Impact of Polymeric Plumbing Materials on Drinking Water Quality and Aesthetics

Timothy Heim

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Andrea M. Dietrich, Ph.D., Chair
Marc Edwards, Ph.D.
Linsey Marr, Ph.D.

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ABSTRACT

The use of polymer pipes is now very common in home plumbing and other parts of the drinking water distribution system. Many taste and odor complaints in drinking water are known to originate from contact of water with materials. The ability of polymer pipes used in home plumbing to affect drinking water quality and aesthetics was investigated using the Utility Quick Test (UQT). Analysis of water quality and aesthetics were conducted in the absence of disinfectant and the presence of either chlorine or chloramines. A Flavor Profile Analysis (FPA) panel was trained according to Standard Methods 2170B to evaluate the organoleptic characteristics of the samples. Laboratory analyses were performed to determine levels of total organic carbon (TOC), disinfectant residual, pH and to attempt to identify specific volatile organics.

The first part of this study investigated HDPE, cPVC and epoxy lined copper pipes using the UQT method. Both HDPE and epoxy-lined copper had significant effects on water quality and aesthetics during the approximately 10 day exposure of the UQT. HDPE and epoxy-lined copper leached significant amounts of TOC and consumed more disinfectant than controls, but in different amounts. cPVC was the most inert of the materials tested and had the least impact on water quality and did not contribute any significant odor. None of the pipes tested appeared to contribute trihalomethanes to drinking water, but further analysis revealed that the compounds may actually be generated and subsequently sorbed into pipe walls. These data show the effects of newly installed polymeric pipe materials and their potential to impact water quality in differing capacities.

The second part of this study compared the results of the UQT on HDPE, epoxy lined copper, cPVC, PEX-a and PEX-b with the goal of comparing and contrasting how five different polymeric plumbing materials can impact drinking water quality. Results demonstrated the short-term ability of all pipe materials except cPVC to impact water quality and aesthetics. This data could potentially be useful in generating selection criteria for homeowners and plumbing professionals regarding the impact of newly installed plumbing materials.

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AUTHOR'S PREFACE

This work is presented in the Virginia Tech Manuscript format. The first chapter is a comprehensive review of the existing literature on the impact of polymeric plumbing materials on taste and odor in the distribution system. It reviews both case studies and laboratory experiments. Chapters II examines the ability of HDPE and cPVC pipe, both commonly available polymer pipe materials, to impact drinking water characteristics. Chapter III examines the effects on drinking water of an *in situ* remediation technique of relining leaking copper pipes with an epoxy resin. Chapter IV provides a comparison of five polymeric plumbing materials via the Utility Quick Test and examines their relative impacts on drinking water quality and aesthetics. This work was prepared for and supported by the National Science Foundation (NSF). Additional support was provided by the Edna Bailey Sussman Foundation. Chapter III entitled "Sensory Aspects of Drinking Water in Contact with Epoxy-Lined Copper Pipe" has been presented at the 7th IWA Symposium on Off-Flavors in the Aquatic Environment in Cornwall, Ontario.

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CHAPTER I

LITERATURE REVIEW

INTRODUCTION

Drinking water aesthetics play a critical role in consumers' perception of the quality and purity of this water, and on their willingness to accept it over alternatives like bottled water, the consumption of which has steadily increased in recent years (McGuire, 1995). In 2004, consumers in the US drank more than 6.8 billion gallons of bottled water, an 8.6% advance over 2003 (BMC, 2005). The perception of tap water as less than ideal may drive the consumer towards bottled water, and generate a lack of confidence in their local water utility, resulting in consumers "paying twice" for their water, once for higher expenditures by water utilities and again for bottled water (McGuire, 1995). Water utilities desire to produce a product that consumers will use with confidence, and depend on the consumer to act as a "sentinel" for the quality and consistency of their water (Whelton, 2003). Consumer confidence and water industry knowledge of aesthetic issues is of even greater importance given the heightened state of awareness concerning bioterrorism. In a 2004 study, Americans identified this type of attack as the one thought most likely to occur in the future (Hart-Teeter, 2004).

While a great deal is known about the effects on taste and odor from microbiological and chemical sources in water supplies, (e.g. cyanobacteria or pollutants from runoff) the effects of the materials making up the distribution system itself are less well realized (Schweitzer et al., 2004). Factors in the distribution system itself include biological causes such as microbial growth on pipe walls, and chemical causes derived from the reaction of disinfectants with natural organic matter (NOM) and leaching from materials in the distribution system (Khiari et al., 1999). Biological and chemical sources can be interrelated as organic matter leaching from plumbing materials may provide a medium for microbial growth. Additionally, the interaction between types of disinfectant used (e.g. chlorine and chloramines) with each other, pipe surfaces and other chemical constituents in the distribution system must also be considered.

Understanding the interaction of the materials from which the distribution system is comprised with drinking water is inherently important to maintaining a high quality product at the tap, and maintaining high consumer confidence. A 1989 AWWA nationwide study reported 65% of water utilities considered the distribution system responsible for their taste and odor problems (Suffet et al., 1995).

As the consumer does not have access to even the most rudimentary water quality analysis equipment, they depend solely on their senses (primarily taste and smell) to judge water quality. Any changes detected in the taste or odor of tap water from what the consumer considers normal could result in the perception that the water is unsafe, unpalatable, and generally less fit to drink (Whelton, 2003, Whelton *et al.*, 2004). This trend had been evidenced in the United States in a study of episodes involving taste and odor problems by consumer descriptions of "foul smelling tap water," with a "grassy and metallic" or "paint thinner" odor and the idea that they are "afraid that some dangerous chemical has been added to the water" (McGuire, 1995). Recent instances of public health problems caused by contaminated drinking water, such as the deaths of 7 people and sickening of thousands more in Walkerton, Ontario, have led to deceased consumer confidence in some areas (Hrudey et al., 2002). It is essential that utilities be able to provide evidence for the actual causes of the odors in order to prevent consumers from assuming a health risk may be present (Jardine et al., 1999).

