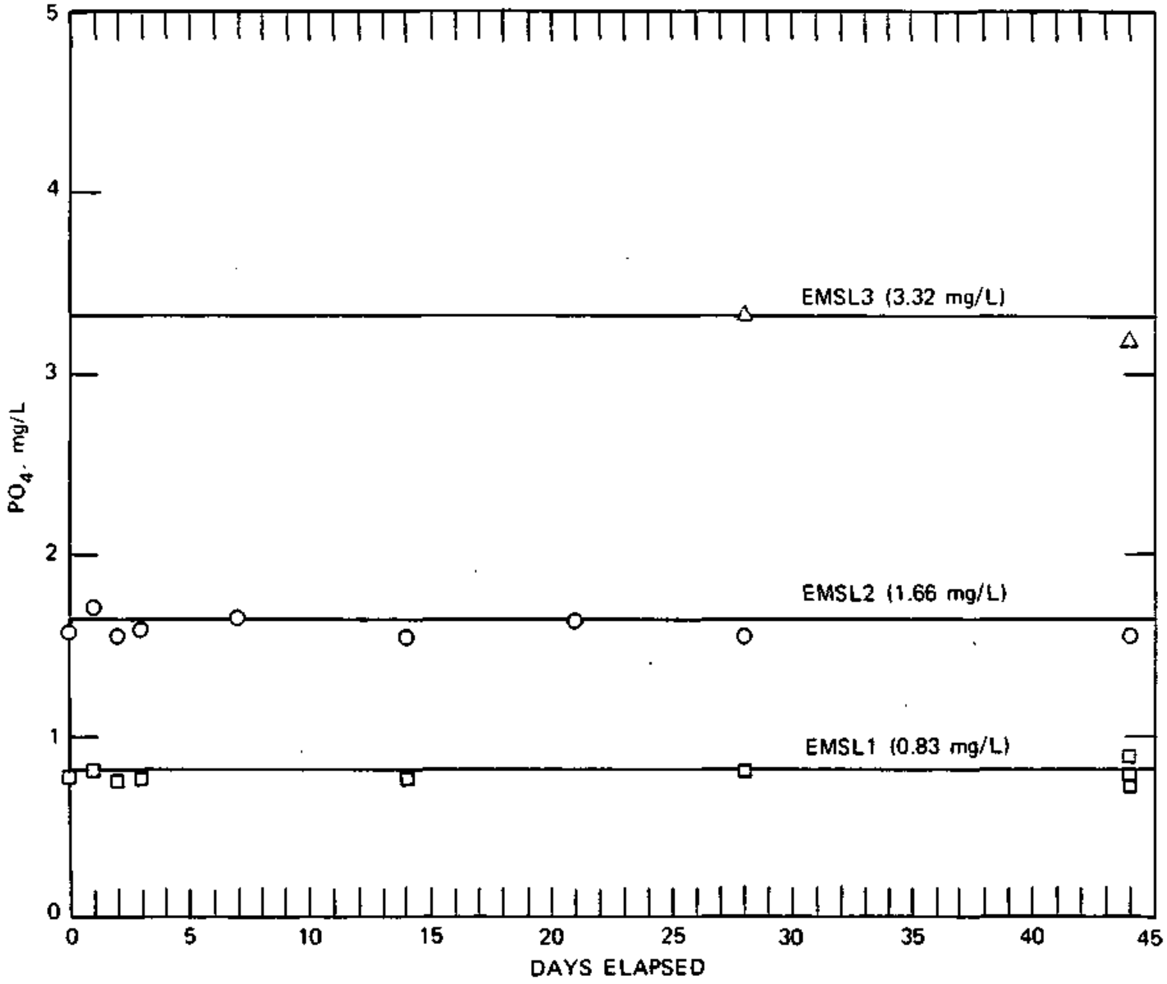

Figure 25. Analyses of USEPA quality control standards for acid hydrolyzable phosphate to check analytical Performance during the stability study. Standards contained only orthophosphate.

The conclusions from this study are the following:

1. Orthophosphate and acid hydrolyzable phosphate data from sites 312 and 313 are reasonable, regardless of time delays before sample analysis.
2. Orthophosphate data from sites 314 and 315 are probably in large error for almost all of the project period. The data are somewhat more reliable after December 1983, but delays of several days were still frequent. No simple correction can be applied to these data.
3. All of the inorganic phosphate treatment dosage may not be accounted for by the analytical procedures used on this project.
4. No statement can be made about the reliability of orthophosphate data from sites 301, 302, 303 or 304 during the periods when polyphosphates were added to that system.

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SECTION 8

LABORATORY CORROSION INVESTIGATIONS

DIFFERENTIATION OF DISSOLVED AND PARTICULATE PRODUCTS

An investigation into the nature of the metal content in the water at several sites was called for because of several observations, including (1) metal concentrations of samples were inconsistent, (2) particulate matter was accumulating on filter membranes, and (3) metal concentrations of samples were exceeding their predicted solubility. The investigation was confined to sites 305, 306, 312, 313, 314 and 315, where a State Water Survey chemist could take the samples and perform the filtration activities at the time of collection.

The published reports of many previous investigations of metal filtration methodologies were examined before the procedure described here was implemented. This procedure follows many of the previous published suggestions.[1-5] Although this procedure was designed to minimize adsorption loss to the filter and apparatus, some small loss (less than 5-10%) was probably inevitable. The procedure described below for sites 305 and 306 is representative of the procedure for all sites where filtered samples were taken.

1. First, a 0.4 µm Nuclepore(R) polycarbonate membrane filter was placed with plastic-tipped forceps into an all-plastic (polycarbonate) 0.47-mm-diameter in-line filtration assembly.

2. The assembled filtration apparatus was rinsed with approximately 500 mL of AR grade 1:1 (v/v) nitric acid by drawing the acid through the line (Tygon(R) tubing) by a peristaltic pump. The filtration apparatus and tubing were then rinsed by approximately one liter of double-distilled deionized water.

3. Immediately, the first 125 mL of water from the galvanized pipe loop were collected directly in a 125 mL standard LPE sample bottle to represent the standing unfiltered sample.

4. A 500 mL high-density linear Polyethylene (LPE) sample bottle was rinsed with approximately 5 mL of sample withdrawn from the galvanized test loop. The rinse water was discarded, and the bottle was rinsed with a second 5 mL portion of sample water.

5. The next 500 mL of sample water were collected in the rinsed LPE bottle.

6. Immediately, the first 350-375 mL of sample were pumped to waste through the filtration assembly. The final 125 mL were collected in a standard 125 mL LPE sample bottle containing the nitric acid sample preservative.

7. The used membrane filter was discarded, and the filtration assembly was briefly rinsed before a new filter was installed. The filtration assembly and a new sample bottle collection were then rinsed as described in steps 1-2, and steps 3-6 were followed for the collection of standing samples from the copper test loops.

3. To collect running samples, the copper loop tap was opened, and the water was allowed to flow for 10 minutes. During this time, the filter membrane was replaced and the apparatus was acid-washed and rinsed as before.

9. A new 500 mL LPE bottle was rinsed as described previously, and both filtered and unfiltered 125 mL samples were collected as given in steps 3~6.

10. The copper loop tap was closed, and the galvanized loop was flushed for 10 minutes. After replacing the filter, cleaning the filtration assembly, and rinsing a 500 mL collection bottle, 125 mL filtered and nonfiltered running samples were collected.

At sites 312 and 313 only running samples were filtered. At sites 314 and 315, two 125 mL standing samples were taken before the filtered standing samples. Running samples were also filtered at these two sites.

At the time these plans were devised, there was not an awareness of the contribution to the observed metal levels by the sampling taps. Thus, some of the results of this investigation are ambiguous. Presumably, in the absence of a contribution by the sampling tap, the metal levels would be constant until the mixing zone between standing and freshly flowing water would be encountered. Thus, the filtered third aliquot of 500 mL from sites 314 and 315 was originally assumed to represent the same chemical concentrations as would be found in the first two 125 mL portions.

At sites 305 and 306 there was little, if any, evidence for particulate metal species (see Tables 10 and 11). With the exception of the initial sampling episode (2/16/83), only a few scattered pairs of analyses would appear to be in any way outside the bounds of analytical precision or possible adsorption loss during filtration. The large differences between filtered and unfiltered copper at site 306 might be attributable to contamination from the chrome-plated brass sampling tap, rather than to the presence of particulate copper species. The cause cannot be determined, because the unfiltered standing sample comprised the initial 125 mL of water

TABLE 10. COMPARISON OF SOME FILTERED AND UNFILTERED STANDING TRACE METAL CONCENTRATIONS FOR SITE 305 (COPPER PIPE LOOP)

	Fe			Cu			Zn			Pb		
	UF*	F*	ΔC*	UF*	F*	ΔC*	UF*	F*	ΔC*	UF*	F*	ΔC*
2/16/83	0.45	<0.04	>0.41	0.62	0.16	0.148	0.18	0.02	0.16	0.071	0.006	0.065
3/8/83	0.05	<0.03	>0.02	0.12	0.10	0.02	0.02	0.02	0.00	0.005	0.003	0.002
14/6/83	0.05	<0.03	>0.02	0.11	0.07	0.04	0.03	0.02	0.01	0.006	0.004	0.002
14/14/83	0.08	<0.03	>0.05	0.16	0.10	0.06	0.07	0.03	0.04	0.018	0.007	0.011
14/21/83	0.06	0.04	0.02	0.15	0.12	0.03	0.04	0.04	0.00	0.010	0.005	0.006
5/3/83	0.05	<0.05	≥0.01	0.14	0.09	0.05	0.12	0.02	0.10	0.010	0.003	0.007
5/24/83	0.05	<0.06	--	0.15	0.12	0.03	0.03	0.02	0.01	0.005	0.002	0.003
6/13/83	0.05	<0.06	--	0.15	0.11	0.04	0.05	0.07	-0.02	0.005	0.003	0.002
6/22/83	0.15	<0.06	>0.09	0.13	0.08	0.05	0.08	0.01	0.07	0.021	0.004	0.017
6/27/83	0.05	<0.07	--	0.09	0.04	0.05	0.02	0.04	-0.02	0.009	0.004	0.005
7/12/83	0.09	<0.07	>0.02	0.11	0.08	0.03	0.014	0.02	0.02	0.016	0.002	0.014

* UF = unfiltered; F = filtered; ΔC = UF minus F, all in mg/L

TABLE 11. COMPARISON OF SOME FILTERED AND UNFILTERED STANDING TRACE METAL CONCENTRATIONS FOR SITE 306 (GALVANIZED PIPE LOOP)

	Fe			Cu			Zn			Pb		
	UF*	F*	ΔC*	UF*	F*	ΔC*	UF*	F*	ΔC*	UF*	F*	ΔC*
2/16/83	0.08	0.04	0.04	0.06	0.02	0.04	0.13	0.12	0.01	0.003	0.002	0.001
3/8/83	0.05	0.04	0.01	0.03	0.01	0.02	0.10	0.09	0.01	0.005	0.001	0.004
4/6/83	0.05	<0.03	>0.02	0.06	0.01	0.05	0.10	0.09	0.01	0.005	0.001	0.004
4/14/83	0.14	0.10	0.04	0.02	0.02	0.00	0.66	0.85	-0.19	0.005	0.007	-0.003
4/21/83	0.28	0.18	0.10	0.29	0.06	0.23	- 0.67	0.71	-0.04	0.017	0.012	0.005
5/3/83	0.12	0.10	0.02	0.02	0.03	-0.01	0.48	0.51	-0.03	0.002	0.003	-0.001
5/24/83	0.15	<0.06	>0.09	0.06	0.03	0.03	0.27	0.23	0.04	0.005	0.005	0.000
6/13/83	0.07	<0.06	>0.01	0.03	0.01	0.02	0.17	0.20	-0.03	0.001	0.002	-0.001
6/22/83	0.17	<0.06	>0.11	0.06	<0.01	>0.05	0.37	0.11	0.26	0.003	0.001	0.002
6/27/83	0.23	<0.07	>0.16	0.17	<0.01	>0.16	0.25	0.15	-0.10	0.012	0.001	0.011
7/12/83	0.11	<0.07	>0.04	0.03	0.01	0.02	0.15	0.09	0.06	0.002	0.001	0.001

* UF = unfiltered; F = filtered; ΔC = UF minus F, all in mg/L

sampled, which was in more prolonged contact with the faucet. Also, because no copper pipe was in the building line to this sampling point, some of the higher copper values are puzzling (if the tap is not the cause). Further evidence for faucet contamination will be presented in a later section.

Tables 12 and 13 show the data from some running samples from sites 312 and 313 that were also filtered by the procedure described. The data show no significant sloughing-off of corrosion products, or the presence of colloidal or suspended particulates in the source water at these sites. The consistency of the data also indicates that the filtration methodology resulted in minimizing the trace metal adsorption losses to the filter membrane, tubing or filter support.

TABLE 12. COMPARISON OF MAJOR METAL CONSTITUENTS IN FILTERED AND UNFILTERED RUNNING WATER SAMPLES FROM SITES 312 AND 313

Date	Ca		Mg		Na		K	
	UF*	F*	UF*	F*	UF*	F*	UF*	F*
Site 312								
2/17/83	12	12	5.6	5.7	310	308	1.4	1.4
4/28/83	17	1b	7.9	7.3	295	313	1.5	1.8
6/28/83	14	14	7.0	6.9	296	298	1.4	1.4
8/25/83	14	13	6.2	6.1	288	235	1.2	1.2
Site 313								
2/17/83	12	12	5.7	6.0	294	288	1.1	1.2
4/28/83	13	13	5.7	5.7	303	300	1.6	1.6
6/28/83	14	13	6.7	6.7	298	296	1.5	1.4
8/25/83	13	13	5.8	5.9	286	298	1.2	1.2

UF = Unfiltered; F = filtered; concentrations are in mg/L

TABLE 13. COMPARISON OF SEVERAL TRACE METALS IN FILTERED AND UNFILTERED RUNNING WATER SAMPLES FROM SITES 312 AND 313

Date	Zn		Fe		Cu		Pb	
	UF*	F*	UF*	F*	UF*	F*	UF*	F*
Site 312								
2/17/83	<0.01	<0.01	0.16	0.09	0.04	0.03	0.003	0.002
4/28/83	<0.01	<0.01	0.08	0.10	0.05	0.03	0.003	0.003
6/28/83	0.01	0.01	0.09	0.07	0.04	0.04	0.002	0.001
8/25/83	0.01	<0.01	<0.06	<0.06	0.03	0.03	0.001	0.001
Site 313								
2/17/83	0.09	0.31	0.09	0.05	0.02	0.02	0.002	0.003
4/28/83	0.03	0.03	0.18	0.09	0.02	0.02	0.002	0.001
6/28/83	0.05	0.08	0.09	0.08	0.02	0.02	0.001	0.001
8/25/83	0.05	0.05	0.06	0.06	0.02	0.02	0.001	0.001

* UF = Unfiltered; F = filtered; concentrations are in mg/L

Tables 14 and 15 show similar data from filtered and unfiltered running samples from sites 314 and 315. Once again, perhaps with the exception of iron, the trace metals and major constituents were apparently present as dissolved species. The observations at these four sites are consistent with the behavior of the polyphosphate treatment chemical as a solubilizing and sequestering agent for a variety of metals. The large amount of particulate iron-containing material observed on filter membranes when unpreserved samples were processed at the laboratory is almost certainly the result of air oxidation, possibly photochemical from ambient light, and longer contact with the chlorine residual in the water. The polyphosphate chemical was effective in sequestering reduced iron (ferrous iron), but after prolonged exposure to strong oxidizing conditions, some of the iron became oxidized and precipitated from solution.

Because filtrations were performed at only six sites, and water characteristics at other locations were considerably different, contribution of particulates to high metal levels in other samples cannot be ruled out.

FIELD INVESTIGATIONS OF CONTAMINATION FROM SAMPLING VALVES

Originally, standing filtered and unfiltered samples were to be taken at sites 314 and 315 to test for contributions from unprecipitated or non-adherent solid material, to complement the running samples described in the previous section. There was also considerable concern by this time that the faucets were contributing copper and zinc to the samples. The concern arose

TABLE 11. COMPARISON OF MAJOR METAL CONSTITUENTS IN FILTERED AND UNFILTERED RUNNING WATER SAMPLES FROM SITES 314 AND 315

Date	Ca		Mg		Na		K	
	UF*	F*	UF*	F*	UF*	F*	UF*	F*
Site 314								
2/19/83	69	64	33	31	164	178	3.3	3.4
2/24/83	118	118	50	51	168	168	3.5	3.6
4/28/83	58	59	27	31	198	194	3.4	3.6
6/28/83	35	34	21	21	198	199	3.3	3.2
8/25/83	77	76	33	33	171	171	3.4	3.4
Site 315								
2/17/83	69	63	33	31	164	180	3.3	3.4
2/24/83	116	115	50	50	169	168	3.5	3.5
4/28/83	58	63	28	30	182	180	3.6	3.6
6/28/83	38	45	22	25	198	197	3.2	3.3
8/25/83	76	77	33	33	169	170	3.3	3.3

* UF » Unfiltered; F = filtered; concentrations are in mg/L

TABLE 15. COMPARISON OF SEVERAL TRACE METALS IN FILTERED AND UNFILTERED RUNNING WATER SAMPLES FROM SITES 314 AND 315

	Zn		Fe		Cu		Pb	
Date	UF*	F*	UF*	F*	UF*	F*	UF*	F*
				Site 314				
2/17/33	0.03	0.04	0.93	0.19	0.01	0.01	0.001	0.001
2/24/33	0.05	0.05	1.48	0.83	0.01	0.01	0.001	0.001
4/28/83	0.03	0.06	0.56	0.39	<0.01	<0.01	0.001	0.001
6/28/33	0.06	0.03	0.89	0.27	0.01	<0.01	0.032	0.001
8/25/83	0.02	0.02	1.06	0.46	<0.01	<0.01	0.012	0.001
				Site 315				
2/17/83	0.02	0.03	0.95	0.20	<0.01	<0.01	0.002	0.001
2/24/83	0.06	0.06	1.47	0.59	<0.01	<0.01	0.004	0.002
4/28/83	0.05	0.03	0.54	0.37	<0.01	<0.01	0.008	0.002
6/28/83	0.09	0.05	1.44	0.54	0.01	0.01	0.003	0.007
8/25/83	0.04	0.04	1.07	1.06	<0.01	<0.01	0.001	0.002

* UF = Unfiltered; F = filtered; concentrations are in mg/L

from observations of the large number of standing samples taken from the galvanized loop that showed copper levels of at least a similar concentration to those found for running samples through the copper loop, and the large number of standing zinc concentrations in the copper loop that exceeded the running zinc concentrations in the galvanized loop.

To test the hypothesis that the chrome-plated brass sampling valves contributed to the metal content of samples, two successive 125-mL portions of sample, followed by a 500-mL sample, were taken at each site. The first two were unfiltered. The first sample was generally comparable to the standing samples contained in the project data base. The third sample was filtered in the manner described previously.

The results of these samplings for some major metals, as well as trace metals, are shown in Table 16. The clear decrease in the trace metal concentration of successive samples is convincing evidence that the faucets made a significant contribution to the metal content of the solution. The low value of the third sample compared to the first two samples cannot be clearly attributed to the presence of particulate material, as had been previously thought before the faucet contamination was discovered.

There are some particularly interesting trends in the trace metal data. If the high zinc levels observed upon standing are presumed to come from the faucet during sampling, then the difference between the first and third sample should be approximately the same for both the galvanized pipe system and the copper system. This hypothesis seems to be supported by the data.

TABLE 16. SUCCESSIVE STANDING SAMPLE PORTIONS FROM SITES 314 AND 315*

Date	Site	Calcium			Magnesium			Sodium			Potassium			Zine		
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
2/21/83	311	73	72	72	31	31	33	171	172	172	3.2	3.2	3.1	0.22	0.10	0.07
M/28/33	311	71	71	73	36	35	35	167	169	177	3.5	3.5	3.5	0.13	0.16	0.08
6/28/83	311	106	107	106	15	15	11	167	165	16t	3.7	3.7	3.6	0.28	0.23	0.15
8/25/83	311	77	76	76	34	31	34	190	136	187	3.6	3.5	3.6	0.27	0.10	0.10
2/21/83	315	73	72	71	34	34	33	173	173	170	3.1	3.2	3.2	1.22	1.21	1.04
M/28/83	315	76	71	76	36	35	35	17t	165	163	3.5	3.5	3.7	1.35	1.23	1.17
6/28/83	315	107	106	107	45	11	15	162	161	163	3.6	3.6	3.7	2.96	2.88	2.64
8/25/83	315	76	76	77	34	31	3t	137	185	186	3.6	3.6	3.6	1.47	1.60	1.23

Date	Site	Iron			Copper			Lead			Manganese		
		1	2	3	1	2	3	1	2	3	1	2	3
2/24/83	314	0.72	0.36	0.16	0.25	0,.10	0.07	0.277	0.037	0.005	0.09	0.08	0.08
1/28/83	314	0.13	0.21	0.17	0.28	0.09	0.06	0.086	0.035	0.015	0.09	0.09	0.08
6/28/83	314	2.00	1.68	0.38	0.37	0..15	0.06	0.085	0.015	0.007	0.22	0.23	0.18
8/25/83	314	1.60	0.60	0.51	0.34	0..09	0.05	0.070	0.007	0.005	0.13	0.11	0.09
2/21/83	315	1.36	1.06	0.21	0.01	0.,02	<0.01	0.089	0.061	0.007	0.10	0.10	0.09
1/28/83	315	2.01	0.38	0.23	<0.01	<0.01	<0.01	0.19t	0.019	0.008	0.09	0.08	0.08
6/28/83	315	2.25	1.18	0.18	<0.01	<0.01	<0.01	0.018	0.008	0.002	0.21	0.24	0.21
8/25/83	315	1.75	2.98	0.10	0.01	0.01	<0.01	0..206	0.037	0.002	0.17	0.10	0.09

* Concentrations are in mg/L. The third portion (3) was filtered through a 0.4-µM polycarbonate merabrane. Portions 1 and 2 were 125 mL; portion 3 was 500 mL.

Many researchers have been concerned over potentially dangerous lead leaching from the zinc coating on the galvanized pipe. High initial lead levels observed at both the copper and galvanized sites dropped extremely rapidly to only several parts per billion by the third aliquot of sample. This indicates not only that there is no important contribution from the galvanizing layer after this length of time (nothing can be said about the earlier samples throughout the project), but that there also is not much of a lead contribution from the solder in the copper loop. These conclusions can be justified only for these two sites without further investigation.

The trend of the running zinc and lead concentrations at the copper loop are somewhat different. After about 9 or 10 months of operation, the lead levels (with three exceptions) tended to stay below about 0.01 mg/L. That possibly reflects the length of time that is necessary to build a passivating coating on the solder, or to remove readily-leachable lead from the sampling taps. The zinc concentrations continued to be highly variable throughout the project. This could possibly indicate that some zinc can still be easily leached from the sampling taps with very Short contact times, via either a solubility or dezincification mechanism.

At sites 305 and 306, the same problem of possible faucet contamination was studied with a similar, but slightly different, approach. At site 306, a new sampling tap of the same general type as thqse employed at the other sites was installed before the galvanized pipe loop (sample valve "x" in Figure 11). This was primarily intended to monitor the levels of zinc, copper, iron and lead going into the corrosion test loop system. A small, new galvanized "T" fitting was also installed to enable the chrome-plated tap to be fitted into the source pipe line.

Initially, only a Single 125 mL standing sample was taken at this location. However, after 97 days of operation, three successive 125 mL unfiltered samples were taken, and this procedure continued through the end of the operation at this site. After 130 days (July 15, 1983), the chrome-plated brass faucet was replaced with one of low density linear Polyethylene (Nalgene(R)). The data from this special study are given in Table 17.

The Information in Table 17 shows clearly that the chrome-plated sampling tap contributed substantial amounts of lead and zinc, and somewhat lesser amounts of copper and iron, to the standing samples. The contamination decreased with time, but still remained considerable after more than five months. The elevated zinc values for the first 125-mL samples with the Polyethylene faucet represent a contribution from the relatively new short galvanized section that was added when the new tap location was added. These data are particularly enlightening, because the low metal levels shown when the plastic tap was used for sampling corroborate the low corrosion rates measured in the weight-loss coupon tests. The high metal levels obtained during the main portion of the study seemed unusually high compared to the measured corrosion rates. The low lead levels indicate insignificant contamination from the galvanized pipe coating.

