

Impact of an Epoxy Pipe Lining Material on Distribution System Water Quality

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Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University in
partial fulfillment of the requirements for the degree of
Master of Science in Environmental Engineering

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May 5, 2009, Blacksburg, VA

Key words: epoxy, in situ lining material, drinking water quality

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Abstract

Corrosion of iron and copper pipes can produce leaks and loss of efficiency in the water distribution system, elevate levels of contaminants at the tap, and cost billions of dollars annually in pipe replacement or rehabilitation. In situ pipe rehabilitation using cement mortar, polyurethane, and epoxy is a commonly employed method of dealing with aging yet structurally sound pipes because it is less expensive and less invasive than replacing pipe infrastructure. Although epoxy has been shown to be an effective solution to pipe corrosion, little research has been conducted regarding its impact on a comprehensive list of water quality parameters. This research addressed that gap in the literature by conducting short-term immersion tests in which new epoxy linings were exposed to reference tap waters containing one of three disinfectant treatments: no disinfectant, free chlorine, or chloramines. As a comparison, an aged epoxy-lined field sample was also tested. Water exposed to the liners under stagnant conditions was analyzed for the following water quality parameters: pH, ammonia, alkalinity, hardness, metals, disinfectant consumption, total organic carbon (TOC), semi-volatile organic compounds (SVOCs), disinfectant byproduct (DBP) formation, and odor. Results of the study showed relatively low impacts on water quality, as all USEPA drinking water regulations were met. Impacts were highest during the first 24 hour exposure period during which time significant disinfectant consumption was shown (> 90% free chlorine consumed, 13% chloramines consumed), high TOC was leached (2.6-6.2 mg/L), trihalomethanes and haloacetic acids were formed (both < 15 ug/L), Bisphenol-A, an endocrine disrupter, was detected (< 35 ug/L), and odor was reported by panelists at a moderate intensity and described as sweet/chemical/burning/chlorinous. Impacts were much less after the initial 24 hours, although odor remained noticeable throughout the 30 day study. Overall, water quality impacts were greatest in chlorinated waters and both new and aged epoxy showed slight differences in results.

Acknowledgements

I would like to express sincere gratitude to everyone who helped me during my research and writing.

In particular I would like to thank Dr. Andrea Dietrich for sharing her knowledge and experience with me. I am grateful for her direction and support as well as her patience and trust in my abilities. I feel very fortunate to have been able to study under such a respected professional.

I would also like to express thanks to the other two members of my committee: Dr. Dan Gallagher and Dr. John Little. Dr. Gallagher has been incredibly helpful in discussing statistical methods and experimental design with me.

I would also like to thank Jody Smiley and Julie Petruska for their vast knowledge and instruction in helping me with lab instrumentation.

Finally I would like to thank my lab partners: Heather Johnson, Dave Clark, James Newbold, Pinar Omur-Ozbek, Andy Whelton, and Jose Cerrato for their help and advice. Heather and Dave in particular spent many hours helping with data collection and interpretation for which I am exceedingly grateful.

Author's Preface

This work is presented in the Virginia Tech Manuscript format. The first chapter consists of a literature review documenting known water quality impacts from epoxy liners. Both laboratory experiments and case studies are included in the review. The second chapter provides the experimental design, data and results, discussion, and possible improvements/future research for the AwwaRF-funded bench-scale epoxy studies.

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Chapter I

Literature Review

I. Introduction

As the drinking water distribution system ages, water mains lose their effectiveness in transporting high quality water (Deb et al., 2006). Corrosion of metal water mains results in leaks and the introduction of metals and other contaminants into the water supply. As the contaminants are scoured from the pipe surface, concentrations of metals sometimes meet or exceed regulated levels as set by the Safe Drinking Water Act (SDWA) and the Environmental Protection Agency (EPA) (Brady et al., 1997). Even if concentrations do not exceed regulatory limits, elevated levels of metals such as iron and copper are still capable of affecting the color or taste and odor of the water supply. Unlined black steel and copper pipes have been reported by the US Army as significant sources of red water in their drinking water systems and severely compromised water quality (Army Corps of Engineers, 2001). Drinking water aesthetics are of particularly high concern to utilities, as consumers' confidence in their water is shaken when water at their tap has an objectionable taste or odor (Khiari et al., 1999). Consumers frequently opt not to use water from their tap in response to taste and odor episodes, choosing the switch to bottled water instead (Khiari et al., 1999). For utilities to meet their customers' needs and preferences, to stay within regulatory limits, and to maintain a properly functioning distribution system, they spend billions of dollars every year on water distribution and compliance. This amounts to approximately 80% of utilities' investments (Deb et al., 1999) and an estimated \$22 billion spent annually for the replacement and rehabilitation of aged water mains in the drinking water distribution system (Brongers, 2002).

The majority of water main replacements in North America have traditionally been performed using open-trench methods where the mains are unearthed and repaired (Deb et al, 1999). This method is costly and can cause significant inconveniences, particularly in heavily trafficked areas. Therefore, if a pipe shows signs of tuberculation or corrosion but is still structurally intact, a popular alternative for replacement or remediation is the use of trenchless technologies (Deb et al, 2006). These include pipe replacement methods of pipe bursting and splitting, pipe pulling, and auger boring, as well as rehabilitation methods of cured-in-place-pipe (CIPP) linings, slip lining, and cement and polymeric in situ linings (Deb et al., 1999). The focus of this review is on in situ pipe relining, a method that has been shown to significantly improve water quality, flow, and pressure, reduce customer complaints, and ultimately improve the long-term performance of the pipe and the reliability of the system (Deb et al, 2006).

The relining process was developed to clean corrosion buildup from structurally sound pipes and install a new corrosion-resistant surface to increase hydraulic capacity and extend the life of the pipe (Deb et al., 2006). Relining creates a barrier between the metal pipe and the water, thereby preventing further leaching of lead from soldered joints and the corrosion of copper and iron pipes (Deb et al., 2006). It also eliminates galvanic corrosion that results from the joining of dissimilar metals (Army Corps, 2001). Finally, relining the pipe allows the water to be restored much faster than traditional open-trench methods, sometimes within 24 hours (Oram et al., 2002).

AwwaRF currently cites an urgent need for pipe rehabilitation in the near future due to the old age and poor condition of many of the existing mains (most are between 40-140 years old), the current low replacement and rehabilitation rates, and the obvious benefits to remediation over complete replacement (Deb et al., 1999). Because of the demand for pipe rehabilitation and the large amount of money invested in drinking water infrastructure, there is significant interest in providing both safe and durable relining materials. In order to be considered safe for use in drinking water systems, relining materials must first pass American National Standards Institute/National Sanitation Foundation (ANSI/NSF) Standard 61 (ANSI/NSF-61, 2000). This set of standards was developed and approved in 1989 by the NSF, American Water Works Association (AWWA), American Water Works Association Research Foundation (AwwaRF), and the Association of State Drinking Water Administrators (ASDWA) in response to requests from the EPA to develop drinking water standards (ANSI/NSF-61, 2000). NSF-61 establishes the maximum contaminant and impurity levels a pipe material can impart into the drinking water through leaching (including organic and inorganic compounds, heavy metals, and any substances posing a potential threat to human health). The standards also set specific guidelines for testing and approving materials for use (ANSI/NSF-61, 2000).

To date, cement mortar has been the most commonly used material for pipe rehabilitation projects and is still the conventional choice to rehabilitate unlined cast iron pipes (Deb et al., 2006, Oram, 2004). It has been used in the US since the 1930s when utilities began to experiment with lining mains 24-in and larger in diameter (Oram, 2004). In the 1950s a remote machine was developed that enabled smaller-diameter pipes to be relined. Since this time millions of feet of pipelines of all diameters have been rehabilitated using cement mortar (Oram, 2004). In recent years, however, analysis has shown many of these cement mortar linings have failed and caused significant deterioration in water quality (Deb et al., 2006, Oram, 2004). In the Southwestern UK, many cement mortar linings installed twenty years ago have failed and resulted in the release of red water caused by corrosion of the iron pipes. This release was further compounded by the presence of sand and residual cement in the pipes from the dissolved lining that exacerbated the corrosion problem (Oram, 2004). Dissolution of the liner was especially problematic in

this part of the UK due to the quality of the water. Soft, aggressive waters erode the cement mortar lining, leaching CaCO_3 , increasing hardness, and raising the pH of the water (Deb et al., 2006, AWWA Permeation). Cement is also known to leach high levels of dissolved aluminum, further compromising water quality (Saegrov et al., 2007). For these reasons utilities concluded that cement mortar was ineffective as a long-term rehabilitation solution in soft, poorly buffered waters (Deb et al., 2006). In addition to its poor performance in certain water types, the thickness of cement mortar linings and the long curing times caused utilities in the UK to shift away from the use of cement mortar linings to more durable and inert polymeric linings. Cement mortar needs to be applied at a minimum thickness of 4-6 mm, making it difficult and impractical to reline pipes smaller than a 4 in-diameter because the lining can significantly decrease flow (Deb et al., 2006). In contrast, polyurethane and epoxy linings can be applied at lesser thicknesses, approximately 1-1.5 mm, allowing smaller pipes to be relined without significantly decreasing flow capacity. The smoother surface of these polymeric linings also results in greater flow capacity, lower energy costs to transport water, less ability for biofilm growth to occur, and easier maintenance (Deb et al., 2006). The curing time of 48 hours is also significantly longer than polymeric linings which take less than 24 hours (Deb et al., 2006).

Despite the obvious benefits, however, epoxy and polyurethane are still not as widely used here in the US for a number of reasons. Thousands of miles of pipe have already been rehabilitated using cement mortar and the vast amount of long-term data ensures utilities know how the liners will perform (Oram, 2004). In contrast, polymeric liners do not possess the same long-term results and utilities express hesitation with using liners that have not been on the market nearly as long (Oram, 2004). Also, polymeric linings are more expensive to apply, require much more highly specialized on-site quality control during application, and fewer contractors are available that are qualified to install epoxy linings (Oram, 2004). Finally, polymeric linings are less forgiving with regard to pipe cleaning and preparation. Due to the thinner application of epoxy and polyurethane, the presence of loose debris or encrustation seriously impacts the quality of adherence, making the liners much more susceptible to failure (Oram, 2004). Taking all of these issues into consideration, utilities choose what lining material ultimately will work best for the system based on past experience, their specific water quality characteristics and water quality needs, and a basic cost evaluation. Peter Oram of Malcolm Pirnie concluded in his review of cement mortar, epoxy, and polyurethane lining materials that it is impossible to answer the question regarding which is the best material for rehabilitation purposes as all three choices offer advantages and disadvantages (Oram, 2004).

II. Epoxy as a Lining Material

Epoxy was first utilized in the drinking water industry in the UK in the late 1970s (Deb et al., 2006). Its initial use came about as an alternative to cement mortar and bitumen linings, both of which had proven to be ineffective under aggressive waters (Deb et al., 2006). The long curing time of cement mortar was also impetus for finding alternative materials that did not require a 48 hour isolation period during which time water was unavailable to customers served by the affected pipe (Oram, 2004). One of the first studies on the effectiveness of epoxy linings was performed by British researchers in 1983. Up to this point epoxy had not been readily used due to uncertainty regarding its long-term performance. Warren et al. (1983) conducted accelerated aging experiments to predict how well epoxy would perform after a considerable amount of time had passed. The experiment utilized aerated rigs containing high concentrations of both disinfectant (150 mg/L as Cl_2) and sulfate (150 mg/L as SO_4^{2-}) at a high temperature (50°C) to gauge epoxy deterioration rates under highly corrosive conditions. The results of the experiment proved favorable, with negligible weathering occurring over an equivalency of 20 years of service time. Simultaneous in-service assessments on different epoxy resins currently in operation performed by the researchers also showed that, after four years of monitoring, no physical deterioration had taken place and all water quality test criteria were satisfied (Warren et al., 1983):

1. No excessive microbial growth was present,
2. No organoleptic or physical deterioration of the water occurred,
3. No toxic metals or cytotoxic compounds were leached.

Although the epoxy was found to temporarily support increased microbial activity, these were shown to be non-pathogenic and to decrease over time. Following these results, epoxy began to be used widely by utilities in the UK, despite a lack of national standards or guidelines (Deb et al., 2006). As application protocol at this time was largely controlled by individual utilities, relining was often found to produce inconsistent results. Later analysis showed the poor performance was due to improper installation and an incorrect formula used to produce the epoxy. Since 1989 a standard quality assurance and quality control protocol was established in the UK to ensure proper application (Deb et al., 2006). Between 1995 and 2000, an estimated 6000 miles of pipe was relined using epoxy, a significantly higher number than anywhere else. The reasoning behind the higher use of epoxy was due to the government involvement in the privatized water industry that has encouraged infrastructure improvement programs (Oram, 2004).

Epoxy use in North America was slower to catch on due to the same lack of operational guidelines and a lack of approval from the NSF (Deb et al., 2006). Implementation of epoxy was significantly increased

after 1993 when an AwwaRF study confirmed the viability of epoxy as an acceptable lining alternative in the US. The 30 day study examined water impacts on a 6-in unlined iron pipe in Chester, Pennsylvania. Results showed the epoxy lining had a minimal effect on leaching and that all primary drinking water standards were satisfied. Furthermore the new lining caused an increase in hydraulic capacity of the pipe by decreasing the roughness coefficient (Conroy et al., 1993). Epoxy was also shown to meet approval of the NSF-61 standard and performed well under accelerated immersion studies to mimic long-term field conditions. This data led researchers to conclude epoxy was a safe and durable material, with an estimated life of 40 to 60 years (Deb et al., 2006).

More recently the use of epoxy resins in the UK has become largely replaced with rapid-setting polyurethanes due to the faster curing time of polyurethane (Oram, 2004). Although polyurethane linings are more expensive than epoxy resin, approximately 75% of in situ pipe rehabilitation in the UK is now being conducted using one of three approved polyurethane materials (Oram, 2004). It is not known whether or not the use of epoxy or polyurethane liners will begin to replace cement mortar as the preferred rehabilitation material in the US as it has in the UK.

III. The Structure of Epoxy

Epoxy is composed of two materials, an epoxy resin and a hardener, or curing agent, that combine to form a hard inert material (Deb et al., 2006). This material provides a stable and impermeable layer that forms an effective barrier between the pipe and water supply. The resin compound is a low molecular weight polymer with epoxy functional groups at each end. Resins are usually classified as either Type 1 or Type 2 materials. Type 1 materials generally refer to the earliest manufactured epoxy resins that have a low viscosity and can be pumped by ordinary hose-lining equipment. These are most commonly used for pipe rehabilitation and are frequently composed of diglycidal ethers of bisphenol-A (DGEBA) and bisphenol-F (DGEBF). Type 2 materials are more recently produced compounds that have a much higher viscosity and require specialized application equipment. Both Type 1 and Type 2 materials share a similar resin structure but vary in the type of curing agent they react with to produce the final epoxy product. In order to be used in potable water mains, resins are required to be (AWWA, 2002):

1. Solvent and benzyl alcohol free
2. High build
3. Slump-resistant

- 4. Rapid-curing
- 5. Moisture-tolerant

Figure 1 below shows a typical resin molecule, a molecule of DGEBA with reactive epoxy groups at each end.

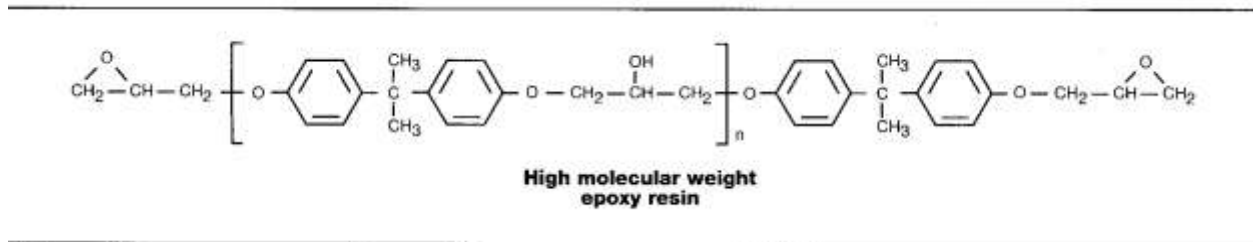


Figure I-1. Epoxy molecule containing reactive epoxy groups at each end

Upon being mixed with the hardener, the epoxy groups on the resin molecules immediately begin to react with hydrogen atoms in the amine hardener in a continuously-branching pattern. This action results in a cross-linking, spaghetti-like network of polymers that grows and tangles, eventually hardening into a solid, insoluble three-dimensional thermoset network. The hydroxyl groups created by the reaction polarize the epoxy layer and are the means by which the epoxy adheres to polar sites on the surface of the pipe (O'Donoghue et al., 1998).

Although the basic formulation of epoxies is fairly similar, the specific structure varies depending upon the type of resin base and hardener used and the ratio of the two components. Epoxy resin manufacturers must specify the ratio needed to ensure the utilities are getting the best adhesion, highest moisture resistance, minimum leaching potential, and correct hardness for their lining (Deb et al., 2006). The presence of additives such as plasticizers (intended to add strength) also affects the chemical characteristics such as hardness and the application process.

IV. Epoxy and Water Quality Issues

Although NSF-61 approved epoxy linings have been proven an acceptable alternative for relining potable water mains, potential problems still exist for utilities and consumers. The most obvious threat to water quality occurs in the case of improperly-installed linings (Deb et al., 2006). Insufficient curing times,

poorly trained staff, poorly maintained equipment, an incorrect ratio of resin to hardener, premature application of the epoxy before the correct ratio is achieved, and poorly-cleaned pipe surfaces are all instances that could result in improperly-installed linings that can likely pose future water quality issues such as increased leached organics (Oram, 2004, Warren Associates, 1997). Assuming proper installation, lab and field tests have generally shown epoxy to have minimal impacts on water quality. Problems that may potentially arise are generally related to the leaching of organic compounds or the increased growth of microbes on the surface of the newly-installed lining (Khiari et al., 1999). Although preliminary tests on epoxy have shown it meets regulations, much research has since been performed on water quality issues related to epoxy linings. These include impacts on pH, disinfectant residual, organic compounds, disinfection byproducts, and taste and odor. The results of many of these studies are summarized below and are divided between inorganic and organic parameters. Some experiments that examined multiple parameters are discussed in different sections throughout the review. Experimental designs and background information are provided during the first discussion of the experimental results.

A. Effect of Epoxy – Inorganic Parameters

a. Disinfectant Residual

Regarding the impact of epoxy linings on inorganic parameters, most of the literature has reported on the impact of epoxy on disinfectant residual. All available literature that examined the interaction between epoxy linings and disinfectant reported epoxy to readily consume disinfectant, especially free chlorine. A 1998 study performed by Holt, Gauthier, Merlet, and Block examined disinfectant consumption in waters exposed to new epoxy-lined pipe and found very high free chlorine consumption rates and significantly lower monochloramine consumption rates. The researchers tested both epoxy and cement lined ductile iron, as well as unlined grey and ductile iron, bitumen, PVC, and polyethylene pipes with 1 mg/L free chlorine or 1 mg/L monochloramine. Pipes (approximately 10 cm in diameter and 50 cm in length) were filled with a commercial mineral water, sealed at both ends, and operated with continuous circulation. Disinfectant concentrations were sampled multiple times an hour. Results of the study found that epoxy consumed free chlorine at a rate of 4-10 times greater than monochloramine, with the exception of highly corroded pipes that consumed both disinfectants rapidly. Results also found epoxy to show a high rate of consumption, more reactive than polyethylene and PVC, but less reactive than cement lined ductile iron, bitumen, and both unlined pipes. In epoxy samples, after 3.75 hours of contact time, the Cl_2 concentration had fallen from 1 mg/L to approximately 0.1 mg/L. After 6 hours contact time in

chloraminated waters, the monochloramine concentration fell from 1 mg/L to approximately 0.6 mg/L. No data were collected after 6 hours. The researchers attributed the disinfectant consumption by the lining materials to the oxidation of molecules at the surface of the pipe, which depended on the individual composition of the materials (Holt et al, 1998).

Heim and Dietrich also reported disinfectant consumption by newly-installed epoxy-lined copper pipe. In their experiment, pipes of 7 ft length by $\frac{3}{4}$ in width were studied using the Utility Quick Test (UQT), a testing protocol that requires pipes be filled with water and allowed to stagnate for 72-96 hours. In this case the pipes were filled with one of three treatments: water containing no disinfectant, water containing 2 mg/L chlorine, or water containing 4 mg/L monochloramine. A set of controls was also prepared that consisted of the same water not exposed to the epoxy-lining. The water used for the study was a low alkalinity, low hardness reference water prepared using a Nanopure system and a series of salts. (The pipes had been previously disinfected for one hour with 50 mg/L chlorine and then rinsed.) The results of the study showed that after 72-96 hours of contact time with chlorinated water, only 0.1-0.2 mg/L chlorine residual was present in the pipes. By contrast, control samples containing no epoxy had a chlorine residual of 1.5-1.7 mg/L, indicating the epoxy lining caused high consumption of free chlorine, approximately 1.5 mg/L. The study also reported relatively high consumption of monochloramine, much higher than the Holt study. The concentration of monochloramine in samples exposed to epoxy decreased from 4 mg/L to 0.3-0.4 mg/L, a substantial change in disinfectant concentration. The control samples, however, also exhibited a high rate of disinfectant consumption, decreasing from 4 mg/L to 1.3-2 mg/L. For these samples, the epoxy lining could be determined to be responsible for consuming approximately 1 mg/L monochloramine. While this study also confirmed a greater rate of consumption for free chlorine than monochloramine, the results contrasted with the Holt study in that the consumption rate was only 1.5 times greater than for monochloramine, not 4-10 times greater like in the previous study (Heim et al, 2007).

Data from both studies showed that epoxy reacts with disinfectant rapidly and that free chlorine is consumed at a greater rate than monochloramine, a finding that supports the ability of monochloramine to remain more stable in the distribution system. Both studies examined only short-term disinfectant consumption and only in newly-installed epoxy.

b. pH

The pH of drinking water is regulated because both acidic and alkaline waters can corrode metal pipes. Galvanized and copper piping is particularly susceptible to this corrosion and the NSF does not

recommend using copper pipes to transport waters below pH 6.5 or above 8.5 (Dunn, 2008). For these reasons it is important to maintain drinking water at a neutral pH. The studies that measured pH in waters exposed to epoxy linings reported no impact from the linings.