Several studies conducted in Canada reinforce the idea that drinking water aesthetics play a key role in consumer acceptance of tap water. Levallois *et al.* reported that in Quebec, over 30% of consumers were unhappy with the taste of their drinking water, and 14% were unhappy with the odor (Levallois et al., 1999). A study done in Toronto reported that less than half (49%) of city residents found their drinking water acceptable, and that 40% of the households studied had changed to an alternative source such as bottled water (Jardine et al., 1999).

The switch by consumers away from tap water is also having more far reaching effects beyond the mere perception of drinking water quality. Dentists at the World Dental Congress in Montreal issued a report suggesting the increased use of bottled water is contributing to a rise in dental cavities in children (AWWA, 2005). While two thirds of American tap water contains fluoride, it is absent in many bottled waters. The switch is being driven by both consumer uncertainty about the safety of tap water sources, and increased consumer standards for aesthetically pleasing tap water.

The combination of increased concern regarding terrorist threats to the distribution system, coupled with heightened consumer standards in regard to tap water necessitate that water utilities produce a consistent high quality product at the tap. The ability to control and understand off-flavors and odors, including those generated by the distribution system is fundamental to this process.

AESTHETIC EFFECTS OF SYNTHETIC PLUMBING MATERIALS

Recent decades have seen the advent of synthetic home plumbing materials and a continuing trend of increased use in homes and distribution systems. Polymers such as High-Density Polyethylene (HDPE), Cross-Linked Polyethylene (PEX), Polyvinyl Chloride and chlorinated Polyvinyl Chloride (PVC and cPVC) make durable, cost effective replacements to traditional materials such as copper. Synthetic pipes can be easier and more cost effective to install due to light weight and increased flexibility, and can be less expensive than copper to produce. Other polymer based materials such as epoxy liners have now become a popular alternative to re-piping in the event of corrosion and copper pinhole leaks.

While type of plumbing material can affect cost and ease of installation, it can also have a significant impact on drinking water aesthetics and has the ability to generate taste and odor problems. The acceptable level of copper in drinking water in terms of health effects has been regulated by the United States Environmental Protection Agency (USEPA) for some time, and recently effects on taste have been examined (Dietrich et al., 2004). Other research has show an even greater potential for synthetic materials to impact taste and odor. (Rigal and Danjou, 1999, Anselme *et al.*, 1985a, Khiari *et al.*, 1999, Tomboulian *et al.*, 2004)

Synthetic plumbing materials have the ability to generate taste and odor problems in drinking water in several ways. One mechanism is the direct leaching of volatile organic compounds (VOCs) from the polymer itself into the exposed drinking water. Another is via microbial growth resulting from the available leached polymer acting as a substrate. Others include polymer permeation and reaction of disinfectants with organics in the pipe.

Studies of the first mechanism show the ability of VOCs to leaching directly from pipe materials and cause odors in drinking water. This was first examined by Anselme in 1985, who demonstrated the occurrence of organoleptic changes caused by defective polyethylene pipe, via both the leaching of polymer additives and oxidation of the surface of the pipe during extrusion. Further studies have confirmed the ability of VOCs to leach from pipes and pipe linings, and effect taste and odor (Skjevrak *et al.*, 2003, Marchesan and Morran, 2004). These VOCs can originate from the pipes themselves, as well as the plasticizers, antioxidants and solvents used in their manufacture.

Anselme et al. (1985) conducted a study of a water pipe causing aesthetic problems which demonstrated the ability of polyethylene (PE) pipe to leach compounds responsible for taste and odor problems. Water passing through a 300 meter length of PE pipe was analyzed via closed loop stripping and simultaneous distillation extraction. Sensory analysis was performed by Flavor Profile Analysis (FPA) and Threshold Taste Number (TTN). Results showed a burnt plastic odor which was attributed to the presence of butylated hydroxyl toluene. Other compounds included 4-methyl-2,6-di-t-butylphenol and alkyl thiophene, which are added as antioxidants, and phthalate and tributyl phosphate used as plasticizers. The problem ceased when the pipe was replaced, and the presence of the odor causing compound was attributed to oxidation of the pipe surface during extrusion. The problems caused by oxidation during the extrusion process were also studied by Rigal and shown to contribute a burned-oil or sweet flavor (Rigal, 1992).

The ability of HDPE to contribute taste and odor causing compounds was studied by Villberg, who investigated the resin used in HDPE manufacturing. The experiment was carried out by analyzing both pure HDPE resin granules and samples of odor free water which had been exposed to the granules and shaken for 4 hours. In this study a gas chromatography mass spectrometry sniffing system and a gas chromatography fourier transform infrared spectroscopy sniffing system were used to identify the odor causing VOCs, while a trained panel was used to determine odor descriptors. A list of organic compounds and the descriptors applied to them, (Table I-1) was subsequently generated (Villberg et al., 1997).

Table I-1. Volatile organic compounds identified from HD-PE resins with corresponding odor descriptors (Villberg et al., 1997)

Compound	**Odor**
2-propanal	Putrid, glue
Ethyl propanate	sweet, candy
C_6-Ketone	Solvent, plastic
Methylpentenone	Plastic
Toluene	Model glue
Hexanal	Leafy
2,4-Heptadienal	Aldehydic
C_7-Ketone	Chemical
Ethylcyclohexanone	Bitter
Butyl acrylate	Glue
C_8-Ketone	Solvent
Methylhexanal	Pungent green
2-Octenal	Mushroom
Pentamethylheptane	Stony, dusty
Nonanal	Bad, aldehyde
Undecadienal	Pungent

Villberg also studied the ability of a combined zeolite called Abscents™ to remove odor causing carbonyl compounds and eliminate odors (Villberg et al., 1998). Samples of HDPE pellets were exposed to odor free water and 4 different concentrations of the zeolite, and then shaken for 4 hours. A gas chromatography mass spectrometry sniffing system was then used to identify odor causing compounds. 7 ketones and 4 aldehydes where identified as causing odor, with isopropylcyclohexanone found to be the cause of the strongest odor. The addition of 0.30 weight percent Abscent was determined to cause the disappearance of carbonyl compounds as well as their resulting odors.