TABLE 17. CONCENTRATIONS (MG/L) IN SUCCESSIVE 125-ML UNFILTERED STANDING SAMPLES FROM THE SAMPLING TAP INSTALLED BEFORE SITE 306

Date	Elapsed days	Zinc			Copper			Lead			Iron		
		1	2	3	1	2	3	1	2	3	1	2	3
3/8/83	1	1.30	--	--	0.73	—		0.099	—		0.11	--	--
4/6/83	30	0.99	--	--	0.31	—	—	0.056	--	--	0.03	--	--
4/14/83	38	2.09	—	—	0.18	--	--	0.059	--	--	0.28	--	--
4/21/83	45	2.66	—	—	0.77	—	--	0.060	—	--	0.93	--	--
5/3/83	57	2.08	--	—	0.06	--	--	0.031	--	—	0.29	--	--
5/14/83	68	1.98	--	--	0.07	--	--	0.075	--	--	0.32	--	--
5/24/83	78	0.65	--	—	0.29	--	—	0.021	--	--	0.09	--	--
6/13/83	98	1.10	0.11	0.18	0.01	0.03	0.01	0.030	0.011	0.008	0.12	0.07	0.10
6/22/83	107	1.01	0.12	0.30	0.06	0.03	0.01	0.019	0.008	0.005	0.36	0.06	<0.06
6/27/83	112	0.75	0.28	0.26	0.08	0.02	0.01	0.015	0.005	0.001	0.52	0.06	<0.07
7/12/83	127	0.68	0.69	0.25	0.03	0.01	0.04	0.013	0.023	0.001	0.28	0.72	0.09
7/16/83	131	0.30	0.20	0.21	<0.01	<0.01	<0.01	0.001	0.001	0.001	0.12	<0.07	<0.07
7/21/83	137	0.22	0.16	0.11	<0.01	<0.01	<0.01	0.001	0.001	0.001	0.13	<0.07	0.07
8/5/83	151	0.35	0.26	0.22	<0.01	<0.01	<0.01	0.002	0.001	0.002	0.17	<0.08	<0.08
8/15/83	161	0.55	0.22	0.01	<0.01	<0.01	<0.01	0.001	0.001	0.001	<0.08	<0.06	<0.06
8/22/83	168	0.16	0.21	0.17	<0.01	<0.01	<0.01	0.001	0.001	0.001	<0.06	<0.06	<0.06

LABORATORY STUDY OF TRACE METAL LEACHING FROM SAMPLING TAPS

To pursue the leaching from the chrome-plated sampling taps Turther, a two-week benchtop experiment was set up. Six new faucets were rinsed copiously with deionized (DI) water, inverted and filled to capacity (approximately 20 mL) with either Champaign tap water from the laboratory, or with deionized water. Three taps were used only for Champaign water, and three were used only for deionized water. The faucets were sealed with new silicone stoppers that had been leached for a week in 10% nitric acid solution, allowing no or minimal air bubbles. The faucets were mounted with finger-clamps on a flexiframe stand in an inverted position until the next day. After samples were withdrawn the silicone stoppers were rinsed with 1:1 HNO_3 and deionized water, the faucets were filled, and the stoppers were replaced.

Because of the restricted sample volume and the need for rapid analysis, water samples were taken on alternate days for either lead and cadmium or zinc, iron and copper, and the samples were mailed to the USEPA Drinking Water Research Division laboratory in Cincinnati for analysis. Samples were acidified with 0.15% v/v ultrapure HNO_3 immediately upon collection. The results of this study are illustrated in Figures 26 through 30.

Figure 26 shows that extremely high amounts of lead can easily be leached from the tap, even after two weeks. The MCL was exceeded by all samples taken. A small amount of cadmium was removed in the first equilibration from the taps containing Champaign tap water, but was not detectable afterwards. More cadmium was removed by the deionized water, and leaching was continuing at detectable levels after two weeks.

Iron leaching was curious, in that more iron was generally taken into the tap water than into the deionized water. A possible explanation would be that less pure oxide or hydroxide passivating films formed in the tap water. It may also be that the oxidation rate was much faster because chlorine and dissolved oxygen species were present in the tap water.

There was considerable zinc leaching with both water types, although there was less from the faucets containing tap water. The leaching of copper behaved very similarly in the two water types, and showed a fairly consistent level after about four days.

These experiments show conclusively that chrome-plated brass sampling taps can be a source of considerable readily leachable lead and zinc, when lead solder, lead pipes, and galvanized pipes are not present. A detailed investigation using other water types and a range of faucet compositions is warranted. The use of such materials might constitute a health risk under some conditions, and they can render data from corrosion studies impossible to interpret in a framework of relating analyzed metal levels to corrosion rates, mechanisms, or pipe solubility. The possible impact of other brass components, such as meters, must also be investigated.

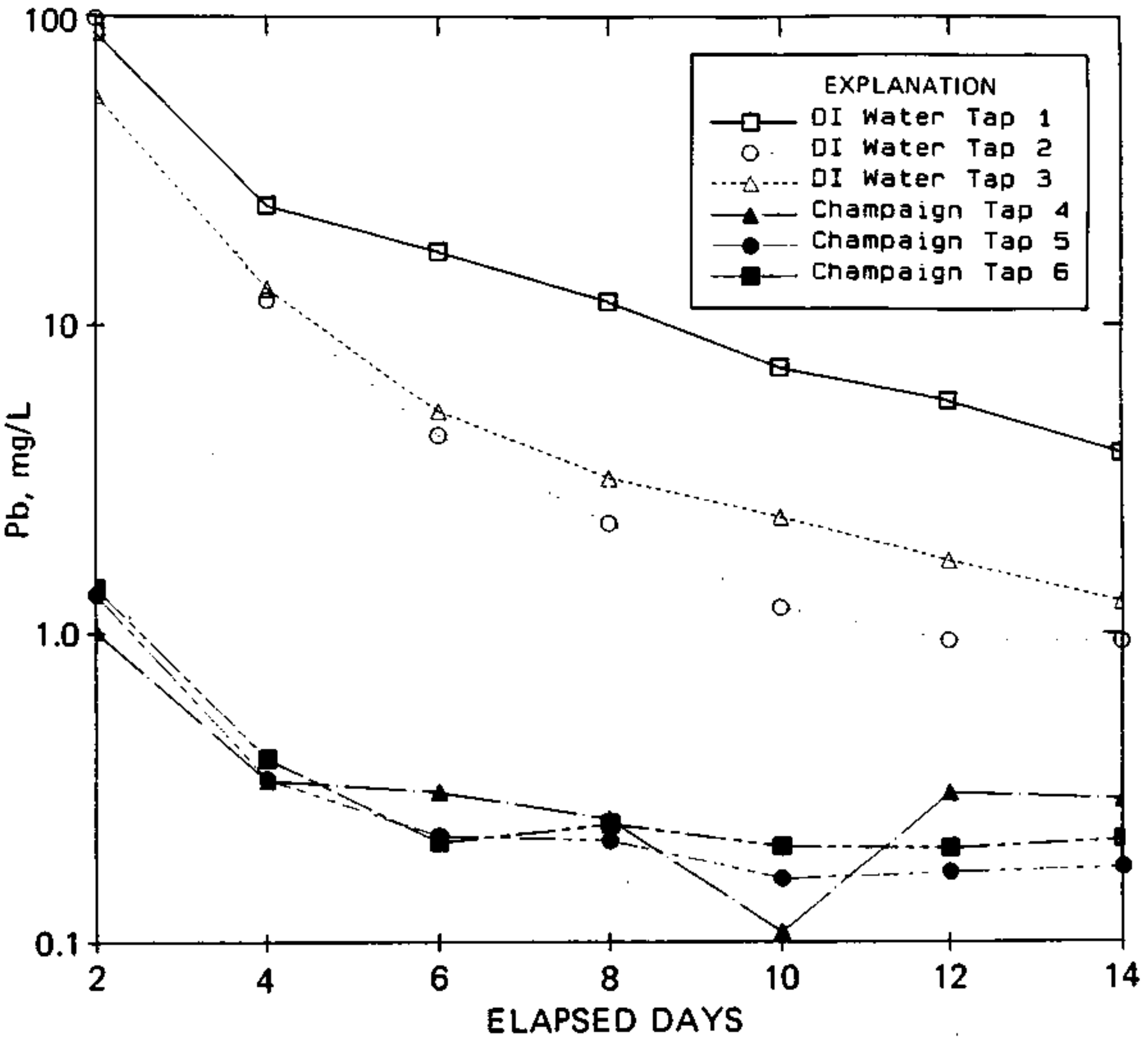

Figure 26. Results of 24-hour leaching study of lead from new chrome-plated sampling taps.

COMPARISON OF FAUCET CONTAMINATION DATA TO OTHER STUDIES

The most similar investigation to this was published during the cburse of this study by Samuels and Meranger.[6] They examined the leaching of copper, zinc, chromium, lead and cadmium from eight kitchen water faucets using several different water types. They performed two 24-hr. leachings with each water type, and found considerable contamination possible from all metals studied except chromium.

In a Danish study, Nielsen found that even when lead pipes were not used, lead can be picked up from household installations.[7] Fittings are frequently made of copper alloys such as brass, which can contain 2-3% lead, or gunmetal, containing 5% lead. Water meters, mixer fittings and other

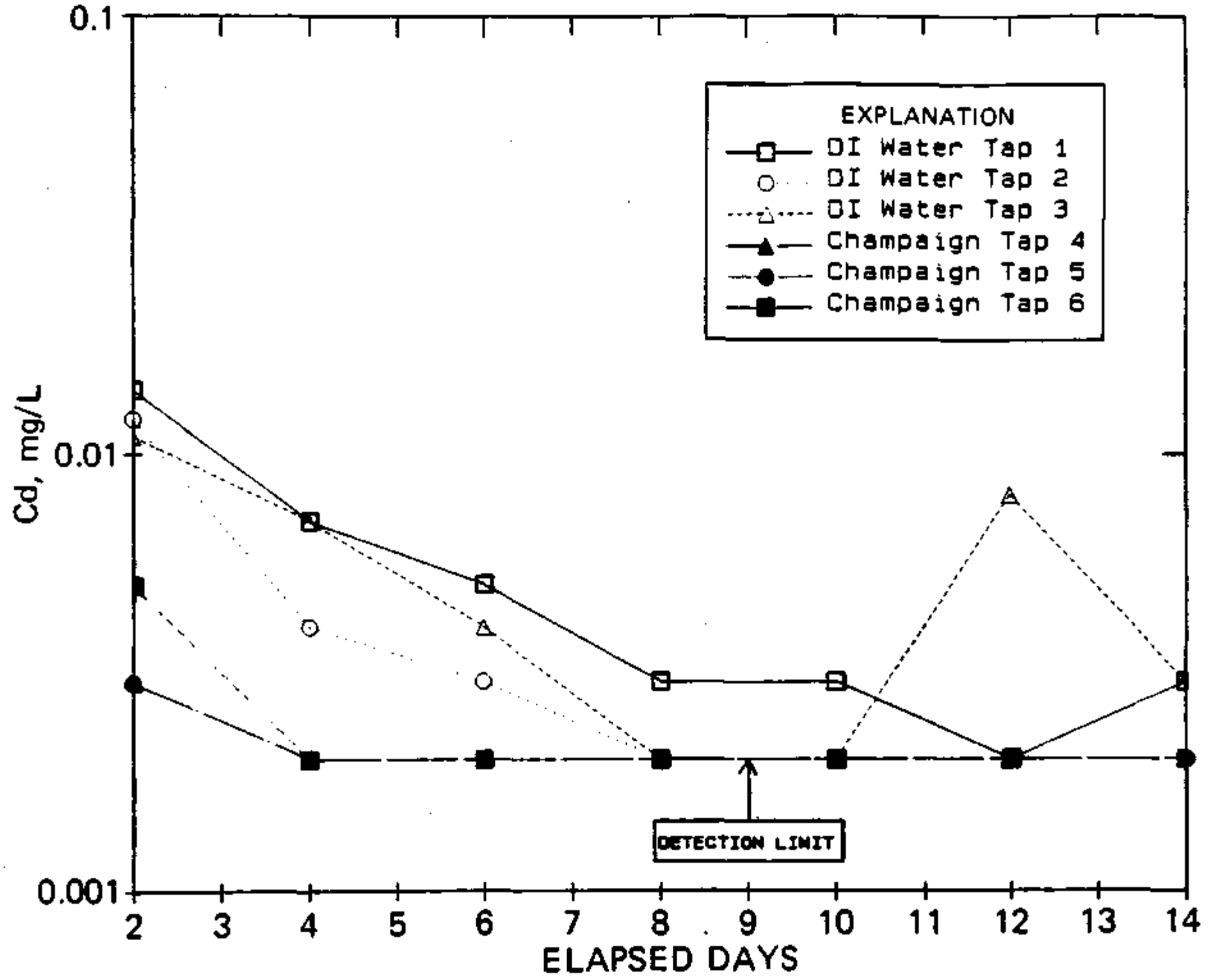

Figure 27. Results of 24-hour leaching study of cadmium from new chrome-plated sampling taps.

fittings are generally made from brass, while main valves and stop valves are often made of gunmetal. The Danish Ministry of Housing currently tests fittings intended for household use for cadmium and lead pick-up.

Nielsen conducted field tests of up to six months using two hard waters and one slightly hard water in the pH range of 7.3 to 7.7. Nielsen concluded that the differences in salt content and hardness had relatively little impact on the metal leaching from galvanized steel, brass and gunmetal. The experiments showed that lead levels generally decreased quickly, to below the 0.05 mg/L water standard in the galvanized steel tubes, but still to a level above the limit in the brass and gunmetal tubes. Nielsen presented a standard test method to evaluate the potential for lead and cadmium leaching from metallic components of drinking water installations.

Mattsson discussed several aspects of dezincification of brass, including some alloying techniques to reduce it.[8] He did not discuss the

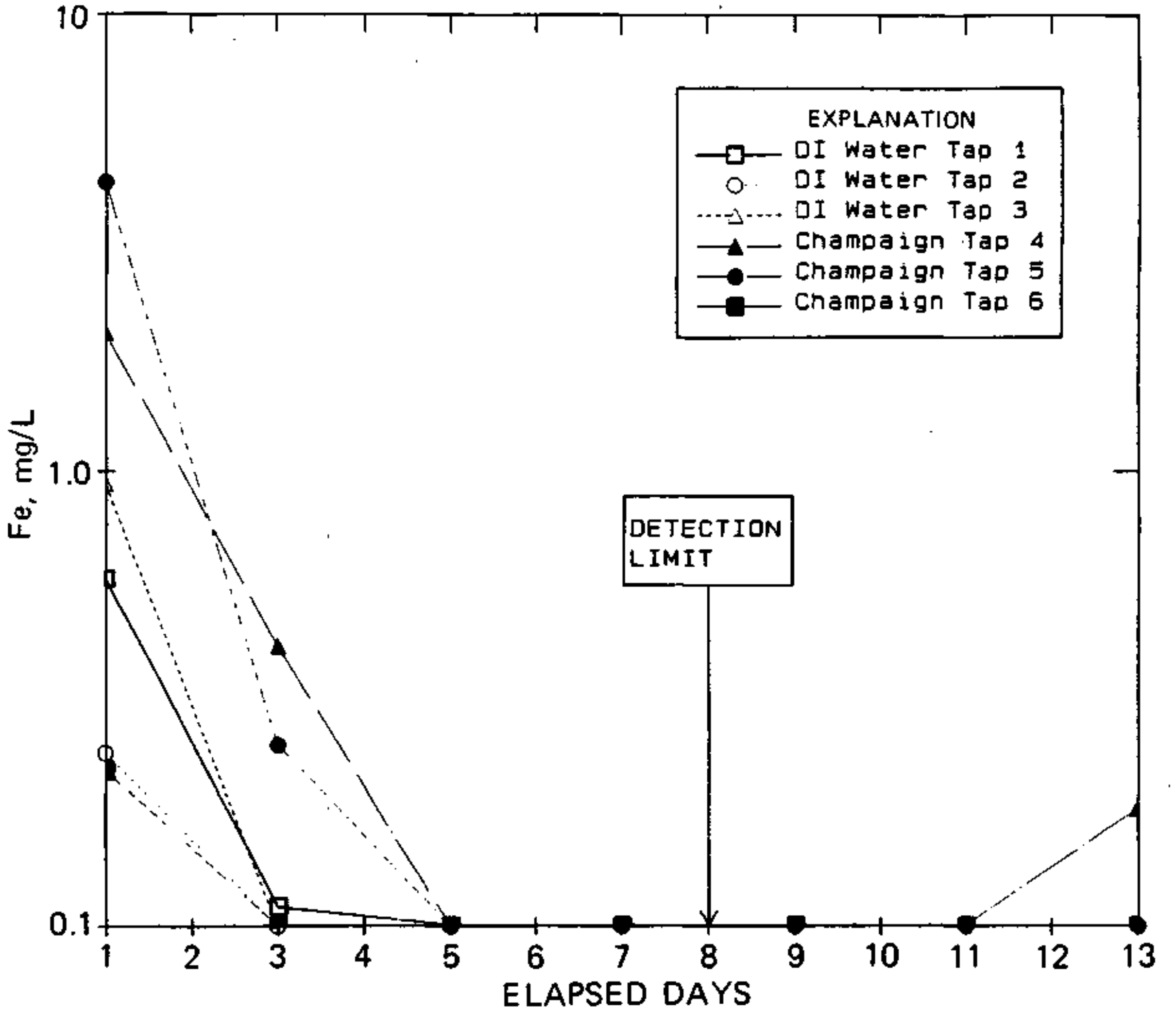

Figure 28. Results of 24-hour leaching 3tudy of iron from new chrome-plated sampling taps.

Potential for metal leaching aside from zinc, but did point out that the presence of copper in the water could sometimes act as an oxidizing agent to accelerate the process. The combination of brass sampling taps and copper plumbing Systems could be a cause of sample contamination in this study, and could be a poor choice for domestic Systems where significant copper solubility occurs.

Kennett has recently attributed dezincification of brass to an imbalance of the ratio of carbonate ion to chloride ion, but also stated that at high pH sulfate ion increases the rate of attack.[9] He also stated that the effect is considerably reduced below pH 8.3. Many of the water Systems in this study had pH values above 8.3, and significant sulfate concentrations (often over 500 mg/L).

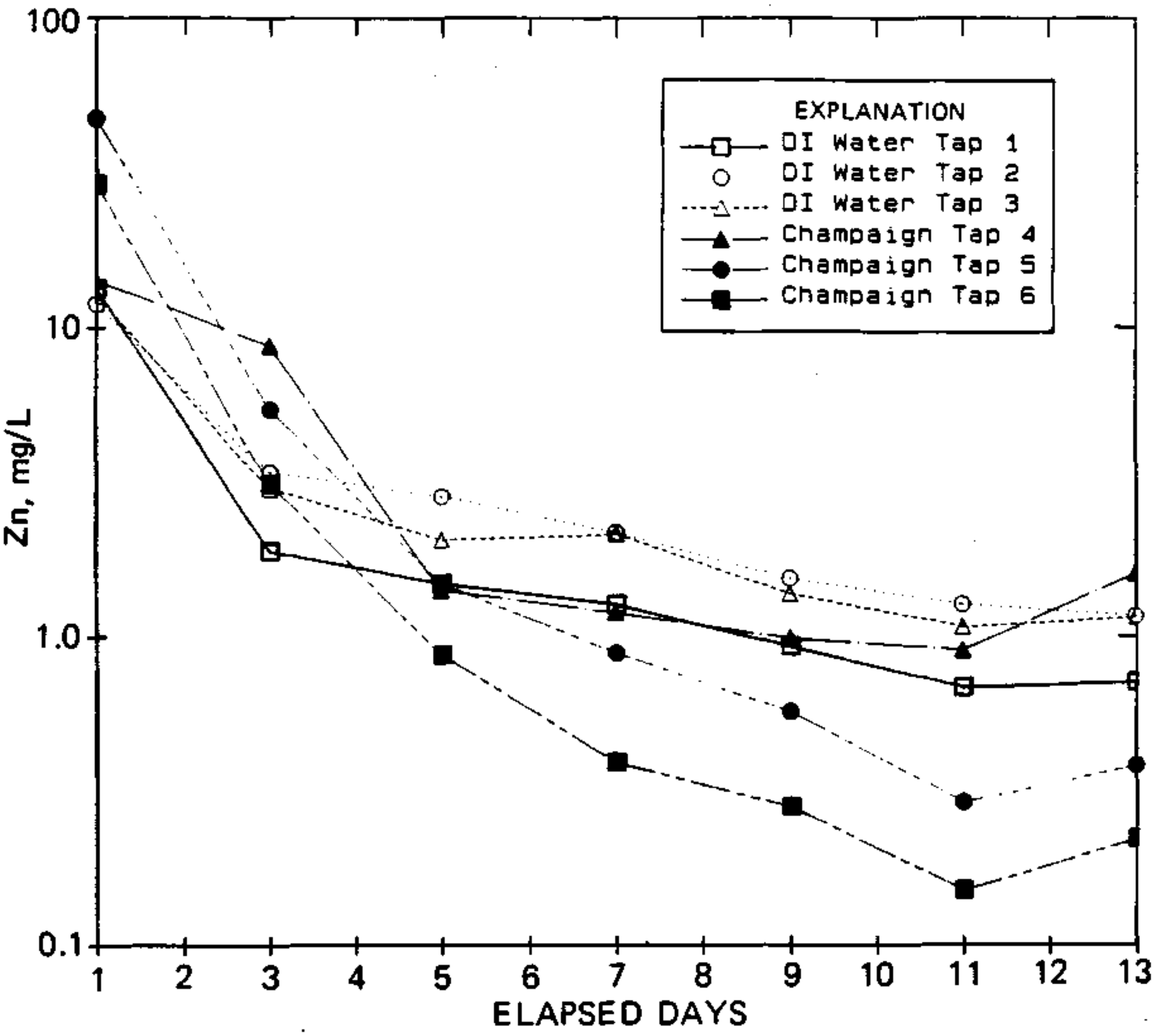

Figure 29. Results of 24-hour leaching study of zinc from new chrome-plated sampling taps.

Jones has indicated that if a brass contains more than 40% copper, it will essentially behave as if it is pure copper.[10] Conversely, if it is below 40% in copper, it will behave like pure zinc. These results were similar to those found by Maahn and Blum.[11] In a laboratory study utilizing a soft, flowing water, Walker found that the corrosion and dezincification of the brass tested appeared to be even dissolution and leaching of both metals from the surface, with the subsequent redeposition of the more noble copper.[12]

Several investigations have been made of the effect of free chlorine and chloramine on brass fittings in drinking water.[13-15] Ingleson et al.[13] studied the pattern of dezincification in ball valves of different brass alloys, and how it related to the construction details of the valves. In

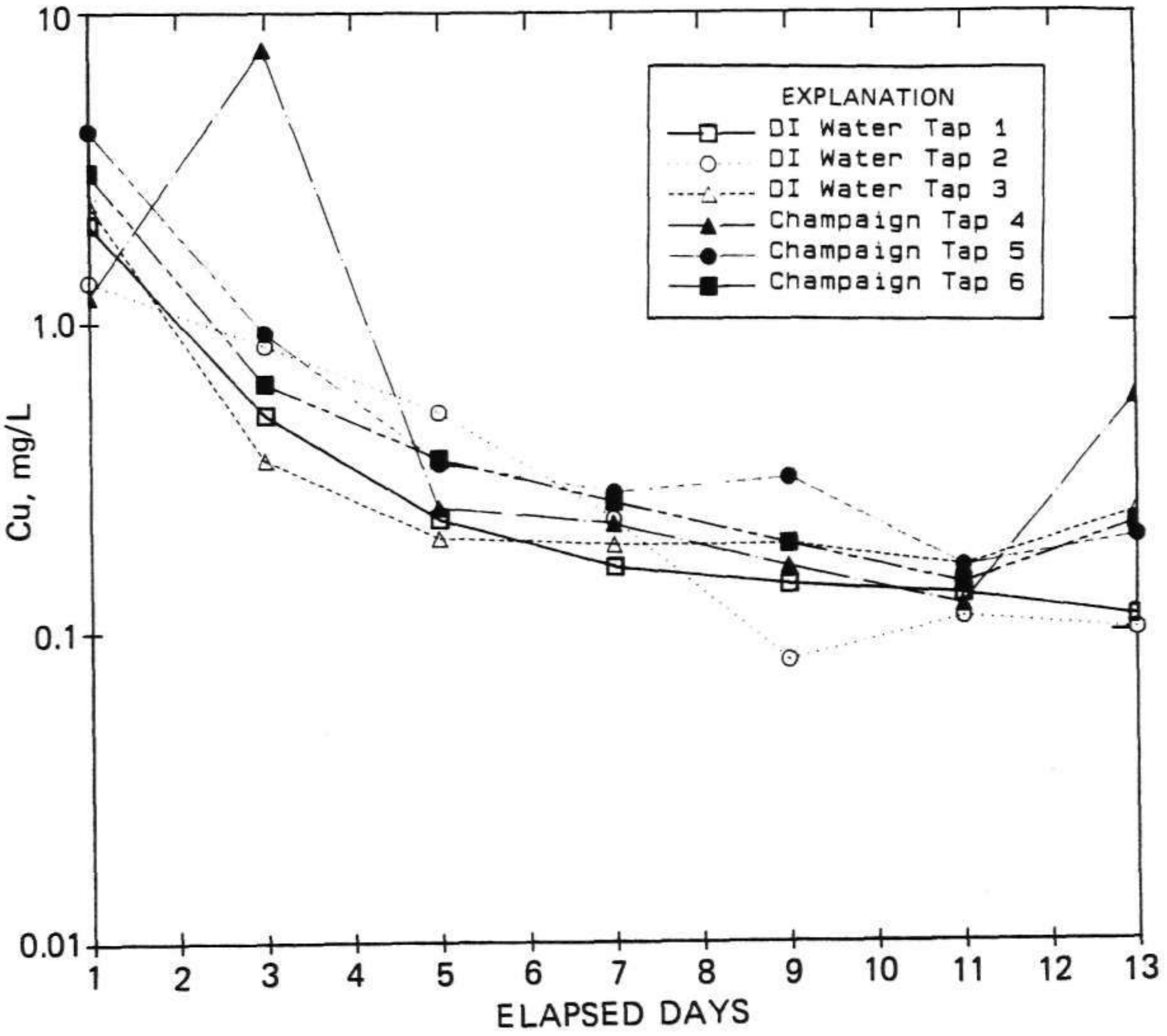

Figure 30. Results of 24-hour leaching study of copper from new chrome-plated sampling taps.

general, they found that though the rate of dezincification did increase with the presence of up to 0.4 ppm of free chlorine, the effect of chlorine was small compared with that caused by variations in the chemical composition of the water.

In 1956, Larson et al. reported on experiences with brass faucets in Champaign-Urbana tap water.[14] At that time, the alkalinity was approximately three times as high, and the pH was approximately 1 .6 units lower than it was during the course of this study. Larson et al. concluded that the cause of the impingement attack was the presence of appreciable chloramine (1-2 ppm as Cl_2) in the greater part of the distribution system.