Concurrent with their UQT experiments, Heim and Dietrich (2007) measured pH and other water quality parameters in household copper plumbing thirty minutes after epoxy installation and initial flushing and again after one week of normal use. They found there to be no change in pH before or after epoxy was installed and concluded epoxy had no impact on pH.

Similarly, a lab immersion experiment performed by Bae et al (2002) also found no significant effect on pH after reference water was exposed to epoxy linings. This study was performed on glass coupons coated with three different epoxy resins that were exposed to two different water treatments: a deionized water and a specified test water containing 30 mg/L as hardness, both at an initial pH of 7.0. The results of the study showed no statistical difference in pH before or after the exposure to epoxy, with pH values ranging from 6.68-8.49.

These two studies suggest epoxy linings have a negligible impact on pH. No articles could be found that related the impact of epoxy linings on alkalinity, hardness, or leached metals, parameters examined later in this research.

B. Effects of Epoxy – Organic Parameters

a. Total Organic Carbon

Total organic carbon (TOC) present in the drinking water distribution system is problematic because it can react with disinfectant in the water to produce highly regulated disinfection byproducts, provide substrate for the growth of microorganisms, and cause taste and odor issues (USEPA, 1998; Russell, 1996; Tomboulion et al., 2004). Much of the concern regarding epoxy as a lining material deals with the ability of epoxy to leach organics upon exposure to water; migration of organic compounds becomes even more problematic in cases where the lining has not been installed properly or has not had sufficient curing time (Alben, 1989).

Heim and Dietrich reported detectable TOC levels in their UQT experiments. They found a statistically significant increase in TOC leached from epoxy-lined copper pipes (0.6-0.9 mg/L) in comparison to controls (0.18-0.22 mg/L). Specific TOC formation rates were not reported but concentrations were measured after an exposure of 3-4 days, indicating the TOC formation rate was in the range of 150-300

ug/L/d. Normalized for surface area, these corresponded to approximately 0.15-0.3 ug/cm²/d. The study reported a difference in TOC concentrations based on disinfectant used; chlorinated waters had higher concentrations of TOC than both chloraminated waters and no disinfectant waters. The no disinfectant water had the lowest TOC levels (Heim and Dietrich, 2007).

A commonly cited 1989 study on TOC migration from epoxy linings reported similar concentrations of TOC leached from recently-lined, epoxy-coated steel panels. Alben et al. exposed these panels to stagnant tap water (pH 8-9) over the course of 30 days, during which time samples were collected for analysis. TOC leached in the water at the beginning of the study was between 40-187 ug/L/d and after 30 days had decreased to a rate of 8-37 ug/L/d (Alben et al., 1989).

In contrast to Heim and Dietrich and Alben et al. who both reported concentrations of TOC in ug/L/d, two separate studies performed by Satchwill (2002) and Russell (1996) detected substantially higher TOC concentrations leached from epoxy linings. Satchwill examined the performance of five epoxy materials at four different curing treatments by exposing newly-lined coupons to 49°C water for 72 hours. Two epoxy coatings were applied and half the linings were exposed to water after 24 hours cure time. The other half were exposed after 72 hours. Half of each batch were rinsed and half left unrinsed to achieve four different test scenarios (24 or 72 hour cure time, rinsed or unrinsed). Immersion tests in 300 mL test vessels were used to simulate no flow conditions, although no information was provided regarding composition of test water or rinse time and no surface area to volume ratio was given. Results of the experiment showed very high concentrations of TOC leached, ranging from 34-345 mg/L after 72 hours. The research showed a large range between epoxy types, suggesting that water quality impacts can vary significantly even among different formulations of epoxy. The experiment also showed that pre-rinsing had no effect on TOC concentrations. The high water temperature most likely attributed to the extreme leaching rates (11.3-115 mg/L/d), as high temperatures are known to cause increased leaching (Bae et al, 2002). However, lack of surface area to volume information makes direct comparison difficult.

The second experiment performed by Russell (1996) involved a design similar to the UQT. This experiment filled 100 m length x 100 mm pipes with water, allowing 72 hours of exposure time, and decanting the water for analysis. The experiment was repeated three times. Although no information was provided regarding the type of reference water used (disinfectant, hardness, pH, etc), the study reported very high TOC formation rates, 0.012 mg/cm²/d during the first exposure period and 0.0007 mg/cm²/d during the last exposure (approximately 0.1-2.4 mg/L/d). The data is summarized in Table I-1.

Table I-1. TOC initial leaching rates for four epoxy migration experiments

Experiment	Epoxy Condition	TOC (mg/L/d)	TOC mg/cm²/d
Alben et al (1989)	New, Lab study	0.04-0.19	NA
Russel (1996)	New, Lab study	0.001-1.6	3.3E-6-0.004
Heim & Dietrich (2002)	New, Lab study	0.4-0.7*	0.00007-0.0001*
Satchwill (2002)	New, Lab study	11.3-115	NA

*Corrected for controls

The TOC data show extremely high variability (two orders of magnitude when normalized for surface area) between experiments which is likely due to differences in both experimental design (water temperature, cure time, disinfectant type used, etc.) and the type of epoxy used. The type of epoxy resin most certainly affected the TOC leached, as Satchwill (2002) reported high variability in TOC leaching rates among the resin types they sampled under identical conditions. Second, the actual design of the experiment (water temperature, flow conditions, contact time, disinfectant treatment, surface area to volume ratio) also likely played a large effect. Although these differences make direct comparison difficult, the results do show the propensity of epoxy linings to leach measurable concentrations of organic carbon into drinking water under both stagnant and dynamic conditions.

In contrast to lab results that showed measurable concentrations of TOC leached from epoxy under stagnant conditions, Heim and Dietrich (2007) found in their field study no difference in leached TOC before and after installation of an epoxy lining under normal flow conditions. This study examined newly-installed epoxy linings under normal flow conditions and found no detectable TOC after flushing the pipes either immediately after installation or after a week of normal use. The results showed that TOC was not a problem when water was not allowed to stagnate and pipes were flushed prior to sampling.

Similarly, in a UK field study examining the impact of aged epoxy samples on water quality, researchers found no statistical differences in TOC between blanks and field samples. This study was commissioned by the Committee on Products and Processes for use in Public Water Supply (CPP) and was intended to test the performance of aged epoxy in existing in situ relined mains. Previous data linking high levels of leached TOC to epoxy had caused the CPP to conclude epoxy was a “high risk material” and could potentially adversely affect the distribution system long-term (Jackson et al., 2007). The study was designed to sample five different aged epoxy resins under different exposure conditions: low and high hardness levels, at low and high free and total chlorine concentrations, and at different ages (1-2 years, 3-6 years, and 7-10 years). Samples were taken during both the spring and fall in order to gauge the effect of water temperature on leaching. Although not every possible combination was taken, a total of 120 samples were collected to analyze TOC levels. Water was allowed to flush through the system for three

minutes before collection to avoid sampling any water that may have stagnated in the pipes. The results of the data from both warm and cold water showed no significant difference in TOC levels between the samples and field blanks, suggesting leaching from the epoxy lining was minimal. They cited no difference in leached organics between water exposed to epoxy and controls. Furthermore, water temperature had no effect on leaching. The results of the study caused the researchers to conclude that experiments performed under stagnant conditions may potentially exaggerate the impacts epoxy has on various water quality parameters (Jackson et al., 2007). However, although the data showed no significant increase of TOC in the water under normal flow conditions, the study did not attempt to address the implications of epoxy on water quality under stagnant conditions. As most homeowners do not practice this technique of flushing the pipes for three minutes before use, it is difficult to gauge whether or not this study in fact understated the effect of epoxy on water quality.

Overall data on TOC was highly variable and relatively inconsistent among experiments. There was shown to be high variability even between epoxy resins that were analyzed under the same test conditions, indicating the specific formulation of epoxy used may be in fact be an important in predicting potential water quality impacts related to TOC.

b. Bisphenol-A and Semi-Volatile Organic Compounds (SVOCs)

As one of the components in many epoxy resins, leached Bisphenol-A in water exposed to epoxy is a possible threat to water quality. BPA has come under scrutiny recently due to its widespread occurrence in a number of different products (baby bottles, food storage containers, etc.) and an extensive database that show BPA causes developmental problems in fetuses during animal studies (National Toxicology Program, 2008). In these studies it has been shown to be an endocrine disrupter, a class of chemicals which can mimic or block the actions of natural hormones. For these reasons, the National Toxicology Program (NTP) has concluded BPA is a chemical of some concern for fetuses, infants, and children at current exposure levels. The NTP cites negligible concern for adults. However, other studies do link exposure to BPA to a number of different cancers and fertility problems in both adult men and women (Bae et al., 2002). Although no MCL exists for BPA, NSF-61 does provide a suggested total allowable concentration (TAC) of 200 ug/L permitted in drinking water. These levels are set for unregulated contaminants detected in drinking water that have yet to receive “normative evaluation criteria established” (ANSI/NSF, 2000). Although the TAC for BPA is set at 200 ug/L by NSF-61, some researchers have claimed concentrations of BPA much lower than 200 ug/L pose serious health threats.

Krishnan et al. (1993), one of the first research groups to study estrogenic effects of BPA, found that concentrations of BPA as low as 6 ug/L can exhibit xenoestrogenic effects in vitro.

Bae et al. (2002) reported in their research on epoxy and BPA a strong correlation between COD levels in the water and BPA concentration. They claimed as organic compounds present in the epoxy resin leach into water, the cross-linking structure of the epoxy weakens and BPA consequently leaches. Therefore as the concentration of organic compounds increase in the water there is a strong indication that BPA levels will also increase.

In an effort to quantify the amount of BPA leached from epoxy linings, Bae et al. (2002) performed immersion tests on new epoxy-lined glass coupons. Coupons were placed in steel containers filled with either deionized water or test water containing 30 mg/L hardness, both at pH 7. Three different epoxy resins were tested at four different temperatures: 20, 50, 75, and 100°C. The results showed BPA leached from each of the samples, with concentrations increasing with increased water temperature.

Concentrations ranged from 0.57 ug/L to 92.39 ug/L, with significantly higher concentrations leached at higher temperatures. Normalized for surface area, concentrations ranged from 1.68 ug/m² to 1735.05 ug/m². This data indicates a fairly high level of BPA leached from the epoxy samples and corresponds to higher risk for BPA leaching during summer months. While these levels fall under the TAC of 200 ug/L of BPA, they are considerably greater than 6 ug/L, the concentration at which in vitro effects can occur according to Krishan et al. (1993). No literature was found that reported detecting BPA in waters exposed to epoxy under dynamic conditions.

In addition to BPA, a number of organic compounds have been reported to leach from epoxy. Utilizing the UQT, Heim and Dietrich (2007) confirmed the presence of BPA as well as phenols, toluene, benzaldehyde, and styrene in waters exposed to new epoxy. The study did not attempt to quantify the actual concentration of these compounds.

In another immersion study, Autret and Saisset (1999) reported the only organic compound detected was a very small concentration of benzyl alcohol (~10 ug/L) and it was only detectable under stagnant conditions. The 1999 study tested performance of newly-coated epoxy-lined stainless steel pipes (150 mm length x 80 mm internal diameter) under numerous water quality parameters and conditions, including two different lining thicknesses (0.5 mm and 1.0 mm), two disinfection products and concentrations (1.5 and 50 mg/L Cl₂, 100, 500, and 1000 mg/L Herlisil), two exposure times (1 hour and 6 hours), various curing temperatures and times (45-50°C and 65-70°C, both for 3 hours or 15-20°C and 40°C, both for 1.5 hours), two water temperatures (8 and 25°C), two flow conditions (stagnant and dynamic), and three different water types (highly corrosive sea water, acid demineralised water, and

urban potable water). They found no difference in lining thickness or disinfectant choice or concentration with regard to leached organics but did detect minor benzyl alcohol concentrations when the curing time was short (< 3 hours) and the curing temperature was low (< 40°C) or the water temperature was high (25°C) (Autret and Saisset, 1999). This study again confirmed that curing time and temperature are factors that contribute to VOC leaching and that these are important things for utilities to consider when applying epoxy. Considering that epoxy linings are now required by NSF-61 to be benzyl alcohol free, the fact that this was the only chemical detectable suggests that epoxy is a negligible source of contamination under normal flow conditions.

In sharp contrast to Autret and Saisset (1999), a study performed by Satchwill (2002) also using immersion tests reported alarmingly high concentrations of BTEX. Their data reported both the highest TOC ranges and the highest identified organic compounds. Concentrations ranged from 0.2 to 48.0 mg/L of BTEX (0.067 – 16 mg/L/d), although they did not differentiate between which BTEX compounds were present. The values were significantly higher than other available data and caused the researchers to conclude that the epoxy linings “can cause significant contamination of the drinking water” and that “careful monitoring of the application process followed by water quality testing is critical when pipe linings are used” (Satchwill, 2002). Again, no information was provided regarding surface area to volume ratio so making a direct comparison is difficult, but the concentration of BTEX was orders of magnitude larger than concentrations of any organic compounds reported in other studies.

The Satchwill report also documented a 1989 Canadian field study in which homeowners had complained about taste and odor issues following relining of a portion of the distribution system using epoxy. Analysis of water showed BTEX in excess of 300 ug/L. Extensive flushing of dead-end zones in the pipes reduced concentrations but BTEX levels could never be reduced less than 10 ug/L. Eventually the utility was able to determine the source of organic contamination and attributed it to a portion of an improperly-installed epoxy lining. After replacing the faulty section with PVC the concentrations immediately fell below detection limits. In contrast to their lab data, field data show with proper installation epoxy linings have a minimal effect on leached organics under normal flow conditions (Satchwill, 2002).

TOC and specific organic compounds leached from epoxy appear to be the primary concern among researchers performing water quality assessments on epoxy linings. There were significant differences between the results of the tests, with some researchers concluding epoxy is a higher-risk material (Satchwill, 2002) and others finding negligible impact on organics. The data show there to be a number of factors contributing to leaching organics (including specific epoxy formulation, curing time,

application conditions, water temperature, pipe flow, and disinfectant used). Each of these is likely to contribute to how well specific linings perform.

c. Disinfection Byproduct Formation

TOC present in water distribution systems is known to react with free chlorine in the distribution system to form trihalomethanes (THMs) and haloacetic acids (HAAs), two disinfection byproducts (DBPs) regulated by the EPA due to their carcinogenic nature. Regulatory limits have been set at 60 ug/L for HAAs and 80 ug/L for THMs (USEPA, 2000). In their research utilizing the UQT, Heim and Dietrich (2007) found that in waters exposed to epoxy trichloromethane was present in concentrations significantly higher than in controls. Chlorinated water was found to have a concentration of 3-9 ug/L while chloraminated water had a concentration of 0-3 ug/L. (TOC concentrations were 0.6 mg/L and 1.5-1.7 mg/L chlorine was consumed.) In a separate experiment, Heim and Dietrich exposed water containing no disinfectant to epoxy. Free chlorine was then added to the water containing leached TOC and allowed to react for 0, 24, and 72 hours. Trichloromethane concentrations were found to increase substantially, with a concentration of 7 ug/L detected upon initial contact and 60 ug/L detected after 72 hours. It was also noted that trichloromethane will decrease over time upon exposure to epoxy. When a solution of water spiked with 48 ug/L trichloromethane was exposed to epoxy, the concentration decreased by 25% over 72 hours. Although a greater decrease than in the control containing no epoxy, the results were not significant. When the concentration was decreased to 17 ug/L and the contact time increased to 7.5 days, trichloromethane concentrations decreased by 50%, significantly higher than controls. The results of the study showed that THMs will decrease over time, possibly as a result of sorption to the epoxy layer. The initial THM concentration and exposure time affects the amount that is consumed.

The data confirm the ability of TOC leached from epoxy to react with disinfectant and produce DBPs. Concentrations in the study, however, were much lower than regulated concentrations so the DBP formation potential of epoxy linings appears to be acceptable.

d. Taste and Odor

Water utilities must provide drinking water free of foul taste and odors because consumers judge the quality and safety of their water based on these aesthetics (Tomboulou et al., 2004). Taste and odor issues in drinking water have been found to occur as a result of both biological causes such as microbial

activity and chemical causes such as reactions occurring between disinfectant and organic matter present in the distribution system (Khiari et al., 1999). Epoxy lining materials, capable of leaching organics, plasticizers, and solvents, can be problematic not only because these compounds are potentially harmful but because they have the capacity to impart taste and odors to the distribution system (Tombouliau et al., 2004). This is a concern for utility companies because certain compounds can result in objectionable odors even when below the action level. Complicating the matter, the US has no aesthetic standards for drinking water so determining what is acceptable or unacceptable can be a difficult and subjective task (Tombouliau et al., 2004). As epoxy linings have been responsible for taste and odor problems in the past (Satchwill, 2002), a fair amount of research has been conducted to attempt to quantify these effects. Many of these researchers have made use of Flavor Profile Analysis (FPA), a sensory method that employs trained odor panelists to rate both the intensity and odor descriptor of the sample being analyzed. FPA is based on a scale of 0-12, where an intensity of 0 represents an odor-free sample, 12 is very strong, and 2 would be considered detectable to consumers.

In their research on synthetic products used in contact with drinking water, Marchesan and Moran (2004) used FPA to examine 343 different materials, 13 of which were epoxy resins used for relining. (This FPA was based on accordance with the Australian water quality standard, AS/NZS 4020, which does set guidelines for both MCLs and taste and odor parameters in drinking water.) Their tests involved immersion of the sample in 20°C, 50 mg/L hardness test water for four 24 hour periods, a single 72 hour period, and then three more 24 hour periods. The experiment was repeated for both no disinfectant test water and 1 mg/L free chlorine. Of these 343 materials, 29 failed to meet the regulations, 2 of which were epoxy materials. The most common complaint for epoxy samples was a plastic/rubbery taste. This taste was even stronger for samples containing free chlorine. Upon completion of the study, the researchers concluded a taste and odor analysis should always be performed in addition to simple chemical and microbiological assessment, as 8.5% of the products passing the chemical assessment still failed to meet taste requirements.

Heim and Dietrich (2007) performed sensory analysis on epoxy-lined pipe samples using FPA. They performed three replicate tests using the UQT in which their pipes were filled with one of three disinfectant treatments: no disinfectant test water, 2 mg/L free chlorine, or 4 mg/L monochloramine. Controls containing no epoxy were also prepared. The results of their tests showed that exposure to epoxy for 72 hours produced a characteristic “plastic/adhesive/putty” odor with an intensity ranging from 3 and 6. They found no major differences between disinfectant type other than the controls having a stronger chlorinous odor due to disinfectant consumption by the epoxy. Heim and Dietrich found that odor was proportional to stagnation time and a one hour exposure was not long enough to produce odor

problems. They also reported that after 30 minutes of flushing at a field site where epoxy had been used to reline copper pipes, no detectable odor was present. Figure I-2 is a table is taken from Tombouliau et al. (2004) and shows a list of organic compounds known to leach from epoxy and to cause taste and odor issues.

Table I-2. Organic compounds known to leach from epoxy and cause taste and odor issues (Tombouliau et al, 2004) and reported associated odors (in red) (Heim and Dietrich, 2007)

1,1 – dichloroethene	ethyl benzene
3-methoxy-2-propanol	Ethylhexanol
4,4-methylenedianiline	isobutyl acetate
Benzaldehyde – “aldehyde”	isopropoxy propanol
Benzidine	methylisobutyl ketone
benzyl alcohol	n-butanol
bisphenol-A – “phenol-like”	n-butyl acetate
bisphenol-A diglycidal ester	Nonylphenol
bisphenol-F	Phenol – “phenol-like”
Butoxyethanol	Styrene – “sweet”
Diethylenetriamine	Toluene – “sweet solvent”
diphenyl ether	tripropylene glycol
Epichlorohydrin	

A French study conducted by Rigal and Danjou (1999) also examined taste and odor analysis on a newly epoxy-lined pipe, but using a different taste and odor assessment tool than FPA. This assessment was based on performing successive dilutions of a sample with reference water until flavor was no longer detectable to panelists. The number of dilutions required before flavor was undetectable was then labeled as the threshold flavor number, or TFN. To perform the study Rigal and Danjou relined a section of pipe using an epoxy resin based on Bisphenol and amines with benzyl alcohol in the hardener. Ideal conditions were used to ensure proper application. After 1 hour of cure time, the pipe was exposed to water and analyzed for taste and odor issues and the presence of organics using GC/MS. Panelists reported a glue/bitter almond flavor and a TFN of 6. At this time benzyl alcohol and a number of derivatives of butane diol were detected at a concentration of approximately 800 ug/L. After 24 hours another panel was conducted, with panelists reporting the flavor as bitter and decreasing to 2.5; no organics were detected at this time. The same analysis was conducted again after 1 week and panelists reported the same bitter flavor at an intensity of 2.5; again, no organics were detected. Although no information was provided as to the composition of test water, the study confirmed that organics leached from epoxy are likely responsible for taste and odor issues, as the presence of organics in the water

correlated to a high intensity on the taste and odor scale. The researchers concluded that the polymerization of the epoxy resin after 1 hr was not yet complete, hence the presence of the organic base components in the water and the high TFN rating. Once the epoxy cured completely, analysts reported a low taste and odor and no detectable organic compounds.

The available data show epoxy linings do have the capability of causing organoleptic problems in drinking water. The literature has shown these problems have generally been encountered in newly-installed epoxy-lined pipes and in areas where water has been allowed to stagnate. In cases of proper installation, flushing appears to be an effective method at removing the odor. Persistent odors would be cause for utilities to analyze the water for the presence of organics and test the lining for possible failure.