The ability of PVC pipe to generate odor causing compounds was examined by a Saudi Arabian study which concentrated on the leaching of vinyl chloride monomer (VCM) from unplasticized PVC pipes. The pipes were filled with waters with varying pH, temperature, total dissolved solids (TDS) and exposure time. pH and TDS were shown to effect VCM concentrations, while temperature had no effect (Al-Malack M.H., 2000). This demonstrated the importance of considering water quality parameters when performing leaching and migration tests.

Further studies were conducted by Brocca in Demark into the leaching of VOCs from four types of polyethylene pipe (Brocca et al., 2002). After a flushing protocol, two types of PEX, medium density polyethylene (MDPE), and low density polyethylene (LDPE) piping were exposed to test water for 7 days. The test water was then analyzed via liquid-liquid extraction by GCMS. 20-30 organic compounds were detected with eight being positively confirmed using commercially or synthesized standards (Table 2) (Brocca et al., 2002). Most of the compounds were comprised of a phenolic ring with hindered alkyl groups substituted into positions 2 and 6 on the aromatic ring.

Table I-2. Organic compounds identified from polyethylene pipe (Brocca et al., 2002).

Compound Identified
4-ethyl phenol
4-tert-butyl phenol
2-6-di-tert-butyl-p-benzoquinone
2-4-di-tert-butyl phenol
3-5-di-tert-butyl-4-hydroxy benzaldehyde
3-5-di-tert-butyl-4-hydroxy acetophenone
3-(3-5-di-tert-butyl-4-hydroxyphenyl) methyl propanoate
3-(3-5-di-tert-butyl-4-hydroxyphenyl) propanoic acid

The Brocca study also examined granules of raw PE material, as well as recently installed PE pipe materials. The raw PE granules were analyzed in order to determine if the odor causing compounds were arising from steps in the manufacturing process. Results showed that a significant number of the compounds arose from either oxidation/degradation products generated during production, or additives used during that time. Samples collected from the recently installed pipes resulted in the detection of 3 of the compounds previously identified.

A Norwegian study (Skjevrak et al., 2003) applied a leaching protocol (CEN 1420) similar to the Utility Quick Test to HDPE, cPVC and PEX, exposing lengths of pipe to test water for 3 successive periods of 72 hours. Organic compounds were concentrated using a purge and trap method based on the open loop stripping principal, and analyzed via GC-MS. Odor analysis was conducted by TON. Results indicated the leaching of 2-4-di-tert-butyl phenol and 2,6, di-tert-butyl-p-benzoquinone from the HDPE pipe, as well as esters, aldehydes, ketones, aromatics hydrocarbons and terpenoids. TON for the HDPE resulted in values ≥4 The PEX pipe leached significant quantities of methyl tert butyl ether as well as unidentified oxygenates and generated TON ≥5. The PVC pipe leached only trace amounts of hexanal, octanal, nonanal and decanal, and did not contribute odor.

A wide ranging study conducted by the Australian Water Quality Centre, examined over 1000 products used in distributions systems worldwide (Marchesan and Morran, 2004). The AS/NZS 4020 standard was applied to various pipes, valves, fittings and other plumbing materials. Particular focus was given to polyethylene pipes, coatings and valves, which have been problematic in some instances. In order to be considered acceptable, the products were not permitted to impart any detectable taste to the water which they were exposed. The study further examined the types of tastes obtained when products were exposed to both chlorinated and non-chlorinated water, and revealed that VOC leaching was accelerated by the presence of chlorine. This demonstrates the importance of using the presence of disinfectants when conducting organoleptic investigations of new plumbing materials.

HIGH DENSITY POLYETHYLENE

Polyethylene was synthesized by accident in 1933 when a reaction between ethylene and benzaldehyde at extremely high pressure yielded white waxy substance that was found to be the result of a polymerization process. The residue polyethylene (PE) resin was a milky white, translucent substance derived from ethylene (CH2=CH2). High-density polyethylene (HDPE) has a density that ranges from 0.94 to 0.97 g/cm3 (Peacock, 2001). Its molecules have an extremely long carbon backbone with no side groups. As a result, these molecules align into more compact arrangements, accounting for the higher density of HDPE.

HDPE is stiffer, stronger, and less translucent than low-density polyethylene. HDPE is formed into grocery bags, car fuel tanks, packaging, and most importantly, polyethylene pipe. HDPE is light weight, flexible, corrosion resistant, and capable of handling the temperatures and pressures found in home plumbing applications. High Density Polyethylene (HDPE) Solid Wall Pipe has been used in Potable Water applications since the 1960's, and has been gaining approval and growth worldwide ever since. HDPE Pipe is approved by both AWWA and NSF standards (PPI, 2006).

CROSS-LINKED POLYETHYLENE

In the late 1950s scientists in Germany attempted to modify the structure of polyethylene to strengthen the connections between the polymer chains. They succeeded in developing ways to create additional ties between the PE molecules through chemical bonding. The result was a PE structure that did not move to a softened state as quickly when temperature was increased. The new polymer came to be known as PEX. Its use subsequently spread across Europe and to the U.S., where it became a popular replacement to copper for home plumbing systems and the drinking water distribution network. Chemically similar to HDPE, PEX enjoys the properties of flexibility, durability, corrosion resistance, and light weight. It is also stable with regard to temperature and pressure, making it a good product for hot and cold home plumbing systems (PPI, 2004). PEX pipes and fittings are approved in all North American plumbing codes for hot and cold potable water distribution systems. Its flexibility makes it easy to coil and carry in large quantities, aiding in ease of installation. PEX is very similar to polyethylene in appearance, but due to its cross-linking, is a thermoset material, so it can not be melted and reshaped.

PEX is the cross linked structure of polymer chains made up of ethylene monomers. The cross linking process is typically done in one of three ways, two chemical: high pressure peroxide and silane, and one physical: radiation. These processes produce products known as PEX-a, PEX-b, and PEX-c, respectively. The first process developed was the high pressure peroxide (also known as Engel) process, which was developed in the 1960's. The Engel process uses free radicals from heat activated chemicals to remove hydrogen atoms from the PE carbon backbone and allow the formation of cross-linking bonds with other PE polymers (PPI, 2004, Peacock, 2001). One potential effect on drinking water aesthetics from this process is the presence of ketones (Peacock, 2001), which are known to impart a "solvent-plastic" odor in drinking water (Villberg et al., 1997).