Wormwell and Nurse also investigated the impact of water composition and chlorination on brass.[15] As with the other studies, their main interest was in corrosion resistance, and trace metal leaching was not measured. They found that the effect of chlorination varied with the type of water involved. At low flow rates (1.2 ft/min.), there tended to be a higher corrosion rate in a very soft and very hard water, and not much effect in some moderately hard waters.

Turner investigated the behavior of brass (60% Cu, 40% Zn) fittings in hot water Systems.'" An examination of the corrosion products found in several Systems where corrosion or deposition of corrosion products was a Problem showed the bulk of the solid to be basic zinc carbonate, with smaller quantities of calcium and magnesium carbonates. Traces of iron, silica and aluminum were also found. His studies indicated that in the presence of calcium and magnesium ions, the meringue dezincification was related to the relative concentrations of chloride and "temporary hardness." Sulfate was also found to have some impact, provided that the chloride concentration was above 90% of that normally necessary to promote dezincification (at a given temporary hardness), and the sulfate concentration was at least three times that of the "missing" chloride. The pH range of the waters studied having this form of dezincification was approximately 8-9, and the corrosion was often associated with lime-softened waters. Turner emphasized that his research pertained only to the meringue type of dezincification.

Regardless of the exact mechanism of dezincification or brass solubility, copper alloy faucets must be investigated further under different flow and chemical quality conditions, to determine the extent and longevity of leaching of noxious trace elements. Such studies are important both from the standpoint of human exposure and from that of effectively isolating the variables to address mechanisms and rates of pipe corrosion and dissolution.

X-RAY DIFFRACTION ANALYSIS OF DEPOSITS FOUND IN CORROSION SPECIMENS

To help get an idea of what solids might be forming on the surfaces of the corrosion specimens, some X-ray diffraction analyses were performed from the scales scraped from the insides of the specimens with the longest exposure times that were available from each site.

Samples were stored in glass bottles with snap-fit plastic caps until the analyses were performed. No special drying or homogenizing was done to the samples. Preparation and analysis was done by students in the Department of Ceramic Engineering of the University of Illinois. The instrument used was a Norelco powder diffractometer located in the Microstructure Characterization Laboratory of the University of Illinois Materials Research Laboratory.

Samples were prepared by first placing double-sided sticky tape on a glass slide. The powders were then spread uniformly across the surface. The instrument was operated with a Cu source tube at 40 kV, with a current setting of 10 mA. A range of 6 to 65 degrees for the 20 value was scanned. Each sample was run at least twice. The first run was a rapid scan of 1 to 2 degrees per minute to examine the gross nature of the pattern. Higher resolution runs were then made at a speed of 1/2 degree per minute, to delineate the structure more clearly.

The experimentally determined 2θ value was compared to reference values computed using the Bragg equation[17]

$$\lambda = 2d \sin \theta$$

for which λ is known (1.542 Å for Cu Kα radiation), and the atomic interplanar spacings (d) were obtained from the ASTM card file. The 29 value was matched as well as possible by manual inspection, and identifications were made.

Table 18 provides a summary of the deposlts found on the corrosion specimens. Available sample quantities did not permit verification by wet chemical analysis. Because the results were not corroborated by other X-ray techniques, the data provided only supplemental Information to the study.

The most interesting finding is the presence of vaterite as the $CaCO_3$ phase. Whether or not this represents the stabilization of a thermodynamically metastable phase by surface adsorption of divalent trace metal ions cannot be clearly determined. If vaterite is the initial or preferred cal-

TABLE 18. COMPOUNDS IDENTIFIED IN CORROSION SPECIMEN DEPOSITS BY X-RAY DIFFRACTION

Site no.	Specimen material	Exposure (days)	Compound(s)
301	Copper	728	CuO
302	Galv.	728	$Na_3Fe(PO_4)\cdot H_2O$, ZnO, $Zn_3(PO_4)_2\cdot H_2O$, ZnS
303	Copper	728	CuO
304	Galv.	728	$Na_3Fe(PO_4)\cdot H_2O$, ZnO, $Fe_2O_3\cdot H_2O$, $Zn_3(PO_4)_2\cdot 4H_2O$, ZnS, UI*
305	Copper	738	UI
306	Galv.	738	$Na_3Fe(PO_4)\cdot H_2O$, $CaSO_4$, SiO_2, ZnO, ZnS?, UI
307	Copper		UI
308	Copper	716	$Cu_2(OH)_2CO_3$, $CaCO_3$ (vaterite?)
309	Galv.	716	$Zn_5(CO3)_2(OH)_6$, $ZnFe_2O_4$,
310	Copper	716	$Cu_2(OH)_2CO_3$, $CaCO_3$ (vaterite?)
312	Copper	555	UI
313	Galv.	555	AM#
314	Copper	727	UI
315	Galv.	556	AM
317	Galv.	755	$Na_3Fe(PO_4)\cdot H_2O$, ZnO,$CaCO_3$ (vaterite), $CaSO_4$, SiO_2, UI
319	Galv.	755	ZnO, $Zn_3(PO_4)_2\cdot 4H_2O$, $ZnFe_2O_4$, ZnS, $Zn_5(CO_3)_2(OH)_6$, $Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$, $CaCO_3$ (vaterite)

* UI - unidentified Compound
# AM - amorphous Compound

cium carbonate precipitate likely to form in a pipe system, then the use of the calcite solubility constant for Langelier Index or calcium carbonate deposition potential calculations would be entirely inappropriate. Pisigan and Singley[18] and Singley et al.[19] have observed aragonite, also a metastable calcium carbonate polymorph, on galvanized and black steel pipes.

The presence of orthophosphate solids of zinc and iron at sites 301-304 is interesting, because the System never employed orthophosphate as an inhibitor, but used a polyphosphate for several months during the early part of this study. Natural orthophosphate levels in the system were low (<0.3 mg PO_4/L, but usually <0.1 mg PO_4/L), so the deposits might represent a residual from the polyphosphate addition period. The interesting aspect is that studies by Koudelka et al.[20] indicated that corrosion protection of iron by polyphosphate solutions resulted from the formation of iron orthophosphate surface films. The zinc orthophosphate deposit at site 319 is perplexing, because no phosphate additive was used, and the natural level appeared to be quite low.

Simple carbonates ($CaCO_3$, $ZnCO_3$) and basic carbonates ($Zn_5(CO_3)_2(OH)_6$ and $Cu_2(OH)_2CO_3$) were not found at as many sites as might be anticipated.

A more thorough investigation of the identities of the solids and the solution chemistry in the pipes is definitely warranted.

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SECTION 9

EVALUATION OF CORROSION DATA

WEIGHT LOSS DATA

As described in Section 5, the ASTM D2688 Method C corrosion tester was employed in this study to measure the corrosion of copper and galvanized steel in the potable water supplies. Two ASTM corrosion test assemblies were installed at each test site. Each test assembly contained two corrosion specimens. At 6-month intervals, each of the corrosion specimens in turn was removed and another specimen was installed in its place. For each test site, seven corrosion specimens were exposed to the water supply for different time intervals during the study. The only exception to the specimen installation schedule occurred at test site 308 where a specimen could not be removed without damage. The specimen was left in place and was removed successfully at the end of the study, providing a duplicate for the 24-month exposure interval. Much of the corrosion data were lost for site 317 due to improper cleaning procedures. The corrosion rates observed during the study for copper and galvanized steel specimens are shown in Table 19 and Table 20, respectively. The complete corrosion results are reported in Appendix B.

TABLE 19. OBSERVED CORROSION RATES FOR COPPER SPECIMENS (mdd)

	Exposure period for specimens (months)						
Site no.	(0-6)	(18-24)	(0-12)	(12-24)	(0-18)	(6-24)	(0-24)
301	1.30	NV	1.09	.51	.65	.32	.59
303	1.16	.72	.91	NV	.62	.40	.60
305	.42	.70	.31	.51	.33	.37	.35
307	1.79	1.59	1.54	1.44	1.25	NV	1.26
308	3.59	NV	2.25	2.53	NV	NV	1.68 1.95
310	3.04	3.02	1.94	2.00	1.66	NV	1.36
312	.65	.96	.57	.59	.42	.40	.41
314	1.25	.70	.75	.27	.47	.28	.42
316	.33	.39	.25	.30	.25	NV	.19
318	.31	.50	.21	.21	.10	.20	.14

NV - no value

TABLE 20. OBSERVED CORROSION RATES FOR GALVANIZED STEEL SPECIMENS (mdd)

	Exposure period for specimens (months)						
Site no.	(0-6)	(18-24)	(0-12)	(12-24)	(0-18)	(6-24)	(0-24)
302	6.47	3.26	5.05	3.11	4.40	3.26	3.88
304	3.76	NV	3.21	1.14	2.38	2.14	2.61
306	.58	.89	.88	.88	.59	.86	.62
309	6.05	3.95	5.95	3.63	4.27	3.86	3.28
311	4.94	4.96	4.17	4.03	2.95	NV	3.51
313	3.19	3.48	1.85	2.29	1.79	2.06	2.04
315	4.97	4.62	4.50	3.65	3.17	3.29	2.81
317	1.57	NV	1.76	NV	1.46	NV	NV
319	3.42	1.23	2.18	1.23	NV	1.33	1.22

NV - no value

TABLE 21. PROCEDURE VARIABILITY OF ASTM D2688, METHOD C, CORROSION TEST

Material	Specimen size I.D. (in.)	Specimen size Length (in.)	Estimate of procedural variability Weight loss (g)	Estimate of procedural variability Corrosion rate (mdd)
Copper	1.025	4.00	±.0356	±.120
	.545	4.00	±.0189	±.064
Galvanized steel	1.049	4.00	±.1961	±.640
	.546	4.00	±.1021	±.333

Laboratory precision Information for reporting weight loss data using the ASTM D2688 method was not available. An estimate of error in the reported weight losses was calculated according to ASTM D4210, Annex A1, Estimating Analytical Procedure Variability by Duplicate Analyses.[1] Numerous corrosion tests employing duplicate specimens have been recorded by the State Water Survey laboratory over the past 15 years. These data were used to calculate the variability in the ASTM method for 1-inch specimens. The variability in the method for 1/2-inch specimens was estimated assuming a linear relationship between the exposed surface area and the variability in weight loss. Table 21 is a tabulation of variability in the ASTM D2688 method employed during this study.

GRAPHIC EVALUATION OF THE CORROSIVITY OF THE WATER SUPPLIES

The results of corrosion tests are commonly reported in terms of a corrosion rate value such as milligrams per Square decimeter per day (mdd). When a Single corrosion rate value has been determined for a material, the implication exists that the corrosion rate is a linear function of the time of exposure. This is seldom true for potable water as corrosion rates normally exhibit an inverse relationship with time of exposure. Reliable long-range estimates of corrosion rates require that several corrosion tests be performed over a sufficient time frame for corrosion rates to stabilize.

A graphic representation of the copper corrosion rates versus exposure time observed during the study is shown in Figure 31 . For the water supplies represented, a minimum exposure period of one year is required to provide a conservative corrosion rate value for predicting the life of copper Systems. The corrosivity of the water supplies can be compared in Figure 31 which indicates sites 307, 308, and 310 being exposed to the more corrosive waters. However, the wall thickness of type L copper tube would be reduced by only 15% when exposed for 20 years to the most corrosive water at Site 308. From a materials selection viewpoint, copper would be a suitable material for installation in all of the water supplies tested.

Figure 32 represents the galvanized steel corrosion rates observed for several exposure intervals during the study. As exhibited by copper exposure in Figure 31, the least corrosive waters reach a stable corrosion rate more rapidly than the most corrosive waters. The corrosion rates reported for galvanized steel are more erratic than the copper values, partially due to the reduced precision of the laboratory procedure. Visual inspection of corrosion specimens and pipe samples indicated that a less uniform type of attack was occurring on the galvanized steel than on the copper. The spotty attack was most evident during the shorter exposure periods for the specimens. Therefore, the reported corrosion values for galvanized steel may not reflect the actual penetration of the zinc coating for galvanized steel specimens. The quality of galvanized steel pipe obtained from local plumbing supply houses for preparation of corrosion specimens has been observed to be inconsistent in appearance, coating thickness, and surface characteristics, which has been reported by others.[2] Estimating the useful life of galvanized steel pipe from corrosion rate measurements becomes very difficult due to the uncertainties involved. Figure 32 must be interpreted with care; however, corrosion rate measurements for galvanized steel apparently require 18-24 month exposure to obtain reliable Information for predicting long-term effects. With zinc coatings varying 3-6 mils in thickness, a uniform corrosion rate of 3.0 mdd would predict penetration of the coating in 5-10 years, an unacceptable value when selecting materials for plumbing installations.

A protective film of zinc corrosion products and/or calcium carbonate can reduce the rate of penetration to more acceptable values. The effectiveness of galvanized steel pipe in building plumbing Systems relies heavily on this protective film to prolong pipe life. The installation experience of galvanized steel plumbing for a particular water supply is

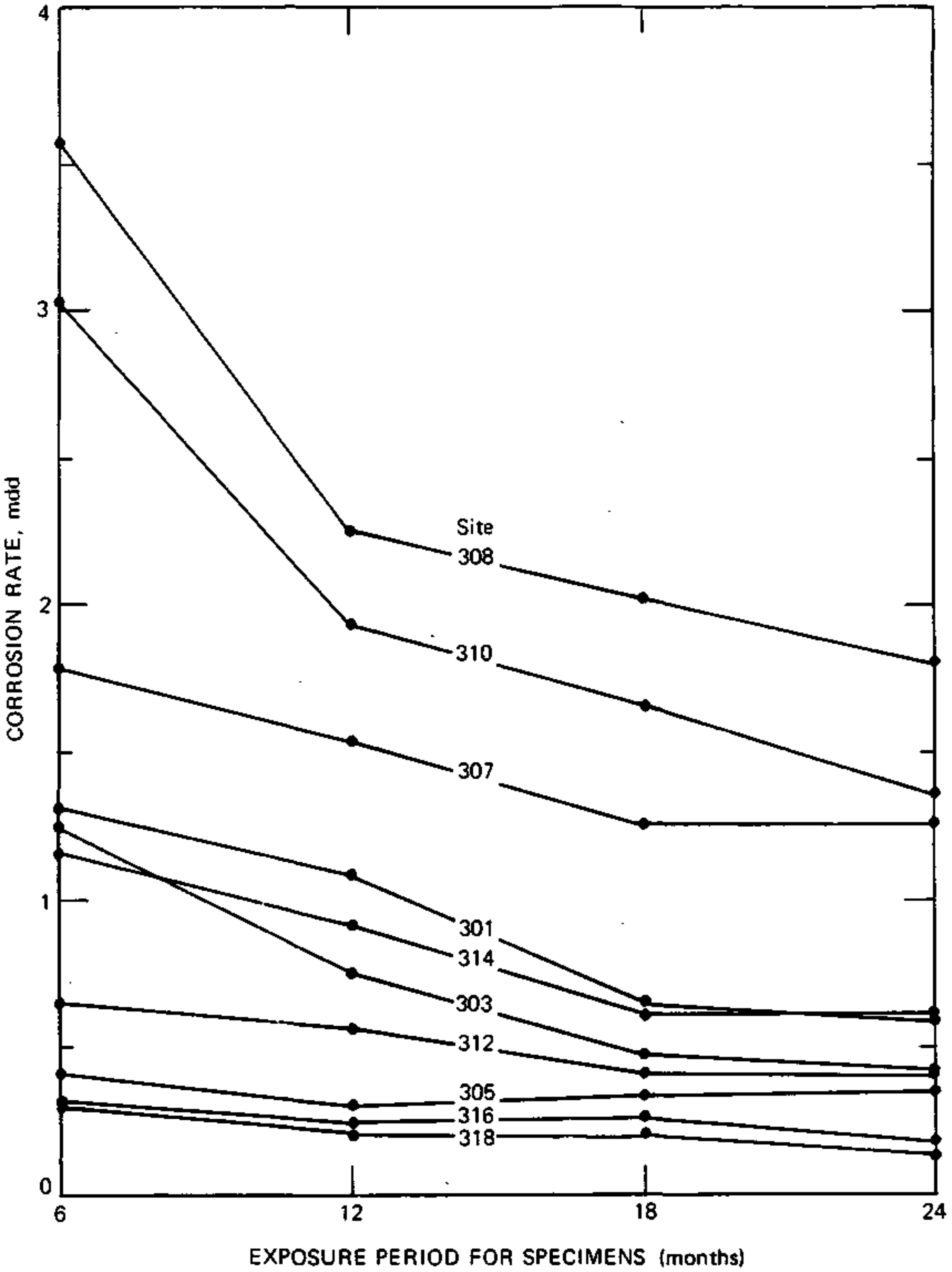

Figure 31. Time-of-exposure effect on copper corrosion rates.

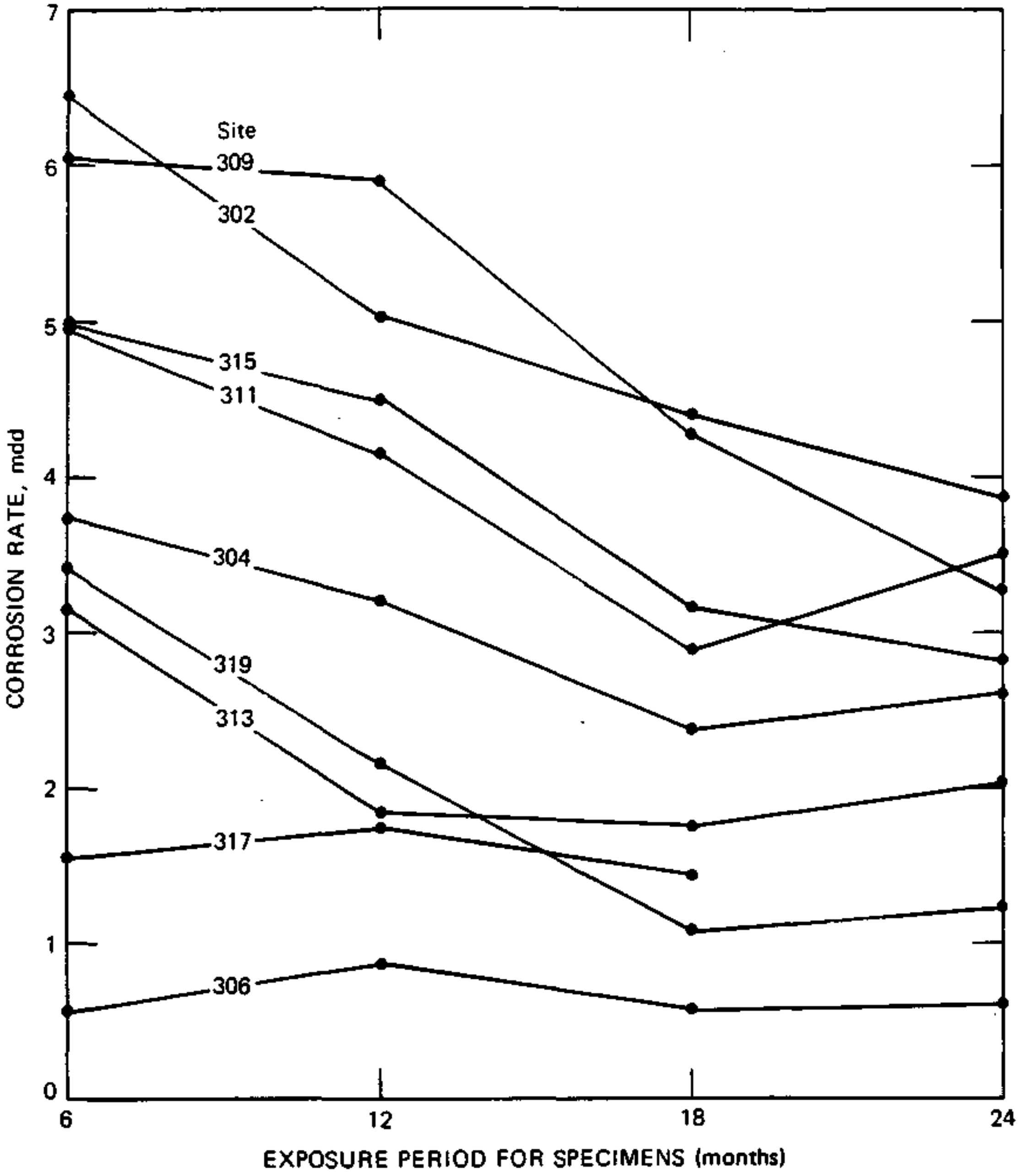

Figure 32. Time-of-exposure effect on galvanized steel corrosion rates.

often more meaningful than actual corrosion measurements in evaluating whether galvanized steel is a suitable plumbing material.

DATA EVALUATION BY THE PLANNED INTERVAL TEST METHOD

The corrosion weight loss data may be employed to differentiate between the corrodibility of metal specimens and changes in the corrosivity of water. The corrodibility of a metal usually decreases with time due to the formation of protective metal oxides; however, it may also increase if corrosion-accelerating scales are formed or the surface layer of the metal becomes more resistant. The corrosivity of the water will change when the corrosive or inhibiting agents vary in concentration. During a long-term corrosion study of public water supplies, the corrosion test method used should be capable of determining a change in corrosivity due to the effects of unidentified inhibiting or corrosive agents. The planned interval test method, described by Wachter and Treseder,[3] was employed in this study for this purpose. The method simply exposes a series of metal specimens to a liquid environment for specified time intervals. The weight loss of a specimen during an early interval of the test program is compared to the weight loss of a specimen during a later interval in the program.

The change in the corrodibility of the metal was adequately shown in Figure 31 and Figure 32. At all test sites, the corrodibility of copper or galvanized steel decreased or remained constant during the course of the study. However, the water supplies were observed to fluctuate significantly in quality during the study, and changes in corrosivity of the water supplies were anticipated.

Corrosion specimens were arbitrarily labeled A,B,C,D,E,F,G for each Site and were exposed for the intervals shown in Figure 33. Comparison of

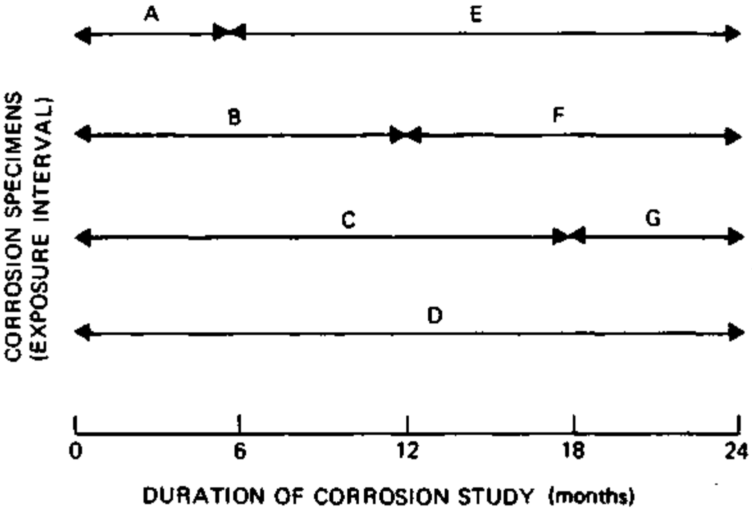

Figure 33. Planned intervals of exposure for corrosion specimens.

the weight loss data between specimens A and G, or between specimens B and F, or between specimens C and E provides the necessary Information for evaluating any changes in water corrosivity during the course of the study. Graphic representation of the data is shown in Figure 34 through Figure 43.

The corrosivity of water supply "A" toward copper specimens is displayed in Figure 34. The corrosivity of water at the water treatment plant (site 301) is not significantly different from the corrosivity of the water from the distribution system (site 303). The weight loss values for specimen G at site 301 and specimen F at site 303 appear somewhat erratic; however, the overall corrosivity of the water on specimens G, F, and C is less than the corrosivity of the water on specimens A, B, and C. This was significant, since the corrosion control program for water supply "A" was changed six months into the corrosion study. A zinc polyphosphate inhibitor was discontinued and the pH of the distribution water was increased from approximately 7.0 to 8.3 for the last 18 months. Figure 35 demonstrates the corrosivity of water supply "A" toward galvanized steel. The change in treatment has reduced the corrosion rate of galvanized steel more significantly than for copper. It also appears that the corrosivity at the water treatment plant (site 302) is greater than the corrosivity in the distribution system (site 304), although the water chemistries of the sites are not significantly different.

The corrosivity of water supply "B" on copper specimens is shown in Figure 36. Although there is no apparent difference in the water chemistries between sites 305 and 307, there is a significant difference in the corrosivities of the water at these test sites. This observation will be discussed in greater detail when velocity effects are discussed in the following sub-section. Examination of the copper weight loss data indicates that the corrosivity of water supply "B" did not change during the study.

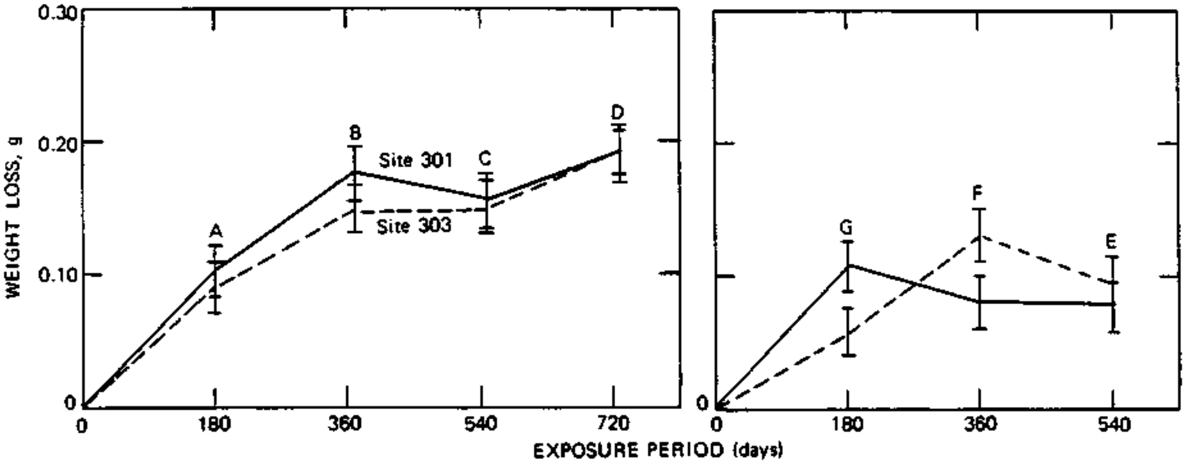

Figure 34. Corrosion of copper specimens in water supply "A".