Another key point made in the literature is that performing taste and odor analysis of epoxy resin materials appears to be a critically-overlooked step in the United States. Considering epoxy is known to leach VOCs and knowing that some of these compounds can be detected by consumers at concentrations lower than the MCL (Tomboulion et al., 2004), American epoxy manufacturers would certainly benefit from implementing a similar taste and odor protocol as required by European and Australian counterparts.

e. Microbial Growth

The available literature on microbial growth related to epoxy linings has found that microbial growth can increase upon exposure to epoxy but that these increases are not likely to be pathogenic or pose a threat to water quality. One of the earliest studies on epoxy linings performed by Warren et al. in 1983 (described earlier) found that epoxy linings did in fact support a greater population of microbes than unlined pipes. Although the bacterial count increased by orders of magnitude when compared with controls, the bacteria were found to be non-pathogenic and after a short period of time leveled back to initial populations.

Bae et al. (2002) also examined the microbial populations during their immersion tests and found that microbial growth significantly increased after exposure to epoxy. The researchers coated a glass container with the three different resins and compared microbial populations in this container with an uncoated stainless steel container. Populations were counted at the beginning of the experiment and again after five to six days. Populations in the epoxy-coated container increased from approximately 370 CFU to 3400 CFU while populations in the steel container increased from approximately 84 CFU to 732 CFU after exposure. The researchers did find that the amount of TOC leached did not correlate with microbial growth, as the resin type that leached the most TOC had the lowest proportion of bacterial colonies. This

caused the researchers to conclude that although the presence of epoxy correlates with increased microbial growth, the actual compounds leaching from the epoxy are not growth-supporting.

The literature shows that while epoxy linings may be capable of supporting increased microbial populations, they indicate the increases are not likely to be a cause for concern.

Chapter II

I. Significance of Research

Although research has been conducted on specific water quality parameters related to epoxy linings, no available literature exists that provides a comprehensive look at the effect of epoxy on multiple water quality parameters immediately following installation. Furthermore, no literature was found that could provide a comparison between how different lining materials perform under identical test conditions. Among existing studies, inconsistencies in experimental designs (including highly variable or unstated water compositions, differing flow conditions, unknown lining material surface area to water volume ratio, etc.) make it difficult to directly compare results and draw conclusions between lining materials. This AWWA-funded research project seeks to fill this gap in the literature by providing practical information regarding the impact of three commonly-used lining materials (epoxy, polyurethane, and cement mortar) on the following water quality parameters: pH, disinfectant residual, ammonia, alkalinity, total hardness, metals, TOC, SVOCs, disinfection byproducts, and odor. Although this paper specifically addresses only data obtained from the epoxy testing, the overall research project was designed with the purpose of providing data that could be used to make a direct comparison between the three targeted lining materials. Identical bench-scale studies are performed to measure impacts on water quality parameters that are of importance to both utilities and public health and perception. Taking into account data that show pipes and lining materials perform differently under different disinfectants, this research also examines three separate disinfectant treatments: no disinfectant, chlorine, and monochloramine. For epoxy, it also compares new and aged epoxy by testing newly-lined glass coupons and an epoxy-lined pipe previously in service. The 30-day study is based upon NSF-61 testing for distribution materials and utilizes immersion tests to mimic zero flow conditions that would occur when water stagnates in a pipe. Stagnant conditions are recommended by ANSI/NSF-61 for experimental design in that they simulate a kind of worst-case situation.

II. Experimental Design and Implementation

A. Experimental Preparation

For the newly-lined glass coupons, coating with epoxy was achieved with the cooperation of an ANSI/NSF-61 approved epoxy manufacturer. The lining was an epoxy material commonly used in water distribution systems. Epoxy was coated on sand-blasted and roughened 8 cm x 8.5 cm x 0.5 cm glass coupons that were shipped to the manufacturer in late February, 2008, encapsulated, and shipped the following day. Coupons cured for 60 hrs before leaching tests were begun. The tests were completed April 5, 2008. All coupons were disinfected prior to beginning the study by soaking the coupons in a 200 mg/L Cl₂ solution for 30 minutes. After being removed, the coupons were thoroughly rinsed with Nanopure® water and allowed to air dry.

A previously used epoxy-lined copper pipe sample from a different manufacturer (26.70 cm in length, 3.63 cm interior diameter) was used as the comparison for aged epoxy. The pipe was approximately 1.5 in. in diameter, less than half the diameter of the pipe the epoxy coupons were meant to simulate, so it had a much greater surface area to volume ratio. The total volume of the pipe was 276.32 cm³ and the surface area was 304.49 cm². The pipe was cut from an active service line in British Columbia and was in service from April 2003 to May 2007 and carried chlorinated water at 140°C. Before beginning the study a 1-in length of the pipe was sawed from the pipe for microbial analysis. The pipe was then thoroughly rinsed with Nanopure® water. The epoxy layer at this time was smooth in finish and had no visible tears or holes. No scale or biofilm could be seen on the surface of the lining prior to the study.

B. Leaching of Coupons

Triplicate borosilicate immersion test vessels of approximately 3 L in volume containing epoxy coupons were prepared for each water type: no disinfectant, 2 mg/L chlorine, 4 mg/L chloramines. The ratio of water volume to epoxy surface area was designed to represent a 4-inch diameter pipe. The experiment was intended to provide a high surface area to volume ratio and so as to maximize water quality impacts. In addition to the triplicate vessels containing epoxy, a single control for each water type was prepared that contained no epoxy coupons. All test vessels were maintained headspace-free and stored in the dark throughout the experiment. The temperature remained between 19 and 23°C. The test vessels were created specifically for this study and, due to construction limitations, had a natural variability to the volume. In order to compensate for the differences and achieve the closest possible surface area to volume ratio, the number of full-sized coupons placed in each vessel was varied between 5½ and 7. The

surface area to volume ratio ranged from 0.351 to 0.375 cm⁻¹. Table II-1 shows the surface area, volume, and number of coupons in each test vessel.

Table II-1. Volume, surface area, and number of coupons in test vessels

Treatment	Apparatus	Coupons	Volume (cm ³)	SA (cm ²)	SA/Vol (cm ⁻¹)
No Dis.	1x	6.5	2910	1027.06	0.352
No Dis.	1y	7	2960	1101.64	0.372
No Dis.	1z	7	3000	1101.64	0.367
No Dis. Control	1c	0	2745	0	0
Cl ₂	3x	6.5	2740	1027.06	0.375
Cl ₂	3y	5.5	2480	869.68	0.351
Cl ₂	3z	7	2970	1101.64	0.371
Cl ₂ Control	3c	0	2840	0	0
NH ₂ Cl	4x	6.5	2920	1027.06	0.352
NH ₂ Cl	4y	7	2945	1101.64	0.374
NH ₂ Cl	4z	6.5	2920	1027.06	0.352
NH ₂ Cl Control	4c	0	3000	0	0

C. Test Water Composition

Reference water was prepared by adding a series of salts to Nanopure® water. Three Pyrex bottles, each containing eleven liters of water, were prepared for each water change/sampling date. One bottle was set aside for no disinfectant and contained only Nanopure water and salts. A second bottle containing 2 mg/L Cl₂ was prepared by adding NaOCl to the finished reference water. Free chlorine concentration was measured after preparation to ensure the concentration was 2 mg/L. Chloraminated test water was prepared by adding NH₄OH while being continuously stirred. After five minutes of mixing on a stir plate, a solution of NaOCl was quickly added to the water and shaken vigorously for 30 seconds. Free and total chlorine was measured to ensure the chloramines concentration was close to 4 mg/L. The make-up of the water was designed as a low alkalinity, low hardness water representative of water typical of the Eastern United States. The three water types are shown below

- No disinfectant, pH 8.0, low alkalinity (35 mg/L as CaCO₃), low hardness (61.7 mg/L as CaCO₃)
- 2 mg/L chlorine, pH 8.0, low alkalinity (35 mg/L as CaCO₃), low hardness (61.7 mg/L as CaCO₃)
- 4 mg/L monochloramine, pH 8.0, low alkalinity (35 mg/L as CaCO₃), low hardness (61.7 mg/L as CaCO₃)

Salts (shown in Table II-2) were added to the reference water at specific concentrations to ensure consistent water. pH of the water was adjusted using dilute HCl.

Table II-2. Reference water composition

Salt	Molarity (M)	Concentration
MgSO ₄	3.292x10 ⁻⁴	39.56 mg/L
NaHCO ₃	6.773x10 ⁻⁴	56.89 mg/L
CaSO ₄	1.452x10 ⁻⁴	19.78 mg/L
CaCl ₂	1.415x10 ⁻⁴	15.70 mg/L
Na ₂ SiO ₃	9.149x10 ⁻⁵	11.16 mg/L
KNO ₃	9.890x10 ⁻⁵	10.00 mg/L

D. Water Changes and Sampling Protocol

A sampling schedule was designed prior to beginning the experiment that designated on which sampling days each water quality parameter would be analyzed. The schedule was loosely modified from NSF-61 sampling protocol for testing of distribution pipe materials. Water changes were performed at approximately the same time every sampling day. To begin the experiment, disinfected and rinsed coupons were inserted into Teflon stands and placed in specified test vessels. Prepared test water was carefully poured into the vessels, completely immersing the coupons. The borosilicate lid was pulled across the surface of the vessel to ensure no headspace was present and the vessels were placed in the dark until the next scheduled water change.

To perform water changes in the pipe, the pipe was filled with the same chlorinated reference water as prepared for the other samples. It was sealed on one side with a Teflon-coated rubber stopper, filled headspace free with the reference water, capped with another Teflon-coated rubber stopper, and stored in the dark adjacent to the test vessels. Figure II-1 below shows one of the test vessels containing epoxy coupons and Figure II-2 shows the epoxy-coated pipe.



Figure II-1. Test vessel containing epoxy coupons



Figure II-2. Epoxy-coated copper pipe

To begin a water change, lids were removed from the vessels and water was collected with cleaned glass beakers and gently poured into cleaned and labeled glass bottles, VOA vials, or flasks. Samples were then sealed accordingly and either immediately analyzed or placed in the refrigerator for later analysis. Bottles and vials containing water intended for organic carbon analysis (TOC, SVOCs, DBPs) were collected, capped with Teflon-faced septa, and stored headspace-free. Vials containing metals samples were acid-washed prior to collection. All samples were analyzed within the allotted time frame according to QA/QC protocol (shown in Table II-4). pH, temperature, disinfectant residual, and ammonia concentrations were always measured immediately after collection. Odor analysis was also conducted within three hours of sample collection; samples were stored in Erlenmeyer flasks and chilled until analysis. After all samples were collected, excess water was poured out and test vessels were refilled with new reference water. Vessels were resealed headspace-free and stored in the dark until the next water change. The sampling schedule is listed in Table II-3, with the water quality parameters and corresponding sample dates shown. Protocols met QA/QC requirements as specified by EPA-SW 846 or Standard Methods protocols.

Table II-3. Frequency for measuring chemical water quality parameters for bench-scale testing for epoxy

Parameter	Standard Method Test Method	Water Change/Sampling Day
pH*	Std Method 4500-H+	1, 2, 4, 9, 11, 14, 15, 19, 21, 30
Disinfectant Residual*	Std Method 2350	1, 2, 4, 9, 11, 14, 15, 19, 21, 30
Ammonia*	Std Method 4500	1, 2, 4, 9, 11, 14, 15, 19, 21, 30
Temperature*	Std Method 4500-H+	1, 2, 4, 9, 11, 14, 15, 19, 21, 30
Alkalinity	Std Method 2320	1, 2, 4, 9, 11, 14, 15, 19, 21, 30
Hardness*	Std Method 3125	1, 2, 4, 9, 11, 14, 15, 19, 21, 30
Metals*	Std Method 3125	1, 2, 4, 9, 11, 14, 15, 19, 21, 30
TOC*	Std Method 5310C	1, 2, 4, 9, 11, 14, 30
Odor	Std Method 2170	1, 4, 9, 14, 19, 21, 30
THMs*	Std Method 6232D	1, 4, 9, 14, 30
HAAs*	EPA Method 552.3	1, 4, 9, 14
SVOCs	Std Method 6410B	1, 4, 9, 14
Total Solids	Std Method 2540B	1, 4, 9, 14

*Indicates tests also performed on aged pipe sample

No SVOCs, total solids, or odor data could be gathered from the mature pipe due to the smaller volume of water obtained from the pipe.

Table II-4. Required containers, preservation techniques, and holding times for sample analysis (EPA SW-846)

Test	Storage Container/ Replicates	Preservation Technique	Holding Time
pH	Glass/3	None	Immediately
Disinfectant Residual	Glass/3	None	Immediately
Ammonia	Glass/3	4°C, pH < 2 using H ₂ SO ₄	7 days
Temperature	Glass/3	None	Immediately
Alkalinity	Glass/3	4°C	14 days
Hardness	Glass/3	4°C, pH < 2 using HNO ₃	6 months
Metals	Glass/3	4°C, pH < 2 using HNO ₃	6 months
TOC	Glass/3	4°C, pH < 2 using HCl	28 days
Odor	Glass/1	None	Immediately
THMs	Glass/3	4°C, dechlorinate	14 days
HAAs	Glass/1	4°C, dechlorinate	14 days
SVOCs	Glass/1	4°C, pH < 2 using HNO ₃	14 days
Total Solids	Glass/3	4°C	7 days

E. Statistical Analysis

Statistical Analysis was performed using R statistical software. Paired t tests were most commonly used as a comparison between the samples and the corresponding controls. Where triplicate samples were collected, the mean value of the three samples was used as a comparison between the control. An alpha value of 0.05 was used for statistical significance. Where appropriate, error bars are drawn on the graphs to indicate the standard deviation between the triplicate samples. No bars are drawn for controls, the aged pipe sample, or hardness and HAAs samples as only one sample was taken and/or analyzed for each. Due to differences in surface area to volume ratio between epoxy coupons and the pipe sample, when making comparisons between new and mature epoxy, concentrations were normalized for surface area.

III. Methods for Chemical Measurements

Samples were collected by following standard methods and protocols and providing adequate QA/QC samples where required. Methods are described below.

pH and Temperature

Temperature and pH were measured using Standard Method 4500-H+ using a Corning 315 pH/ion probe that was calibrated using standard pH solutions 4, 7 and 11 (BioWorld).

Total Alkalinity

Alkalinity was measured using Standard Method 2320. H₂SO₄ (CAS# 7664-93-9) with concentration 0.0190 N was titrated into 100 mL samples to pH 4.5.

Disinfectant Residual

Disinfectant Residual was measured using Standard Method 2350 with a HACH® kit (HACH®, free chlorine CAT# 21055-69, total chlorine CAT#21056-69) measuring free and total chlorine. Free chlorine was used to measure the chlorinated sample water. Monochloramine was calculated using free and total chlorine (Total – Free = Chloramine).

Nitrogen-Ammonia (N-NH₃)

Nitrogen-Ammonia (N-NH₃) was measured using Standard Method 4500 with a HACH® kit using salicylate (HACH, CAT# 26522-99) and cyanurate reagents (HACH, CAT# 26531-99).

Solids

Total Solids (TS) was measured using Standard Method 2540B. Selected samples were filtered through a 0.5µm filter to measure dissolved solids and particulate solids.

Elemental Analysis for Metals, Non-Metals, and Hardness

Selected trace metals (Sodium (Na), Magnesium (Mg), Aluminum (Al), Potassium (K), Vanadium (V), Chromium (Cr), Iron (Fe), Manganese (Mn), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Molybdenum (Mo), Cadmium (Cd), Tin (Sn), Barium (Ba), and Lead (Pb)), non-metal (Sulfur (S), Phosphorous (P), Chlorine (Cl), and Silicon (Si, a semi-metal) were measured. Standard Method 3125 was used and the samples were analyzed on ThermoElectron Corporation inductively coupled plasma mass spectrometer (ICP-MS) X-Series. Hardness, as the sum of calcium and magnesium concentrations, was measured using the elemental analysis results.

Total Organic Carbon (TOC)

Total organic carbon (TOC) was measured using Standard Method 5310C using a Shimadzu TOC-V Total Organic Carbon Analyzer. The samples were acidified to < pH 2 using Nitric acid (CAS# 7697-37-2). Two measurements were taken from each replicate, if the samples were not within 20% a third sample was taken and an average was calculated to give the TOC concentration for that sample.

Trihalomethanes

Trihalomethanes were analyzed using Standard Method 6232D using Tre Metrics 9001 gas chromatograph, Tracor 1000 Hall® Detector, Purge & Trap Autosampler Tekmar 2016 and Purge & Trap Concentrator Tekmar 3000. The column used was a DB-624 with helium as the carrier gas with the initial oven temperature at 45 °C and held for 3 minutes, increasing at 11 °C/min with a maximum oven temperature of 200 °C. Standard curves were performed for each run unless run sequentially (THM-521-1 Ultra 5000 µg/mL standard).

Haloacetic acids (HAA5)

The HAA5 extractions were performed following EPA Method 552.3 using liquid-liquid extraction, derivitization, and gas chromatography with electron capture detection. The standard (Methylated

Haloacetic Acid Standard, Chem Service, West Chester, PA) contained concentrations of HAA5 ranging from 20 µg/L-60 µg/L. The GC column used was a DB-1701 (30 m length, 0.25 diam., 0.25 µm film) with helium as the carrier gas and nitrogen as the makeup gas. Initial oven temperature was 35 °C, which was held for 10 min and increased at 5.7 °C/min to 75 °C and held for 5 min. Temperature was again increased at 5 °C/min to 100 °C and held for 5 min, then increased at 20 °C/min to 140 °C and held for 5 min. After being removed and equilibrating to room temperature, the samples were identified and quantified using procedural standard calibration.

Semi-volatile organic compounds (SVOCs)

Semi-volatile organic compounds (SVOCs) were measured using Standard Method 6410B which is a liquid-liquid extraction using methylene chloride and then concentrated using a Kaderna-Danish apparatus at 75 °C water bath. The samples were analyzed using a gas chromatograph-mass spectrometer (GC-MS) using a DB-5 column (30.0 m x 250 µm x 0.30 µm). The initial oven temperature was 40 °C and was held for 3 minutes then increased by 8 °C/min to 200 °C and held for one minute. The column was then heated by 10 °C/min to 300 °C and held for 11 minutes. The targeted compounds were identified using standard NIST elution times as well as mass spectra. Non-targeted compounds were tentatively identified based on library matching of mass spectra. For Bis-Phenol A, chemical standards were prepared and retention times and mass spectra compared to confirm their qualitative identity and measure quantitative amounts.

Odor Analysis

Odor analysis was performed using the Flavor Profile Analysis (FPA) using Standard Method 2170 where FPA participants underwent a one day long training session to learn the Flavor Profile Analysis method. The study protocol was approved by the Institutional Review Board for Research Involving Human Subjects at Virginia Tech. The FPA intensity scale is 0: odor free (OF), 1: threshold, 2: very weak, 4: weak, 8: moderate, 10: strong, 12: very strong. The weak intensity corresponds to the sweetness of canned fruit (for comparison, FPA taste intensity of 8 is moderate and corresponds to canned soda while an FPA intensity of 12 is strong and corresponds to syrup or jelly).

Trihalomethane Sorption/Formation Experiment

An issue for leaching tests, including those described in NSF-61, is that DBPs can form in the water during leaching and then be re-sorbed into the lining material and consequently not measured. This phenomenon was investigated for selected trihalomethanes. The formation of trihalomethanes from the

reaction of TOC leached from the lining material and added chlorine used for disinfection was investigated by placing coated coupons in reference water with no disinfectant and allowing leaching to occur over a 72 hour period under headspace free conditions at room temperature. The TOC was then measured from aliquots of the leached water that were placed in headspace free VOA vials with the addition of free chlorine. At 0, 24 and 72 hour time intervals, 0.0250 N sodium thiosulfate solution was added to quench the THM formation reaction. The samples were then analyzed for disinfectant residual and THMs. To investigate if THMs could sorb into the lining material, coated coupons were immersed headspace free for up to 72 hours in reference water containing 15-100 $\mu\text{g/L}$ of THMs and no free chlorine. Lining material coupons were placed in the test apparatus with the standard water without disinfectant for 72 hours under headspace free conditions. The sorption of trihalomethanes into the lining was tested by determining the concentration of THMs in the water over time.

IV. Data and Results

A. Inorganic Water Quality Parameters

a. pH

No difference in pH was seen between any of the three water types exposed to new epoxy and their controls and no change in pH over time was found (Figure II-3). pH of the waters was shown to naturally fluctuate between 7.8 and 8.2, but these differences were generally mirrored in control samples. Upon addition of chloramines to the chloraminated test water, the pH was found to increase to approximately pH 9 and to resist initial adjustment back to pH 8.0. Following Day 2, dilute HCl was continuously added to the reference water to ensure the pH returned back to 8.0. Chloraminated water from Days 1 and 2 shows this large increase in pH (present in both test samples and controls), which is due to the addition of chloramines and is not a result of interaction with the epoxy. Statistical analysis using paired t tests confirms no statistical difference between the test waters and the controls ($p = 0.102, 0.180, 0.232$ for no disinfectant, chlorinated, and chloraminated waters, respectively). The data indicate the new epoxy lining has no effect on pH in any of the three water treatments.

For the aged pipe sample filled with chlorinated test water, the pH was shown to decrease marginally but consistently over the experiment when compared with the chlorinated control (Figure II-4). The pH dropped approximately 0.3 pH units on average, an insubstantial but statistically significant decrease when compared with controls ($p < 0.001$, one-sided t test). It is uncertain whether or not the specific formulation of the epoxy, the presence of bacteria on the surface of the lining, or another factor is responsible for the small but detectable change in pH. The results of the data are insignificant, however, because such a minor pH change would not affect water quality nor pose problems for utilities as the pH values fall within the EPA recommended range of 6.5 to 8.5 (USEPA, 2000). Overall the pH data supports the available literature that epoxy has no significant impact on pH.