The silane or “moisture cure” process for cross-linking polyethylene involves the use of silane molecules and steam to form a silane bridge that links together multiple polyethylene chains. This is initiated by organic peroxide and occurs via a radical reaction between silane molecules and the carbon chain PE backbones. The presence of moisture allows hydrolysis, which leads to the formation of the siloxane bridges. High temperatures increase the reaction rate (Peacock, 2001).

The third cross-linking process is physical rather than chemical and utilizes electron beam cross-linking controlled by the strength of an ultraviolet radiation beam to initiate cross linking of PE molecules. This process requires the presence of a photoinitiator, whose purpose is to initiate radical free polymerization and a bridging agent to facilitate cross-linking (Peacock, 2001).

POLYVINYL CHLORIDE AND CHLORINATED POLYVINYL CHLORIDE

Polyvinyl chloride, commonly known as PVC, is a member of the ethylene family of polymers. Vinyl chloride, the monomer from which PVC is made, was first synthesized in the laboratory of Justus von Liebig in 1835. PVC itself was synthesized in 1872. In the late 1920s that the first commercial production of PVC took place in the USA and subsequently spread across Europe (ECVM, 2006). PVC is produced by combining chlorine and ethylene to form ethylene dichloride, which is then converted into the monomer vinyl chloride, the basic building block of polyvinyl chloride.

Chlorinated Polyvinyl chloride (cPVC) possesses the same chemical resistance of PVC, but offers superior performance to PVC in applications where higher heat resistance is required. cPVC can withstand short term exposure up to 230 degrees F, while PVC has a maximum permissible temperature on a short term basis of 140 degrees F.

EPOXY LINED COPPER

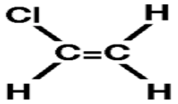
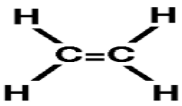
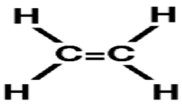
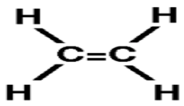
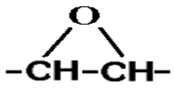
The study of synthetic plumbing materials includes not only those polymer-based pipes which are installed as substitutes for older materials like copper, but also synthetic materials which may be added to existing pipes for the purpose of repair and remediation. Distribution system corrosion is a serious problem in drinking water systems. Repair costs related to corrosion for public utilities in the United States are estimated at 22 billion US dollars per year (Brongers, 2002). Estimates for private infrastructure are even higher; with the potential cost of 1 Trillion US dollars to replumb every household in the US (Edwards, 2004). One solution to the corrosion problem is to repair leaking pipes by means of *in situ* remediation. This generally involves scouring the pipes via grit blasting, followed by the application of epoxy paint liners injected at high pressure to coat and seal pipe surfaces from further corrosion (Engineers, 2001). One of the most popular and effective of such liners is epoxy based coatings, which have become a popular solution to residential copper pinhole leak problems.

Epoxy was first used as a lining material over 40 years ago to prevent corrosion in Japanese industrial processes, and spread quickly to other applications. Epoxy is essentially a combination of two compounds. The first is a low-molecular-weight polymer with *epoxy* groups at each end, the second is diamine (Dekker, 1988). The two groups of molecules combine to form a cross-linked network which is extremely strong and durable (Center, 2002).

Epoxy lining is now used in a variety of applications. These include water main and reservoir linings, and *in situ* remediation of home plumbing systems with pinhole leaks. It has also been used extensively by the navy for shipboard pipe remediation (Brady and Adkins, 1994, Engineers, 2001). The liner used for these applications is certified by the National Sanitation Foundation under protocol NSF-61 for use as a plumbing material, and is capable of carrying hot and cold water.

A study done by the Army Engineering Research Laboratory evaluated the effectiveness of in-situ epoxy coatings for inhibiting metal corrosion under a spectrum of water quality parameters. In-situ coating was compared to zinc orthophosphate chemical inhibitor treatment to prevent corrosion in a model of a home plumbing system. Results indicated that epoxy coating provides an effective alternative to chemical treatment for the prevention of lead and copper corrosion. Both treatments effectively reduced metals levels below the USEPA Action Level of 15 µg/L for lead and 1.3 mg/L for copper in drinking water (Hock et al., 2005).

Table I-3. Common Polymeric Pipe Materials

Name	Monomer	Monomer Structure	Common Uses	Used In US Since
cPVC	vinylchloride		hot and cold water distribution systems in home plumbing	1952
HDPE	polyethylene		home plumbing and distribution mains, sewerage and drainage	Early 1970's
PEX-a	polyethylene		hot and cold water plumbing systems, radiant heating systems, snow melting applications	Early 1980's
PEX-b	polyethylene		hot and cold water plumbing systems, radiant heating systems, snow melting applications	Early 1980's
Epoxy-Cu	epoxy		relining copper pipes to treat pinhole leaks, lining for tanks and water towers	Early 1990's

LEACHING AND MIGRATION EVALUATION METHODS

The effect aesthetic quality of tap water has on consumer confidence and perception necessitates the use of a method to assess the impacts on taste and odor that new plumbing materials may have when introduced into the distribution system. In recent decades, Europe, Australia and New Zealand have developed standard methods to analyze taste and odor impact in new plumbing materials to a greater extent than the United States. Examples of this include the AFNOR XP41, used in France, the BS 6920-2.2.1 used in the United Kingdom, EN 1420-1, which is utilized by other parts of Europe, and most recently, AS/NZ 4020, the standard for Australia and New

Zealand. The goal of these methods is to ensure that materials to be used in the distributions system are subjected to a thorough organoleptic assessment prior to their approval for use.

The French protocol AFNOR XP41 which went into effect in 1997, states that a material being tested must pass organoleptic, chemical and toxicity requirements before being approved for use (Rigal and Danjou, 1999). In France and all other European countries, the first requirement in the approval process for a new synthetic material is that it passes an organoleptic evaluation, only then can the chemical and toxicity test be performed. In the Southern Hemisphere, AS/NZ 4020 uses a variety of protocols to assess the effects on taste and odor of both polymer and metal derived plumbing materials. Research conducted using AS/NZ 4020 has shown the significant failure rate which can be attributed to taste and odor problems, with 8.5% of the materials tested failing to pass the organoleptic portion of the test, even after they had passed chemical and microbiologic standards (Marchesan and Morran, 2004). Even if new plumbing materials successfully complete testing by aesthetic standards noted above, complications may still arise in the field due to installation, interaction between adhesives and fittings, and local water quality characteristics (such as type of disinfectant). This illustrates the importance of testing new materials for specific locations and the respective conditions to which they will expose the pipes.