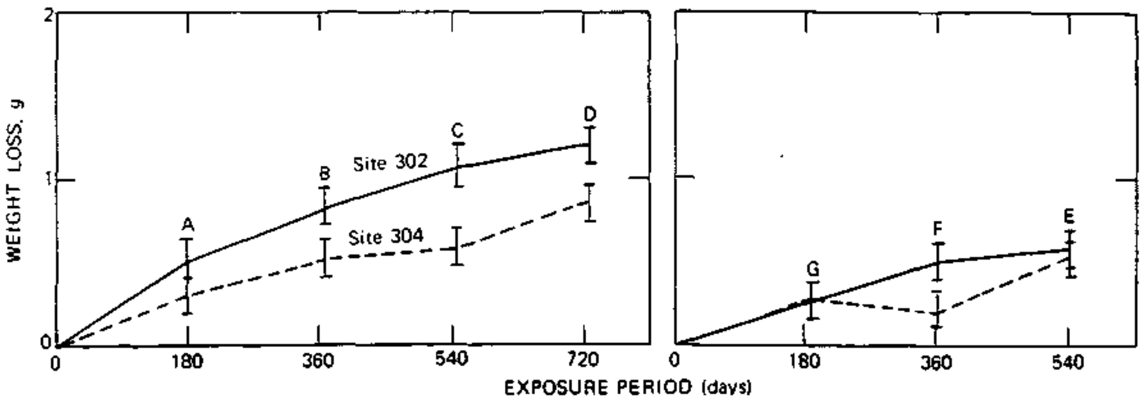

Figure 35. Corrosion of galvanized steel specimens in water supply "A",

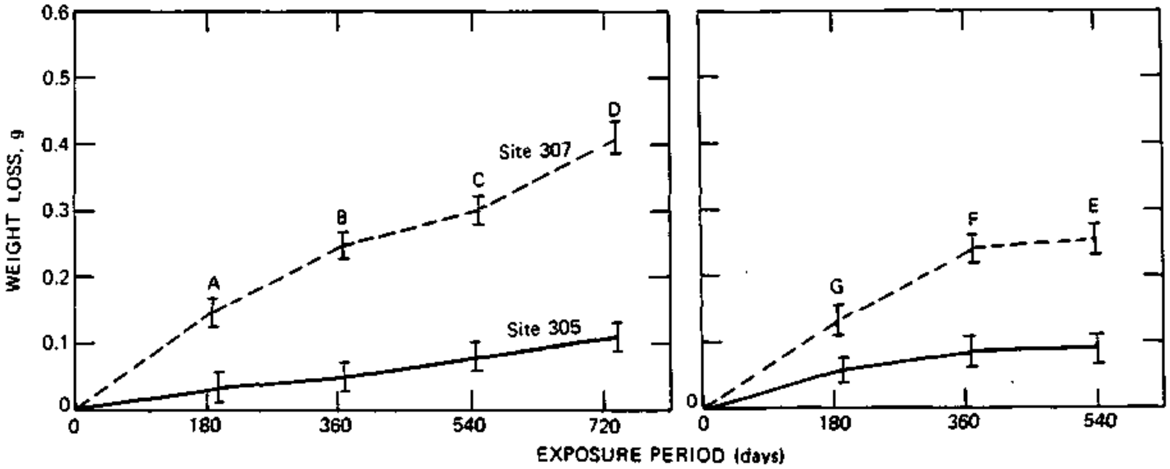

Figure 36. Corrosion of copper specimens in water supply "B".

Only one galvanized steel corrosion test site (site 306) was located in water supply "B". The corrosion weight loss data for this site are shown in Figure 37 which also indicates that the water corrosivity did not change significantly during the study. The corrosion rate at this site was the lowest value observed for galvanized steel for any of the water supplies.

Water supply "C" was selected for the study because the water corrosivity was anticipated to be high. Site 308 and site 309 were intended to reflect the corrosivity of the untreated raw water supply; however, installation difficulties dictated use of water treated to reduce corrosion in the distribution system. Site 310 and site 311 were located in the distribution System of water supply "C", receiving water of similar quality to site 308 and site 309. Figure 38 displays the corrosivity of the water experienced by copper specimens at the two locations. The corrosivity of water supply

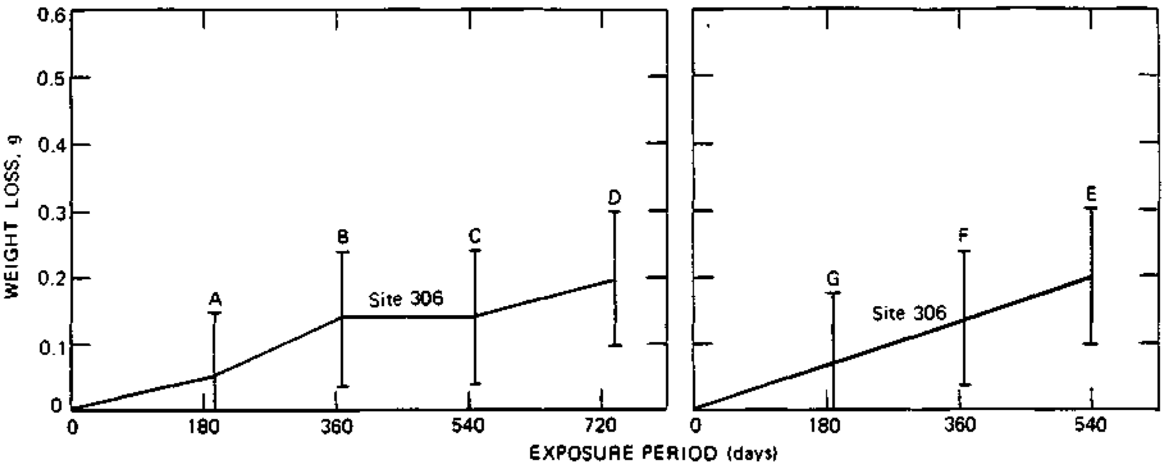

Figure 37. Corrosion of galvanized steel specimens in water supply "B".

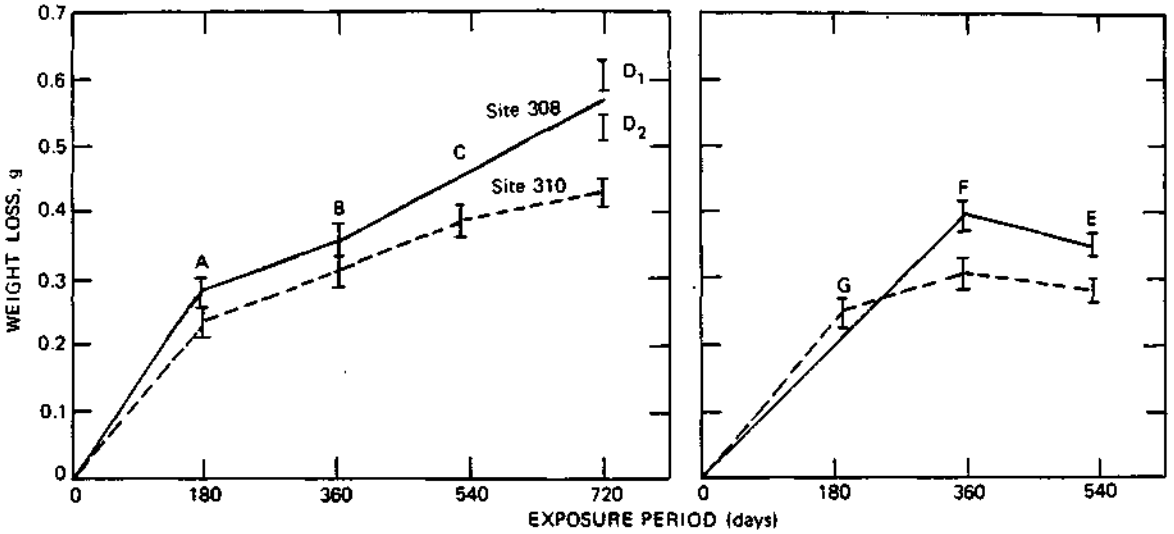

Figure 38. Corrosion of copper specimens in water supply "C".

"C" was the highest observed during the study for copper specimens. A slight difference in corrosivity was observed between the two site locations. Site 308 was occasionally exposed to the untreated water which may have contributed to the observed difference in corrosivity; however, stabilization of the water after silicate-caustic soda treatment in the distribution system is more likely to be responsible for this slight difference in corrosivity. Figure 39 shows similar corrosivity characteristics for galvanized steel specimens exposed to water supply "C". No significant change in corrosivity of the water supply was observed during the study and

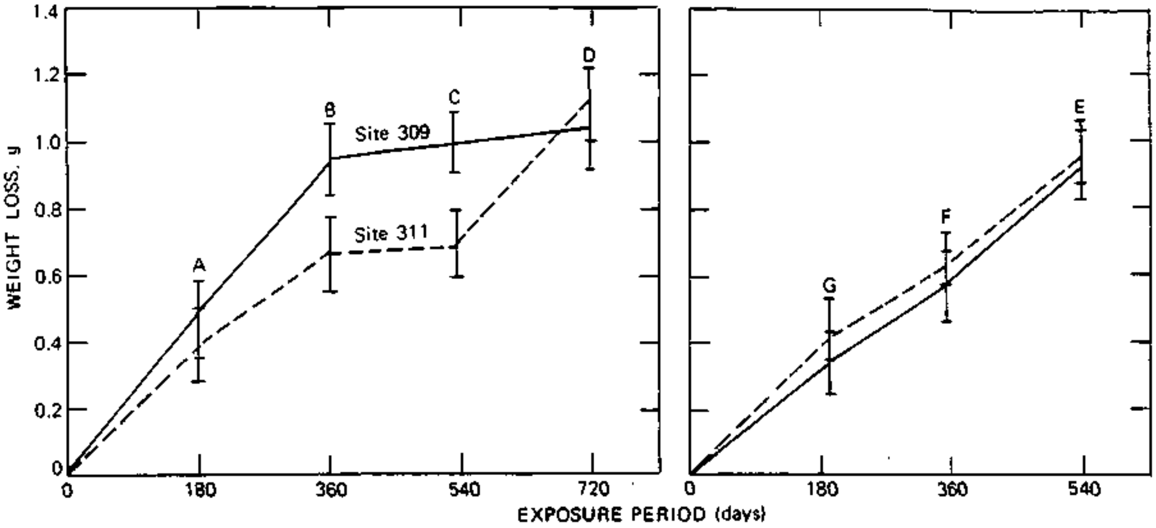

Figure 39. Corrosion of galvanized steel specimens in water supply "C".

differences in corrosivity were insignificant at the two test site locations, although two excursions in water quality occurred during this period in water supply "C". Failure of Well No. 2 occurred for 40 days early in the testing period and again during the last 45 days of the study. Well No. 1 was employed during the outages and the corrosion specimens were exposed to a major change in sulfate, chloride, and sodium concentrations (Appendix A, sites 308-11). Either the change in water quality did not alter the corrosivity significantly or the surface film on the specimens was resistant to the change in quality.

The corrosivities of water supplies "D" and "E" are compared for copper specimens in Figure 40, since only one test site was located in each water supply. A significant change in corrosivity is observed for site 314 (supply "D") which is not apparent at site 312 (supply "E"). Interpolation of the weight loss data suggests the corrosivity was reduced during the last 18 months of testing. The total copper concentration of samples from site 314 also decreased dramatically which appears to confirm the change in corrosivity. The water chemistry of samples collected from the two sites was observed to fluctuate widely throughout the study due to well pumping schedules detailed in Section 4. There is no apparent relationship between the observed change in water corrosivity for copper at site 314 and the fluctuations in water quality which were also occurring at site 312.

Examination of the weight loss data for galvanized steel specimens, shown in Figure 41 , indicates that the water corrosivity did not change during the investigation for either water supply. The corrosivity was observed to be lower at site 313 (supply "E") than at site 315 (supply "D"). At site 313, the hardness of water supply "D" has been reduced, sodium Silicate has been added, and the pH has been adjusted with caustic soda to

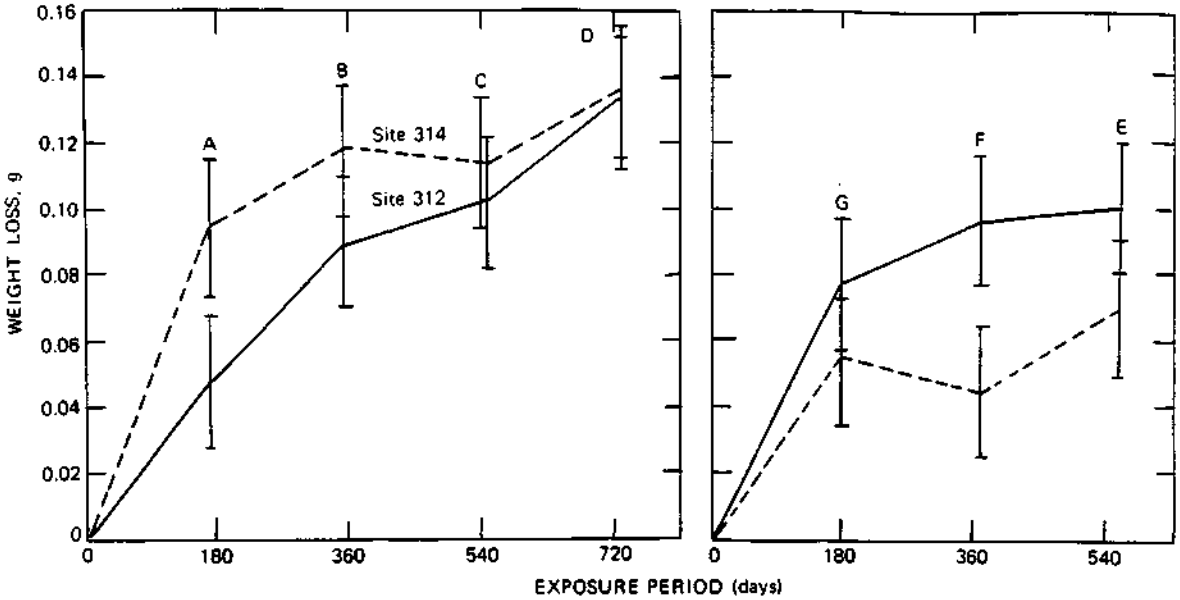

Figure 40. Corrosion of copper specimens in water supplies "D" and "E".

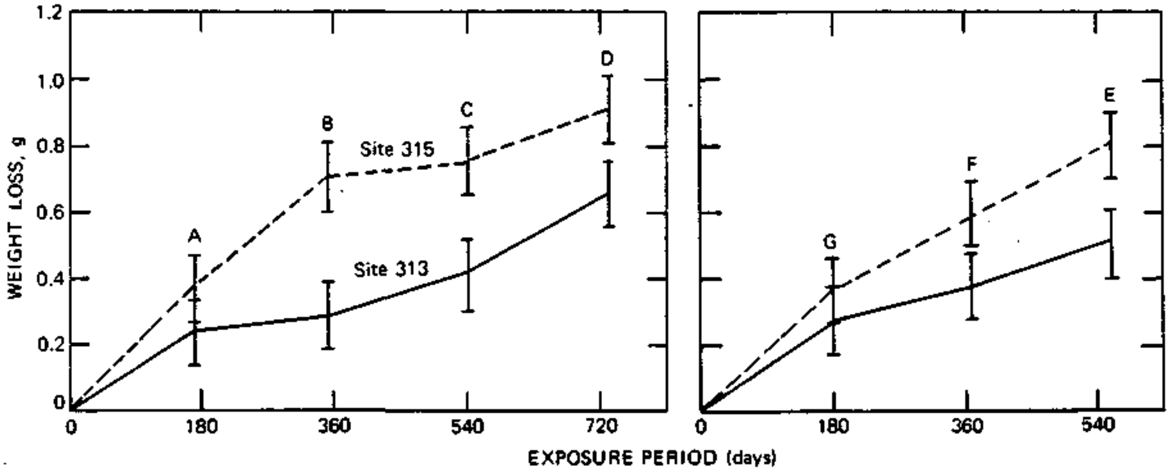

Figure 41. Corrosion of galvanized steel specimens in water supplies "D" and "E".

reduce the corrosivity. This treatment is observed to be effective for galvanized steel, although little benefit is seen for copper. Significant concentrations of polyphosphate were found at both sites which may have likely influenced the observed weight loss measurements.

Water supply "F" experienced contamination problems during the study, serious enough to require "boil" notices to the public and to drastically alter the disinfection treatment program. Chlorine residuals were increased from <1.0 mg/L combined chlorine to 3.0 mg/L free residual chlorine, while the pH of the water supply was increased from approximately 9.5 to 10.0 or above. The overall change in water quality was expected to influence the corrosivity of the water supply. However, examination of the corrosion weight loss data by the planned interval method as shown in Figures 42 and 43 does not indicate a change in corrosivity. The corrosion weight losses of copper and galvanized steel specimens in water supply "F" were among the lowest values observed; therefore the variability in the weight loss method overshadows any minor change in corrosivity that may have occurred. Also, the weight loss data from sites 316 and 317 are not for the

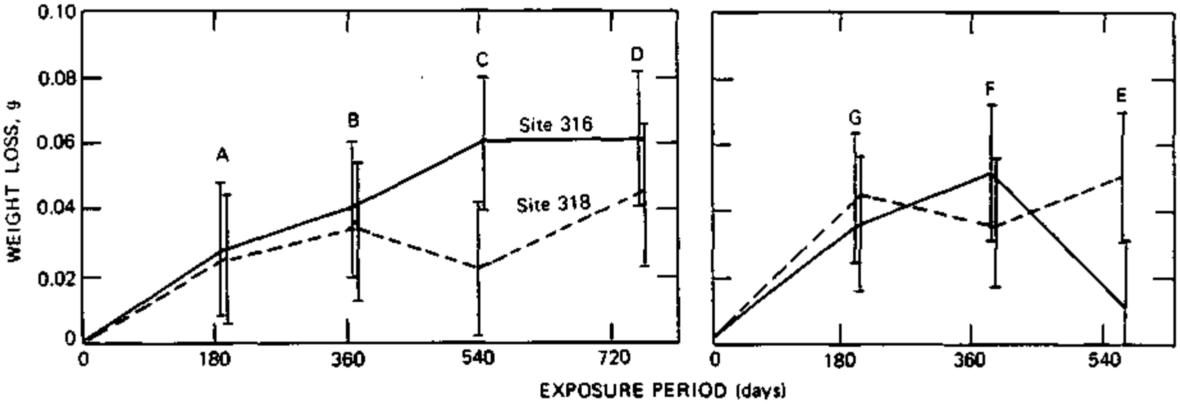

Figure 42. Corrosion of copper specimens in water supply "F".

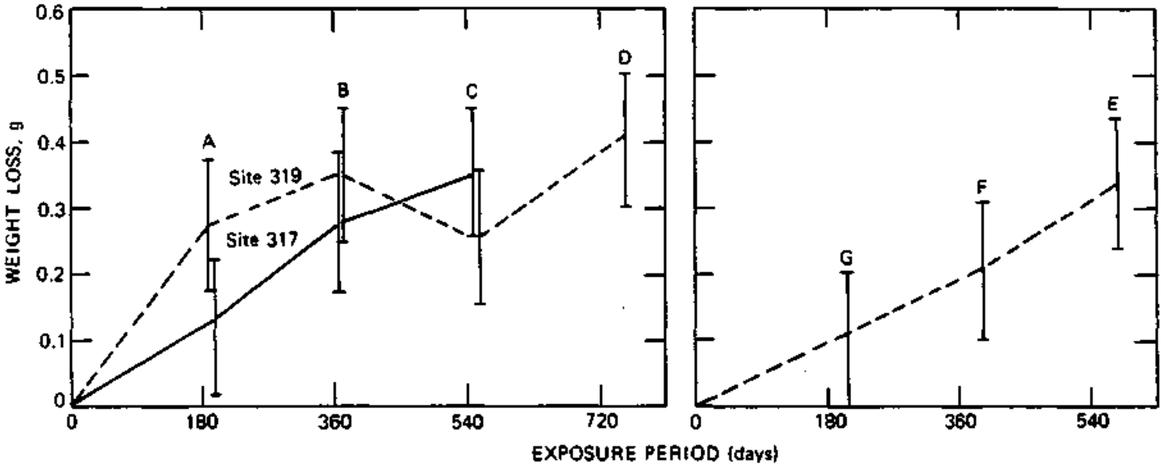

Figure 43. Corrosion of galvanized steel specimens in water supply "F".

same installation period as those from sites 318 and 319, making a direct comparison of changes in corrosivity impossible. The overall oorrosivity of water supply "F" at the water treatment plant site and at a site some distance away was not significantly different for either copper or galvanized specimens.

WATER VELOCITY EFFECTS ON COPPER

Excessive water velocity through copper plumbing materials will cause rapid thinning of the copper tube wall which is normally first observed near obstructions or bends in the tubing. This type of attack is known as erosion-corrosion. The National Association of Corrosi'on Engineers (NACE) has recommended a maximum design water velocity of 1.22 m/s (4.0 f/s) for type K copper tube and suggests that lower design velocities be employed for type L and type M copper tube because of reduced wall thickness.[4] The effect of water velocity on the erosion-corrosion of copper tube may be compounded when the water chemistry is particularly aggressive.

The instantaneous peak water velocities for the corrosion test sites were expected to be less than 0.9 m/s through both the simulated test loops and the actual home installations. During the corrosion study, the 24-hour average water velocities for the copper test sites were observed to range from .03 m/s to .12 m/s. However, the average velocities were not representative of the instantaneous peak velocities experienced by the corrosion specimens. The peak velocities for the simulated test loops were estimated to be 12-20 times the reported water velocities. Therefore, the instantaneous peak water velocity may have exceeded 1.22 m/s at sites 308, 310, and 316, where simulated test loops were installed. Furthermore, by applying this ratio to the corrosion test sites in homes, the peak water velocity may also have exceeded 1.22 m/s at sites 301 and 307.

Since the peak velocity experienced by the corrosion specimens was not actually determined, a plot of the copper corrosion rate versus the water velocity for each site was made to graphically examine the influence of water velocity on the observed corrosion rates (Figure 44). The 24-hour average velocity was adjusted to reflect the actual velocity averaged over the interval when water was actually used at each site. This period varied from 8 to 18 hours between sites. Figure 44 indicates that the highest copper corrosion rates occurred at the highest water velocities. The 6-month, 12-month, and 18-month corrosion rate data, which are not shown, also displayed the same characteristics.

The copper corrosion rates for sites 307, 308, and 310 appear to be influenced by the higher water velocity. The instantaneous peak velocity to adjusted velocity ratio was calculated for the simulated test loops based on a 6.5 minute timer setting and was estimated to be 9.2 times the adjusted average velocity. Multiplying the adjusted average velocity for each site by this estimated factor indicates that sites 307, 308, and 309 exceeded the NACE standard of 1.22 m/s.

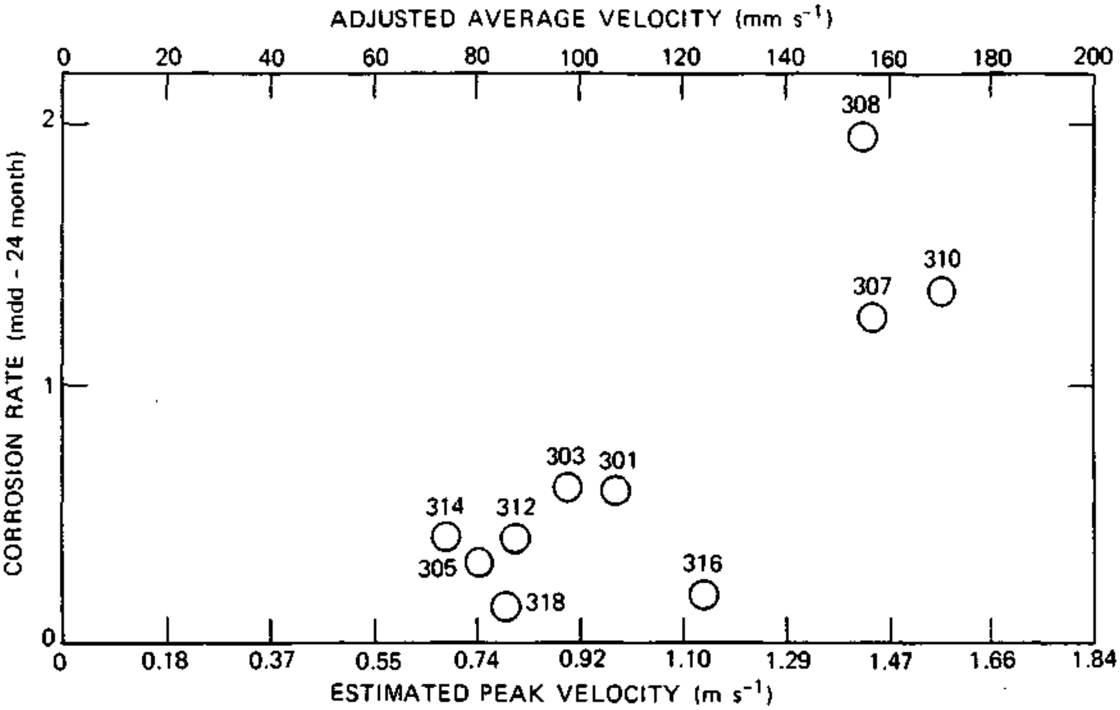

Figure 44. Effect of water velocity on corrosion rate of copper.