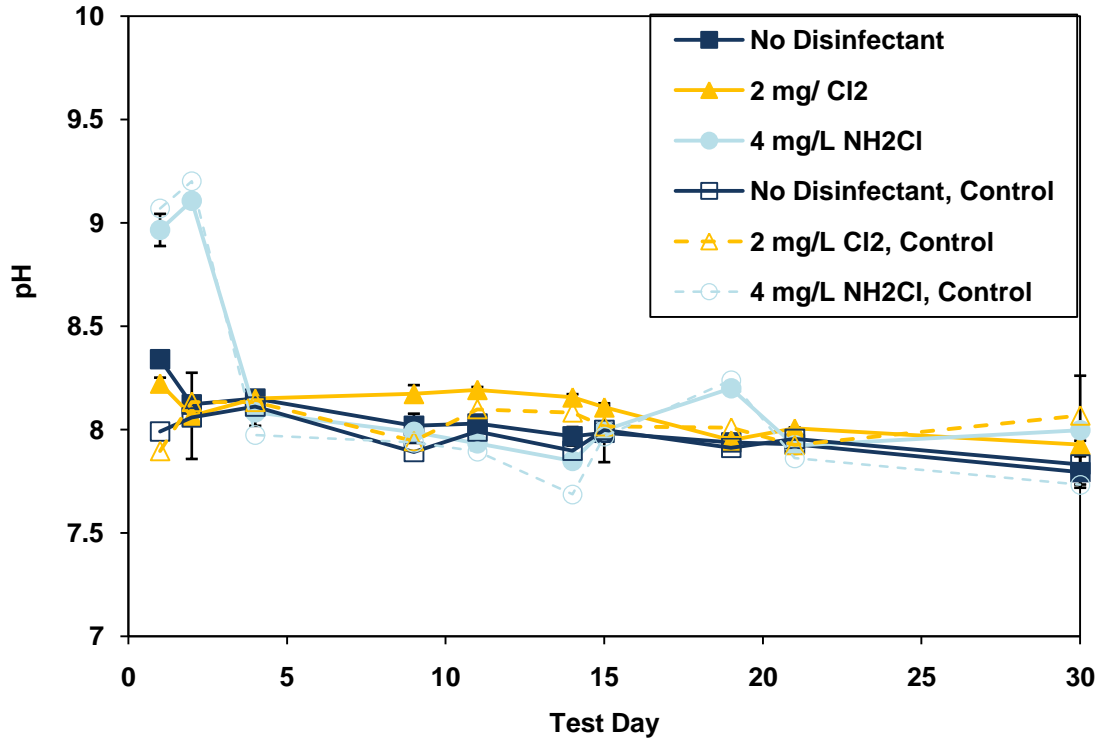


Figure II-3. pH as a function of time for all three water treatments and corresponding controls; error bars indicate standard deviations

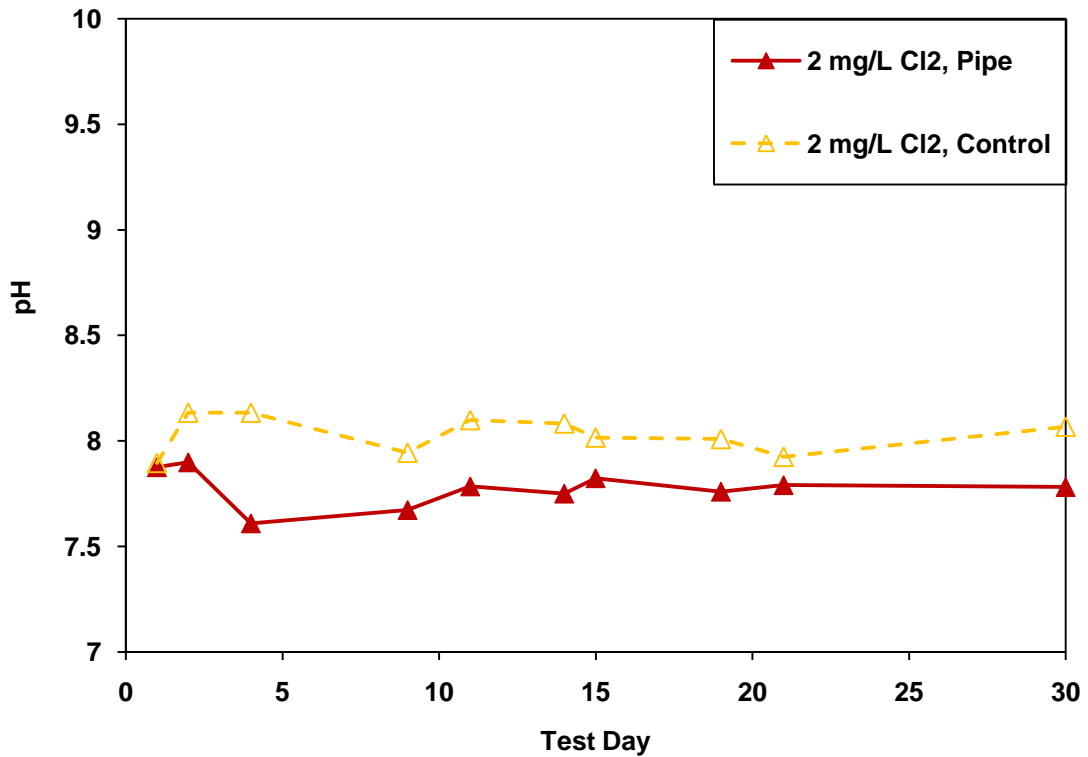


Figure II-4. pH as a function of time for chlorinated aged pipe sample and chlorinated control

b. Alkalinity

No difference in alkalinity was detected between any of the three disinfectant treatments and their controls ($p = 0.939, 0.995, 0.599$ for no disinfectant, chlorinated, and chloraminated waters, respectively, paired t tests). The higher alkalinity readings on Days 1 and 2 in both the chloraminated test waters and chloraminated controls correspond to the higher pH readings on both days as a result of the addition of monochloramine (Figure II-5). The target alkalinity for the reference waters was prepared as 35 mg/L as CaCO_3 . Again, with the exception of Days 1 and 2 for chloraminated samples and controls, alkalinity was shown to remain within approximately 3 mg/L as CaCO_3 of the target alkalinity.

Analysis performed to compare alkalinity in the aged pipe sample to the chlorinated control also showed no difference between alkalinity in the chlorinated mature pipe sample and in the control ($p = 0.121$, paired t test). Both analyses indicate that neither the new epoxy coupons nor the aged pipe sample have any effect on alkalinity.

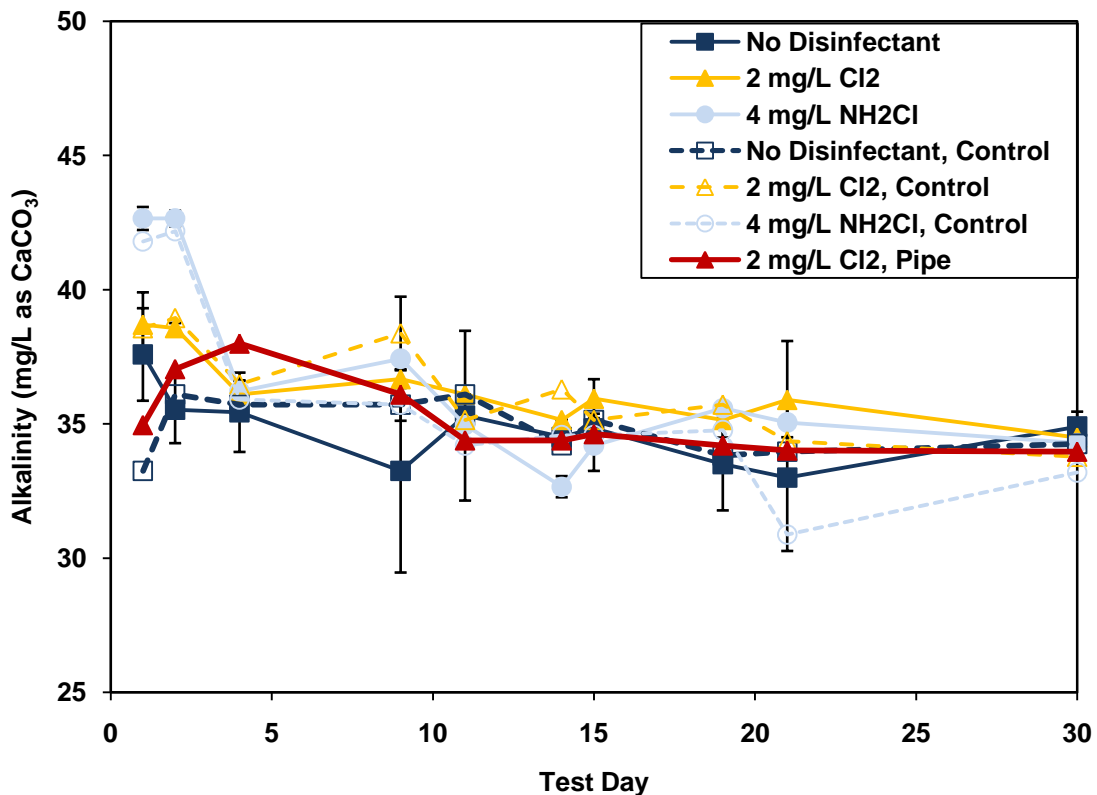


Figure II-5. Alkalinity as a function of time for all three water treatments and corresponding controls; error bars indicate standard deviations

c. Hardness

No impact on hardness was seen in waters in contact with epoxy. The two primary constituents of hardness in the waters are calcium and magnesium, both added as salts to the test waters at a concentration of 11.5 mg/L Ca and 8 mg/L Mg (61.7 mg/L total hardness as CaCO₃). Hardness concentrations were identical in samples exposed to epoxy liners and controls. Data for the samples from exposed to epoxy (including the aged pipe sample) are shown in Figure II-6. Analysis using paired t tests confirms no difference between test waters and controls (p = 0.900, 0.605, 0.324 for no disinfectant, chlorinated, and chloraminated waters, respectively).

Similarly, there was no statistical difference in hardness between the aged pipe sample and the chlorinated control (p = 0.439, paired t test). Neither new nor aged epoxy was shown to have an impact on total hardness. These results were expected. (Controls are not shown but also showed no deviation from the target alkalinity of 61.7 mg/L as CaCO₃.)

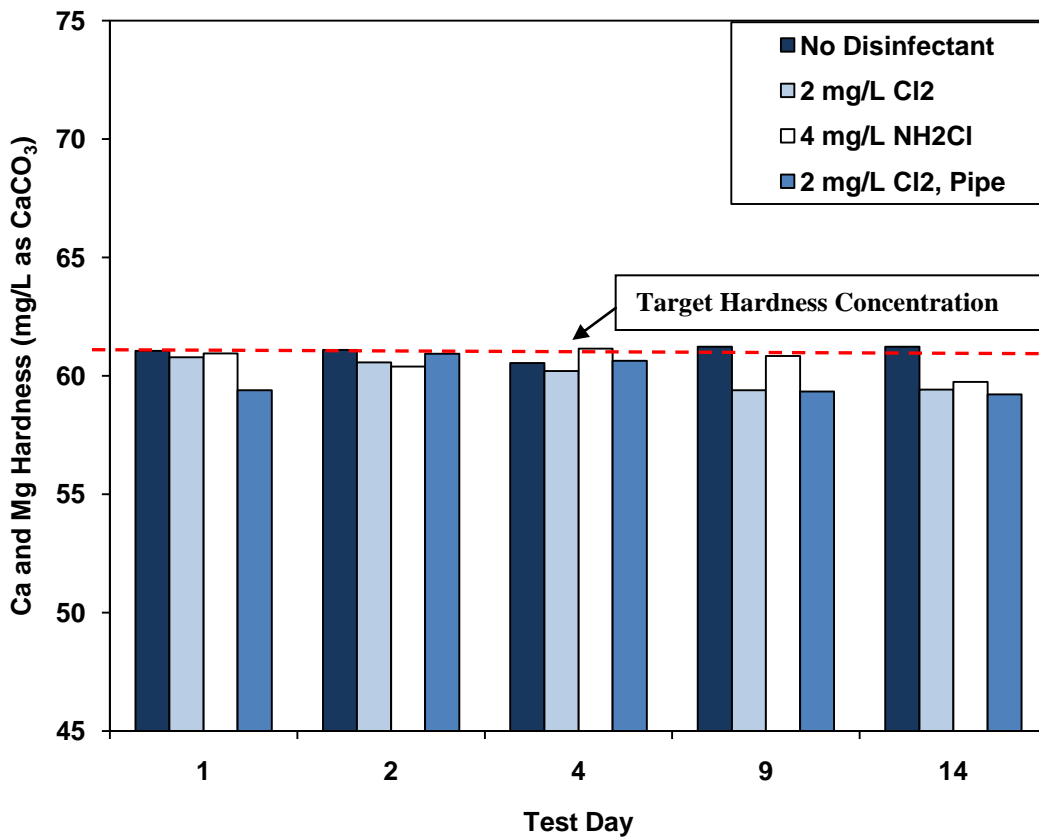


Figure II-6. Total Hardness (Ca and Mg, mg/L as CaCO₃) for all three water treatments and aged pipe sample as a function of time

d. Elemental Analyses

No trends concerning selected trace metals and nonmetals were found in any of the three water types exposed to new epoxy. ICP-MS was used to quantify specific trace metals (Sodium, Aluminum, Potassium, Vanadium, Chromium, Iron, Manganese, Cobalt, Nickel, Copper, Zinc, Arsenic, Molybdenum, Cadmium, Tin, Barium, and Lead) and non-metals (Sulfur, Phosphorus, Chlorine, and Silicon). Analysis using paired t tests shows no statistical difference between the concentration of Na, Al, Cr, Fe, Mn, Ni, Cu, Zn, Pb, S, P, or Si between the test waters and the controls ($p > 0.05$ for all treatments). Concentrations of V, Co, As, Mb, Cd, and Sn were below detection limit on most test days and so could not be statistically analyzed.

With the exception of copper, analysis comparing metals and nonmetals concentrations in the aged pipe sample to its chlorinated control also failed to detect a statistical difference between any of the elemental concentrations ($p > 0.05$ for all tests). Copper concentrations in the aged pipe ($< 35 \text{ ug/L}$ on all test days) were shown to be significantly higher than in controls ($p = 0.00016$, paired one-sided t test) which is almost certainly due to either copper filaments that were stuck to the epoxy layer after the pipe was cut or exposure to the pipe edges (Figure II-7). Inspection of the epoxy layer revealed no holes, tears, or failure that would result in copper released from the pipe wall itself. Other than copper present in the aged sample, both new and aged epoxy were not found to have an effect on selected metals or nonmetals concentrations in the water. These findings were expected, as epoxy is used as a corrosion preventative that is meant to decrease metals concentrations in water scoured from pipe walls.

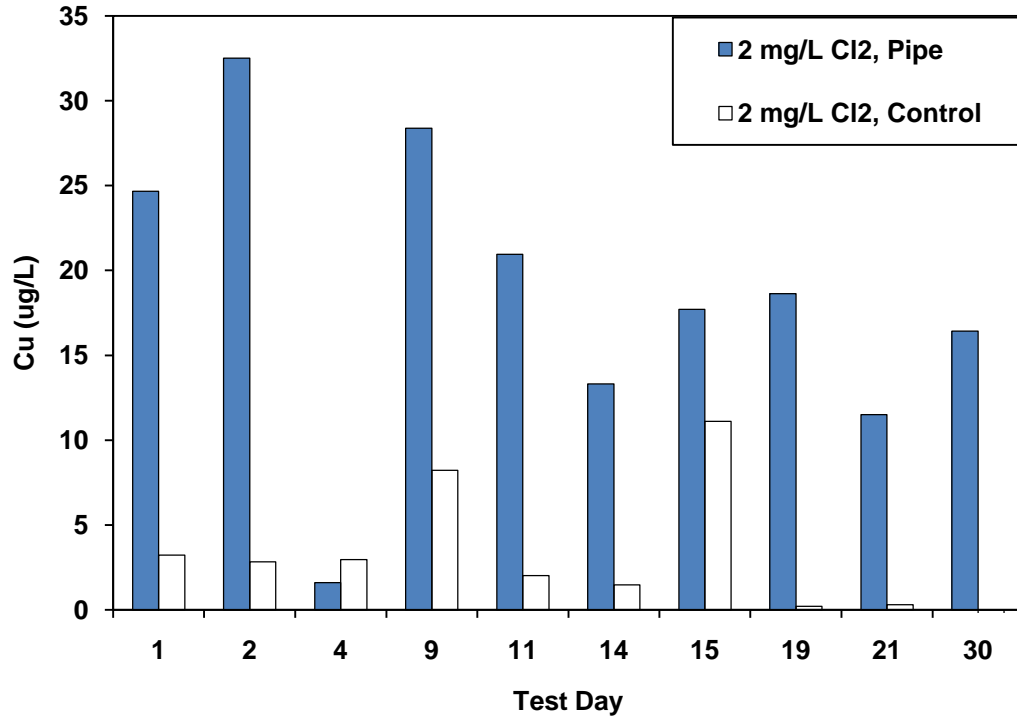


Figure II-7. Copper concentrations (ug/L) in aged pipe sample and chlorinated controls as a function of time

e. Total and Dissolved Solids

The total solids concentrations (soluble solids + suspended solids) of the three sample waters and controls were not found to be different than the controls or follow a trend over time. Sample water was clear of particulate solids and total solids were recovered in approximately the same concentrations in both test waters and controls (data not shown). Paired t tests were used to compare total solids concentrations in the test waters with the controls and confirmed that the concentrations of solids in all three treatments were no different than controls ($p = 0.887, 0.915, 0.828$ for no disinfectant, chlorinated, and chloraminated waters, respectively). The data indicate epoxy does not contribute to the presence of solids in the waters.

f. Disinfectant Residual

The presence of epoxy had a significant effect on disinfectant residual in the reference waters for both chlorinated and chloraminated waters and for new as well as aged epoxy. Compared with controls, paired t tests confirmed both waters exposed to new epoxy had significantly lower disinfectant residuals ($p = 2.18E-08$ and 0.0005 , for chlorinated and chloraminated waters, respectively). As consistent with the literature, contact with epoxy had the greatest effect on free chlorine in the water. During the first 24

hour exposure period, the residual decreased over 90%, from 2.1 mg/L to 0.2 mg/L as Cl₂ in water exposed to new epoxy. (For comparison, the control decreased only 13% as a result of natural chlorine decay.) Upon subsequent exposure periods the demand decreased notably, with less chlorine consumption occurring during equivalent exposure periods. However, longer exposure always corresponded to increased chlorine demand and even at the end of the study, 9 days of contact time resulted in total chlorine consumption (compared with only a 14% reduction as a result of decay and a residual of 1.77 mg/L in the control) (Figure II-8).

Interestingly, the aged epoxy sample also showed a much higher tendency to consume disinfectant over the course of the study. Whereas the new epoxy showed a decreasing tendency to consume chlorine over time, the aged pipe sample maintained a disinfectant residual that averaged only 0.05 mg/L over the study (Figure II-10). Even when normalized for surface area, the disinfectant was still significantly lower than the new epoxy exposed to chlorinated water ($p = 0.006$, one-sided paired t test). There is a strong possibility that the slightly higher concentration of copper metal present in the water was contributing to the increased chlorine demand, as metal pipes generally exhibit high disinfectant demand.

Chloraminated water exposed to new epoxy also exhibited higher demand than controls but the chloramines residual present in the water was much greater than for free chlorine (Figure II-9). The first 24 hour exposure period showed high disinfectant demand, with a 32% decrease in monochloramine from 4.4 mg/L to 3.0 mg/L. (By contrast, the control showed no decay). After this first exposure, however, there was an observable decrease in demand and by the end of the study the consumption after 9 days of exposure was only 0.7 mg/L. Consistent with the literature, chloramines exhibited a greater stability in the water and maintained a higher residual and overall lower demand over the 30 days.

Figure II-10 show the disinfectant loss in mg/L as Cl₂ for both chlorinated and chloraminated waters. (The no disinfectant treatment water is not shown, as there was no detectable free or total chlorine in the initial reference water or at any point during the study.) The data were consistent with the literature in showing that exposure to epoxy results in high disinfectant demand, with notably higher consumption of free chlorine than monochloramine occurring. Because maintaining a disinfectant residual of at least 0.2 mg/L at the tap is necessary for utilities, they should be aware of the potential problems faced with lining pipes with epoxy in chlorinated drinking water systems, particularly if those portions of the distribution system are in dead-end zones where stagnation is allowed to occur.