The NSF 61 standard, from the American National Standards Institute/National Sanitation Foundation International evaluates only for compliance with health requirements. NSF 61 certification conveys that a material has not been found to leach compounds acknowledged by the EPA as causing adverse health effects (ANS/NSFIS, 2000). NSF 61 testing protocols vary depending on whether the material in question is to be utilized for hot or cold water conveyance or storage, but generally involve exposing a pipe to water for a predetermined period of time, then analyzing for specified contaminants based on the material's chemical properties. A small diameter pipe is rinsed in cold water followed by a rinse in deionized water, then filled with water containing 2mg/l chlorine. The water in the pipes is then changed ever 24 hours for a period of 14 days, and the water sample produced is analyzed for contaminants according to the EPA Methods for Chemical Analysis of Waster and Wastes (EPA 600/4-79-020). HDPE is tested for VOCs, metals, and phenolics, cPVC is analyzed for VOCs, metals, phenolics, tin, antimony and residual vinyl chloride monomer (RVCM) and PEX is tested for VOCs, metals, phenolics, methanol, and tert-butyl alcohol.

Currently, The United States has no standard method to provide an evaluation of aesthetic effects from synthetic plumbing materials such as those that exist in Europe. Based on the findings of an international workshop of drinking water experts, as well as the opinions of experts in the field, the Utility Quick Test (UQT) was developed in 2001 to constitute the US equivalent of an organoleptic assessment tool for synthetic plumbing materials (Schweitzer et al., 2004). The UQT involves a flushing and disinfection protocol, followed by the exposure of the test material to extraction waters for a 72 hour period. The water samples are then analyzed in comparison to control by trained panelists via Flavor Profile Analysis (FPA). This process seeks to generate sensory data which help to understand the leaching of volatile organics from the plumbing materials being tested, and predict the effects such materials might have on the distribution system. Water used in the test can be varied from highly pure sources like carbon filtered D.I. water to tap water which represents local water quality. The type and concentration of disinfectant utilized can also be varied to examine the effects that this might have on leaching and odors.

FLAVOR PROFILE ANALYSIS

Flavor Profile Analysis (FPA) is a standardized method of gathering sensory data which was first developed by the food industry and later adapted for use by water utilities. Its use can be an effective alternative to complicated and expensive equipment for the identification of odor causing compounds (Morran and Marchesan, 2004). The method involves five to seven panel members who undergo a significant amount of training to make them familiar with an odor intensity scale (0-12) and commonly used odor descriptors. FPA as several advantages over the more commonly used Threshold Odor Number (TON) (Rashash et al., 1997). TON uses an open-ended scale, and can be highly influenced by the sensitivity of an individual to a particular odor. TON generates information on composite odors, while FPA can break odors down by using specific individual descriptors. In addition to this, the dilution used in TON can influence the odors perceived in a particular sample. FPA is conducted in accordance with the procedures found in Standard Methods 2170.

DISINFECTANT AND DRINKING WATER AESTHETICS

The ability of drinking water disinfectants to affect taste and odor at the tap has been demonstrated in the literature. Disinfectants may increase, decrease or completely mask odor intensity from other sources. The presence of disinfectants has also been shown to affect the rate of leaching from plumbing materials. The two most commonly used disinfectants are hypochlorous acid (HOCl), known as "free chlorine," and chloramines (NH_2Cl, $NHCl_2$, NCl_3), known collectively as "total chlorine". The use of these disinfectants is critical in maintaining safe drinking water and protecting against waterborne diseases. The United States Safe Drinking Water Act (SDWA) states that chlorine residual in the distribution system must be between a minimum of 0.2 mg/L for disinfection and limited to a maximum of 4 mg/L to prevent formation of Trihalomethanes (THMs) (USEPA, 1996). It is important to consider the effects that the addition of a disinfectant may have on taste and odor data during a leaching and migration test, as well as other factors effecting water quality, including pH, and temperature.

Chlorinous odors from chlorine and chloramine are detectable by sensory panelists at concentrations as low as .05 mg/l for French consumers and .25 mg/l for Americans (Bruchet A., 2004, Krasner S.W., 1984). The effects of chlorine and chlorine on drinking water odors have been demonstrated by several studies; most commonly these disinfectants mask or reduce the perceived intensity of other odors which may be present.

Research at the Philadelphia Water Department showed that chlorine and chloramine have the ability to remove odor. Some water utilities were found to use disinfectant to control odors from geosmin and MIB (Burlingame et al., 1986). In a specific instance, odor caused by trans-2-cis-6-nonadienal present in Delaware River water was removed by increased levels of chlorine. Initially this was discovered when water treatment plants with higher levels of chlorine residual did not experience taste and odor complaints relating to the compound (Burlingame et al., 1992). A more recent study demonstrated the ability of chlorinous odors to reduce sensory panelists' ability to detect other odors. Panelists presented with samples of 30 ng/l geosmin in the presence of 1 mg/l free chlorine gave an average FPA odor intensity of 0.5. The same panelists gave an identical concentration of geosmin an intensity rating of 4.1 when no chlorine was present (Worley J.L., 2003). This data indicates that chlorinous odors reduce the perception of other odors in drinking water.

In related findings, a study conducted by Oestman *et al.* demonstrated the ability of trained panelists to sense geosmin and MIB when chlorine and chloramines were present using pairwise ranking test and FPA. The study determined that panelists could distinguish between different concentrations of geosmin and MIB when chlorine and chloramine were present at levels representative of those found in the distribution system, but showed that some masking of the musty odor caused by these compounds occurred when disinfectant concentrations were increased (Oestman E., 2004).