Visual examination of the corrosion specimens and copper pipe sections did not show evidence of erosion-corrosion attack sufficient to remove protective oxide coatings although velocity effects were observed on the surface of pipe sections removed from site 307. Striations of the thin blue film coating the pipe wall appeared to be due to turbulence around bends and fittings. The velocity effect on copper tubing apparently was limited to an increase in the general corrosion rate and was not sufficient to cause localized attack of the copper.

Mattsson[5] discusses the velocity effect on copper tube and presents regulations of the Swedish Board of Physical Planning and Building for maximum flow rates in copper tube in respect to temperature, type of installation, and accessibility (Table 22). He reports that small diameter copper tubes can tolerate higher flow rates than large diameter tubes and that continuous flow is more likely to cause erosion-corrosion than intermittent flow.

The corrosion rates observed in this study suggest that the corrosion of copper increases because of an increase in water velocity prior to the actual eroding of the surface film and exposure of bare metal. The more conservative NACE standard of 1.22 m/s, therefore, may be more reliable in predicting the onset of corrosion due to velocity, while the Swedish regulations may be more valid in predicting the actual erosion of surface films.

TABLE 22. SWEDISH FLOW RATE REGULATIONS FOR COPPER TUBE

Type of installation	Accessibility of piping	Maximum permissible flow rate (m/s) at temperature 10°C	50°C	70°C	90°C
Distribution main	Exchangeable	4.0	3.0	2.5	2.0
	Nonexchangeable	2.0	1.5	1.3	1.0
Service lines	Exchangable	16.0	12.0	10.0	8.0
	Nonexchangeable	4.0	3.0	2.5	2.0
Continuous circulation		2.0	1.5	1.3	1.0

CORROSION 0F PLUMBING MATERIALS DURING LONG-TERM CURTAILMENT 0F WATER USAGE

The plumbing Systems of newly constructed homes and other buildings are often exposed to water for long periods when water usage is very low and the materials have the highest corrosion potential. Plumbing Systems in older homes experience similar exposure when residents leave for extended periods for vacations or move to another home. The consumption of water during the nonuse period may lead to exposure to increased metal concentrations due to corrosion of the plumbing materials.

The unanticipated failure of the timer mechanism Controlling the water usage at corrosion test sites 316 and 317 provided an opportunity to observe the influence of water stagnation on the corrosion rates of copper and galvanized steel. The long delay experienced in replacing the timer mechanism resulted in four corrosion specimens of each material being exposed to a very low throughput of water for 113 days. The specimens were removed and new specimens were installed after the simulated corrosion test loop was operating as designed. The corrosion rates of the two sets of specimens were compared to provide additional Information concerning the influence of water usage on corrosion. The corrosion rate data are presented in Table 23.

The corrosion of copper was not influenced by the usage of water in this particular water supply. However, the galvanized steel specimens exposed to stagnant water experienced appreciably higher corrosion rates than when exposed to the intermittently flowing water. Visual inspection of the specimens exposed to the stagnant water revealed scattered large mounds of white deposit and numerous small diameter pits less than .005 inch in depth. The pitting occurred along the bottom half of the horizontally orientated specimens. The specimens exposed to intermittently flowing water did not experience the pitting and the white deposit was more uniformly distributed over the surface.

The corrosion rates for copper and galvanized steel in water supply "F" were among the lowest values observed during the study; however, the metal

TABLE 23. EFFECT OF WATER FLOW ON CORROSION RATE

Site no.	Plumbing material	Flow condition	Specimen corrosion rates (mdd) No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
317	Galv. steel	No flow*	5.2	2.0	7.4	3.2			
		Intermittent flow#	1.6	1.8	1.5				
316	Copper	No flow*	0.23	0.35	0.33	0.34			
		Intermittent flow#	0.33	0.25	0.25	0.19	0.05	0.30	0.39

* - 113 day exposure
\# - 189-755 day exposure

TABLE 24. EFFECT OF WATER FLOW ON METAL CONCENTRATIONS IN WATER

Site no.	Plumbing material	Flow condition	Exposure period (days)	Total metal concentration (mg/L) Cd	Pb	Cn	Zn	Fe	Mn
317	Galv. steel	No flow	15	.009	0.77	0.88	67.6	18.3	0.22
		No flow	28	--	0.71	2.82	11.2	41.3	0.20
		Intermittent flow	120	--	0.00	0.00	0.2	0.1	0.02
316	Copper	No flow	15	.006	11.00	1.69	70.2	14.3	0.17
		No flow	28	—	2.24	0.34	78.0	7.4	0.11
		Intermittent flow	120		0.01	0.00	0.2	0.1	0.01

concentrations were very high in water samples collected during the first 28 days when no water flow was occurring. Two sets of samples were collected during this period in which total cadmium, lead, zinc, copper, iron, and manganese concentrations were determined. The analytical data for these samples are shown in Table 24. Although the total concentrations are highly variable, the results reveal the potentially high values which can occur in new plumbing Systems where water usage is limited. Insoluble corrosion products are the likely major constituent of the total concentrations, with significant soluble species also present. Further investigation is required to determine the speciation of the metal concentrations.

The lead and copper concentrations observed at site 317 are apparently due to the corrosion of the brass sampling valve, since no other copper alloy materials were present in the simulated test loop. The zinc concentrations found at site 316 may also be evidence that the sampling valve is a major contributor to the metal concentrations, although the transport of zinc could also occur from the galvanized steel section of the loop. The lead concentrations at site 316 are much higher than at site 317, which indicates that the lead-tin solder used in the copper test loop is a significant contributor to the observed metal concentrations.

A thorough flushing of new plumbing installations is obviously required to remove suspended and soluble corrosion products prior to consumption of the water. Metal concentrations in water will tend to be at higher levels in newly installed copper or galvanized steel plumbing until the corrosion mechanisms reach an equilibrated state. This process is very slow in potable water and was observed at several sites during this study. Preconditioning treatment may be necessary to reduce the corrosion of plumbing Systems by some water supplies.

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SECTION 10

STATISTICAL ASSOCIATION ANALYSES

INTRODUCTION

The chemical and physical Information gathered from the sample collection and corrosion specimens can be separated into two general categories, the independent and dependent variables, for the purpose of statistical analysis of the data. Depending upon the exact question to be addressed, different combinations of dependent and independent variables could be selected. Tables 25, 26, and 27 list the set of variables used in the attempt to relate observed trace metal levels to major water quality characteristics or to relate observed corrosion specimen weight losses to the major chemical characteristics.

TABLE 25. ANALYTICAL INDEPENDENT VARIABLES* CONSIDERED IN THE REGRESSION ANALYSES FOR WEIGHT LOSS CORRELATIONS

Symbol	Independent variable
PH	pH (Standard units)
ALK	Total alkalinity ($CaCO_3$)
MG	Magnesium (Mg)
CA	Calcium (Ca)
NA	Sodium (Na)
K	Potassium (K)
CL	Chloride (CD
SO4	Sulfate (SO_4)
NO3	Nitrate (NO_3)
PO4	Orthophosphate (PO_4) = (PO4T - PO4X)
PO4X	Polyphosphate (PO_4)
SIO2	Silica (SiO_2)
TDS	Total dissolved solids
TOC	Total organic carbon (C)
CL2F	Residual free chloride (Cl_2)
CL2T	Residual total chlorine (Cl_2)
DO	Dissolved oxygen (O_2)
TC	Temperature, flowing (°C)
TCS	Temperature, standing (°C)
VEL	Velocity (mm/s)

* Concentrations are expressed in mg/L, except as noted

TABLE 26. COMPUTED INDEPENDENT VARIABLES, DERIVED USING THE FLOWING SAMPLE AND AN ENHANCED VERSION OF THE WATSPEC COMPUTER PROGRAM*

Symbol	Computed independent variables
FREE C02	mg/L free carbon dioxide content, computed
LARRAT	Larson's ratio, which includes SO4, CL and ALK. A possible corrosion tendency indicator
PHS	Computed hypothetical pH for calcium carbonate Saturation
PMTIC	-log (total inorganic carbon concentration, in moles/L)
MGLTIC	Total inorganic carbon concentration in mg $CaCO_3$/L
BETA	Buffer intensity, equivalents/pH unit
I	Ionic strength
SIARAGON	Saturation index of aragonite form of calcium carbonate
SICALCIT	Saturation index of calcite form of calcium carbonate
SICHAL	Saturation index for microcrystalline silica form
SIDOLO	Saturation index for $(Ca,Mg)(CO_3)_2$, dolomite
SIGYPSUM	Saturation index for calcium sulfate (gypsum) $CaSO_4 \cdot H_2O$
SIHMG	Saturation index for hydromagnesite, a hydrated magnesium carbonate
SIMAGNES	Saturation index for magnesium carbonate (magnesite)

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* Wigley, T. M. L. WATSPEC: -. A Computer Program for Determining the Equilibrium Speciation of Aqueous Solutions. British Geomorphol. Res. Group Tech. Bull., 20 (1977).

TABLE 27. ANALYTICAL DEPENDENT VARIABLES FOR REGRESSION ANALYSES OF TRACE METAL CONCENTRATI0NS*

Symbol	Dependent variables
CUR	Copper, running sample, mg/L Cu
CUS	Copper, standing sample, mg/L Cu
ZNR	Zinc, running sample, mg/L Zn
ZNS	Zinc, standing sample, mg/L Zn
PBR	Lead, running sample, mg/L Pb
PBS	Lead, standing sample, mg/L Pb
FER	Iron, running sample, mg/L Fe
FES	Iron, standing sample, mg/L Fe
MNR	Manganese, running sample, mg/L Mn
MNS	Manganese, standing sample, mg/L Mn
GMSLOST	Weight loss of specimen, g
MPY	Corrosion rate, mpy

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* Cadmium was deleted from statistical analysis because all values were at or below the detection limit.

The modeis tested in this project consisted only of untransformed multiple linear regressions. The SAS statistical package[1] was used for these analyses. Three classifications were investigated:

1. The relationship of the trace metals at each site to the independent variables at each site
2. The relationship of the trace metals to the independent variables among sites
3. The relationship of the measured weight loss to the measured water quality variables among sites

Sample concentrations below the detection limits were set to the detection limits before the statistical analyses were performed. This is known to be somewhat biased, but no practical alternative with demonstrably better accuracy was known. With the elimination of cadmium from the statistical computations, only a relatively small number of trace metal analyses were below the detection limits of the methods used. Thus, the impact of this assumption will be greatest with independent variable constituents such as orthophosphate or nitrate, which were frequently present at low levels and for which the analytical methods were relatively poor.

METALS ESTIMATED BY WATER QUALITY VARIABLES WITHIN AND BETWEEN SITES

For each site and metal concentration variable, a stepwise regression program was run to choose a model with the metal concentration as the dependent variable and the water quality variables as the independent variables. PROC STEPWISE in SAS with the default option "STEPWISE" was used.[1] Because there are 19 sites and 10 trace metal concentration variables, 190 modeis were generated. A significance level of 0.15 was selected as the acceptance criterion for each independent variable in the model.

Tables 28 through 33 show the variables found to be significant in these modeis, and indicate whether they are associated with increasing or decreasing concentrations of copper, zinc, and lead. The modeis for iron and manganese are not included because the high levels in many of the source waters make finding true relationships with pipe loop corrosion impossible. In these modeis, negative signs indicate an association with decreasing metal concentrations, and positive signs indicate an association with increasing concentrations. For example in Table 28 at site 301 , higher levels of nitrate in running samples are associated with increasing copper levels.

No variable appeared in all of the modeis, and many variables appeared in some modeis with a positive sign and others with a negative sign. Overall, there was little consistency, and few data indicative of the chemical processes of corrosion or inhibition of metal leaching can be inferred.

TABLE 28. VARIABLES FOUND SIGNIFICANT IN PREDICTING THE CONCENTRATION OF COPPER IN THE RUNNING SAMPLES FROM EACH SITE

Site	Correlation coefficient (Model r^2)	Model terms*
		Copper pipe loop
301	0.15	+ NO3
303	0.55	+NO3, +ALK, -PH, -CL2T
305	0.33	+ALK, +TC, -CL2T
307	0.26	+SIO2, -PH, -CL
308	0.39	+SIO2, -CL2F, -NO3
310	0.16	+TC, -CL2T
312	0.13	+CL2T
314	0.42	+PH, +CL, -NA
316	0.09	+TC
318	0.19	+SO4, -CL, -NO3
All	1 .00	+CL, -MG, -K
		Galvanized pipe loop
302	0.33	+K, +TC, -CL
304	0.27	-CL2F, -PH, -S04
306	0.20	+MG, -NA, -TDS
309	0.36	+SI02, -CL2F
311	0.48	+TC, +N03, -CL2F
313	0.31	-CL
315	0.43	+PH, +NO3, +CL2F, -TC
317	0.17	+TC, +MG, -CL2T
319	0.34	+PH, +K, -CL, -CA
All	1 .00	+PO4X, -CL, -K, -TDS, -BETA, -LARRAT

* Positive terms are associated with increasing copper concentrations and negative terms are associated with decreasing copper concentrations. Symbols are explained in Tables 25 and 26.

TABLE 29. VARIABLES FOUND SIGNIFICANT IN PREDICTING THE CONCENTRATION OF COPPER IN THE STANDING SAMPLES FROM EACH SITE

Site	Correlation coefficient (Model r^2)	Model terms*
	Copper pipe loop	
301	0.28	+CL, +ALK, +SO4
303	0.88	+CA, -PH, -MG, -CL2T
305	0.06	+ALK
307	0.34	+TCS, -PH, -NA, -CL
308	0.09	+K
310	0.34	+NO3, +TCS, -CL2F
312	0.30	+TC, -PH, -MG
314	0.16	+SIO2, -SO4
316	0.12	+TCS
318	0.31	+CL2T, TCS
All	0.97	+CL, +NA
	Galvanized pipe loop	
302	0.06	+K
304	—	None
306	0.16	-CL2T, -NA
309	0.37	+SIO2, -PH, -CL2F
311	0.25	+MG, -CL2T
313	0.29	+ PH, CA, -SIO2, -NA
315	0.23	+PH, +CL2T
317	0.13	+TCS
319	0.14	+TCS, -CL2T
All	0.85	+CL

* Positive terms are associated with increasing copper concentrations and negative terms are associated with decreasing copper concentrations. Symbols are explained in Table 25.

TABLE 30. VARIABLES FOUND SIGNIFICANT IN PREDICTING THE CONCENTRATION OF ZINC IN THE RUNNING SAMPLES FROM EACH SITE

Site	Correlation coefficient (Model r^2)	Model terms*
		Copper pipe loop
301	0.17	-PH, -MG
303	0.71	+CA, -CL2T, -PH, -TC
305	0.21	+CL, -PH, -CL2T
307	—	None
308	0.33	+SIO2, -CL2T, -NO3
310	0.17	-CL2F
312	0.45	+TC, +NA, + ALK, -PH, -S04
314	0.29	+TC, +MG, +ALK
316	0.10	-CL2T
318	0.14	-NA
All	0.92	+K
		Galvanized pipe loop
302	0.06	-S04
304	0.25	-NA
306	0.71	+K, +CL2T, -PH, -SIO2, -TC, -TDS
309	0.07	-K
311	0.28	-N03, -CL2T
313	0.05	-TC
315	—	None
317	—	None
319	—	None
All	1.00	+PMTIC, +CL2F, +CL, +TC, +ALK, -LARRAT, -K, -NA

* Positive terms are associated with increasing zinc concentrations and negative terms are associated with decreasing zinc concentrations. Symbols are explained in Tables 25 and 26.

TABLE 31. VARIABLES F0UND SIGNIFICANT IN PREDICTING THE CONCENTRATION OF ZINC IN THE STANDING SAMPLES FR0M EACH SITE

Site	Correlation coefficient (Model r^2)	Model terms*
		Copper pipe loop
301	0.51	+MG, +CL, + NA, +CA, -NO3, -SIO2, -TCS
303	0.80	+CA, +SO4, -CL2T, -PH, -TCS
305	0.30	+K, -PH, -CL2F, -SO4
307	0.11	-NA
308	0.26	+SIO2, -CL2F
310	0.52	+MG, +TCS, +TDS, -CA, -CL
312	0.52	+CL2T, +TCS, +TDS, +SO4, -MG, -SIO2, -NA
314	0.44	+PH, +NO3, +SIO2, +TCS
316	0.19	-K, -MG
318	0.24	+SIO2, -TDS
All	0.85	+K
		Galvanized pipe loop
302	0.61	+N03, +TCS, -PH, -NA
304	0.42	+TDS, -PH
306	0.26	+ALK, -CL2T, -S04
309	0.37	NA, -CL2T, -N03, -K
311	0.30	+TCS, +MG
313	0.21	+CA, -SI02, -NA
315	0.40	+CL2F, +CL2T, +SI02, +CL
317	—	None
319	—	None
All	0.91	+LARRAT, +TCS, +MG

* Positive terms are associated with increasing zinc concentrations and negative terms are associated with decreasing zinc concentrations. Symbols are explained in Tables 25 and 26.

TABLE 32. VARIABLES FOUND SIGNIFICANT IN PREDICTING THE CONCENTRATION OF LEAD IN THE RUNNING SAMPLES FROM EACH SITE

Site	Correlation coefficient (Model r^2)	Model terms*
		Copper pipe loop
301	0.10	-PH
303	0.66	+SIO2, +CL, +TC, +TDS, -CL2T, -NA
305	0.16	-CL2T
307	0.34	+TDS, -PH, -TC
308	0.11	-TC
310	0.07	+CL
312	0.25	+SIO2, -PH, -CL2T
314	0.47	+CL2T, +CA, -SO4
316	0.09	+TC
318	0.06	+SO4
All	1.00	+PO4X, +CL2F, -PO4, -FREECO2, -TC
		Galvanized pipe loop
302	0.11	+NA, +K
304	0.16	-CL2F
306	—	None
309	0.15	-K
311	0.42	+MG, -ALK
313	0.27	+CL2F, -CL2T, -ALK, -SO4
315	0.33	+NO3, -CL2T, -TC, -MG
317	0.31	+TDS, -CL2F, -SIO2, -SO4
319	—	None
All	0.67	+K

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* Positive terms are associated with increasing lead concentrations and negative terms are associated with decreasing lead concentrations. Symbols are explained in Tables 25 and 26.

TABLE 33. VARIABLES FOUND SIGNIFICANT IN PREDICTING THE CONCENTRATION OF LEAD IN THE STANDING SAMPLES FROM EACH SITE

Site	Correlation coefficient (Model r^2)	Model terms*
		Copper pipe loop
301	0.28	+CL, +ALK, +SO4
303	0.61	+K, +CA, -MG, -NO3, -ALK
305	0.45	+ ALK, -PH, -CA, -SO4
307	0.14	+TCS
308	0.32	-K, -ALK
310	0.17	+PH, +TCS, -SIO2
312	0.62	+CL2F,+CA, +SIO2, +CL, +TDS, -PH, -MG
314	0.55	+PH, +TDS, -K, -SO4
316	0.09	+TCS
318	0.06	+TCS
All	1.00	+PO4X, +CA, -BETA, -TCS, -SO4
		Galvanized pipe loop
302	0.45	+MG, +CL2T, -SIO2
304	0.34	+TDS, -NO3, -PH
306	0.35	+CL, +ALK, -K, -CL2F, -SI02
309	—	None
311	0.38	+TDS, -K
313	0.10	+CL2F
315	0.23	+TCS, -CL2F
317	0.10	+TCS
319	0.53	+K, +TCS, +N03, +ALK, -SI02
All	0.97	+TCS, +CA, +CL

* Positive terms are associated with increasing lead concentrations and negative terms are associated with decreasing lead concentrations. Symbols are explained in Tables 25 and 26.

In order to look at the case that is perhaps most interesting, that of predicting metal levels at different sites from a Single model, the independent variable data had to be pooled. For each site, the average of each metal concentration and water quality variable was calculated. For each pipe type (copper and galvanized steel), a stepwise regression was run with the average metal concentrations as dependent and the average water quality variables as independent variables. The "observations" were sites. As before, the PROC STEPWISE procedure[1] with the option "STEPWISE" was used. The data are listed in Tables 28 through 33 under the site "All."

One significant problem inherent in this approach is that there is a small number of observations (9 or 10 sites) and a larger number of variables (34). The main question to ask about these models is whether the presence of particular variables in a particular model is due to actual scientific truth or just random Variation. Part of the difficulty lies in the large number of water quality variables that have to be dealt with. To explain possible problems, consider the following idealized Situation.

Suppose we have 34 orthogonal variables $x_1, \ldots, X_{34}$ (e.g., the water quality variables) with which we want to explain variable y (e.g., the metal concentrations or corrosion rates) using a linear model of the form

$$y = \alpha + \sum \beta_i x_i + e$$

Choosing a model involves choosing a subset of the x_i's for the summation. Suppose that in reality y is independent of the variables x_i, that is, the true model is

$$y = \alpha + e$$

What model is the statistical procedure used likely to pick? For simplicity, suppose we are just going to choose from the models with at most one x_1 in them. Thus, only those of the form

$$y = \alpha + \beta_i x_i + e$$

are considered, plus the true model. The procedure is to fit each model using the data. If none of the 34 models has a β_i which is determined to be significantly different from zero at the α level, then we take the true model. If one or more of the models has a significant β_i, then we take the model with the most significant β_i. Taking $\alpha = .15$ (as we did in our models), we have that

$$P\ (\text{We will not choose the true model}) = 1 - (1 - \alpha)^{34} = .996\ (99.6\%)$$

Thus, we are almost certain of finding a model with a significant β_i, even though the true model has no β_i's.

The idealized model is not exactly what we have (our x_i's are not orthogonal, and we consider models with one or more x_i's), but it serves to give an idea of what can happen.

Alternatively, one may wonder how many variables x_i would be expected to appear in a model. For the idealized model, we would expect 34 (.15) = 5, even though in reality we should have 0. Looking at the metal concentration versus water quality variables within sites, we find that there is an average of only about 2.4 x_i's per model.

Thus, there is not much evidence that the models found are reflective of mechanisms or extents of chemical reactions rather than random associations.

ESTIMATION OF WEIGHT LOSS FROM WATER QUALITY: STATISTICAL BACKGROUND

The actual weight loss of the corrosion specimens was selected as the most important parameter indicative of the corrosive nature of the waters, as was discussed in an earlier section. The experiment design dictated a complicated procedure to effectively deal with the data, which is summarized below.

For each pipe type, we are interested in a regression model with weight losses of the specimens as the dependent variables and the water quality variables as the independent ones. The smallest time period over which weight loss was measured was six months, so the observations for this section are averages for each site and six-month period. Thus, there are four observations from each site. The averages for the weight losses cannot be directly calculated from the data because the weight losses for some specimens were measured only after 12, 18 or 24 months. Thus, the first task was to obtain for each site and six-month period an estimate of weight loss, as well as an estimate of the variability of the weight losses.

The actual observed weight losses y for the seven pipe specimens at one site can be represented as follows:

```
             Six-month period
First    Second    Third    Fourth
--y1--|------------y2----------
------y3--------|-------y4------
----------y5------------|----y6-
---------------y7---------------
```

Here y_1 is the weight loss for the first specimen, which was in the study for the first six-month period; y_2 is the weight loss of the secpnd specimen, which was in the study for the last three six-month periods, etc. For each specimen, the weight loss y_i is actually a sum of weight losses y_{ij}, where y_{ij} is the weight loss of specimen i during time period j. These weight losses are represented as follows:

Six-month period

First	Second	Third	Fourth
-y11	-y22--	--y23--	-y24-
-y31	-y32-	-y43--	-y44-
-y51	-y52-	-y53-	-y64-
-y71	-y72--	-y73-	-y74-

Thus, $y_1 = y_{11}$, $y_2 = y_{22} + y_{23} + y_{24}$, etc. Notice that y_2 is measured, but y_{22}, y_{23}, and y_{24} are not. The model for the y_{ij}'s is

$$y_{ij} = \beta_j + \gamma z_{ij} + e_{ij}$$

where β_j is the average weight loss during time period j, e_{ij} is the error, and γz_{ij} is a term taking into account the fact that specimens show a decreasing corrosion rate as time proceeds. For y_{ij}, the variable z_{ij} is defined as follows:

$$z_{ij} = \begin{cases} 3 & \text{if } j \text{ is the first time period for specimen } i \\ 1 & \text{" " " " second " " " " "} \\ -1 & \text{" " " " third " " " " "} \\ -3 & \text{" " " " fourth " " " " "} \end{cases}$$

The Y is the coefficient which measures the decrease in corrosion rate over time. We assume the e_{ij}'s are distributed normally with means 0 and variances σ^2

As only the y_i's were observed, we have to find the model for these by adding up the models for the y_{jj}'s. This model is as follows:

$$\begin{aligned}
y_1 &= \beta_1 + 3\gamma + e_1 \\
y_2 &= \beta_2 + \beta_3 + \beta 4 + 3\gamma + e_2 \\
y_3 &= \beta_1 + \beta_2 + 4\gamma + e_3 \\
y_4 &= \beta_3 + \beta_4 + 4\gamma + e_4 \\
y_5 &= \beta_1 + \beta_2 + \beta_3 + 3\gamma + e_5 \\
y_6 &= \beta_4 + 3\gamma + e_6 \\
y_7 &= \beta_1 + \beta_2 + \beta_3 + \beta_4 + 0\gamma + e_7
\end{aligned}$$

Now $e_1 = e_{11}$, $e_2 = e_{22} + e_{23} + e_{24}$, etc. Because each e_i is a sum of a number of independent errors with variances σ^2, it follows that

$$\text{Var } (e_i) = (\text{number of time periods}) \, \sigma^2$$

The main objects of interest are the β_j's.