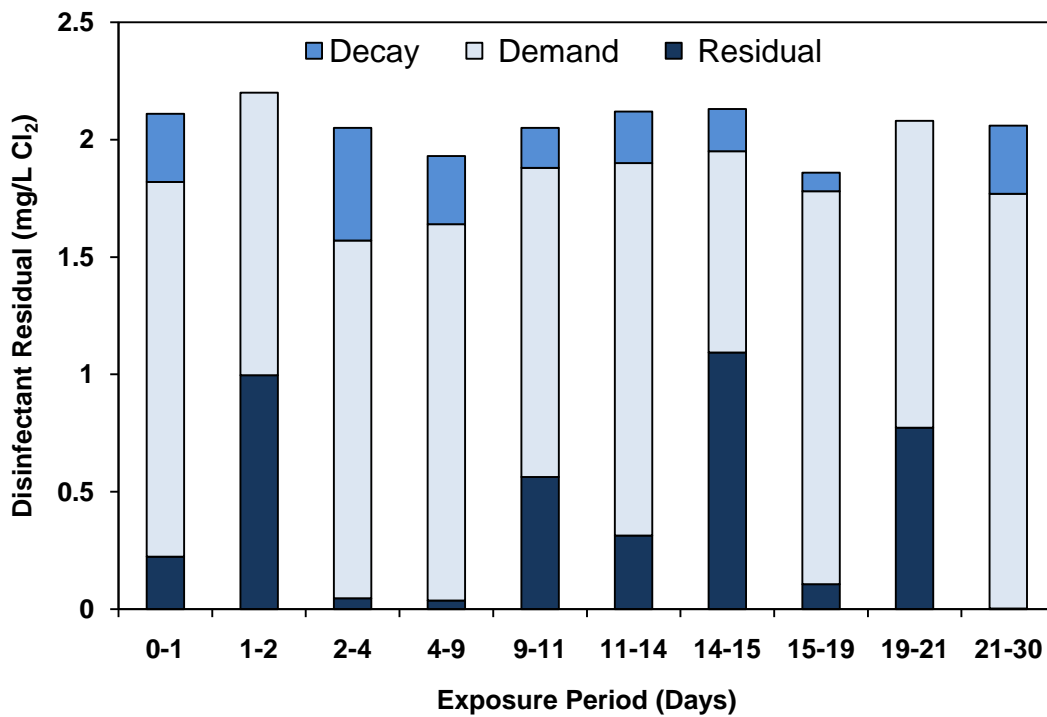


Figure II-8. Fate of chlorine, showing disinfectant residual, disinfectant consumption, and natural disinfectant decay (as measured in controls) as a function of time

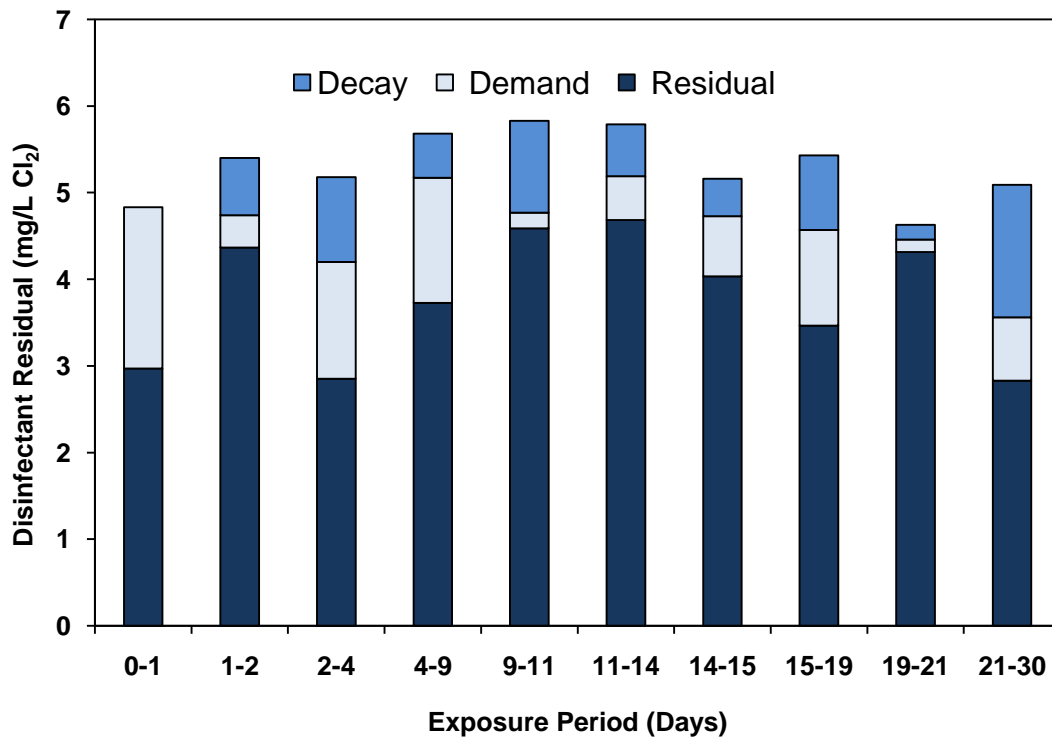


Figure II-9. Fate of monochloramine, showing disinfectant residual, disinfectant consumption, and natural disinfectant decay (as measured in controls) as a function of time

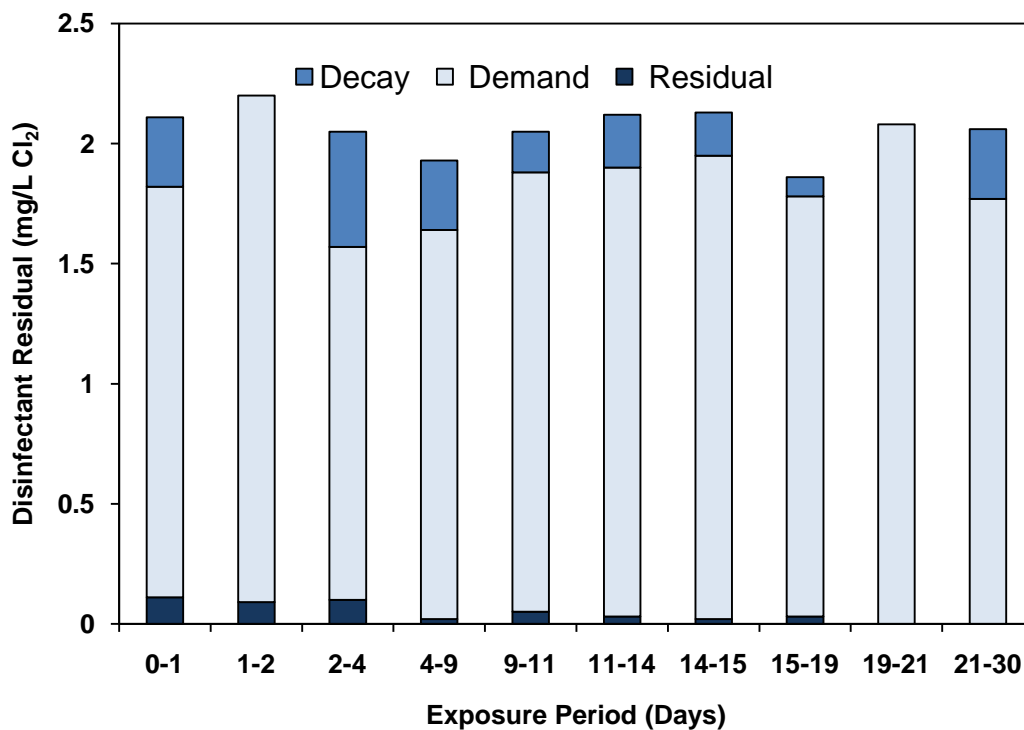


Figure II-10. Fate of chlorine decay in the aged pipe sample, showing disinfectant residual, disinfectant consumption, and natural disinfectant decay (as measured in controls) as a function of time

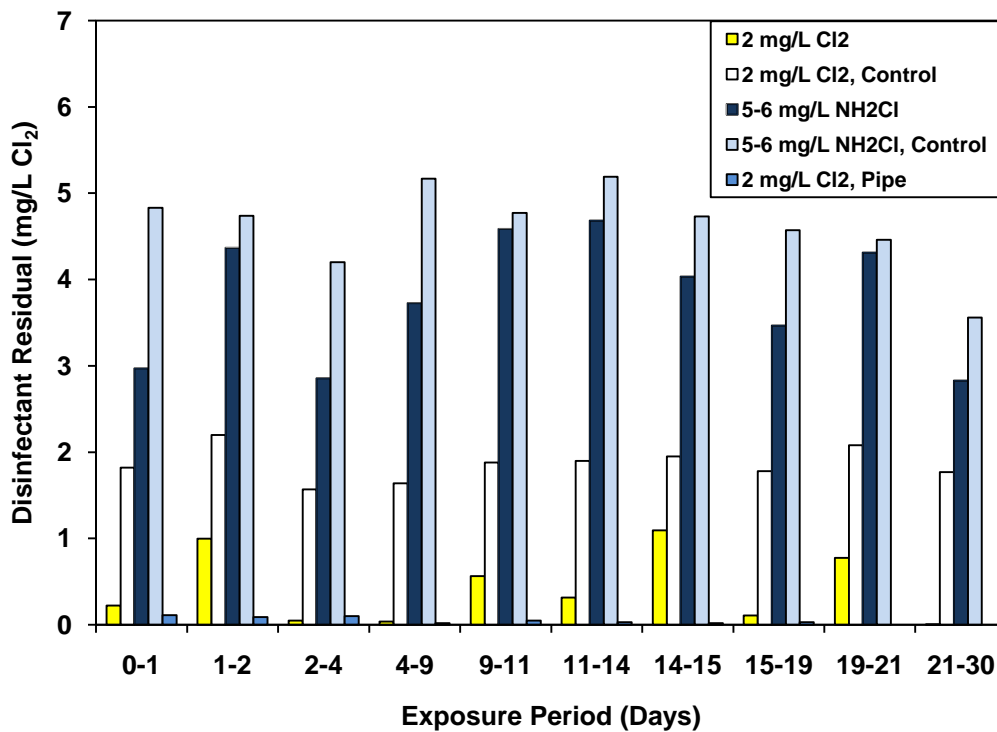


Figure II-11. Chlorine and monochloramine residuals (mg/L Cl₂) in new and aged epoxy samples and controls, as a function of time

g. Ammonia

No significant changes were seen in ammonia concentrations in reference waters upon exposure to epoxy. Neither the no disinfectant water nor the chlorinated water had ammonia levels above background levels so Figure II-11 shows only ammonia concentrations in chloraminated water. The figure shows similar concentrations of ammonia in both the sample and control waters and statistical analysis using paired t tests showed no difference between the N-NH₃ concentration in the chloraminated test waters and controls ($p = 0.522$). This is understandable in that ammonia in equilibrium with free chlorine would be measured as ammonia in the water. Interestingly Day 1 did have a measurable difference in ammonia of approximately 0.6 mg/L as N. As the concentrations of ammonia in no disinfectant waters and chlorinated water had no detectable concentrations released from the lining, it's likely the difference is attributable to the monochloramine and its equilibrium products. It is possible that the high monochloramine demand on Day 1 in samples exposed to new epoxy released free ammonia into the water and caused there to be a higher reading of ammonia for those samples. Other than the higher concentration detected on Day 1, epoxy had no discernible effect on the concentration of ammonia in the water.

Also of note is the trend seen in the ammonia concentration in the mature pipe sample. The concentration of ammonia, while very low, was consistently and significantly higher than the concentration in the chlorinated control waters ($p = 0.0004$, paired t test). The slightly higher concentration of N-NH₃ found in the pipe samples, which averaged 0.06 mg/L over the course of the study (compared with 0.00 in the control), could possibly be due to the presence of bacteria on the surface of the epoxy. Given the low oxygen conditions present in the pipe, heterotrophic bacteria (which were detected on the lining) could have dissimilated nitrate added to the water as KNO₃ back into ammonia. The low concentrations of 0.06 mg/L of ammonia, however, are unlikely to negatively affect water quality in any measurable way.

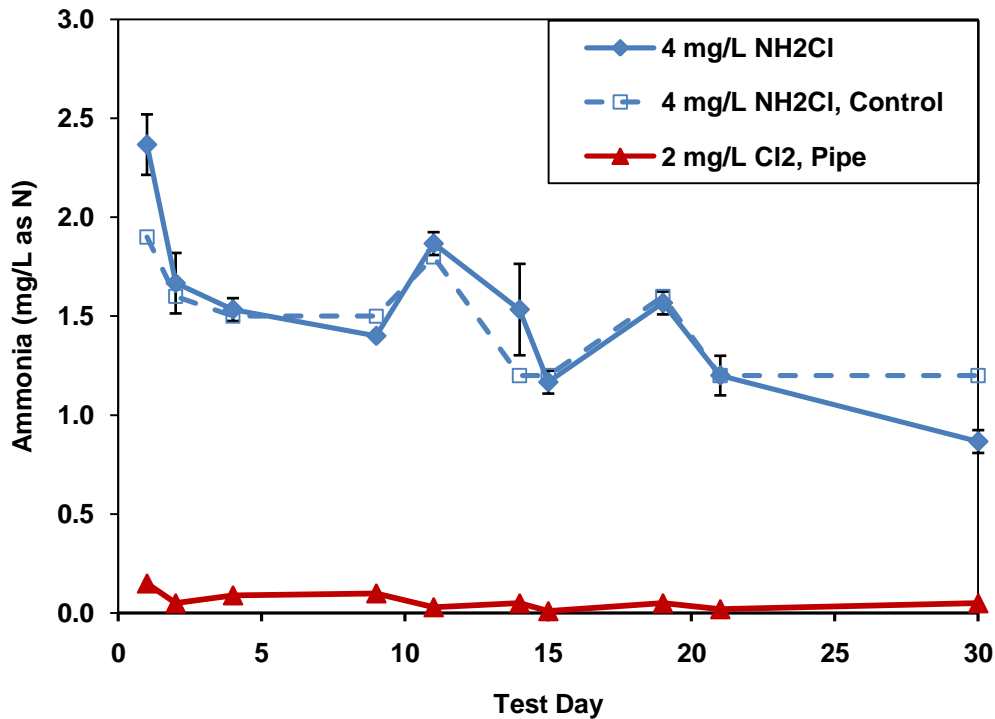


Figure II-12. Ammonia (mg/L as N) in chloraminated sample and control waters (4 mg/L NH₂Cl), as a function of time

B. Part 2: Organic Water Quality Parameters

a. Total Organic Carbon

The test waters all show significantly higher TOC concentrations than the controls ($p < 0.05$, paired Wilcoxon test). The highest concentration of TOC leached in each of the samples was on Day 1; by Day 2 concentrations in all treatments had decreased significantly. The highest initial TOC concentration was found in the no disinfectant water, with slightly lower concentrations in the chlorinated water; chloraminated water had a noticeably lower TOC concentration on Day 1. TOC was still leaching from the epoxy after 30 days of exposure to test waters, with higher concentrations leached after longer exposure times. Data in Figure II-13 is normalized for epoxy surface area (mg/cm^2) to show a comparison between the new epoxy coupons and the mature pipe.

The concentration of TOC in the aged pipe sample (mg/cm^2 surface area) exposed to chlorinated water was significantly higher than was expected, given that the sample had been in service for four years. TOC was lower on Day 1 (2.6 mg/L) than in waters exposed to new epoxy but was higher than new

epoxy than all other test days. Because the sample was four years old, it is unlikely that the TOC in the water was due entirely to organic carbon leached from the epoxy, as leaching rates as high as those detected in the aged pipe samples would most likely be too great for the lining to still be intact. Rather, it is probable that a substantial portion of the TOC is from biomass present on the surface of the epoxy lining. The presence of heterotrophic bacteria on the lining is almost certainly a source of much of the TOC detected in the samples.

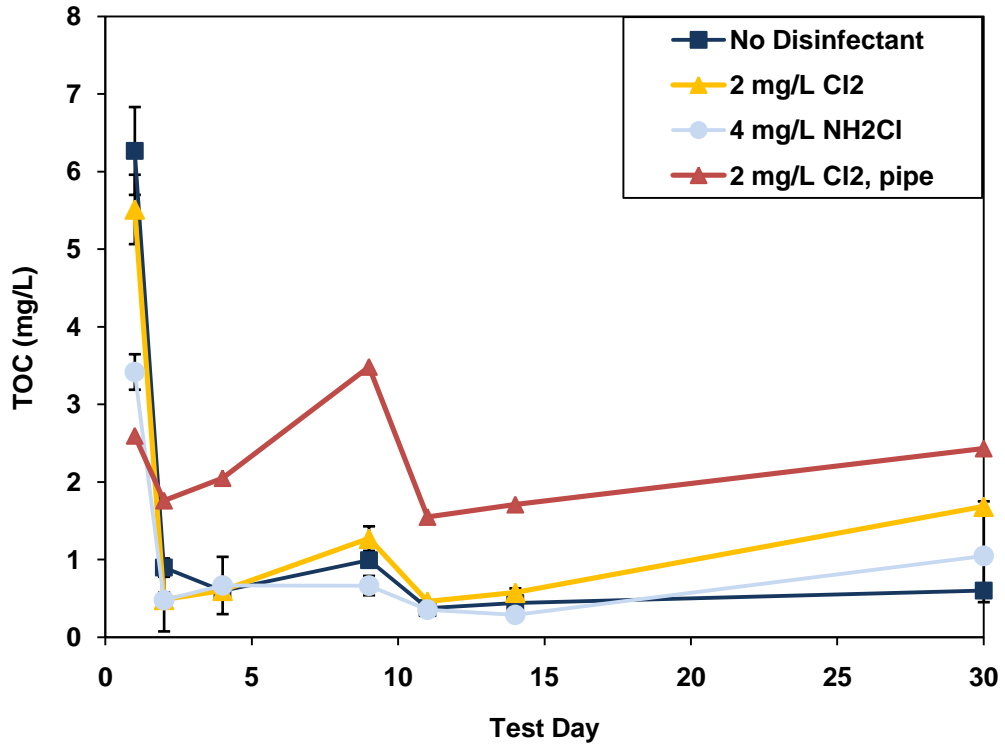


Figure II-13. TOC (mg/L) as a function of time for all three water treatments and aged pipe; errors bars indicate standard deviations

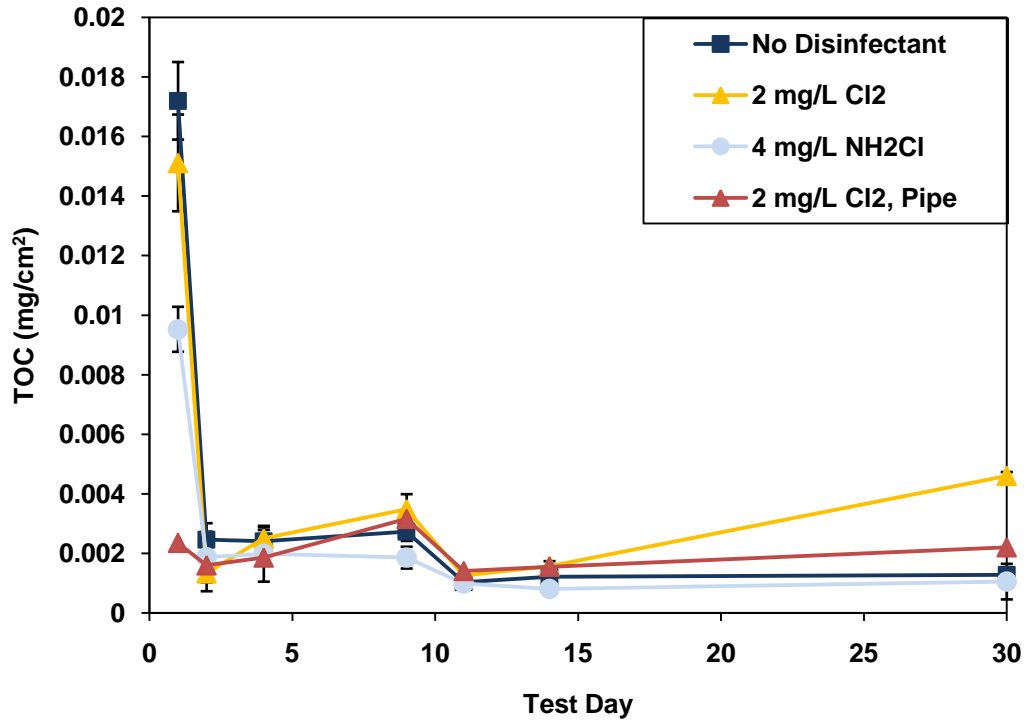


Figure II-14. TOC (mg/cm²) as a function of time for all three water treatments and aged pipe; error bars indicate standard deviations

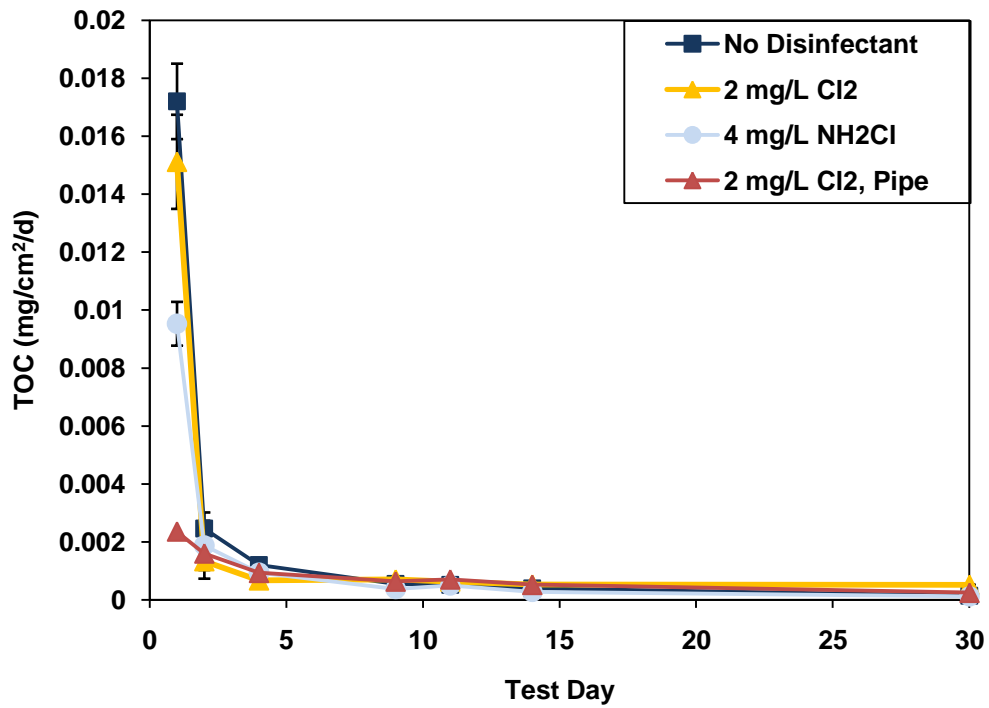


Figure II-15. Rate of TOC leached (mg/cm²/d) as a function of time for all three water treatments and aged pipe; errors bars indicate standard deviations

b. Semi-Volatile Organic Compounds (SVOCs)

None of the SVOCs analyzed for (as listed in Standard Method 6410B) were detected in sample waters exposed to new epoxy. (Due to the small volume of water held by the aged pipe, no SVOC analysis could be performed on waters removed from the pipe.) In addition to the targeted compounds, samples were analyzed for any other SVOCs using a GC/MS library search. Surprisingly, although samples contained high TOC concentrations, only one compound was positively identified from the library search, Bisphenol-A. These results could indicate that most of the TOC present was either volatile organics that volatilized in the headspace during the extraction procedure or non-volatile organics that were not able to be detected through gas chromatography.

c. Bisphenol-A

Bisphenol-A (BPA) was detected on three separate sampling days. Concentrations (22-33 ug/L) were highest during the first exposure period and decreased significantly on later sampling days. Concentrations of BPA were detectable in controls on some of the days but, with the exception of one sample, were always lower than concentrations in samples exposed to epoxy. Figure II-15 shows the concentrations in waters exposed to the epoxy samples less the concentrations in controls. BPA levels were the highest in chloraminated water and lowest in no disinfectant water, the exact opposite trend of TOC concentrations. As Bae et al (2002) reported a correlation between BPA and COD, these results were somewhat surprising. However, given that the concentrations were extremely low and only differed by 11 ug/L, the numbers most likely don't show any significant trend. These initial concentrations were notable but not alarming by drinking water standards, as the total allowable concentration (TAC) for BPA as recommended by ANSI/NSF-61 is 200 ug/L (ANSI/NSF-61, 2000). By Day 4 the levels had fallen substantially and they remained very low to non-detectable for the remainder of the study. The aged pipe was not sampled for BPA due to the smaller water volume of the pipe. As there was significant TOC leaching in the aged pipe, there is potential for BPA to be leached as well and future studies comparing BPA in aged and new epoxy might be useful. Judging from the existing data for new epoxy linings, there do not appear to be major water quality impacts from BPA, particularly under normal flow conditions.