While chlorinous odor itself has been demonstrated to interfere with panelists' ability to detect other odor causing compounds in some cases, other research has shown the ability of its oxidizing properties to increase migration of compounds from pipes and plumbing materials via degradation of pipe materials(Heitz et al., 2002). This could potentially increase the concentration or presence of odor causing compounds.

CASE STUDIES

There are several of examples of taste and odor problems generated by the distribution system in the literature. Sources include newly installed pipes, reservoir or tank linings and coatings, as well as the interaction of disinfectant with organic matter within the distribution system. Tromboulian et al. published a review of case studies and information from the National Sanitation Foundation database regarding the leaching of organic compounds from materials found in the distribution system (Tomboulian et al., 2004). The NSF study was conducted using the ANSI/NSF Standard 61 for the testing of new materials to be used in the distribution system. The review provided an extensive list of the compounds which can potentially leach from a spectrum of synthetic plumbing materials, as well as the odor descriptors associated with many of the compounds. The review also references the taste and odor descriptors with those described by the "Drinking Water Taste and Odor Wheel 2000" (Suffet, 2000). The Drinking Water Taste and Odor Wheel is a tool developed to help identify odorants commonly found to cause problems in drinking water. The concept of the wheel has its origins in the beer and wine industry, and includes 8 classes of odors, the four tastes, as well as a mouth/feel, nose/feel category.

Khiari examined four examples of distribution generated taste and odor phenomena in France and Spain by means of FPA and GC-MS(Khiari et al., 1999). All of the problems were originally reported via consumer complaints about the quality of their tap water. In the first case, a newly installed reservoir coating was found to be leaching chloro- and bromophenols, generating a medicinal odor. The second case involved the installation of a new water main with a bituminous coating. Consumers complained of a "paint/putty" odor, which was likely from alkyl benzenes and naphthalenes identified to be leaching into the system from the main. The other two cases involved odors derived from chemical reactions within the distribution system. One involved the chlorination of phenols which had leached from a reservoir coating resulting in a medicinal odor. In the last case, medicinal tastes and odors in tap water were determined to originate from the interaction of NOM with residual disinfectants.

Rigal conducted several more studies related to taste and odor problems in the distribution system in France utilizing GCMS to identify compounds and both Threshold Odor Number (TON) and Threshold Flavor Number (TFN) to record aesthetic data (Rigal and Danjou, 1999). In one study, a fiberglass and polyester resin lining in a recently refurbished water tower caused consumers to complain of a "chemical" taste and odor in their tap water. The odor causing compound was identified as styrene. A second problem originating from a recently refurbished water tower was determined to be caused by leaching of styrene, acetone and isobutylketone from a vinyl-based coating. The presence of these compounds gave an odor of solvent or petroleum to the dairy products which it was being used to produce. A third case study, this time involving a water reservoir lined with a cement containing organic additives, was conducted after consumers complained of a strong "medicinal" smell and taste. After analysis, the off-odor was attributed to the release of the plasticizer triphenylphosphate, which was present in a PVC net and leached due to increased pH from the lime leaching from the cement.

Also reported by Rigal were the results of relining an experimental network of pipes with an epoxy resin system. The system was analyzed after 1 hour, 1 day and 1 week. Results after 1 hour indicated that the presence of the epoxy was detected by odor analysis as having a “glue-bitter almond” odor with a TFN value of 6. Compounds responsible for the odor included benzyl alcohol, ether of butane diol and diaminodiphenylmethane. After 1 week, the TFN value was reduced to 2.5 and the descriptor was given as “bitter.”

The studies reported above detail the ways in which components of the distribution system can contribute compounds to the drinking water distributions system which can negatively impact taste and odor. The studies also illustrate the willingness of consumers to readily notice and report changes to their tap water. This demonstrates both the sensitivity of consumers to aesthetic changes, and their usefulness as sentinels as described by Whelton.

SIGNIFICANCE OF RESEARCH

This research project seeks the better the understanding of the effect of synthetic plumbing materials on drinking water aesthetics. As the popularity of polymer based pipes continues to increase, the need to study the potential for taste and odor problems related to the exposure of these materials to water in the distribution system becomes increasingly important. Past studies have repeatedly shown the ability of synthetic plumbing materials to impart taste and odor in the distribution system under both field and laboratory conditions. In addition to examining synthetic pipes, *in situ* remediation techniques such as epoxy lined copper must also be studied, as issues similar to those involving plastic pipes may arise from their use. Furthermore, little research has been done to study the possible effect of disinfectants on these materials, necessary as the trend to switch from chlorine to chloramines as a means of disinfectant continues in the US.

CHAPTER II

SENSORY ASPECTS OF CHLORINATED AND CHLORAMINATED DRINKING WATER IN CONTACT WITH HDPE AND cPVC PIPE

T. H. Heim and A. M. Dietrich
Civil and Environmental Engineering, Virginia Polytechnic Institute and State
University, 418 Durham Hall, Blacksburg, VA, 24061-0246 USA
(E-mail: *heimt@vt.edu; andread@vt.edu*)

Abstract

Pipes constructed with high density polyethylene (HDPE) or chlorinated polyvinyl chloride (cPVC) are commonly used in drinking water distribution systems and home plumbing. In this comprehensive investigation, the effects on odor, organic chemical release, THM formation and disinfectant consumption in water exposed to HDPE and cPVC pipes were examined, and the results were compared. The study was conducted in accordance with the Utility Quick Test (UQT), a method for utilities to conduct sensory analysis of materials in contact with drinking water. A migration test was performed using water with no disinfectant and levels of chlorine and monochloramines representative of those found in North American distribution systems. Panelists consistently attributed a “waxy/plastic/citrus” odor to the water from the HDPE pipes, while no difference from control was detected in the cPVC samples. The odor intensity generated by the HDPE pipe remained relatively constant for multiple pipe flushes, while the descriptor given for the odor was affected by disinfectant type. Water samples stored in both types of pipe showed a significant increase in the leaching of organic compounds when compared to glass controls, with HDPE causing a significantly greater increase than cPVC. Both pipe materials showed a slight increase in THMs. Water stored in both types of pipe also showed an increase in disinfectant demand relative to the water stored in glass control flasks for both types of pipe. The results demonstrate the impact that synthetic plumbing materials can have on water quality, as well as the significant variations in water quality generated from different materials.