We want to combine all sites and time periods into two large models, one for the copper specimens and one for the galvanized steel specimens. For Site k, we write the model in matrix form as

$$\underline{y}^{(k)} = A \, \underline{\beta}^{(k)} + \underline{c} \, \gamma + \underline{e}^{(k)}$$

The vector $y^{(k)}$ contains the seven weight losses at site k, the vector $\beta^{(k)}$ contains the four average weight losses (one for each time period) for site k, and c is the vector of Z_{ij}'s, i.e.,

$$\underline{c}' = (3\ 3\ 4\ 4\ 3\ 3\ 0)$$

$\underline{e}^{(k)}$ is the vector of errors, and A is the design matrix

$$A = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 1 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 1 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 1 & 1 & 1 \end{pmatrix}$$

The errors have covariance matrix $\sigma^2 D$, where

$$D = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 4 \end{pmatrix}$$

That is, the diagonal elements of D indicate how many time periods the corresponding specimens remained in the study. Now the large model combines everything as follows:

$$\begin{pmatrix} \underline{y}^{(1)} \\ \underline{y}^{(2)} \\ \cdot \\ \cdot \\ \underline{y}^{(p)} \\ \cdot \end{pmatrix} = \begin{pmatrix} A & 0 & 0 & 0 & \underline{c} \\ 0 & A & 0 & 0 & \underline{c} \\ \cdot & \cdot & A & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & A & \underline{c} \end{pmatrix} \begin{pmatrix} \underline{\beta}^{(1)} \\ \underline{\beta}^{(2)} \\ \cdot \\ \cdot \\ \underline{\beta}^{(p)} \\ \gamma \end{pmatrix} + \begin{pmatrix} \underline{e}^{(1)} \\ \underline{e}^{(2)} \\ \cdot \\ \cdot \\ \underline{e}^{(p)} \end{pmatrix}$$

where p is the number of sites. For copper, p = 10, and for galvanized steel, p = 9. The above model can be written more compactly as

$$\underline{y} = X \begin{matrix} \beta \\ \gamma \end{matrix} + e$$

The covariance matrix for the vector of all errors is $\sigma^2 H$, where

$$H = \begin{pmatrix} D & 0 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & D & 0 & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & 0 & 0 & D \end{pmatrix}$$

The procedure GLM in SAS was used. Since the errors had variances proportional to the number of time periods the corresponding specimen was in the study, we had to do a weighted regression. This was done by setting the WEIGHT parameter in GLM to a variable we called WAIT, which for each specimen had a value of 1/(number of time periods the specimen was in).

Some observations were eliminated after their y values and their residuals from the model were examined. These are

COPPER: Site 308 . . . 18A and 24
Site 310 . . . 24
Site 307 . . . 18B
STEEL: Site 304 . . . 12B
Site 319 . . . 18A
Site 317 . . . 6B, 12B, 18B, and 24.

Some of these observations were actually eliminated earlier, because of questions concerning their analytical processing.

The estimates of the ß's must now be used as dependent variables. The water quality variables, averaged over each time period, must be taken as the independent variables. An important technical problem which arises is that the estimates are not independent, having been estimated all together in the large model. The following approach was taken. The model is

$$\begin{pmatrix}\beta\\ \gamma\end{pmatrix} = \alpha_1 \begin{pmatrix}w_1\\ 0\end{pmatrix} + \alpha_2 \begin{pmatrix}w_2\\ 0\end{pmatrix} + \cdots + \alpha_m \begin{pmatrix}w_m\\ 0\end{pmatrix} + \gamma \begin{pmatrix}0\\ 1\end{pmatrix} + \begin{pmatrix}f\\ g\end{pmatrix}$$

where the β and γ are the estimates from the large model. The w_i's include vectors of water quality observations and vectors indicating which site applies to each variable, and f and g are the errors. This model can be written compactly as

$$\begin{pmatrix}\beta\\ \gamma\end{pmatrix} = W \underline{\alpha} + \underline{f}$$

The covariance matrix for the errors in this model is obtained from the previous section as $\sigma^2 V$, where

$$V = (X' H^{-1} X)^{-1}$$

The objective is to choose a subset of the w_i variables which best fits the model above. PROC STEPWISE is what we would like to use, but it assumes the errors are independent. In order to satisfy this requirement, we multiply everything by $V^{-1/2}$, i.e., the square root of the inverse of V. Thus,

$$V^{-1/2} \begin{pmatrix}\beta\\ \gamma\end{pmatrix} = V^{-1/2} W \underline{\alpha} + V^{-1/2} \underline{f}$$

so that now

$$\mathrm{Cov}\,(V^{-1/2} \underline{f}) = \sigma^2 I$$

where I is the identity matrix. This model was then fed into the PROC STEPWISE of SAS. Both STEPWISE and BACKWARD options were used.

The final models obtained are in Tables 34 through 37. Some of the models examined have one intercept term. Another model considered for copper had a separate intercept for each site: S301 for site 301, etc. For the galvanized steel specimens, both MGLTIC, which represents inorganic carbon concentration as mg $CaCO_3$/L, and PMTIC, which is essentially -log(MGLTIC), appear in the models. The models were refit eliminating the PMTIC parameter, but no significantly better prediction was obtained. Also, two models were fit for the copper specimens using only velocity as a variable. One of the models assumed one intercept, while the other allowed a separate intercept for each site.

ESTIMATION OF WEIGHT LOSS FROM WATER QUALITY: SUMMARY OF MODELS

The estimates of the variability of the weight losses obtained by the procedure given in the previous section are .00027 for the copper specimens and .0018 for the galvanized steel specimens for within-period variability. The estimates of between-period variability were 0.0087 and 0.0398 respectively. If a model using the water quality variables is to adequately explain the weight losses, then the residual variances from the linear models should be close to the variances above. However, the best models

TABLE 34. LINEAR REGRESSION MODEL FOR THE WEIGHT LOSS OF COPPER SYSTEMS, WITH NO SITE-SPECIFIC TERMS*

Term	Coefficient
Intercept	-3.0613
SO4	0.0158
CL	0.0200
K	0.0192
TDS	0.0023
MG	0.0523
N03	0.0075
PO4X	-1.1957
PO4T	1.0133
TCS	-0.0041
I	-855.6832
FREECO2	-0.0054
LARRAT	-0.1622
PMTIC	1.1590
MGLTIC	0.0082

* Symbols are explained in Tables 25 and 26.
Model correlation coefficient (r^2) was 0.74.

TABLE 35. LINEAR REGRESSION MODEL FOR THE WEICHT LOSS OF COPPER SYSTEMS, ADDING SITE-SPECIFIC INTERCEPTS (S301... 319)*

Term	Coefficient
S301	-2.1540
S303	-2.3138
S305	-2.5605
S307	-2.5895
S308	-6.3571
S310	-6.4960
S312	-6.4005
S314	-4.6942
S316	-2.6028
S318	-2.5831
SO4	-0.0043
CA	-0.0749
NA	-0.0368
TC	-0.0133
TDS	0.0058
MG	-0.0762
PO4X	-1 .8177
PO4T	1.5315
TCS	0.0138
I	607.1954
PMTIC	0.5826
MGLTIC	0.0027
BETA	189.2508

* Symbols are explained in Tables 25 and 26.
Model correlation coefficient (r^2) was 0.87.

found had residual variances which were 4.22 and 10.78 (respectively) times too large. These values are highly statistically significant. The copper model in Table 35 includes site Parameters, implying that there are differences between sites not explained by the water quality variables. The best model for the copper specimens not including site parameters had a residual variance 8.2 times too large. Thus, we conclude that these modeis are inadequate.

This inadequacy implies that there are variables which have not been included in the modeis but should be. We cannot estimate the effects of the

TABLE 36. LINEAR REGRESSION MODEL FOR THE WEIGHT LOSS OF COPPER, CONSIDERING ONLY VELOCITY*

Term	Coefficient
	All site's
Intercept	0.027775
VEL	0.000035
	With Site intercept term
5301	0.086072
S303	0.145168
S305	0.0143176
S307	0.097190
S303	-0.045961
3310	0.004618
S312	0.161332
S314	0.061527
S316	0.110107
S313	0.013436
VEL	-0.000294

* Model correlation coefficients (r^2) for all sites and with site intercept term included were 0.65 and 0.87, respectively.

TABLE 37. LINEAR REGRESSION MODEL FOR THE WEIGHT LOSS OF GALVANIZED STEEL, WITH NO SITE-SPECIFIC TERMS*

Term	Coefficient
Intercept	0.1924
S04	-0.0172
CL	-0.0186
K	0.0305
ALK	-0.0184
TDS	-0.0033
CA	-0.0226
N03	0.0241
CL2F	0.1616
I	-979.7432
LARRAT	-0.5413
SI02	-0.0398

* Symbols are explained in Tables 25 and 26. Model correlation coefficient (r^2) was 0.58.

missing variables, because we do not know what they are; however, failure to include them in the modeis renders the resulting estimates erroneous. There are many candidates for missing variables or causes for the apparent absence of important variables. Four possibilities that seem to be the most likely are:

1. Important characteristics of the water were not measured;
2. The values of the water quality variables did not stay constant between sampling dates. In other words, the measurements taken were not adequately representative of the water quality throughout the study;
3. There are interactions between two or more variables that were not integrated into the modeis; and
4. The variables need to be transformed, e.g., by using other concentration units, taking logarithms, etc.

Of these possibilities, the first one is the most unlikely. The wide fluctuations in water chemistry at several of the sites indicate that possibility number 2 operated to at least some extent. The wide variations would certainly change the corrosive environment of the samples a great deal, and the kinetics of the competing reactions would become highly significant. The third possibility is known to be a potential problem, as pH, alkalinity, computed total inorganic carbon, and computed free CO_2 are good examples of variables that are mutually interdependent.

The last possibility is also interesting, and is a potential area for future investigation. The difference in the magnitude, and sometimes the sign of MGLTIC as opposed to pMTIC, is evidence that different units certainly can impact the regression equation a great deal. Recently, Pisigan and Singley found a regression model that had good agreement with laboratory corrosion rate data, and which was based on logarithmic transformations.[2] Further investigation could not be pursued during this study because of time constraints.

The inadequacies in the study design cannot be overcome simply by using more sites. The unmeasured variables, if they exist, will still remain unmeasured. Possibly, monitoring the water quality variables more frequently would help, but unless they are monitored almost continuously (which is prohibitively expensive), obtaining representative water data could still be a problem. A blind search for interactions would probably not be very fruitful. There are about 200 pairs of variables, and 1200 triples, so that the problem of having too many variables is greatly exacerbated. A possible approach would be to be more selective in restricting the modeis to more plausible chemical variables, but it would still be difficult, if not impossible, to "control" for the other background fluctuations.

CONCLUSIONS AND RECOMMENDATIONS

There are too many possible relations to examine and too much variability between sites and within sites to expect an uncontrolled field study of this type to reach many definitive conclusions. At best, one may hope that some relationship is strong enough that it will rise above everything else and be noticed. Unfortunately, this did not happen here. The study is important because it gives strong evidence that there are more factors and interrelationships affecting corrosion rate than have been taken into account by a simple linear regression model. This occurred even though an effort was made to obtain sites which were fairly stable.

Thus, we strongly recommend that controlled laboratory studies be pursued. A few variables can be studied at a time with the, other variables held constant, so that one can be reasonably sure that the differences in corrosion rates that are observed are due to the isolated variables. In this way, a general model built on basic chemical reactions can be developed and extended to Systems of increasing complication. This would provide the optimum method of predicting pipe behavior at new locations across the state and country.

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SECTION 11

SIGNIFICANCE OF METAL CONCENTRATIONS OBSERVED IN PUBLIC WATER SUPPLIES

INTRODUCTION

During the corrosion study, determinations were made of the total concentrations of several trace metals in drinking water which have been identified as potential threats to human health. The chemical analyses were confined to the total lead, zinc, copper, cadmium, iron, and manganese content. Corrosion of copper plumbing materials may contribute to the copper, lead, and zinc content while corrosion of galvanized steel materials may contribute to the zinc, iron, and cadmium content of drinking water. Iron and manganese are naturally occurring metals common to Illinois water supplies.

The National Interim Primary Drinking Water Regulations (NIPDWR)[1] have established maximum contaminant levels for lead and cadmium at 0.05 mg/L and 0.01 mg/L, respectively. The National Secondary Drinking Water Regulations (NSDWR)[2] have established MCL limits for copper, zinc, iron, and manganese at 1.0 mg/L, 5.0 mg/L, 0.3 mg/L, and 0.05 mg/L, respectively. Several aesthetic parameters of drinking water were also limited by the NSDWR, such as chloride, sulfate, TDS, pH, and corrosivity. The USEPA states that the direct measurement of the specific corrosion by-products in water may be the only suitable alternative for assessing exposure to these contaminants.3

The appropriate methods for obtaining representative water samples have not been established by the regulations; therefore, the influence of sampling procedures on the contribution of these metals to drinking water was also investigated.

SAMPLES EXCEEDING MCL STANDARDS

A significant percentage of the water samples collected at each test site over a 24-month period exceeded the established MCL standard for one or more metals. All samples were acid-preserved to determine the total concentration of each metal of interest. At a few sites, a procedure for differentiating between soluble and particulate metal species was used which was reported in a preceding chapter.

The percentage of samples collected which exceeded the MCL for each metal is shown in Table 38. The iron and manganese exceeded the MCL in a high percentage of both running and standing samples. This was anticipated, as many Illinois water supplies have naturally occurring iron or manganese

TABLE 38. FREQUENCY WITH WHICH SAMPLES EXCEED THE MCL FOR TRACE METALS

Metal	MCL mg/L	Standing samples		Running samples	
		Total no.	% >MCL	Total no.	% >MCL
Pb	0.05	830	17.1	836	3.1
Zn	5.00	833	11.8	835	2.2
Cu	1.00	832	10.6	835	4.4
Cd	0.01	194	0.0	197	0.0
Fe	0.30	833	25.6	836	16.0
Mn	0.05	832	14.5	836	11.6

in the water source. Any contribution of iron or manganese to the drinking water by corrosion in plumbing Systems will be concealed somewhat by this influence.

The lead, copper, and zinc content exceeded the MCL in a surprisingly high percentage of the samples, although the MCL's were exceeded in a significantly smaller number of running samples than standing samples. This fact has been reported by other investigators employing similar monitoring programs and points up the need for flushing newly installed plumbing Systems.

Cadmium concentrations were found to be extremely low in both standing and running samples. The cadmium MCL was not exceeded in a Single sample collected during the study. Cadmium concentrations were considered a poor indicator of the corrosivity of the water supplies investigated. Similar cadmium values have been reported by other investigators, which raises questions regarding the justification for monitoring cadmium in public water supplies.

Examination of the samples exceeding the metal MCL's in respect to specific test. sites revealed that certain water supplies were responsible for the major contribution of samples exceeding the MCL for a specific metal. The age of the plumbing installations was also found to be a major influence on the observed metal concentrations -in the water supplies. Table 39 provides a Synopsis describing each test site by the age of the piping and brass sampling valves. All sites where plumbing existed prior to the start-up of the study exceeded 15 years of age.

Manganese

Figures 45 through 49 illustrate the test sites where the metal concentrations in running and standing samples exceeded the MCL for manganese, iron, zinc, copper, and lead, respectively. For example, the manganese concentrations (Figure 45) exceeded the MCL in approximately 80% of the

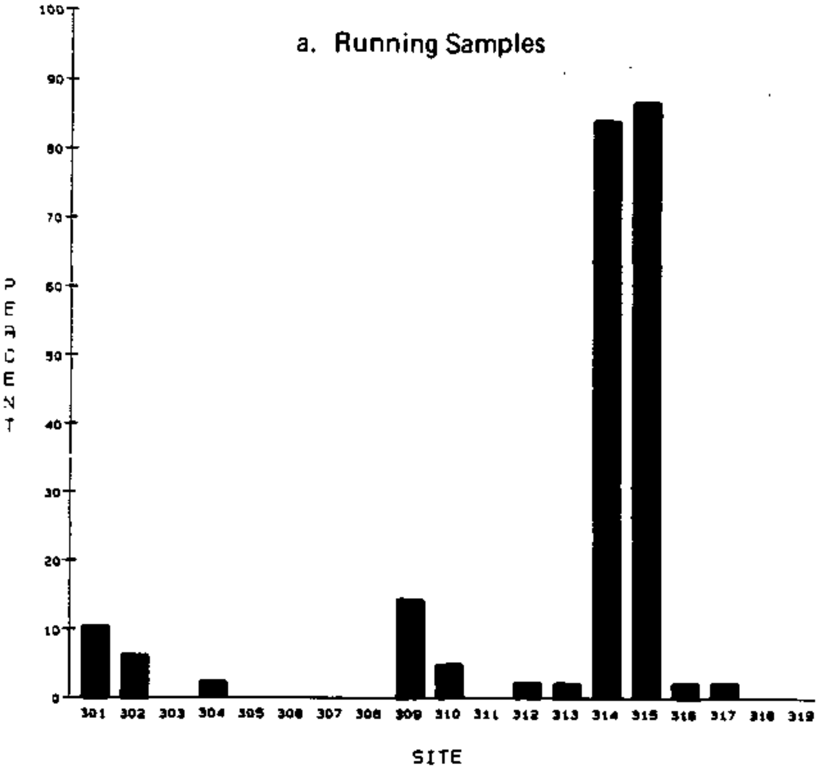
TABLE 39. AGE OF PLUMBING SYSTEMS AT EACH TEST SITE

Site (No.)	Water supply	Description of plumbing system (Pipe material)	(Piping age)	(Valve age)
301	A	Copper	New	New
302	A	Galv. steel	Existing	New
303	A	Copper	Existing	Existing
304	A	Galv. steel	Existing	Existing
305	B	Copper	New	New
306	B	Galv. steel	New	New
307	B	Copper	Existing	Existing
308	C	Copper	New	New
309	C	Galv. steel	New	New
310	C	Copper	New	New
311	C	Galv. steel	New	New
312	E	Copper	Mix	New
313	E	Galv. steel	Existing	Existing
314	D	Copper	New	New
315	D	Galv. steel	New	New
316	F	Copper	New	New
317	F	Galv. steel	New	New
318	F	Copper	New	New
319	F	Galv. steel	New	New

running samples and 94% of the standing samples in water supply "D" (sites 314, 315). The mean manganese concentration was 0.14 mg/L for all samples from this supply. Water supply "A" also exhibited a similar high percentage of samples exceeding the MCL for manganese. However, a sudden reduction in manganese occurred after six months of sampling which coincided with a change in treatment from a polyphosphate-based corrosion inhibitor to caustic soda. A polyphosphate inhibitor was also applied continuously to water supply "D", with correspondingly high manganese concentrations occurring throughout the study. Since the major portion of the manganese content was soluble (as shown in a previous section), the conclusion is that the manganese is strongly complexed by polyphosphate inhibitors added to public water supplies. This poses a potential problem for a water supply where a corrosion control program is required and manganese occurs naturally or is added in the water treatment process.

Iron

The polyphosphate influence was confirmed by examining the iron concentrations found at sites 314 and 315 (Figure 46). Nearly 100% of both running and standing samples at these sites exceeded the MCL for iron whether from a galvanized steel or a copper plumbing installation. As previously described, the polyphosphate Compound is being applied (4-5 mg/L as PO_4) at water supply "D" to control "red" water and also to remove tuberculation in cast-iron mains. The analytical data confirm the complexa-



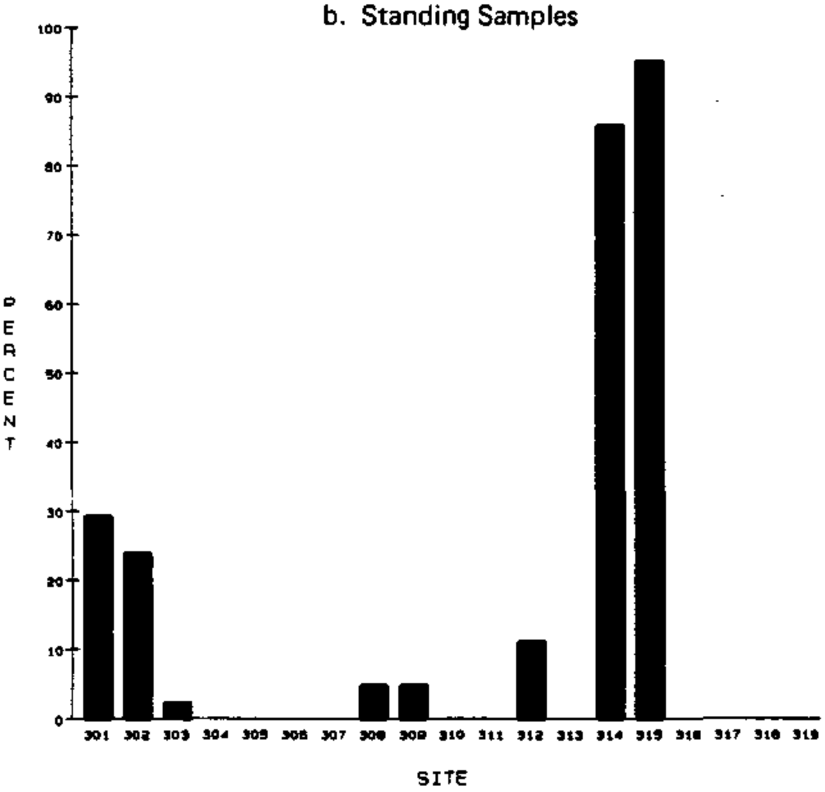


Figure 45. Percent of samples exceeding the MCL for manganese.

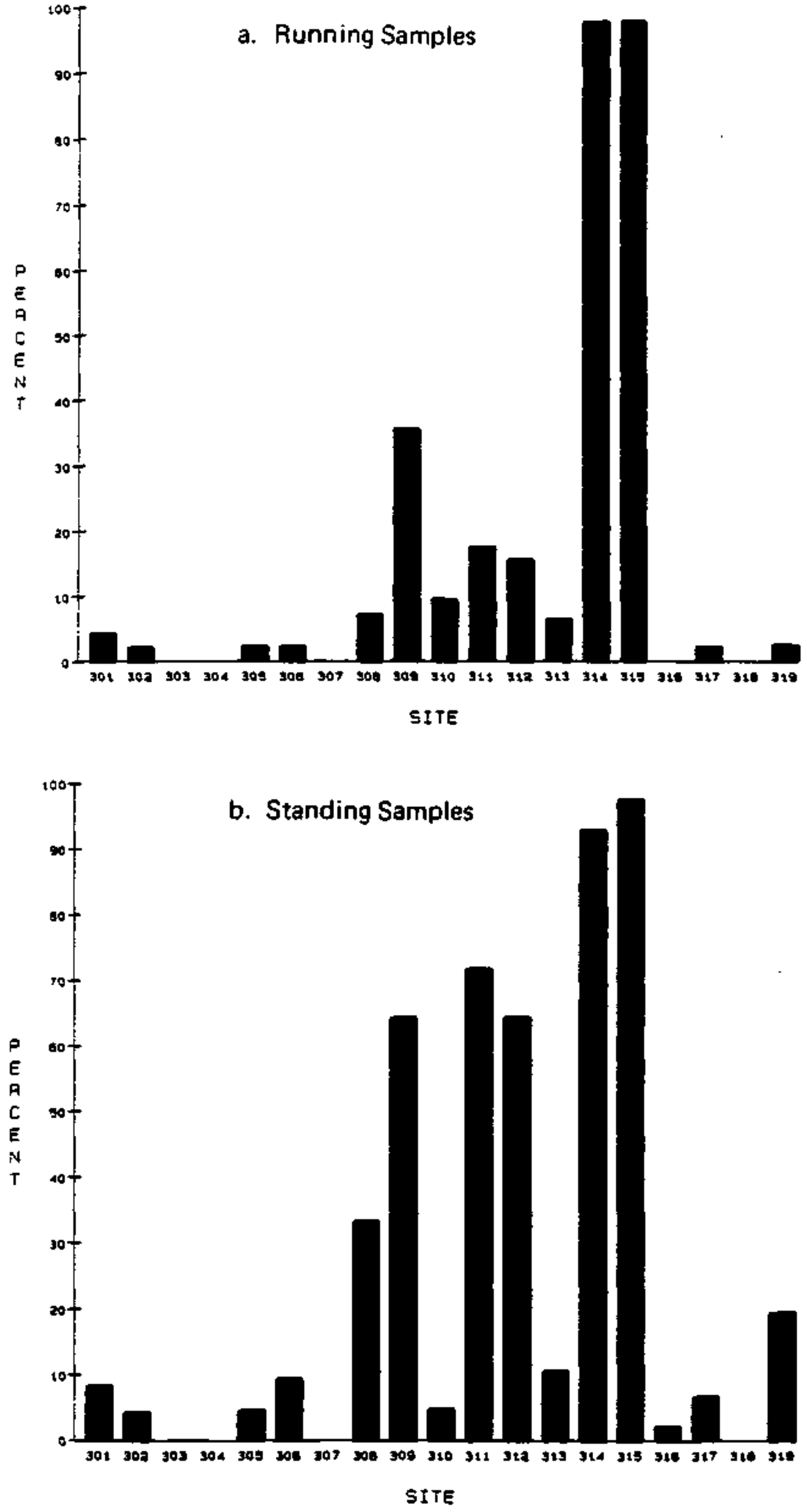


Figure 46. Percent of samples exceeding the MCL for iron.

tion of iron, as the mean iron concentration was 1.10 mg/L (as Fe) for 88 running samples which approximates the average iron content of the five wells used as the source of water. The polyphosphate has been responsible for maintaining the iron content in excess of the MCL for this water supply. At water supply "A" where the polyphosphate application was discontinued, the effect on iron was not apparent, as the concentration was near or at the minimum detectable limit (MDL) throughout the study. However, many of the samples were above the MDL when polyphosphate was being applied and were below the MDL when polyphosphate was discontinued.