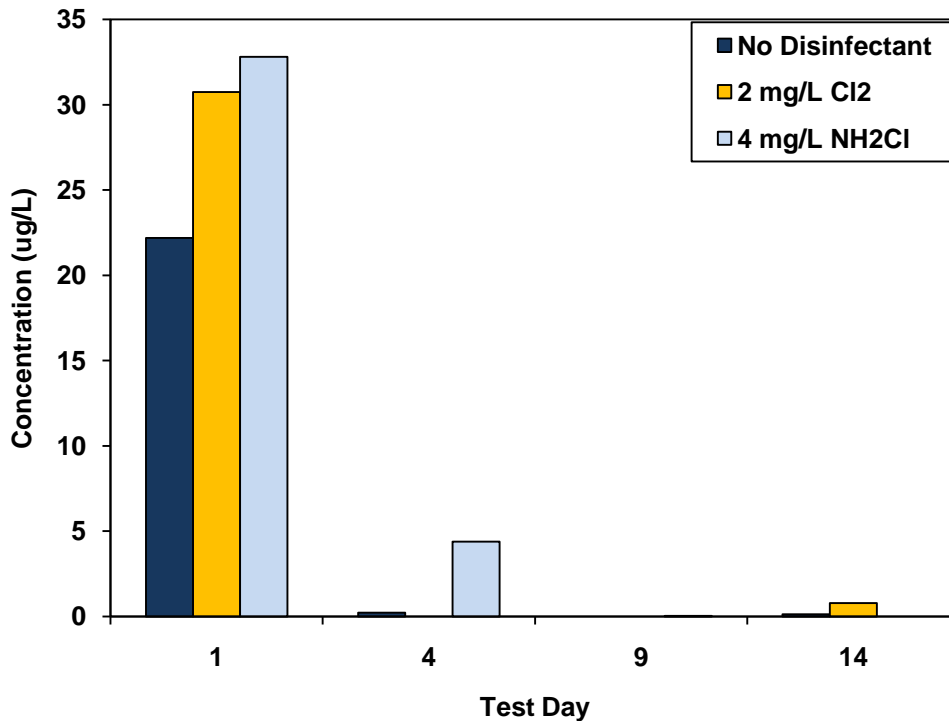


Figure II-16. Bisphenol-A concentrations (ug/L) for all three water treatments as function of time, corrected for controls

d. Disinfection Byproducts

i. Trihalomethanes

Trihalomethanes (THMs) were detected only in chlorinated waters exposed to new epoxy; no detectable concentrations were present in either chloraminated water or no disinfectant water. Chloroform (CHCl₃) was the only THM present and was detected each test day in greater concentrations than in control samples (Figure II-17). Concentrations ranged from 0.3 to 11.8 ug/L above background levels in the controls. Normalized for surface area, the concentrations ranged from 9.11E-05 to 0.032 ug/cm². This data was consistent with earlier data from Heim and Dietrich (2007) that detected concentrations of CHCl₃ ranging from 3-9 ug/L in chlorinated waters. That study, however, also detected CHCl₃ in chloraminated waters but at lower concentrations, 0-3 ug/L. Interestingly, although the highest TOC concentrations were leached and the most chlorine was consumed during the initial 24 hour exposure period, THM concentrations were lower than on later test days. It is not well understood why THMs

appeared to increase toward the end of the study, with the highest concentrations detected on Day 30. When normalized for THM formation rate, however, the graph exhibited a rather uniform shape (with the exception of Day 2), indicating CHCl_3 formed at a fairly constant rate over the study (Figure II-18). Concentrations of CHCl_3 in the aged epoxy sample fell almost entirely below the background concentration in the controls, showing negligible levels of THMs were produced in the chlorinated water exposed to the aged pipe sample. Although similar concentrations of TOC were leached from the aged pipe epoxy as from new epoxy, THMs were formed in far greater concentrations in waters exposed to new epoxy.

Even though CHCl_3 concentration detected in the water is significantly lower than the MCL for total THMs, the data confirm earlier studies that show epoxy does react with disinfectant present in the water (particularly free chlorine) to produce detectable levels of CHCl_3 . However, given that high disinfectant consumption occurred and high concentrations of TOC were leached, the low concentrations of THMs detected suggests that the TOC leached from epoxy linings does not readily produce THMs. Also, considering that the study was performed under stagnant conditions at a high surface area to volume ratio, it is suspected that THM formation will not be a major problem for epoxy linings.

For Figures II-17 and II-18, the sample size on Days 1 and 2 was lower due to sample loss. Therefore only one sample was available on Day 1 and two samples on Day 2. This low sample size and the relatively high error bars depicted in the two figures thus warranted performing another experiment to confirm the validity of the data. This experiment, described in the following section, also examined the relationship between free chlorine consumption by TOC leached from epoxy and the concentration of THMs formed. After normalizing these results for surface area to volume ratio, the concentration of CHCl_3 detected fell within the same range as that present during the earlier immersion study, giving further credence to the data.

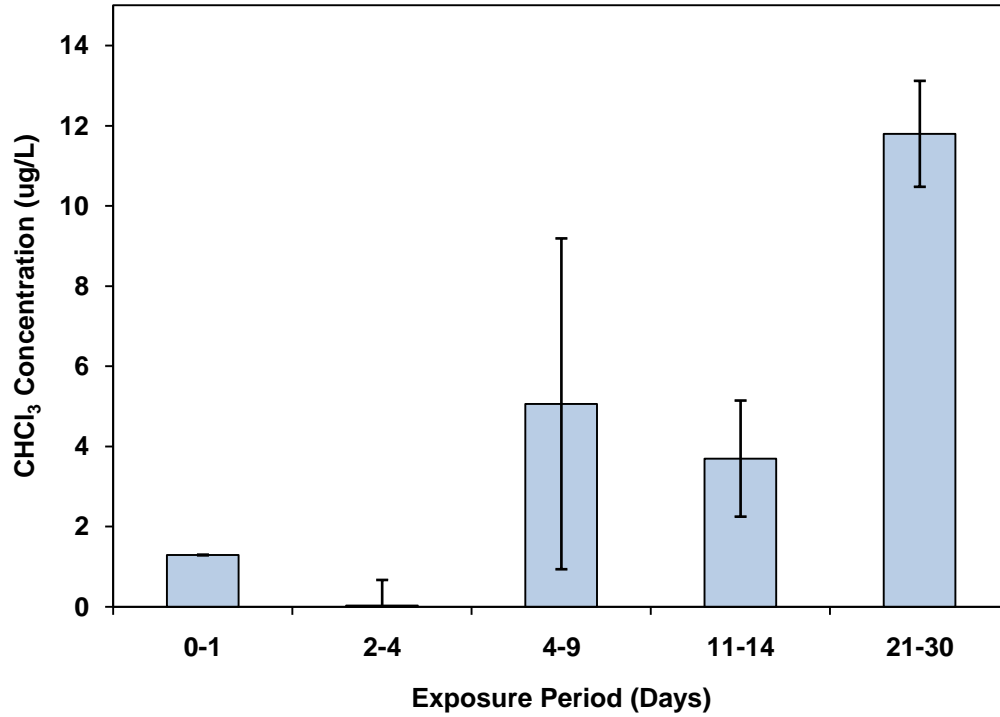


Figure II-17. THM concentrations (ug/L, Chloroform) in chlorinated samples exposed to new epoxy; error bars indicate standard deviations

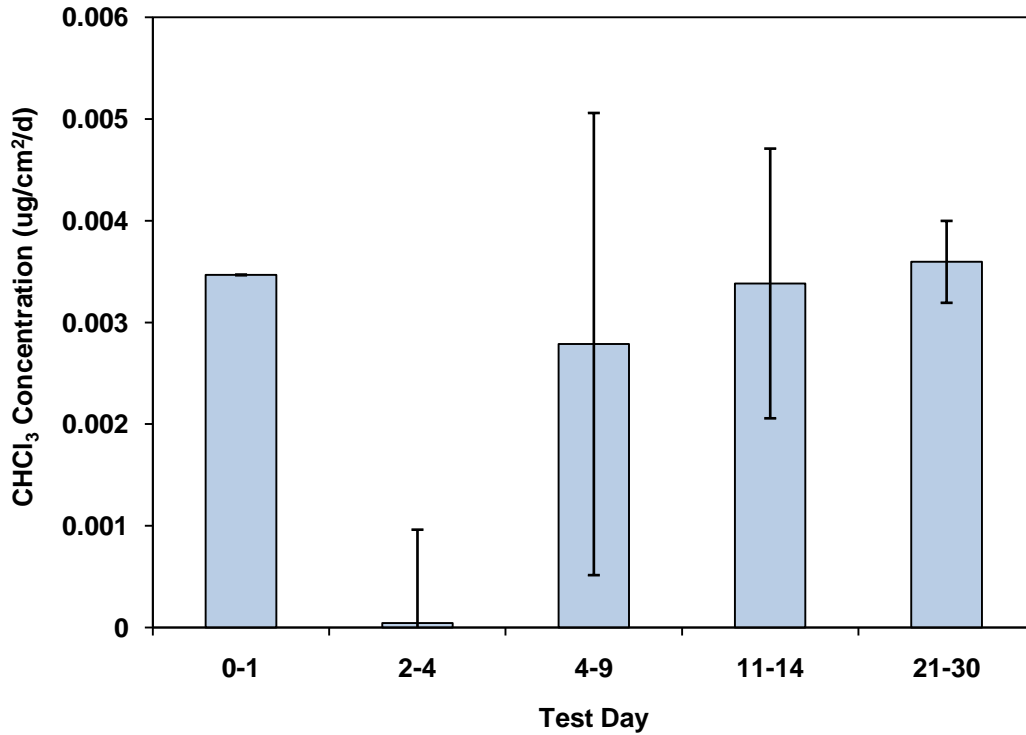


Figure II-18. THM formation rate (ug/cm/d, Chloroform) as a function of time in chlorinated samples exposed to new epoxy; error bars indicate standard deviations

ii. THM Formation/Sorption

A separate two-part study was conducted using the same test vessels and new epoxy-coated coupons to measure THM-formation and sorption potential in waters exposed to epoxy. The impetus for this research was to determine 1) whether higher concentrations of both TOC and free chlorine would produce higher concentrations of THMs and 2) whether THMs formed from the interaction between disinfectant and TOC were remaining in the water or were sorbing back into the epoxy surface layer. The experimental design involved exposing 10 coupons to no disinfectant reference water for 72 hours, under the same identical test conditions as the bench-scale studies. The total surface area of the coupons was 1573.8 cm² and the total volume was 2970 cm³, giving a surface area to volume ratio of 0.53 cm⁻¹.

After the coupons had been exposed to no disinfectant reference water for 72 hours, samples were removed and spiked at a concentration of 6.7 mg/L. This arbitrary concentration was used simply because it was high enough to provide a detectable residual (0.7 mg/L) in the samples a few minutes after the samples were spiked. One hour after being spiked with chlorine, the chlorine residual in the reference water exposed to the epoxy had decreased even further to 0.3 mg/L. After 24 hours of exposure, free chlorine had been completely consumed. TOC concentrations in the no disinfectant reference water prior to being spiked with chlorine were 7.5 mg/L and decreased slightly over the three day study. CHCl₃ again was the only THM formed upon exposure to chlorine and a concentration of 10 ug/L was detected. When normalized for surface area, the amount of CHCl₃ produced averaged 0.018 ug/cm². These values fell within the range detected during the 30 day immersion study (< 12 ug/L, 0.032 ug/cm²) and confirmed the propensity of epoxy to react with chlorine to produce relatively low but detectable concentrations of CHCl₃. It showed that with a high surface area to volume ratio of epoxy to water there was complete chlorine demand, even at very high disinfectant levels (6.7 mg/L). Also, high levels of TOC were again leached from the epoxy lining. Normalized for surface area, initial leached TOC concentrations were very similar to initial values obtained during the immersion study (0.012 mg/cm² and 0.017 mg/cm², respectively) yet when converted to a rate the initial leaching rate was much lower than the initial leaching rate during the immersion study (0.004 mg/cm²/d and 0.017 mg/cm²/d, respectively). Most likely the differences are a result of comparing different exposure periods, one day in the immersion study and three days for the THM formation study.

Some of the data was surprising, however. First, significantly higher disinfectant levels (6.7 mg/L compared with 2 mg/L) combined with higher TOC concentrations did not result in significantly increased THM formation. Presumably higher disinfectant levels coupled with higher TOC would have resulted in increased concentrations of CHCl₃. Also unexpected was the decrease in TOC seen across the three days. TOC decreased from an initial high of 7.5 mg/L to 5.1 mg/L. Although this decrease was

consistent in all samples it was not well understood. Finally, the slight apparent increase in CHCl_3 from 9.7 to 11.0 $\mu\text{g/L}$ after 72 hours could not be explained by the residual and is likely due to statistical variability, as all chlorine had been consumed after 24 hours of exposure. Figure II-19 shows the results of the study.

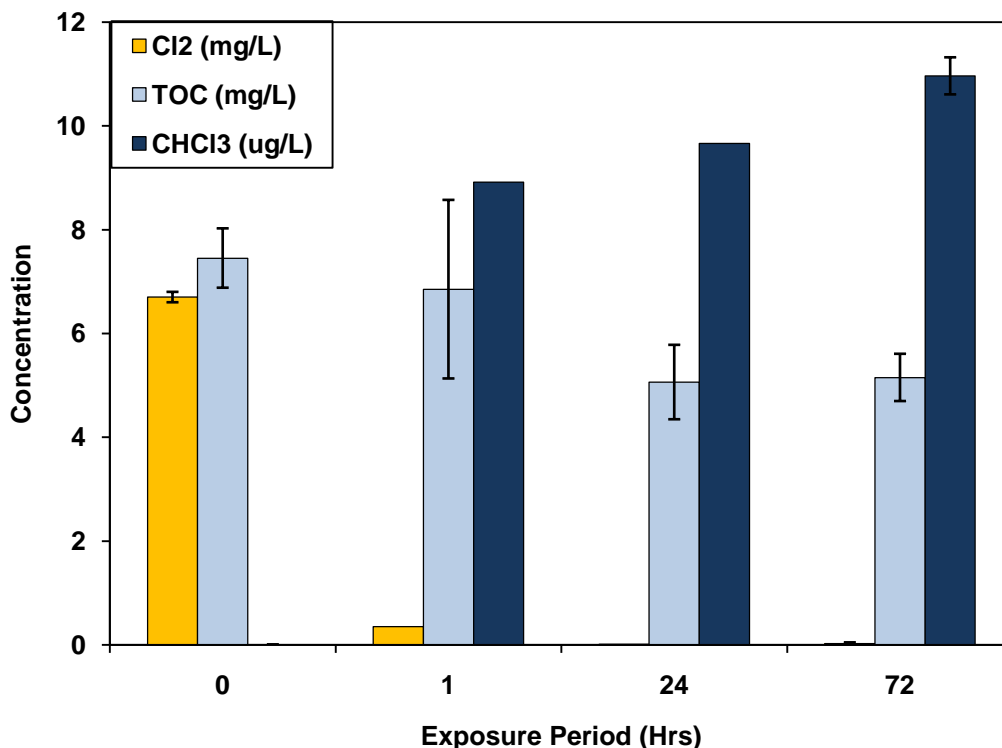


Figure II-19. Concentrations of disinfectant residual (mg/L), TOC (mg/L), and THMs ($\mu\text{g/L}$) as a function of time after exposure to 6.7 mg/L chlorine

A THM sorption experiment was also conducted to address the possibility that a portion of the THMs formed from the chlorination of TOC was in fact sorbing back into the epoxy layer, a phenomenon that might explain why much higher TOC levels and higher disinfectant consumption did not produce higher CHCl_3 in the water. If sorption was occurring in the water it would likely under-represent the effect epoxy linings have on THM formation.

This experiment was performed under the same test conditions and again used new epoxy-coated coupons. 10 coupons were exposed to no disinfectant reference water spiked with approximately 14.5 $\mu\text{g/L}$ of CHCl_3 . Samples were collected from the headspace-free vessels after 8, 24, 48, and 72 hours to determine CHCl_3 concentration in the samples. After analysis the concentration of CHCl_3 in the samples remained constant and there was no statistical change in CHCl_3 observed over the 72 hours ($p = 0.689$,

linear regression) (Figure II-20). Thus epoxy does not absorb CHCl_3 and all THMs formed from the chlorination of organic carbon were likely still present in the water.

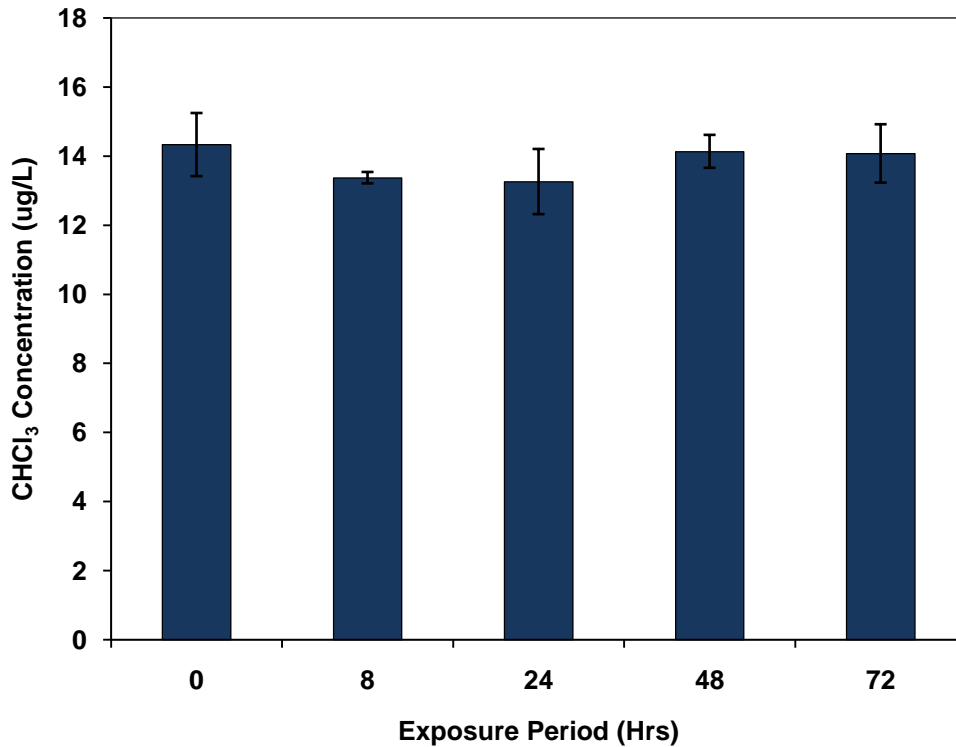


Figure II-20. CHCl_3 concentration (ug/L) in waters spiked with 14.5 ug/L CHCl_3 as function of exposure time (hrs)

iii. Haloacetic Acids

In contrast to THMs that were only detected in chlorinated waters exposed to new epoxy, Haloacetic Acids (HAAs) were present in all reference waters exposed to both new and aged epoxy, although concentrations were always well below the total MCL of 60 ug/L, as specified by the EPA (2000). HAA analysis examined only HAA-5, the five regulated HAAs consisting of mono-, di-, and tri-chloroacetic acids (MCAA, DCAA, and TCAA, respectively) and mono- and di-bromoacetic acids (MBAA and DBAA). HAAs detected in the water consisted primarily of DCAA and TCAA and no brominated HAAs were found. HAAs were present in very low concentrations in both samples exposed to epoxy and controls, although concentrations were typically higher in the samples exposed to epoxy. Figure II-21 shows HAA concentrations in samples exposed to epoxy less the concentrations detected in the controls. HAAs in samples exposed to new epoxy were not found to be statistically higher than in controls for any

of the three water treatments ($p > 0.05$ for all three treatments). HAAs in the aged pipe sample were statistically higher than controls ($p = 0.0112$, one-sided paired t test), with concentrations ranging from 13.5-20.8 ug/L, compared with 3.1-8.6 ug/L in controls. When normalized for surface area, however, the concentrations were much closer (Figure II-22) and statistical analysis showed no difference between normalized concentrations in the two chlorinated waters exposed to epoxy ($p = 0.5598$, one-sided paired t test).

Consistent with the THM data, the highest overall concentrations of HAAs were found in chlorinated waters, although statistical analysis found statistically greater concentrations only when compared with no disinfectant water ($p = 0.045$, one-sided paired t test), not with chloraminated samples ($p = 0.1104$)

The data confirm the potential for TOC leached from epoxy to react with disinfectant (particularly chlorine) to form HAAs as well as THMs. Given the high amount of TOC leached, HAA concentrations remained considerably low and the impact of epoxy on HAA formation appears to be low.