Keywords
cPVC; disinfectant; drinking water; Flavor Profile Analysis; odor; HDPE; utility quick test

INTRODUCTION

Recent decades have seen the advent of synthetic home plumbing materials and a continuing trend of increased use in homes and distribution systems. Plastic pipes currently make up about 54% of the all pipes installed worldwide. Polyvinyl chloride (PVC) makes up 62% of this demand, and polyethylene (PE) in its various forms about 33.5% (Raynaud, 2004). Polymer pipes such as high density polyethylene (HDPE) and chlorinated polyvinyl chloride (cPVC) make durable, cost- effective replacements to traditional materials such as copper. Synthetic pipes are easier for plumbing professionals to work with due to their lighter weight and increased flexibility, and can be less expensive than copper to produce and install. Increased use of synthetic pipes has been further motivated by the problem of pinhole leaks via corrosion of metal pipes which has had a significant economic impact in some parts of the country (Edwards, 2004). Leaching of lead from these pipes into the drinking water supply also constitutes a serious health threat (Edwards, 2004).

While type of plumbing material can affect cost and ease of installation, it can also have a significant impact on drinking water aesthetics and has the ability to generate taste and odor problems. Research has shown a considerable potential for synthetic materials to impact taste and odor via the leaching of volatile organic compounds (VOCs) into water stored in the pipes. (Rigal and Danjou, 1999, Anselme *et al.*, 1985a, Khiari *et al.*, 1999, Tomboulian *et al.*, 2004) As distribution systems are continuously expanded and older metal pipes replaced with synthetic materials, it is critical to consider the effects on taste and odor, and thus consumer perception, that these changes will have (Dietrich, 2006).

Understanding the interaction and effect of the materials from which the distribution system is comprised is inherently important to maintaining a high quality product at the tap, and maintaining high consumer confidence. A 1989 AWWA nationwide study reported 65% of water utilities considered the distribution system responsible for their taste and odor problems (Suffet et al., 1995). These aesthetic issues have great significance to both utilities and the public, as consumer awareness of water quality is heavily influenced by taste and odor perception at the tap (McGuire, 1995, Whelton, 2003). If newly added materials cause water from the distribution system to be unpalatable to the consumer, other benefits of their physical properties may be negated.

While the impact on drinking water aesthetics resulting from exposure to cPVC and HDPE has been investigated, little work has been done to determine the sensory effects of water with disinfectant species and concentrations comparable to those found in the actual distribution system. This knowledge is especially important in light of the widespread effects caused by the switch from chlorine to chloramine in North America and elsewhere that has exacerbated lead release (Edwards and Dudi, 2004).

The United States currently has no standard method to provide an evaluation of aesthetic effects from synthetic plumbing materials such as those that exist in Europe. The NSF 61 Drinking Water System Components - Health Effects standard, from the National Sanitation Foundation, evaluates only for compliance with health requirements. NSF 61 certification means that a material has not been found to leach selected compounds known to cause adverse health effects. The standard establishes the minimum health effects requirements for chemical contaminants and impurities that may be leached into drinking water (ANS/NSFIS, 2000). During the testing protocol, a small diameter pipe is rinsed in cold water followed by a rinse in deionized water, then filled with water containing 2mg/l chlorine. The water in the pipes is then changed ever 24 hours for a period of 14 days, and the water sample produced is analyzed for contaminants according to the EPA Methods for Chemical Analysis of Waster and Wastes (EPA 600/4-79-020). HDPE is tested for VOCs, metals, and phenolics, cPVC is analyzed for VOCs, metals, phenolics, tin, antimony and residual vinyl chloride monomer (RVCM). The NSF standard uses a standard water and does not take into account local water quality. Based on the findings of an international workshop of drinking water experts, as well as the opinions of experts in the field, the Utility Quick Test (UQT) was developed in 2001 to constitute the US equivalent of an organoleptic assessment tool for synthetic plumbing materials under realistic water quality conditions (Schweitzer et al., 2004). This process seeks to generate sensory data which help to understand the leaching of volatile organics from the plumbing materials being tested, and predict the effects such materials might have on the distribution system.

HDPE is light weight, flexible, corrosion resistant, and capable of handling the temperatures and pressures found in home plumbing applications. It is synthesized via the polymerization of ethylene into long carbon backbone polyethylene molecules with no side groups, resulting in its high density (Peacock, 2001). HDPE pipe has been used in potable water applications since the 1960's, and has been gaining approval and growth in municipalities ever since. Its use is approved under AWWA C901 and NSF 61 standards (PPI, 2006).

The ability of VOCs to leach directly from polyethylene pipe materials and cause odors in drinking water has been demonstrated repeatedly. Organoleptic changes to water quality have been caused by defective polyethylene pipe, via both the leaching of the polymer additives and oxidation of the surface of the pipe during extrusion (Anselme et al., 1985a). The main compounds identified included antioxidants (4-methyl-2,6-di-t-butylphenol, alkyl thiophene), several aldehydes and plasticizers (phthalates and tributyl phosphate). The burnt plastic odor was found to be due to butylated hydroxy toluene. Studies done by the French Centre de Recherche et de Controlle des Eaux showed insufficiently controlled extrusion conditions can result in the formation of oxidation products such as aldehdyes, ketones or quinones which can convey burned-oil or sweet flavor to drinking water (Rigal, 1992).

Further studies have confirmed the ability of VOCs to leach from pipes and pipe linings, and effect taste and odor (Skjevrak *et al.*, 2003, Marchesan and Morran, 2004), and a number of the odor causing compounds have been specifically identified (Villberg *et al.*, 1997, Brocca *et al.*, 2002, Skjevrak *et al.*, 2003).