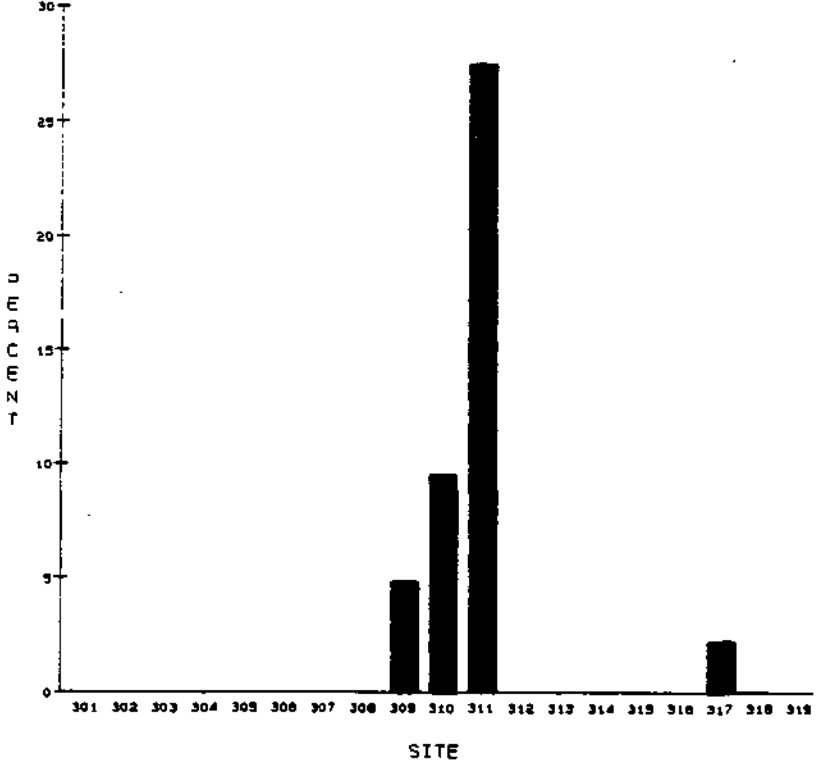
Iron most frequently exceeded the MCL standard for both running and standing samples when compared to the other metals which were monitored. Copper plumbing installations were comparable to galvanized steel installations in the number of samples found to exceed the MCL, which indicates that corrosion of galvanized steel was not contributing significantly to the iron content. The iron content at many sites appeared to be generated in the distribution systems, most likely in the particulate form if polyphosphate or naturally occurring iron were not a factor. Neither iron nor manganese were found to be reliable indicators of water corrosivity of the public water supplies investigated in this study.

Zinc

The MCL for zinc was exceeded in samples from three of the water supplies studied (Figure 47). However, two of the water supplies were responsible for the majority of these samples, as the MCL was exceeded at every sampling site for these supplies. Water supply "C" was the most serious offender, as 27% of the running samples from site 311 exceeded the MCL standard of 5.0 mg/L. The unusual aspect of the zinc concentrations observed in this water supply was a significant trend for the zinc concentrations to increase during the last 24 months of the study. Both copper and zinc exhibited this steady trend to higher concentrations which was observed at all four corrosion test sites in water supply "C". Standing and running samples exhibited the same phenomenon. The increase was attributed to corrosion of the plumbing materials, as the zinc and copper content was affected more significantly than lead, iron, cadmium, or manganese content.

The water of water supply "C" is highly mineralized and is considered to be very corrosive. Silicate and caustic soda have been applied for over 15 years at this supply to control corrosion of galvanized steel piping. Partial softening by ion exchange has reduced the hardness content. Examination of the galvanized steel and copper pipe specimens removed after the two-year study indicated that a satisfactory coating had formed in the piping and no visible indication of significant corrosion was seen. The deposits removed from the corrosion specimens were given an abbreviated analysis, shown in Table 40. The composition of the deposits was very similar to that of deposits found on copper and galvanized steel specimens from the other water supplies studied.

The MCL for zinc was also exceeded in standing samples from water supply "F", although in fewer samples than in water supply "C". The mean zinc concentration of the standing samples from site 319 was 7.22 mg/L Zn


a. Running Samples

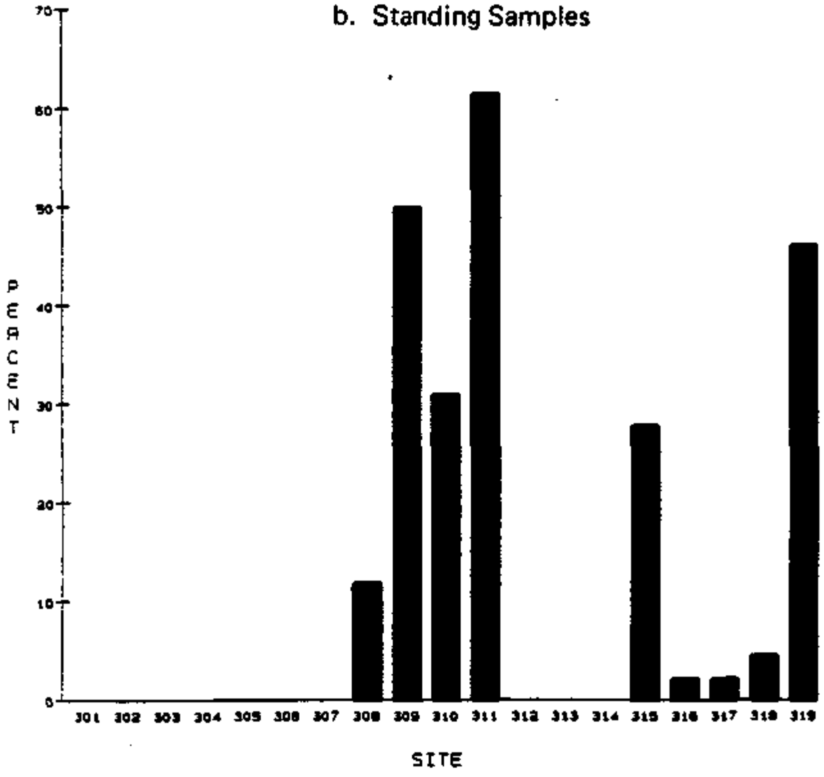

b. Standing Samples

Figure 47. Percent of samples exceeding the MCL for zinc.

TABLE 40. COMPOSITION OF DEPOSITS IN CORROSION SPECIMENS, WATER SUPPLY "C"

Site (No.)	Specimen (Material)	Chemical composition (%) (Zn)	(Cu)	(Fe)	(Ca)	(Mg)	(CO_2)
303	Copper	1.1	15.8	1.9	1.4	0.7	1.1
309	Galvanized	41.3	0.2	0.6	0.6	0.3	41.3
310	Copper	1.4	21.9	2.2	1.1	0.6	1.4
311	Galvanized	41.2	0.3	0.7	0.9	0.3	41.2

and was influenced by a 24"-long galvanized pipe nipple between the sampling valve and the test loop. The zinc concentrations within this nipple were not subjected to the diluting effects during operation that occurred in the shorter 6"-long pipe nipples used at the other sites; therefore, the zinc values in standing samples exceeded the MCL more frequently at this site than others in water supply "F".

Site 315 exhibited a very high incidence of zinc concentrations exceeding the MCL in standing samples (28?). The frequency of these occurrences decreased with time, although the zinc concentration remained high. The simulated test loop at this site was installed in a vertical configuration which tended to concentrate particulate corrosion products near the sampling valve. The presence of polyphosphates may also have interfered with the formation of a passivating film on the galvanized steel, producing a less adherent coating of corrosion products. In any case, the corrosion of zinc piping materials contributes significantly to the total zinc content found in drinking water. The zinc content was influenced by many factors (i.e., piping configürations, water usage, water quality, etc.) which impedes any correlations between the zinc concentration and corrosivity of water.

Copper

Water supply "C" exhibited the greatest frequency of samples exceeding the MCL for copper (Figure 48). The copper concentrations of running samples were the highest values observed from any site from the standpoint of mean concentration and frequency in excess of the MCL. Standing samples more frequently exceeded the standard than did running samples. Copper plumbing (sites 308 and 310) contributed more copper to standing samples than galvanized steel plumbing (sites 309 and 311); however, in running samples the copper concentrations were not significantly influenced by the plumbing materials. In fact, the copper concentrations of samples from the galvanized steel sites were equivalent to copper concentrations found in samples from the copper sites, although no copper materials were present other than the brass sampling valves. The source of the exceedingly high copper content in this supply was not identified. Copper was not present in the water source or treatment plant effluent. As previously discussed, sampling procedures were investigated and found to be carried out as

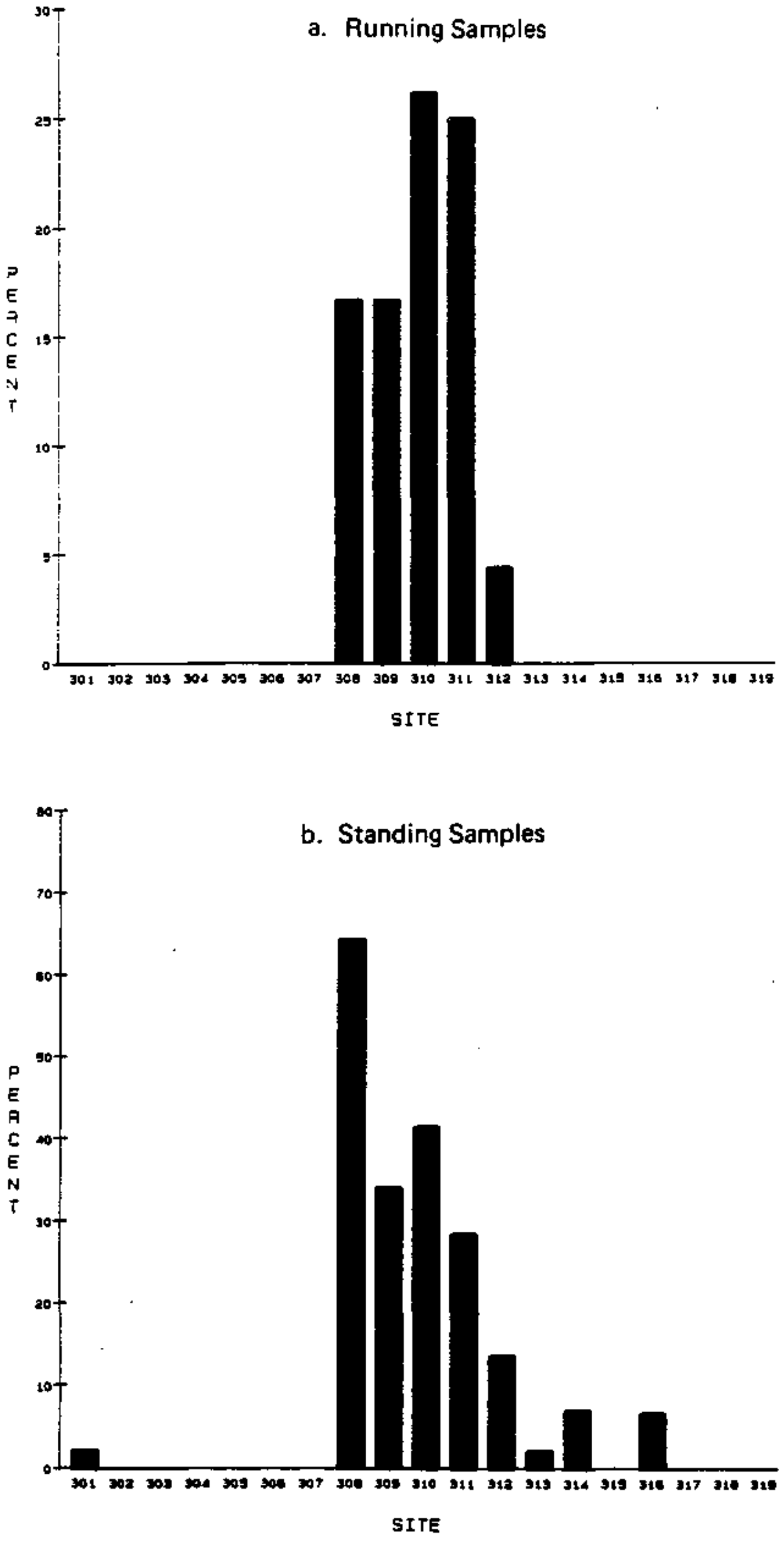


Figure 18. Percent of samples exceeding the MCL for copper.

recommended. Corrosion of the brass valves appears to be the only source of copper in the galvanized steel test sites. The trend toward increased copper concentrations in water supply "C" during the last 12 months of the study was also unexplained.

Water supply "E" was the only other water supply which exceeded the MCL for copper in running samples. The mean concentration for copper was also higher than desired for both running and standing samples, 0.26 and 0.68 mg/L, respectively. One factor, common to water supply "C" and water supply "E", was the use of sodium silicate to control corrosion of galvanized steel. Further investigation is needed to determine if Silicates may be influencing copper dissolution in household plumbing Systems.

Lead

The most disturbing observation during the corrosion study was the frequency with which the lead concentrations exceeded the MCL (Figure 49). Of the nineteen test sites, eight sites exceeded the MCL in over 20% of the standing samples collected. Five of the remaining sites exceeded the MCL in 2-10% of the standing samples, while only six sites were below the standard in all samples. Running samples also exceeded the MCL at six of the nineteen sites. Examination of the corrosion data revealed that the lead concentrations were prone to wide variations in concentration from sample to sample. The mean lead concentrations may be abnormally high due to one or two samples exhibiting very high lead content. Samples exceeding the lead MCL were rechecked to authenticate the "spikes" in the observed lead concentration. Generally, the spikes occurred at most sites during the early stages of the study, although they also occurred at reduced frequency in later samples.

Site 314, copper, and site 315, galvanized steel, exhibited the highest mean lead concentration for standing samples: 2.13 and 0.23 mg/L Pb, respectively. Thirty of forty-two 3tanding samples exceeded the MCL at site 314, whereas nineteen of forty-three standing samples exceeded the MCL at site 315. Apparently the corrosion of the lead-tin solder in the copper plumbing at site 314 was contributing more to the lead content of water than was the galvanized steel plumbing at site 315. The lead concentrations observed from site 315 can most likely be attributed to corrosion of the brass sampling valve, although lead is an impurity in galvanized materials. Running samples from this site did not exceed the MCL for lead, and the lead content remained very low (>0.01 mg/L Pb) throughout the study.

The running samples which exceeded the MCL for lead were from five sites with copper plumbing and from only one site with galvanized steel plumbing (site 309). The "spikes" in lead content of these samples did not follow a distinct pattern such as appeared only during the early stages of sampling. The "spikes" were generally several magnitudes higher than the background lead concentration. Sporadic spalling of lead corrosion products apparently occurs, which is observed for several months in newly installed plumbing. Copper Systems employing lead-tin solder were more prone to this problem than the galvanized steel Systems, although brass materials may also behave in a similar manner.

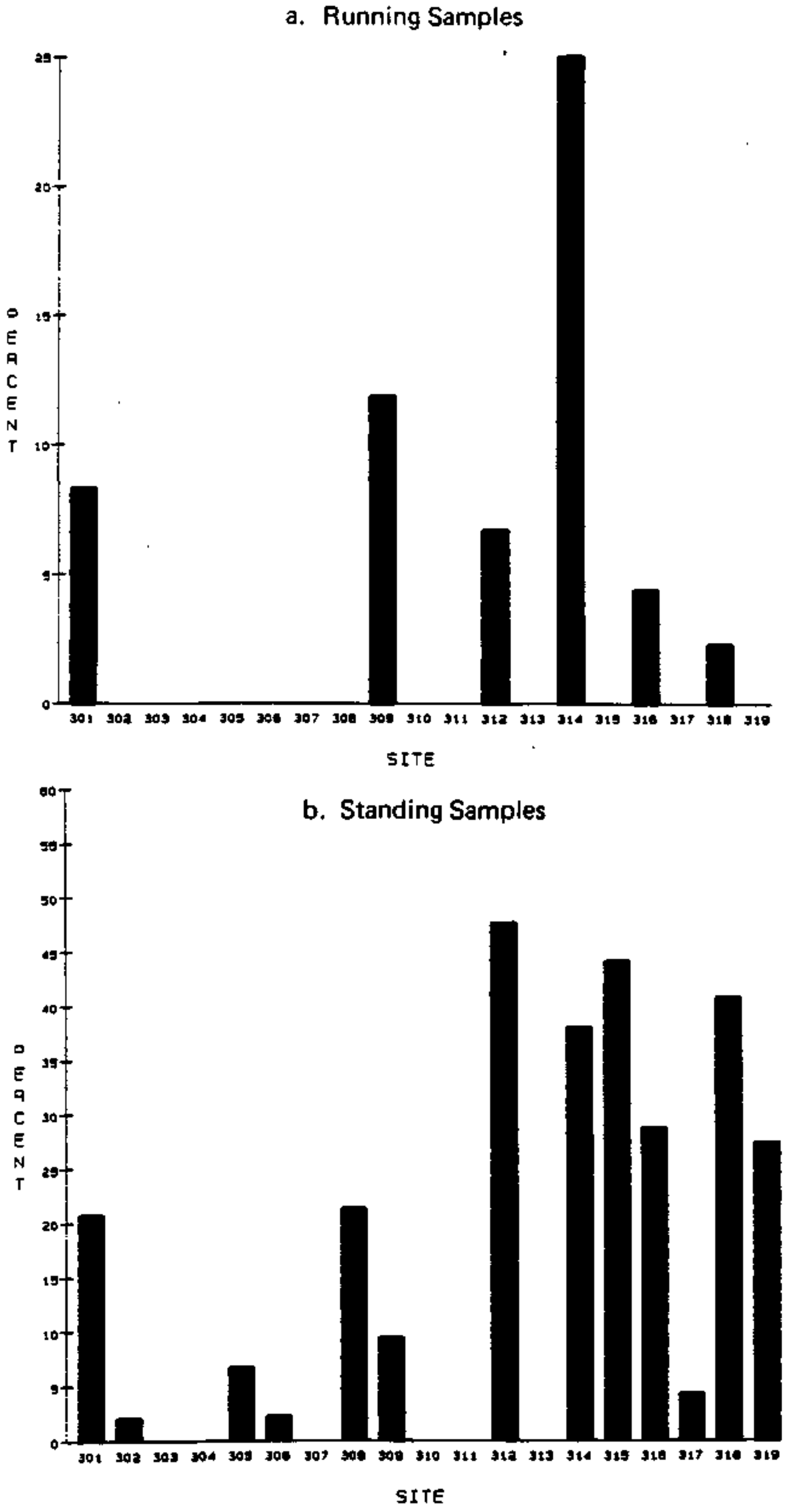


Figure 49. Percent of samples exceeding the MCL for lead.

The standing samples exhibited a more pronounced effect, with increased frequency and higher concentration levels of lead occurring than observed in running samples. Galvanized steel Systems exhibited similar characteristics to copper Systems, except at reduced frequency and reduced lead concentration. The plumbing in four of the six sites which did not exceed the MCL for lead in a Single standing or running sample had been installed several years prior to the study. The age of the plumbing materials is an important factor influencing the lead content of public water supplies.

The influence of brass sampling valves pn the lead concentration is also significant, and these valves may be the primary source of lead in standing samples. Polyphosphate or Silicate corrosion inhibitors, while perhaps producing a positive benefit regarding corrosion of copper or galvanized steel in some water supplies, may at the same time have an adverse effect on the lead, copper, or zinc concentrations found in drinking water.

VARIATION OF METAL CONCENTRATIONS IN SAMPLES

The monitoring of the total metal concentrations in drinking water is the only method currently available which is capable of assessing exposure of consumers to these contaminants. However, the metal content must be evaluated carefully when attempting to relate concentration to the corrosivity of water. Iron, cadmium, and manganese may be totally unrelated to the corrosion of plumbing materials in public water supplies, as was shown by the MCL evaluation. Although copper, lead, and zinc may be found in drinking water as a result of the corrosion of piping materials, their concentrations were not useful in pred'icting the degree of corrosivity of the particular water supply. The metal content of water samples was observed to fluctuate significantly during this study and was often characterized by the "spikes" in concentration reported previously.

For example, the zinc concentrations found in standing samples from Site 313 and site 315 are shown in Figure 50. The decrease in zinc concentration with time and the decrease in the magnitude of the "spikes" with time are probably typical of most new galvanized plumbing installations exposed to a corrosive water supply like that represented by Site 315. Older installations of galvanized steel plumbing materials are represented by site 313 where zinc concentrations of standing samples had reached a plateau prior to the study. The lower concentration level and the reduced frequency and magnitude of "spikes" are typical of older installations. New installations of galvanized steel may require two years to approach a similar plateau in zinc concentration, as shown by data from site 315.

The copper concentrations of standing and running samples from new copper plumbing, represented by site 314 in Figure 51, exhibited similar characteristics for copper content to that observed for zinc content in samples from galvanized plumbing materials. Running samples from the copper System were approaching the concentration plateau after nine months of sampling, while standing samples required 15-18 months of sampling to reach a similar plateau.

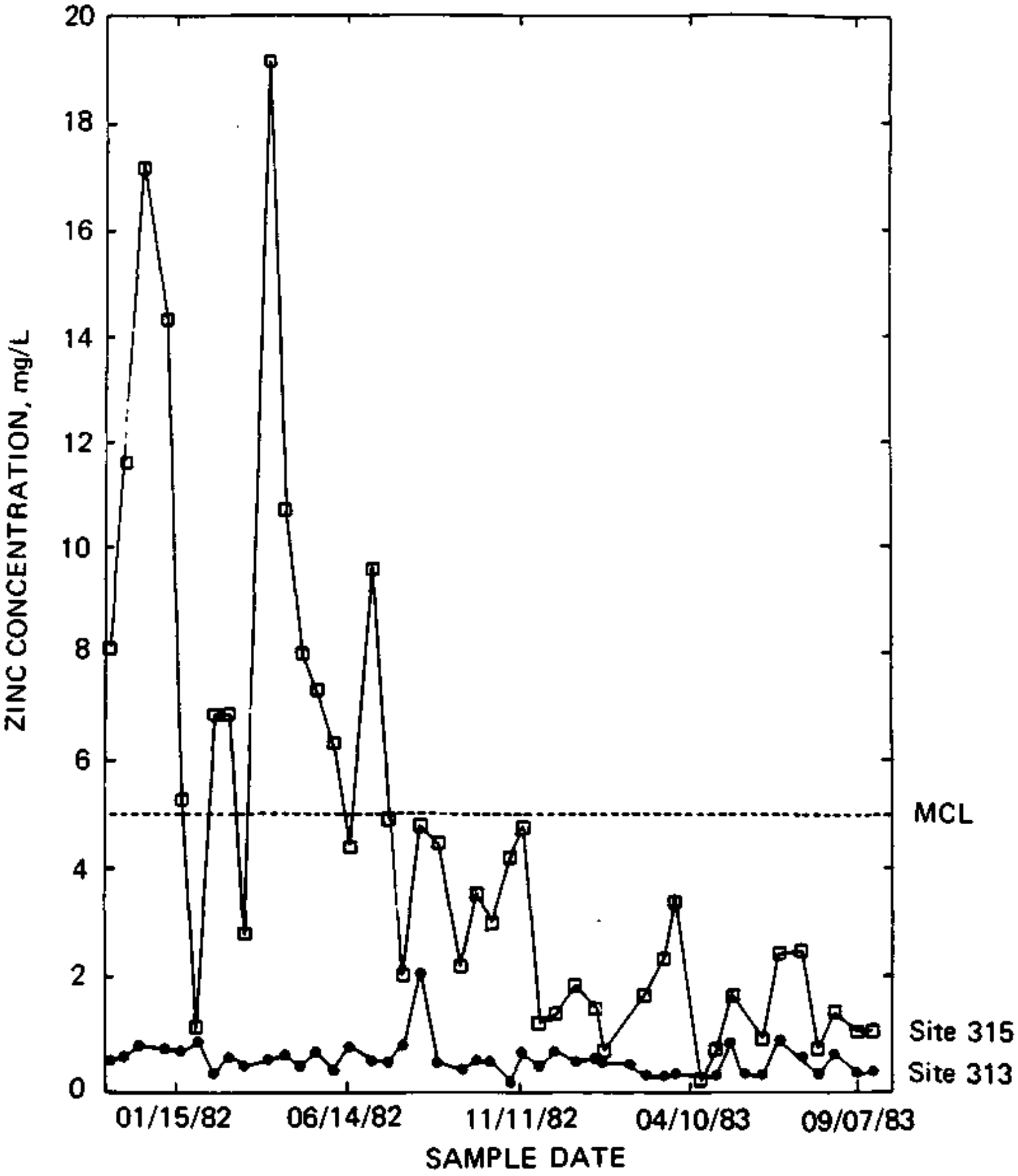


Figure 50. Zinc concentrations of standing samples from sites 313 and 315.