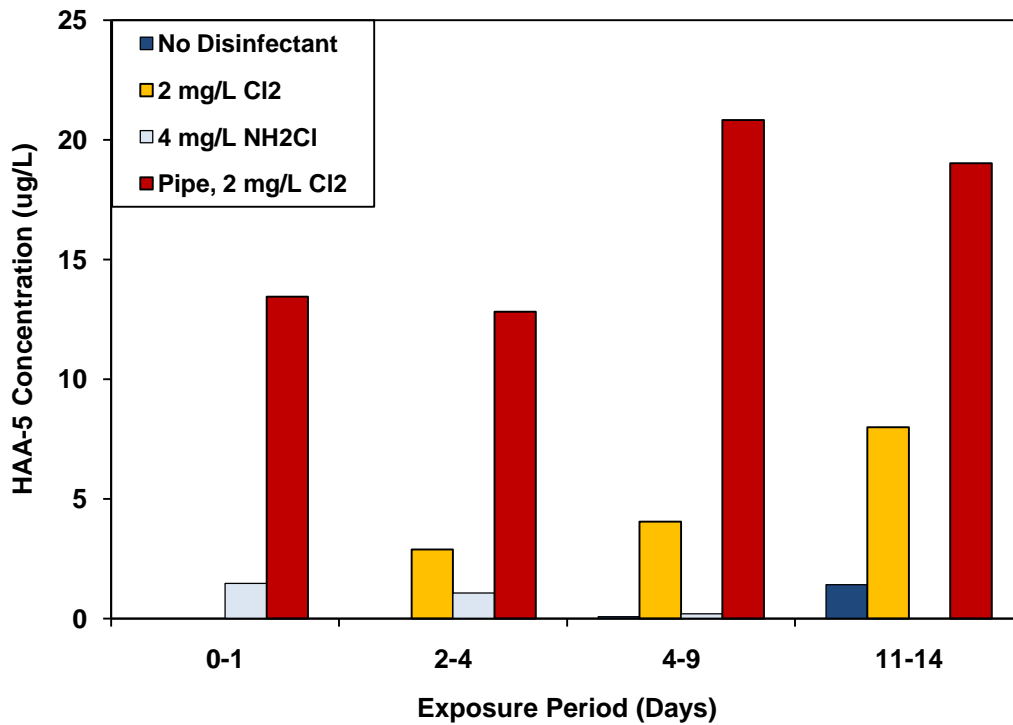


Figure II-21. HAA-5 concentrations (ug/L) as a function of time for all three water treatments and aged pipe sample

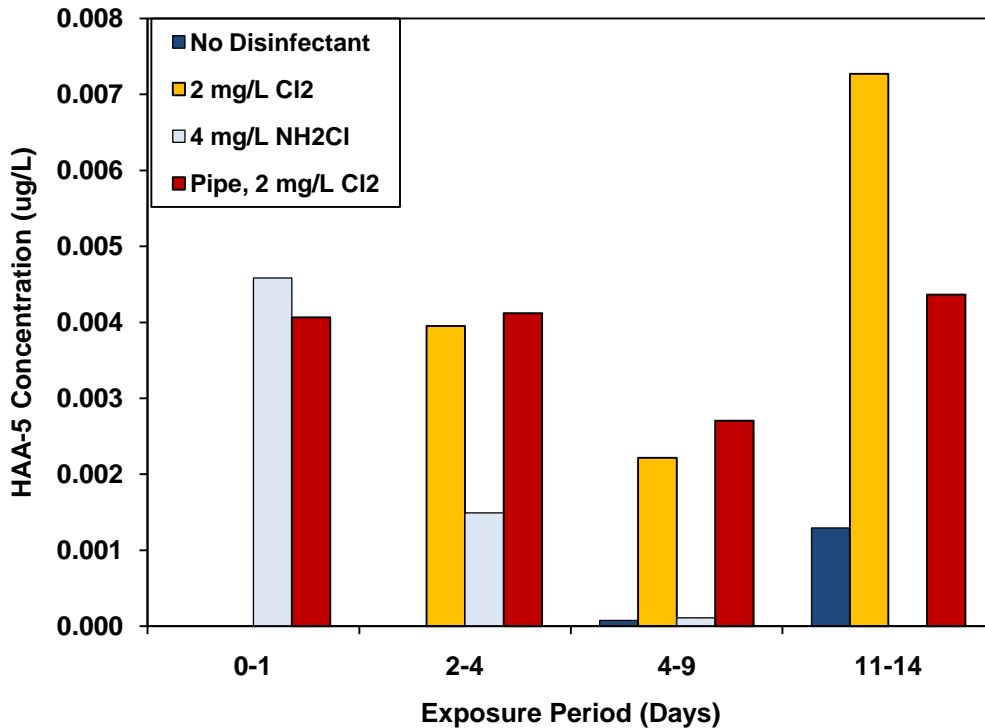


Figure II-22. HAA-5 formation rate (ug/cm²/d) as a function of time for all three water treatments and aged pipe sample

e. Odor

Flavor Profile Analysis (FPA) panelists reported a moderate intensity odor in all waters exposed to new epoxy, although there were distinct odors associated with each disinfectant type. (No odor panel was performed on aged epoxy because the volume of water held by the pipe was again not large enough.) The most commonly used odor descriptors for the water were chlorinous, sweet, plastic, and chemical. For the purpose of quantifying the odor intensity of the waters according to descriptors, two categories were used: chlorinous and sweet/plastic/chemical, as panelists commonly used sweet, plastic, and chemical interchangeably to describe a similar odor. Of the test waters, the chlorinated samples had the highest overall odor intensity, followed by chloraminated samples and then no disinfectant samples. None of the odor intensities of the test waters changed statistically over time (linear regression, $p > 0.05$ for all samples)

The no disinfectant test water had an average intensity of 3.0 over the seven test days, falling above the odor threshold for detectable odors as listed by FPA. Panelists described the no disinfectant samples as having an overall pleasant odor and used the labels sweet, chemical, plastic, and waxy to describe it. By comparison, the no disinfectant control had an average intensity below the odor threshold of 1 over the

test days and the odor was described as either undetectable or an unidentifiable threshold odor. Data for no disinfectant samples exposed to epoxy is shown in Figure II-23.

Panelists reviewing the chlorinated test waters could detect both a strong chlorinous odor and a strong plastic/chemical odor on most test days. They commonly described the chlorinous odor as burning and the plastic/chemical odor as burning chemical or burnt rubber. The combined effect of chlorine with epoxy had a synergistic effect on the intensity and odor descriptors, with panelists no longer describing the odor as sweet/pleasant but offensive/burning chemical with a much stronger intensity. Over the seven test days the average intensity of the chlorinous odor was 7.0 and the intensity of the plastic/chemical odor was 7.6. Intensity was highest on days 4, 9, 14, 19, and 21, with lower intensities found on both the first and last test days. Notably, on day 30, after an exposure period of nine days and no chlorine residual present in the test water, panelists could no longer detect a chlorinous odor and described the plastic/chemical odor for the first time as sweet and having a weak intensity. By contrast, the chlorine control still maintained a strong chlorinous odor on Day 30, consistent with the 1.8 mg/L Cl_2 residual that was present in the water. Overall the chlorinated control maintained a constant odor intensity averaging 7.1 and described as simply “chlorinous.” Data is shown in Figure II-24.

Panelists reported the chloraminated test waters also had both a chlorinous and plastic/chemical odor, but with weaker intensities of both chlorine and plastic. The chlorinous odor appeared to be masked by the plastic/chemical odor on Day 1 and had a much lower intensity than in chlorinated test waters, averaging only 2.7 over the study. The plastic/chemical odor was also not as intense as in chlorinated test waters, averaging 4.4, and panelists frequently described the odor as sweet and pleasant. The sweet descriptor was also commonly used to describe the chloraminated control water, most likely due to chloramines having a characteristically sweeter odor. Data is shown in Figure II-25.

The odor intensity from all three samples would exceed the FPA readily-detectable threshold of 2 and would likely warrant complaints from customers. Flushing the pipes would certainly decrease the intensities but the results do show that, given stagnant conditions and high disinfectant concentrations (particularly chlorine), odor may be problematic.

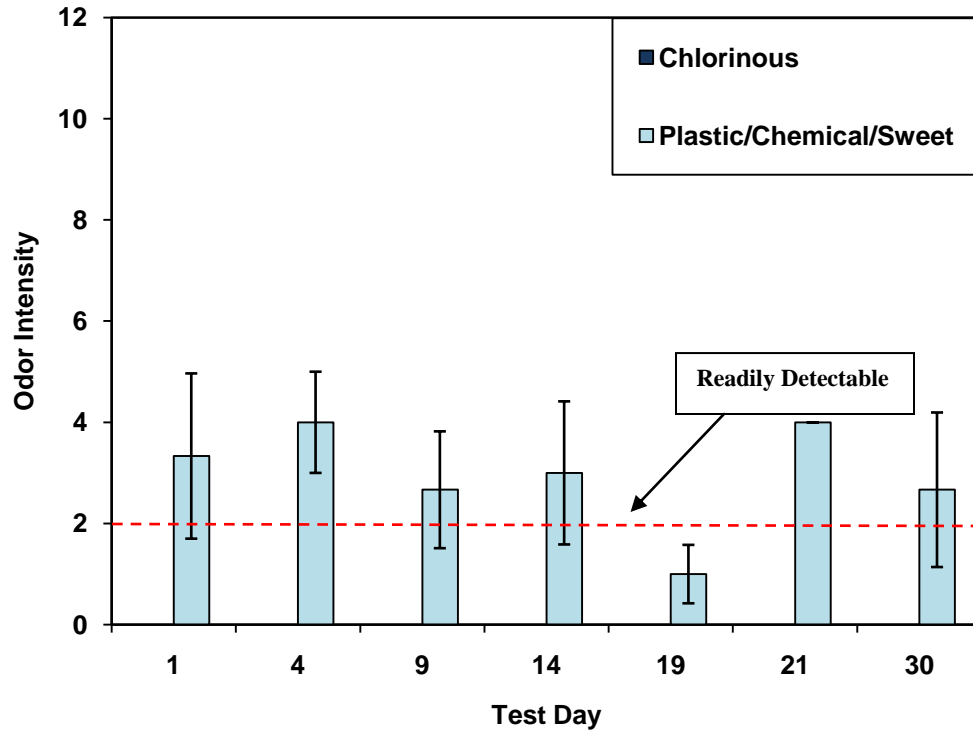


Figure II-23. Odor descriptors and intensities for no disinfectant samples as a function of time; error bars indicate standard deviations

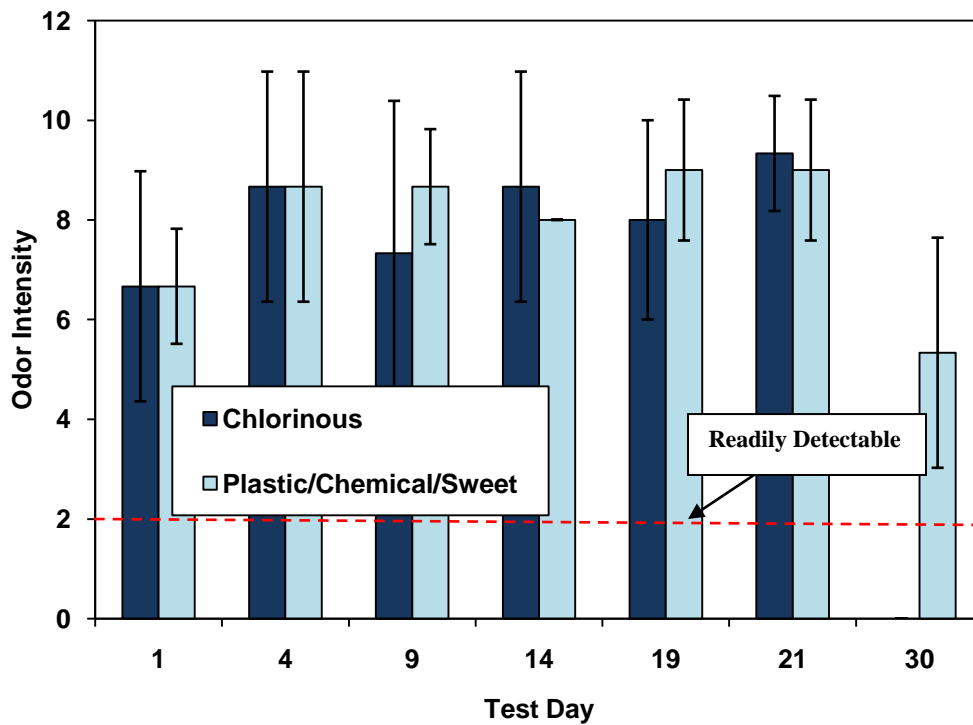


Figure II-24. Odor descriptors and intensities for chlorinated samples as a function of time; error bars indicate standard deviations

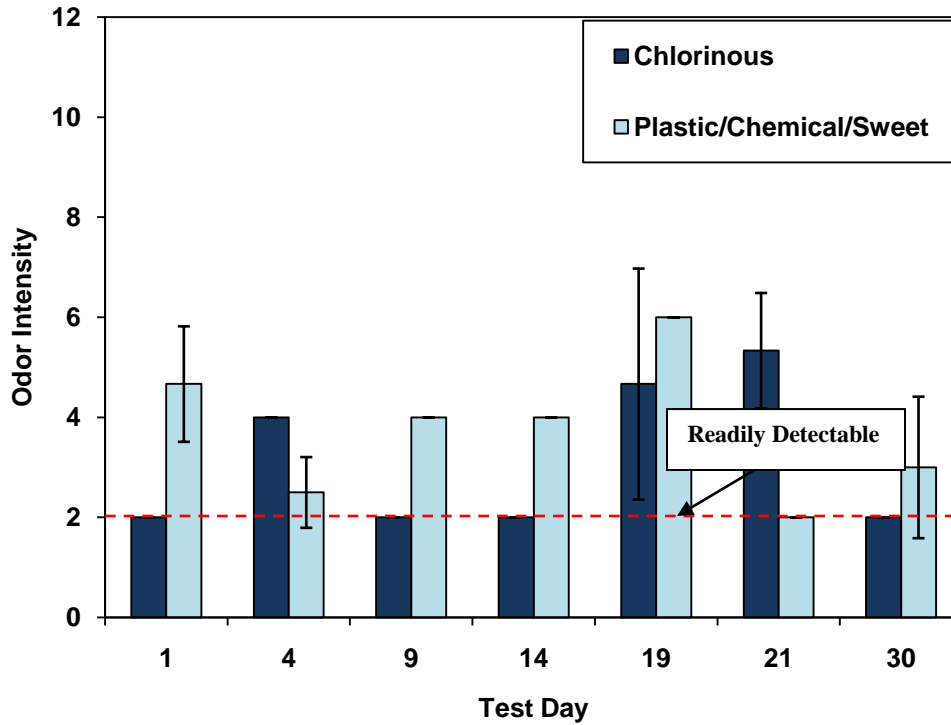


Figure II-25. Odor descriptors and intensities for chloraminated samples as a function of time; error bars indicate standard deviations

f. Microbial Growth

Although no visible biofilm was present on the surface of the aged epoxy sample, microbiological analysis was performed to determine whether the epoxy lining was supporting significant microbial populations. To perform the analysis a 2 cm² area was scraped using a spatula, swabbed for bacteria, and added to a sterile tap water solution for culturing. Detection of heterotrophic organisms was performed using both R2A and PCA Agar. MacConkey (lactose) Agar was used for detection of fecal coliforms. The results of the analysis are as follows.

Table II-5. Results of microbiological analysis of 2 cm² of mature epoxy pipe surface

Plate	Plate Counts (CFU/cm²)	Morphological Description
R2A – Original Sample	103	Diverse circular colonies of different colors: pink, yellow, and white.
R2A – Diluted x 10 ⁻¹	0	NA
PCA – Original Sample	4	Circular colonies, one pink one yellow, and two white.
PCA – Diluted x 10 ⁻¹	0	NA
McConkey – Original Sample	0	NA
McConkey – Diluted x 10 ⁻¹	0	NA

Results of the analysis confirmed the presence of a small number of heterotrophic bacteria. As the numbers were relatively low and the literature has not shown a correlation between epoxy and pathogenic bacteria, the water quality impact from the bacteria is expected to be inconsequential.

Chapter III

Summary and Discussion

I. Summary

This 30-day immersion study was conducted to examine the water quality impacts from two epoxy liners: 1) a newly applied epoxy cured for 60 hours immediately before beginning the study and 2) a length of aged epoxy-lined pipe that had been taken from a service line where it had been in operation in a chlorinated drinking water distribution system for four years. The water quality parameters measured in the study were pH, ammonia, alkalinity, hardness, metals, disinfectant consumption, total organic carbon (TOC), semi-volatile organic compounds (SVOCs), disinfectant byproduct (DBP) formation, and odor. The new epoxy lining was used to encapsulate glass coupons that were immersed in test vessels containing reference tap water. The low alkalinity, low hardness water (pH 8) was decanted from the vessels and analyzed. Epoxy was exposed to identical reference water containing three different disinfectant treatments: no disinfectant, 2 mg/L chlorine, and 4 mg/L monochloramine. The aged pipe sample was sealed with Teflon stoppers, filled with the same chlorinated reference water, and water samples were then extracted for analysis. Water changes were performed on Days 1, 2, 4, 9, 11, 14, 15, 19, 21, and 30, although not every water quality parameter was analyzed during each sampling date.

The results of the study confirmed most existing data that reported properly-installed epoxy linings have a minimal impact on water quality parameters. This summary of the results is organized into two sections. The first section documents major and minor impacts on water quality from the new epoxy lining while the second section addresses major and minor impacts from the aged epoxy.

A. New Epoxy Lining

a. Major impacts observed under the conditions of the study:

- 1) Epoxy reacted readily with both chlorine and chloramines during the first 24 hours of exposure. After the initial 24 hours exposure, free chlorine was consumed at a greater rate and to a much greater extent than chloramines. The disinfectant consumption rate decreased over the thirty days for both disinfectants but longer exposure times corresponded with higher consumption. Even after 30 days of exposure, the epoxy liner still showed a high chlorine demand, with no detectable

residual present after the nine day exposure period (compared with 1.77 mg/L present in the chlorinated control and compared with 2.83 mg/L in the chloraminated sample).

- 2) Epoxy exposed to each of the three water types produced significant concentrations of TOC (6.3 to 3.5 mg/L) during the first 24 hours of exposure to water. By the second 24 hour exposure period TOC had decreased substantially (0.98 to 0.19 mg/L). Epoxy exposed to both chlorinated and no disinfectant water leached the highest concentrations of TOC. By the end of the thirty days, each of the water types exposed to epoxy had TOC present in concentrations between 1.7 – 0.5 mg/L, with chlorinated water having the highest TOC concentration.
- 3) Disinfectant byproducts were present in most samples, with the highest concentrations detected in chlorinated water. Trihalomethanes were present only in the chlorinated water exposed to the epoxy and at relatively low levels (< 12 ug/L). Chloroform was the only THM detected. Haloacetic acids were present in all three water types and the highest concentrations were found in chlorinated waters. Concentrations in waters exposed to epoxy were never greater than 8 ug/L above the controls. Both DBPs were well within regulatory limits.
- 4) Bis-Phenol A was detected in concentrations of 33 to 22 ug/L during the first 24 hours in all three waters exposed to epoxy. Concentrations decreased substantially by the second test day but trace amounts of BPA were still detected by the last test day. No other SVOCs were identified in the samples and it is not known what organic compounds contributed to the high TOC levels.
- 5) Weak to moderate odor intensities were released from epoxy exposed to all three disinfectant types which persisted all thirty days. Overall the intensities from any of the waters exposed to epoxy would be objectionable to consumers (≥ 3 SMCL-TON) and water allowed to stagnate in newly-installed epoxy-lined pipes would almost certainly warrant complaints from customers. The odor was strongest in chlorinated waters, with panelists detecting both a chlorinous and a burnt plastic odor. In chloraminated and no disinfectant waters panelists detected a sweet and pleasant odor, in addition to a less intense chlorinous odor in chloraminated waters.

b. Minor impacts observed under the conditions of the study:

- 1) Ammonia was present in slightly higher concentrations in water exposed to epoxy only during the first 24 hours.

B. Aged Epoxy

a. Major impacts observed under the conditions of the study:

- 1) Free chlorine exposed to the mature pipe was almost completely consumed by each test day. In contrast to the new epoxy, the pipe did not show a decrease in disinfectant demand over the thirty days. At least a portion of the demand can be attributed to higher levels of copper present in the water.
- 2) Higher concentrations of copper (< 33 ug/L) were detected in the water and most likely impacted both pH readings and disinfectant demand.
- 3) TOC leached from the mature pipe sample ranged in concentration from 1.6-3.5 mg/L. There was a slightly higher TOC concentration leached during the first 24 hours but overall the leaching rate remained constant over the experiment.
- 4) Disinfection byproducts were formed in chlorinated water exposed to the pipe. Only HAAs were detected (and, when normalized for surface area, these were formed at the same concentration as in the chlorinated samples exposed to new epoxy).

b. Minor impacts observed under the conditions of the study:

- 1) pH in the mature pipe sample was found to decrease slightly when compared with the chlorinated control. The pH consistently dropped approximately 0.3 pH units on each test day; most likely this is due to the increased copper concentrations in the water.
- 2) Ammonia was statistically higher in the pipe sample than in controls, but only by 0.6 mg/L. The slightly higher ammonia concentration in the pipe sample could be due to the presence of bacteria.

II. Discussion

Based on the available literature on new epoxy linings, the results of the study were not unexpected. Other than disinfectant consumption and odor there was very little impact on inorganic water quality parameters which was consistent with earlier studies performed by Bae et al (2002) and Heim and Dietrich (2007). Interestingly, pH in waters exposed to new epoxy remained unchanged, but this study demonstrated that the pH of water exposed to aged epoxy decreased slightly but consistently. It is unknown what caused this small but consistent decrease in pH but it's possible the higher presence of copper metal in the water had an influence on this drop in pH. As the pH of drinking water should stay within the range of 6.5 to 8.5 according to National Secondary Drinking Water Regulations (USEPA, 1998), the pH falls well within this range and epoxy linings are shown to have no severe impact on pH.