The copper concentrations found in the first running samples from old copper plumbing (site 307) exposed to a water of low corrosivity were observed to be at a concentration plateau from the beginning of the study. Within one month, the standing samples had also reached a concentration plateau. The expanded scale shown in Figure 52 reveals that even under these conditions of low corrosivity and old plumbing materials, the fluctuations in copper concentrations continue to exist. A mean value for copper has been established for both the running and standing samples due to the Variation in concentration. This Variation was much greater than the varia-

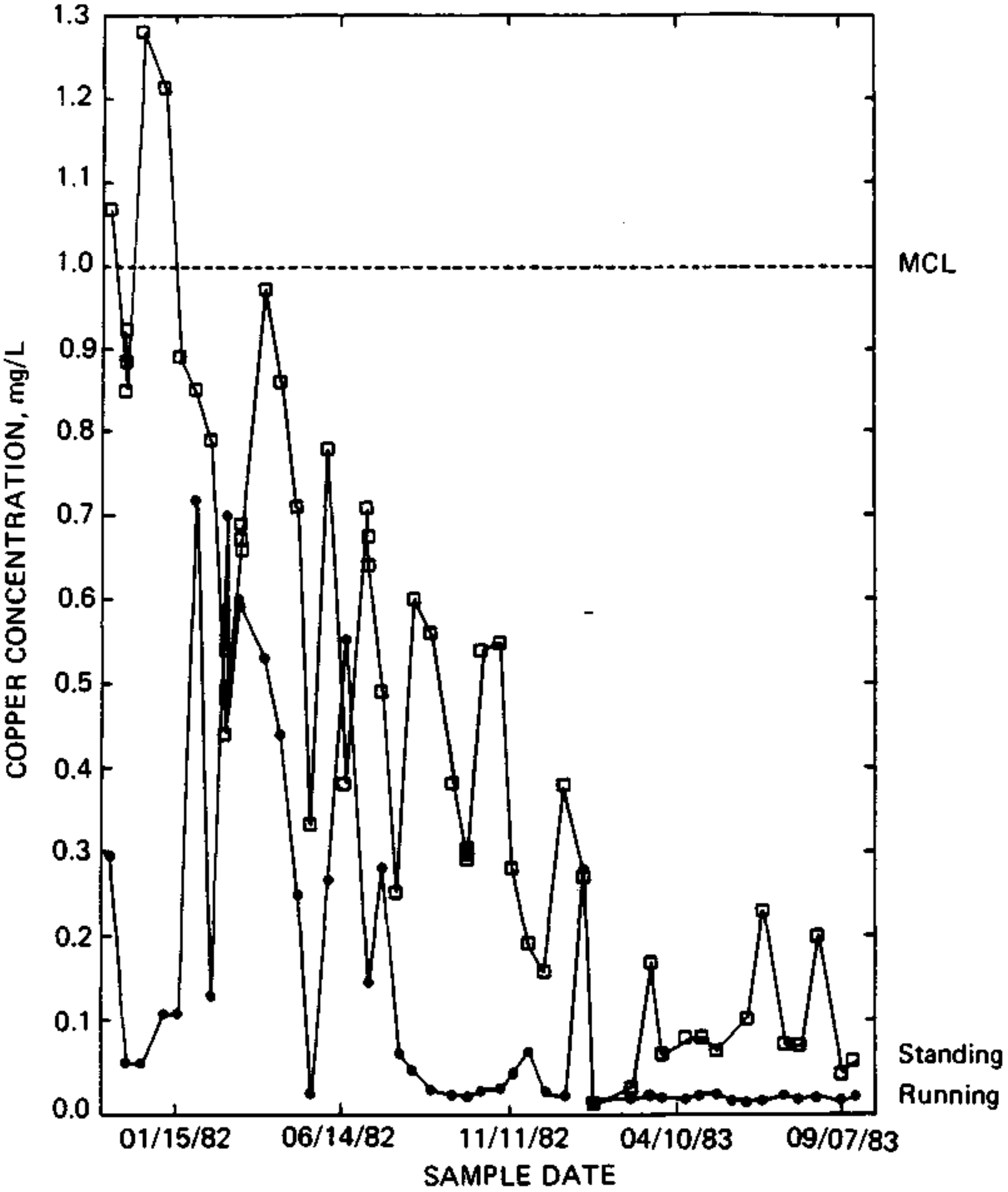


Figure 51. Copper concentrations of samples from site 314.

bility attributed to the analytical method used for copper, but may have been influenced by sampling procedures.

The "spikes" in copper and zinc concentrations found in water samples are generated by the corrosion of the plumbing materials. The normal trend is for the concentration "spikes" observed in samples to decrease in frequency and mean concentration with time as the plumbing materials approach an equilibrium with the water supply. The time required for samples to attain the concentration plateau was a function of the corrosivity of the

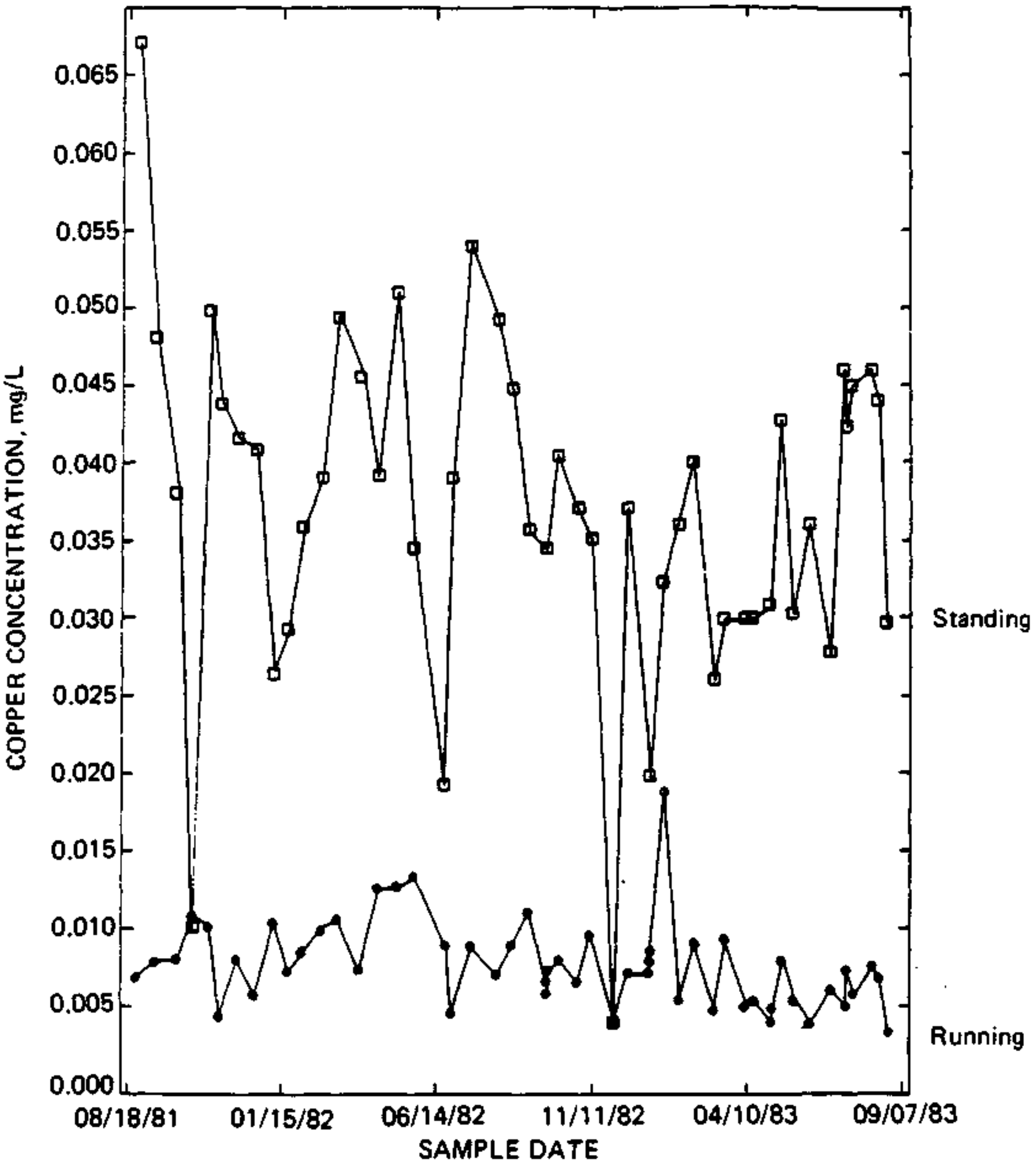


Figure 52. Copper concentrations of samples from site 307.

water, plumbing materials, age of the plumbing, and water usage within the system. The observed trend in metal concentration conforms with fundamental corrosion mechanisms. Soluble metal and particulate metal species were found to be at higher levels in the early stages of the corrosion study.

An unusual trend was observed at sites 308, 309, 310, and 311 located in water supply "C". At these sites, the metal concentrations of both running and standing samples exhibited the normal trend during the first 8-10 months of the study. During the last 12 months of the study, the trend was reversed as the copper and zinc concentrations steadily increased as illustrated by Figures 53 and 54. The copper and zinc concentrations exceeded the MCL for most of the samples collected during this period. The very high metal concentrations were unanticipated and were suspect when first observed. After sampling techniques and analytical procedures were eliminated as causes for error in the reported metal content, the reported values were accepted as the true copper and zinc concentrations for the samples. Both the zinc and copper concentrations exceeded the predicted solubility of the respective metal, which indicated that the particulate metal species were primarily responsible for the increase in the metal content of the samples. The increased frequency and increased magnitude of the "spikes" in copper concentration at site 310 are illustrated in Figure 53. At this site, the zinc concentrations were also observed to behave in a similar manner, as shown in Figure 55, although the plumbing materials in the immediate vicinity of the sampling valve were copper and copper alloys. Particulate zinc was probably responsible for the major portion of the total zinc concentration found in samples from the copper plumbing at site 310. The source of the zinc was not identified, but zinc may have been transported from the galvanized steel piping installed prior to the copper loop or may have been derived from the brass sampling valve.

The effect of the particulate species on metal concentration was not anticipated for running samples, since the plumbing and valves were flushed for a minimum of five minutes prior to collecting the sample. The galvanized steel section of the simulated test loops was effectively flushed more than ten minutes prior to collecting the running samples from the copper System. Flushing was generally successful in reducing the total metal content of running samples when compared to the metal content found in standing samples, as illustrated in Table 41. However, significant metal concentrations in running samples continued to persist after five minutes of flushing at certain sites. The flushing period was inadequate at water supply "C" as the mean copper and zinc concentrations in running samples were extremely high. The mean lead concentration of running samples from site 314 also indicated that the flushing was inadequate prior to sampling. The median lead concentration for the running samples at this site was 5 µg/L Pb as compared to the mean value of 422 µg/L. This points out the effect of random particulate metal species in samples on the mean concentrations observed.

A stringent sampling protocol is required to obtain representative Information on metal concentrations in public water supplies. In addition to the influence of water quality, the sampling valve material, age of the plumbing system, flushing rate and interval, piping configurations, and water usage were observed in this study to influence the total metal concentrations found in water samples.

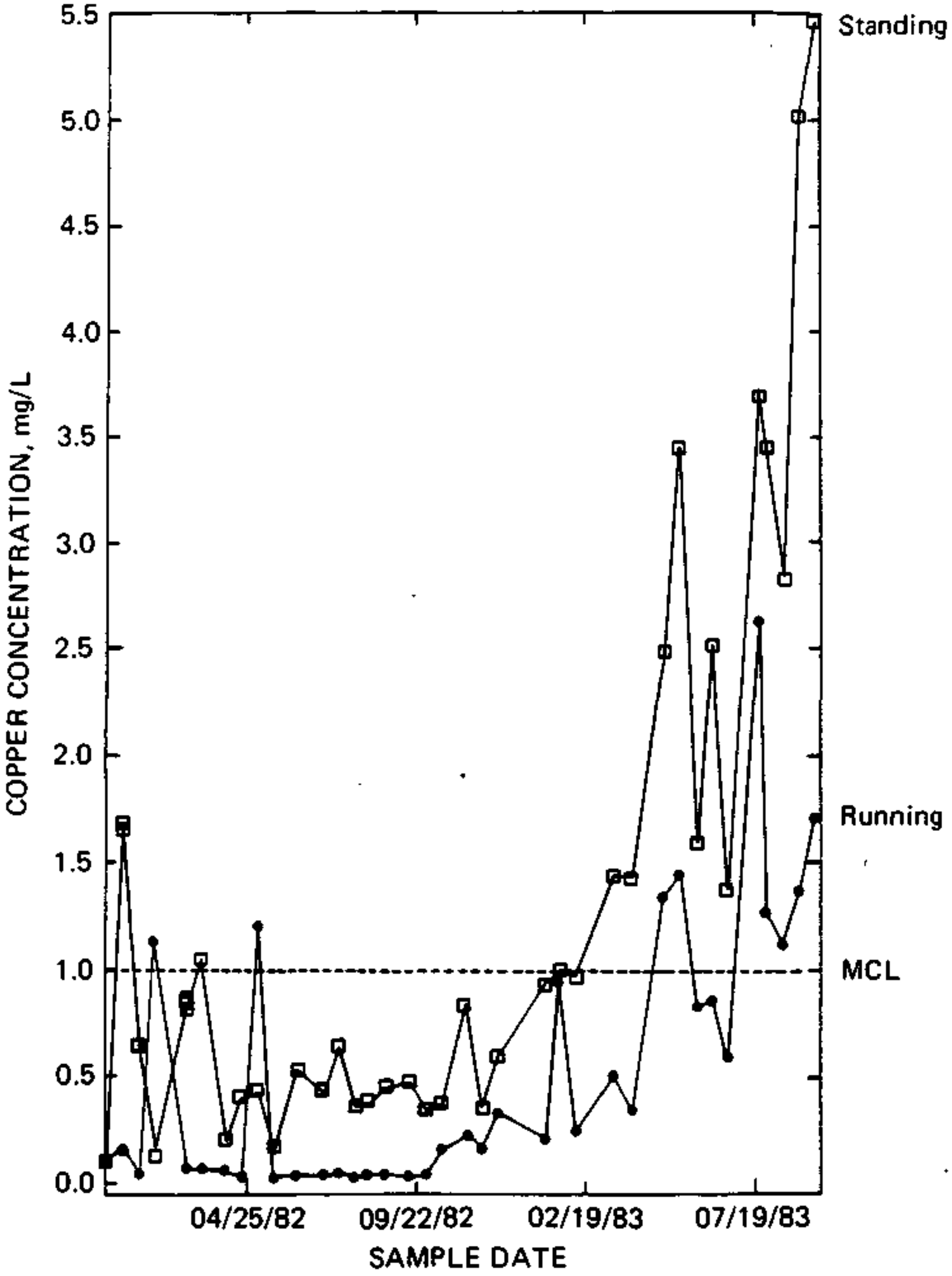


Figure 53. Copper concentrations of samples from site 310, copper System.

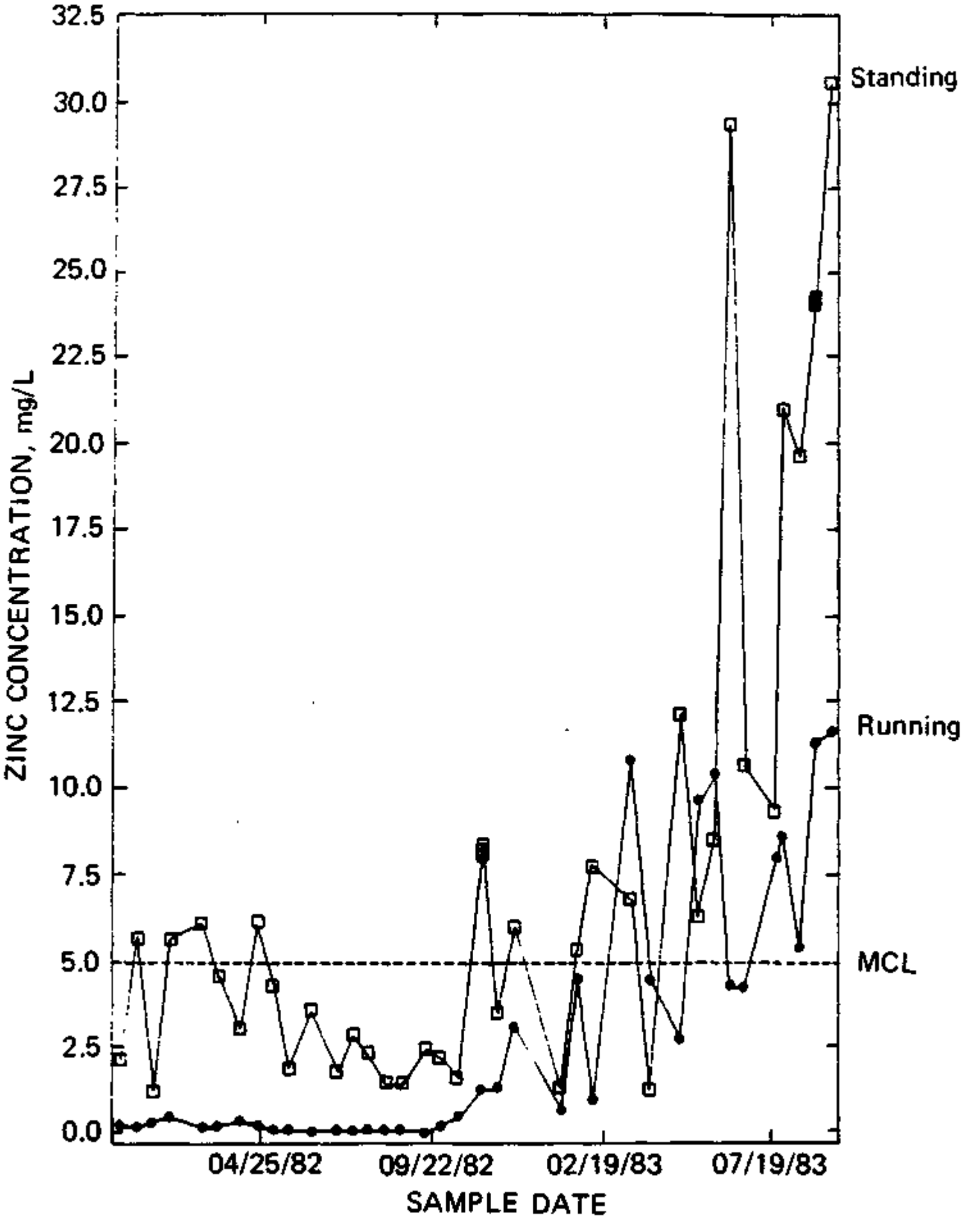


Figure 54. Zinc concentrations of samples from site 311, galvanized steel system.

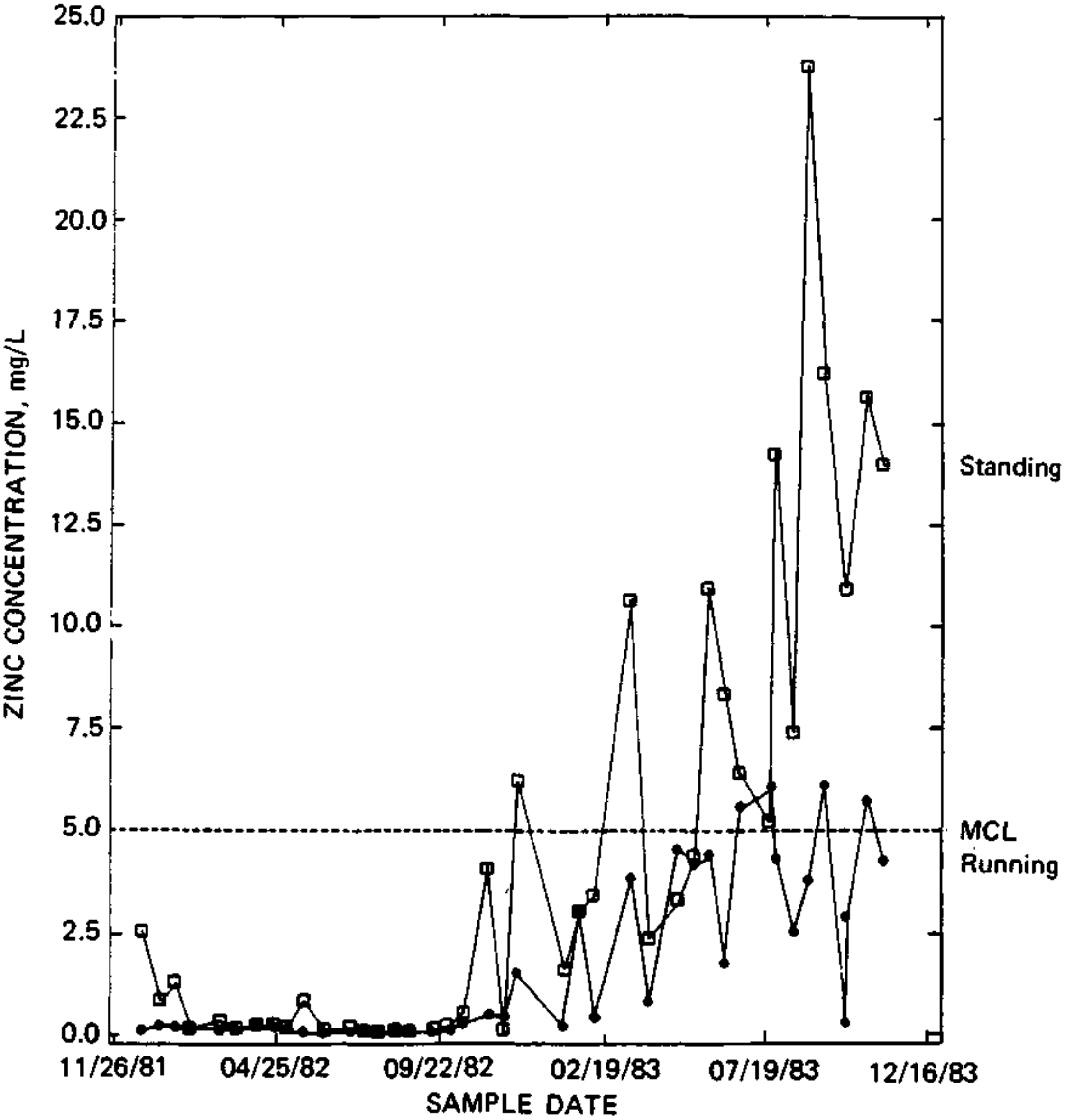


Figure 55. Zinc concentrations of samples from site 310, copper system.

TABLE 41. MEAN METAL CONCENTRATION VALUES FROM TEST SITES

Site (No.)	Supply	Lead (Pb), µg/L (standing)	Lead (Pb), µg/L (running)	Copper (Cu), µg/L (standing)	Copper (Cu), µg/L (running)	Zinc (Zn), µg/L (standing)	Zinc (Zn), µg/L (running)
Galvanized steel systems							
302	A	7	1	11	9	135	77
304	A	3	1	39	3	118	56
306	B	13	1	88	8	425	100
309	C	17	13	766	538	5919	2214
311	C	16	5	1479	772	10198	3500
313	E	8	14	79	27	418	156
315	D	225	4	39	10	4439	291
317	F	15	2	47	3	3889	213
319	F	85	3	17	5	7227	227
Copper Systems							
301	A	82	14	250	37	398	169
303	A	3	1	25	7	85	27
305	B	17	1	190	26	79	27
307	B	2	1	37	8	23	20
308	C	42	4	1327	489	2358	1116
310	C	10	5	1273	555	4331	1678-
312	E	173	30	682	263	206	25
314	D	2128	422	408	113	336	213
316	F	155	12	250	13	364	26
318	F	71	4	97	10	69	97

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SECTION 12

PROJECT SUMMARY

The primary objectives of the project were to investigate the influence of selected water supplies on the corrosion rates of galvanized steel and copper materials and to monitor the impact of these materials on the trace metal concentrations found in drinking water. The study was not designed to provide solutions for all of the corrosion problems occurring in public water supplies, but was an attempt to identify or verify difficulties associated with the monitoring of corrosion, water quality, and trace metal content of potable water from plumbing Systems in buildings.

The project was a long-term effort by many individuals and encountered numerous delays associated with field studies. Problems developed due to relocation of facilities, personnel changes, equipment failures, delays in site preparations, and many other minor inconveniences. A large volume of analytical data was generated from 19 corrosion test sites located in 6 public water supplies. Considerable effort was necessary to insure the reliability of the data and to prepare the data for statistical evaluation. Hopefully, the data base developed in this study and presented in Volume II (appendices) of this report will be useful to others investigating correlations between water quality and corrosion.

The most significant finding of this research was that brass sampling taps were contributing significant quantities of lead, copper, and zinc to water samples collected from the plumbing Systems in buildings. Leaching studies were conducted using new brass sampling taps which confirmed that the brass material was a source of these trace metals when lead-tin solder, lead pipe, copper tube, or galvanized steel pipe were not present. The impact of brass and other copper alloys on the trace metal content of drinking water has not been adequately studied. Because water samples were collected from brass sampling taps during many previous studies, the lead content attributed to lead pipe or lead-tin solder may be suspect where the contribution of brass was not recognized. Further investigation is warranted concerning the effects of water quality and composition of copper alloys on the trace metal concentrations in drinking water.

In a similar context, the effects of applying polyphosphates to public water supplies should be investigated. Many water supplies in Illinois are using polyphosphates for a variety of purposes: (1) to inhibit calcium carbonate deposition on sand filters, (2) to Sequester soluble iron and manganese found in ground water, (3) to inhibit corrosion within the distribution System, and (4) to solubilize iron corrosion products in distribution mains. The authors suspect that the presence of polyphosphate may have additional detrimental effects on the trace metal content of drinking water than those effects observed in this study. It would not be surprising to find that polyphosphates are affecting the deposition or dissolution of metal oxide films on the surface of plumbing materials.

Preliminary observations from the corrosion study were presented during the 1983 National Association of Corrosion Engineers Conference,[1] during the USEPA National Seminar on Plumbing Materials and Drinking Water Quality,[2] and in a research report published by the AWWA Research Foundation.[3]

REFERENCES

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2. Plumbing Materials and Drinking Water Quality: Proceedings of a Seminar. USEPA Report EPA/600/9-85/007, Feb. (1985).

3. Internal Corrosion of Water Distribution Systems. AWWA Research Foundation Research Report (1985).