Disinfectant consumption by both new and aged epoxy linings was significant. Based on the literature epoxy linings were expected to exhibit a relatively high chlorine demand, as both Holt et al (1998) and Heim and Dietrich (2007) reported significant disinfectant consumption from epoxy linings. During the first 24 hours, chlorine decreased from 2.1 mg/L to 0.2 mg/L, a 90% decrease in the residual (compared with only a 13% decrease in the control). At the same time period monochloramine decreased from 4.8 mg/L to 3.0 mg/L, a 38% decrease (compared with no decrease in the control). After this initial exposure there was a sharp decline in the disinfectant demand in chloraminated waters while chlorinated water maintained high consumption rates. On average, after Day 1 monochloramine demand from the liner only contributed to approximately 14% loss of the initial monochloramine while chlorine demand was responsible for a decrease of approximately 70% of the initial chlorine. Notably, on Day 30 there was no chlorine residual left in water exposed to new epoxy while a residual of 1.77 mg/L was still present in the control. The monochloramine residual was 2.83 mg/L in samples exposed to new epoxy while 3.56 mg/L was still present in the control. (As a rate of consumption, free chlorine demand averaged 0.72 mg/L/d over the study while monochloramine demand averaged 0.45 mg/L/d.) The rate of chlorine consumption was approximately 1.6 times higher than that of monochloramine, consistent with data from Heim and Dietrich (2007) that reported a chlorine consumption rate 1.5 times higher than monochloramine. By contrast, Holt et al (1998) reported epoxy exhibited a chlorine consumption rate 4-10 times higher than monochloramine.

Surprisingly, for aged epoxy linings there was essentially complete chlorine consumption on every test day (0.01 mg/L when averaged over the 30 days). It is speculated that the higher concentration of copper detected in the water in the aged pipe sample contributed to the extreme chlorine demand. It is likely the

chlorine consumption rates would have been even higher as there was no essentially no chlorine residual left in the new epoxy samples to be consumed (< 0.05 mg/L) on three of the ten test days and no residual left in the aged pipe. Taking into account the high rate of chlorine consumption and that the initial concentration of monochloramine in the distribution system is typically twice that of chlorine (4 mg/L monochloramine, 2 mg/L chlorine), chlorine is not only a much less stable disinfectant but there is less of it to lose. (As a comparison to chlorine, monochloramine residual never fell below 2.83 mg/L.) For these reasons utilities ought to be aware of the capacity of epoxy linings to consume chlorine and should gauge whether the length of pipe needing relining is in a dead-end zone or if water is expected to remain in contact with the lining for an extended period of time. If so, the utility should consider carefully monitoring water from the taps of customers at the ends of the service lines to ensure a disinfectant residual is present, particularly for the first few days after installation of a lining.

Regarding the presence of ammonia in the water, the only notable difference in ammonia concentrations was in the aged pipe sample. In waters exposed to new epoxy, ammonia was detected only in chloraminated waters, as would be expected from the presence of the amine group in chloramines. There was no difference in concentration between samples and controls, with the exception of Day 1 when there was slightly higher ammonia (0.6 mg/L) in samples exposed to new epoxy. This is most likely insignificant but this difference could be due to the significantly higher concentration of free ammonia that was released as monochloramine was consumed at a high rate during that initial exposure. Theoretically the concentration should not have changed as the HACH kit measures total ammonia but this significant increase in free ammonia could possibly have been measured at a higher concentration than the complexed amine groups. Given that no ammonia was detected in the no disinfectant or chlorinated samples during this period it seems unlikely that the higher concentrations are due to any compounds leached from the epoxy. Regarding the aged pipe sample, low concentrations of ammonia were present every test day in higher levels than in the chlorinated control. While these concentrations (averaging 0.05 mg/L) pose no threat to water quality, it was puzzling why ammonia was detected in the chlorinated water. It is possible that the heterotrophic bacteria were dissimilating the nitrate that was added as a salt back to ammonia under low oxygen conditions that were likely present in the stagnant water. Regardless, the impact on ammonia concentrations in the water is low.

The other inorganic water quality parameters of alkalinity, hardness, and metals remained unaffected by the presence of new epoxy linings. These results were not surprising, as the pH remained unchanged and no literature was found to report that epoxy linings can leach metals. The literature has shown epoxy to be an effective barrier between the metallic pipe and the water source, thereby preventing any leaching or

corrosion from occurring. Regarding the presence of solids in the water, no visible particulate matter was present and analysis showed no dissolved or particulate matter was detectable. For the aged pipe sample, analysis of the water did show detectable concentrations of copper in the range of 2-33 ug/L. It is unlikely that copper was leached into the water through the epoxy lining itself but rather through the act of cutting the pipe. Low copper concentrations were likely introduced into the pipe that would have affected other parameters such as disinfectant demand and possibly pH.

Possibly the most significant impact on water quality was the high amount of leached organic material from both new and aged epoxy linings. Although a study performed by Satchwill et al (2002) reported significantly higher TOC leaching rates from new epoxy linings in their lab study (up to 115 mg/L/d), the TOC data from the new epoxy were higher than most of the literature available (3.4-6.3 mg/L/d, after the first 24 hour exposure). Even more surprising was the high TOC leached from the aged epoxy. It was believed that after years of service the epoxy lining would have stabilized to the point where leaching was negligible. This was not the case, however, as concentrations never dropped below 1.6 mg/L and remained fairly constant across the 30 days. With the exception of Day 1, TOC levels were always highest in chlorinated waters, consistent with findings from Heim and Dietrich (2007) that reported chlorine was correlated with increased TOC leaching. The separate THM formation study also confirmed the tendency of new epoxy to leach TOC in similar concentrations as reported during the immersion study. 7.5 mg/L TOC was leached from the coupons in no disinfectant water after an exposure of 72 hours (0.012 mg/cm^2) compared with 0.017 mg/cm^2 in the immersion study after 24 hours. Although the exposure periods differed, both studies showed that a long initial exposure to water does not produce substantially higher TOC.

When samples from the new epoxy linings were analyzed for the presence of 61 regulated SVOCs, none of the compounds were detected in the samples. The samples were also analyzed by performing a GC/MS library search and only one of the compounds from the samples could be identified, Bisphenol-A (BPA). BPA was present in the samples from 22-33 ug/L on Day 1 but decreased significantly after the first exposure and remained very low for the remainder of the study. Interestingly BPA was highest in chloraminated waters and lowest in no disinfectant waters, although concentrations differed by only 11 ug/L. Concentrations of BPA in all three waters dropped substantially after Day 1, coinciding with a sharp drop in TOC and consistent with research from Bae et al (2002) that predicted a direct correlation between BPA and COD. Detecting BPA in the samples was not surprising as it is one of the chemicals used in the manufacture of some epoxy liners. However, controversy surrounds the use of BPA in drinking water materials due to its potential to mimic hormones and interfere with the endocrine system.

Fortunately concentrations in the water never exceeded the Total Allowable Concentration (TAC) of 200 ug/L as recommended by NSF-61 and from the trend seen in the data it is expected BPA levels will remain low. It is presumed that these concentrations would be effectively decreased by flushing and are far enough below the TAC to be deemed acceptable. The absence of other identifiable organic compounds was surprising, considering the high amount of leached TOC in the water. Because only semi-volatile organics were analyzed for, it's likely that a substantial portion of the leached TOC were either volatile organics that were lost to the headspace during the extraction procedure or heavier, non-volatile compounds that were not detected by chromatography. Further analysis using other extraction and detection procedures would be useful in determining what organic compounds were present in the water. Analysis of the aged pipe sample would also be useful to see if the TOC leached from the aged liner also contained levels of BPA; however, limitations with the volume of water in the pipe precluded testing for organic compounds. Overall this data fit within the available literature and showed that epoxy liners do leach relatively high concentrations of TOC.

Also consistent with findings from Heim and Dietrich (2007) was the data that showed the potential for disinfectant byproduct (DBP) formation in waters exposed to epoxy linings. Data from this experiment showed the greatest concentration of haloacetic acids (HAAs) and trihalomethanes (THMs) in chlorinated waters, consistent with the two previous experiments on polyurethane and cement mortar linings and also consistent with the knowledge that free chlorine reacts more readily with TOC to form DBPs than does monochloramine. For new epoxy linings both THMs and HAAs were present, although chloroform was the only THM detected and only chlorinated HAAs were detected. These findings were logical in that no bromine was present and Heim and Dietrich (2007) also reported detecting only chloroform during their THM analysis. Surprisingly chloroform showed a trend of increasing concentrations over the study but the highest concentrations present (12 ug/L) were significantly below the MCL of 80 ug/L (USEPA, 2000). HAAs did not show a trend in formation and concentrations never exceeded 8 ug/L, much lower than the MCL of 60 ug/L (USEPA, 2000). The THM formation study confirmed the ability of only chloroform to form from the reaction of chlorine with leached TOC with very similar results: approximately 10 ug/L CHCl_3 . Analysis of the aged pipe sample showed no THMs formed in spite of higher HAA concentrations present, approximately 13-22 ug/L. When normalized for surface area these fell within the range for new epoxy. Given the extreme disinfectant demand of the aged epoxy and the high TOC levels in the water, it was not surprising to detect higher concentrations of HAAs, although the absence of THMs is not well understood. Overall DBP concentrations were well below regulated levels and the effect of epoxy on these regulated compounds is presumably low, in spite of considerable TOC present in the water and high disinfectant demand.

The other major concern for epoxy linings other than TOC and disinfectant consumption was odor. Odor was described by panelists as having a moderate intensity, meaning customers would almost certainly object to their drinking water containing an odor at that level of intensity. As the Flavor Profile Analysis (FPA) lists 2 as readily detectable, all of the samples would meet or exceed the recommended level. Panelists reported the chlorinated samples as containing the highest odor intensity and the most offensive “burning/chemical” odor, averaging 7.6 for the chemical odor and 7.0 for the chlorinous odor. The intensity on Day 30 was notable in that, after nine days of exposure, all the disinfectant was consumed and panelists reported the chemical odor as “pleasant.” The trend shows that with higher disinfectant concentrations and a subsequent high chlorinous odor, the epoxy contributed a more offensive odor. Chloraminated waters produced lower intensity odors and panelists reported a more pleasant odor (averaging 4.4, sweet chemical; 2.7, chlorinous). The no disinfectant waters exposed to new epoxy had the lowest odor intensities across the experiment (averaging 3, sweet/chemical). Although all the intensities were reported as relatively strong, it is likely that dynamic conditions experienced during normal flow would significantly decrease the odor intensity. Utilities would be encouraged to tell consumers to flush their pipes for a few minutes if they experience issues with odor. However, based on research from Marchesan and Moran (2004), epoxy manufacturers should perform odor assessment of epoxy formulations prior to mass manufacturing their product as some products were shown to produce significant odor yet still pass organic leaching tests. More research would be useful to determine what length of exposure time and what flow conditions will produce detectable odors in the water.

Microbial analysis was only performed on the aged pipe sample and showed low concentrations of bacteria on the surface of the aged pipe sample (< 105 CFU/cm²). The analysis showed the bacteria were heterotrophic and so were likely using TOC present in the water as their carbon source. It is impossible to know from the analysis whether or not these bacteria would be problematic but it is highly unlikely that this low concentration of bacteria poses any threat to water quality, as no literature could be found linking epoxy linings to the presence of disease-causing bacteria. Although Bae et al (2002) found an increase in CFU in waters exposed to epoxy linings, they found no correlation between the amount of TOC leached and the number of bacteria. It is not well-understood exactly what effect the presence of this epoxy lining has on the bacterial count but the impact does not appear to be harmful.

Overall the factors influencing water quality during the study were shown to be surface area to volume ratio and disinfectant treatment. The surface area to volume ratio was critical in that, when concentrations were normalized for this ratio, levels of TOC and DBPs between the new epoxy, aged pipe, and THM formation tests were all very similar. Concentrations prior to being normalized were always higher given

higher surface areas. This is an important factor for utilities to consider in that smaller-diameter epoxy-lined pipes can almost certainly be expected to transport lower-quality water. This is of particular concern if household plumbing is relined, where pipes are not only smaller but stagnation is much more likely to occur. For these reasons pipes ought to be flushed well in the days following lining and water at the tap should be monitored for the presence of organics. Also, the disinfectant used by a utility will be a factor in how many DBPs are formed and the ability to maintain a residual at the consumer's tap.

Although there are potential water quality issues to face with epoxy linings, in situ rehabilitation using epoxy is a cost-saving, proven alternative to pipe replacement or the use of cement mortar or polyurethane to reline. More long-term monitoring of existing epoxy liners is recommended as very little data exists here in the US and, as a result, utilities are still somewhat hesitant to incorporate epoxy linings into their rehabilitation projects. Hopefully this study has confirmed the ability of epoxy to perform within regulatory limits as set by ANSI/NSF-61 and the EPA and provide them with a comparison to cement mortar and polyurethane regarding their performance on the specified water quality criteria.

III. Potential Improvements to the Experimental Design

After completion of the study it was realized there were some design issues that could be improved upon to make the study more efficient and to make statistical analysis of the results more practical.

1) Adjust the sampling schedule to a more consistent pattern. This proposed schedule change would sample at regular intervals and have consecutive water changes performed after the same length of time. This would mean instead of the water change schedule of Days 1, 2, 4, 5, 9, 11, 14, 15, 19, 21, and 30, water changes would be performed after three 24 hour exposure times on Days 1, 2, and 3 followed by three 48 hour exposure times on Days 5, 7, and 9, then three 72 hour exposure periods on Days 12, 15, and 18, and finally three 96 hour exposure periods on Days 22, 26, and 30. This would allow better statistical analysis to be performed in that leaching and disinfectant consumption rates could be analyzed using linear regression. Trying to analyze the rates at the current sampling schedule is not practical because the exposure times are not the same.

The initial sampling schedule was designed around an ANSI/NSF-61 schedule and was planned with two primary purposes in mind: to sample most intensively at the beginning of the study and to allow enough time in between water changes to run analysis of time-sensitive samples. Due to the enormous amount of samples collected during a short time period, time had to be set aside for both preparation and sample analysis. And because some of the samples required extremely labor-intensive lab work, the current schedule was produced that would allow enough time to prepare and process the data. This proposed schedule takes into account these requirements but also would allow more thorough statistical analysis to be performed.

2) Adjust the frequency with which certain parameters were measured. After analyzing the data, it was obvious that some of the most interesting data had some of the fewest data points, making statistical analysis of these samples even more difficult. As previously discussed, the schedule was designed to allow enough time to process the samples in between water changes. This meant that not all parameters were collected every sampling day. TOC, THMs, and HAAs specifically were only analyzed on specified sampling days due to their time-intensive analysis, while most of the inorganic parameters were analyzed at every water change. Because epoxy is a polymeric lining, the most significant impacts on water quality were related to its capacity to leach organics and form disinfection byproducts. Anticipating this from the literature, it would have been more practical to sample parameters like alkalinity less frequently and focus more on the organic parameters. Because determining alkalinity was

also very time-intensive, spending less time analyzing these samples that were not expected to be impacted from a polymer lining could have meant more time analyzing other organic parameters.

3) Obtain test vessels of the exact same dimensions. Even though concentrations and rates were normalized for surface area to make comparisons, the difference in the number of coupons between test vessels (5.5, 6, 6.5, or 7 coupons) could have been an additional factor that affected the results and this would be one less element to consider.

4) Obtain a larger pipe sample and a larger sample size. The small amount of water volume held by the pipe did not allow for analysis of SVOCs or odor, two parameters that would have been interesting to know. Having more than one length of pipe would also provide more confidence in the results, that they were reproducible with multiple samples.

IV. Future Research

As discussed earlier in the text there were a few areas of research that could use further exploration. It would be useful to perform a more thorough analysis of the organic present in the water to determine the exact composition of the leached compounds. Obtaining a basic formulation for the epoxy would also be of use to compare how the organic matter in the water reflected the composition of the epoxy liner itself. Considering the small length of pipe used for the aged epoxy analysis, another practical area to explore would be to obtain a larger pipe or multiple samples to test the parameters that were not able to be analyzed due to limitations with water volume. Also, as data from Satchwill et al (2002) showed that different formulations of epoxy can perform very differently with regards to leached TOC, a practical application would be to compare different epoxy linings under the same conditions to determine how parameters do differ according to the type of epoxy used. Finally, performing similar leaching tests under dynamic conditions to represent dynamic flow patterns in pipes would provide a helpful comparison for utilities to understand how flow can affect water quality.

References

- Alben, K., Bruchet, A., and Shpirt, E., (1989) *Leachate from Organic Coating Materials Used in Potable Water Distribution Systems*. Denver, CO, AWWARF
- American National Standard/NSF International Standard 61. (2000) Drinking water system components – health effects: <http://www.nsf.org>
- AWWA (2002) Permeation and Leaching. Prepared for USEPA, Office of Water.
- AWWA (2002) AWWA standard for spray applied in situ epoxy lining of water pipelines – draft. ANSI/AWWA CB1X-xx. Denver: AWWA
- Autret, E., Saisset-Costel, C., Khahil, A., Diagouraga, B., Boireau, A. (1999) In situ resin lining of potable water mains: a comprehensive approach for process optimization and product performance assessment. *Pipeline Protection*. **37**, 207-214.
- Bae, B., Jeong, J., Lee, S. (2002) The quantification and characterization of endocrine disrupter bisphenol-A leaching from epoxy resin. *Water Science and Technology*. **46**, 381-387.
- Brady, R. & Adkins, J. (1997) Control of lead in drinking water. Naval Research Laboratory, Washington, DC.
- Brongers, M.P.H. (2002) Drinking water and sewer systems in corrosion costs and preventative strategies in the United States. Report FWHA-RD-01-156, US Department of Transportation Federal Highways Administration, Appendix K.
- Conroy, P., Hughes, D., Wilson, I. (1993) Demonstration of an innovative water main rehabilitation renewal technique: in situ epoxy lining. Denver: AWWA
- Deb, A., Snyder, J., Hammel, J., Tyler, E. (2006) Service line analysis of water main epoxy lining. American Water Works Association Research Foundation (AWWARF).
- Deb, A., Hasit, Y., Norris, C. (1999) Demonstration of Innovative Water Main Renewal Techniques. American Water Works Association Research Foundation (AWWARF).
- Dunn, D. (2008) Water delivery report 2008: the science behind water quality and pipe restoration.
- Heim, T., Dietrich, A. (2007) Sensory aspects and water quality impacts of chlorinated and chloraminated drinking water in contact with HDPE and cPVC pipe. *Water Research*. **41**, 757-764.
- Heim, T. Dietrich, A. (2007) Sensory aspects of drinking water in contact with epoxy lined copper pipe. *Water Science and Technology*. **55**, 161-168.
- Holt, Gauthier, Merlet, Block. (1998) Importance of disinfectant demand of materials for maintaining residuals in drinking water distribution systems. *Water Supply*. **16**, 181-191.
- Jackson, P., Warren, I., James, H. (2007) The long term migration of substances from in-situ applied epoxy resin coatings: final report to the drinking water inspectorate.

- Khiari, D., Bruchet, A., Gittelman, T., Matia, L., Barret, S., Suffet, I., Hund, R. (1999) Distribution-generated taste-and-odor phenomena. *Water Science and Technology*. **40**, 129-133.
- Krishnan, A., Stathis, P., Permeth, S., Tokes, L., Feldman, D. (1993) Bisphenol-A: an estrogenic substance is released from polycarbonate flasks during autoclaving. *Endocrinology*, **136**, 2279-2286
- Marchesan, M., Morran, J. (2004) Tastes associated with products in contact with drinking water. *Water Science and Technology*. **49**, 227-231.
- National Toxicology Program (2000) Department of Health and Human Services: <http://ntp-server.niehs.nih.gov/>
- O'Donoghue, Garrett, R., Datta, V. (1998) Optimizing performance of fast-cure epoxies for pipe and tank linings. *Journal of Protective Coatings and Linings*. **15**, 36-51.
- Oram, P., Brown, D., Jennings, K. (2002) The benefits of lining large diameter pipes with polyurethane. *International Water Engineering*. **22**, 52-55.
- Oram, P., 2004. Spray applied linings for water main rehabilitation: good or bad? New Orleans, North American Society for Trenchless Technology, NO-DIG 2004.
- Rigal, S., Danjou, J. (1992) Taste and odors in drinking water distribution systems related to the use of synthetic materials. *Water Science and Technology*. **40**, 203-208.
- Russell, J. (1996) Development of epoxy resins for potable water mains. Engineering and Construction Conference. Denver, CO.
- Saegrov, S., Bjorgum, A., Rodum, E., Haugen, M., Wermskog, L., Reksten, K. (2007) Degradation of lining systems for drinking water networks. *Presentation LESAM 2007*.
- Satchwill, T. (2002) The impact of pipe coatings on drinking water quality. City of Calgary, Engineering and Environmental Services Department.
- Schweitzer, L., Tombouliau, P., Atasi, K., Chen, T., Khiari, D. (2004) Utility quick test for analyzing materials for drinking water distribution systems for effect on taste-and-odor. *Water Science and Technology*. **49**, 75-80.
- Tombouliau, P., Schweitzer, L., Mullin, K., Wilson, J., Khiari, D. (2004) Materials used in drinking water distribution systems; contribution to taste and odor. *Water Science and Technology*. **49**, 216-226.
- United States Army Corps of Engineers (2001) In-situ coating for metallic pipe.
- United States Environmental Protection Agency (USEPA) (2002) Permeation and leaching: <http://www.epa.gov/safewater/tcr/pdf/permeleach.pdf>
- United States Environmental Protection Agency (USEPA) (1998) Stage 1 disinfectants and disinfection byproduct formation: <http://www.epa.gov/safewater/contaminants/index.html#dbps>
- Warren, I. (1983) Factors influencing the choice of materials for epoxy resin renovation of water mains. *Chemistry and Industry*, **17**, 673-678.
- Warren Associates (Warren Associates (Pipelines) Ltd.). 1997. Yorkshire Water Services Ltd. Report on Epoxy Resin Lining Assessment Western Area (Vol.1 of 3), First Draft. 8 Prince Maurice Court,

Hambleton Avenue, London Road, Devizes, Wiltshire SN10 2RT, England: Warren Associates Pipelines) Ltd.