PVC is produced by combining chlorine and ethylene to form ethylene dichloride, which is then converted into the monomer vinyl chloride, the basic building block of polyvinyl chloride. Chlorinated polyvinyl chloride (cPVC) is PVC that has been chlorinated via a free radical reaction with chlorine. This reaction is initiated by application of thermal or UV energy. Chlorine gas is decomposed into free radical chlorine which is then reacted with PVC, replacing a portion of the hydrogen in the PVC with chlorine. The chlorine content may vary from the base PVC 56.7% to as high as 74%, but typically falls with in the range of 63% to 69%. cPVC possesses the same chemical resistance of PVC, but offers superior performance to PVC in applications where higher heat resistance is required. Common additives to cPVC include stabilizers, impact modifiers, pigments and lubricants. cPVC is commonly available in home supply stores and is installed whenever conveyance of hot water is required. PVC has not been known to cause significant odor during migration tests (Skjevrak et al., 2003). Migration of chlorinated organics and organotin compounds has been reported however (Sadiki *et al.*, 1996, Sadiki and Williams, 1999, Mallevialle and Suffet, 1987).

The intent of this research was to comprehensively evaluate changes in sensory and chemical water quality when cPVC and HDPE pipe were contacted with drinking water containing representative levels of chlorine and monochloramines. Specific objectives of this research were to determine if the polymers contributed odor to the water and to examine the effects of HDPE and cPVC on TOC, THMs, and disinfectant residual.

MATERIALS AND METHODS

Plumbing Materials

cPVC and HDPE pipe with internal diameters of ¾ inches were acquired from local building supply companies. The HDPE pipe was manufactured by Aquajet Inc. and the cPVC pipe by Nibco Inc. Both materials were certified according to National Sanitation Foundation (NSF-61) standards, based on health effects, for use in hot/cold potable water systems and suitable for use in home plumbing systems in the United States.

Utility Quick Test

To conduct the Utility Quick Test, 7 foot lengths of cPVC and HDPE pipe were flushed using distilled water for 1 hour, filled with water containing 50mg/L free chlorine for 3 hours for disinfection, and flushed again with distilled water to eliminate any chlorine residual. "Reference" water was then prepared to simulate tap water typically found in the Eastern US. The reference water was synthesized using Nanopure (Barnstead® Nanopure Filter) water combined with salts equaling 8 mg/L Mg^{2+}, 46 mg/L SO_4^{2-}, 20 mg/L Na^+, 0.05 mg/L Al^{3+}, 11 mg/L Ca^{2+}, 2.6 mg/L SiO_3^{2-}, 4 mg/L K^+, 1.4 mg/L NO_3^- as N, 0.002 mg/L PO_4^- as P. Three separate batches of the water were then prepared, one containing 2 mg/L free chlorine, one containing 4 mg/l monochloramine, and one containing no disinfectant. pH in the waters was adjusted to between 7.7-7.9 and the pipe lengths were filled to their entire volume to eliminate headspace and capped with Teflon lined VOA vial caps and sealed with Parafilm®. No additional natural organic matter was added to the water. The pipes were stored undisturbed at room temperature and pressure for 72 hours (3 days), after which the leachate water was removed for analysis. The fill and drain process was repeated 2 additional times for each UQT. Each UQT was subsequently repeated to ensure accuracy of results. Controls were prepared with the 3 types of disinfection content as the pipes samples, and stored separately in 500 ml glass Erlenmeyer flasks with stoppers, and stored in the dark covered in aluminum foil for identical time periods as the pipes (72 hours). Controls were conducted for each experimental condition investigated.

Flavor Profile Analysis

FPA was conducted in accordance with the procedures found in Standard Methods 2170. Odor free water was obtained from a Barnstead® Nanopure filter. All samples were prepared in 500 mL Erlenmeyer flasks with ground-glass stoppers and heated to 45° C in a water bath for 15 minutes prior to testing. Five to seven panelists from a trained group of ten were presented with the flasks in random order at two minute intervals. Prior to sampling, and between each subsequent sample, panelists sniffed flasks filled with odor free water to calibrate themselves and clear their noses. Panelists were asked to give a descriptor and intensity rating (0-12) of the odor of the water in the flasks in accordance with their FPA training. Training and research was approved according to the standards of the Virginia Tech Institutional Review Board (IRB) for human subjects.

Water Quality Analysis

TOC Analysis. Analysis of total organic carbon (TOC) concentration content of water samples from the UQT was performed using a Sievers® 800 Portable TOC analyzer, and the parameters described in Standard Methods 5310C.

Disinfectant Residual. Residual for free chlorine, total chlorine and monochloramine was determined by measuring the concentration of these species before and after they were stored in the pipes and control flasks. Concentrations of the disinfectant species were determined using appropriate powder pillows and a HACH® Pocket Colorimeter II and HACH® DR/2400 Portable Spectrophotometer.

Trihalomethane Analysis. Trihalomethane (THM) content of water samples used in FPA was performed according to USEPA Method 502.2 (USEPA 1995). The instrument was a Tremetrics 9001 gas chromatograph with a 1000 Hall detector, Tekmar 3000 purge trap and concentrator and Tekmar 2016 Purge Trap autosampler.

Formation and Sorption of Trihalomethanes. The fate of THM's in water exposed to HDPE pipe was investigated by examining whether or not THMs could form from leached TOC and chlorine during the UQT and then sorbed into the polymer pipe. To investigate THM formation from leached TOC, reference water with no disinfectant was used to fill sections of HDPE pipe as well as glass control flasks and allowed to remain under static conditions for 72-96 hours. The water was then drained from the pipes and controls into 40 ml amber vials with Teflon lined caps. Hypochlorous acid was added at 2 mg/l as Cl_2. Sodium thiosulfate was subsequently added to quench the THM formation reaction at 0, 24 and 72 hours. The samples were then analyzed for concentration of THMs and TOCs.

An investigation into the sorption of THMs into the HDPE pipe wall itself was conducted by filling one foot lengths of HDPE pipe and amber glass controls with synthetic water representative of tap water as described previously containing 60 µg/L trichloromethane diluted from a stock solution. The vials and pipes were filled to eliminate headspace and sealed with PTFE caps and Parafilm® and allowed to rest horizontally for 72 hours. Following the contact period, pipes and vials were sampled through the PTFE caps using 5ml glass single-use hypodermic needles to prevent exposure to air. Following needle extraction, samples were injected into purge trap samples ports for analysis conducted by correlation with a five point standard curve.

pH Analysis. pH was determined using the Accumet® (cat# 13-620-287) electrode and the Accumet® pH Meter 910 purchased from Fisher Scientific. pH values were measured and recorded prior to exposure to pipe samples and after each subsequent flush period.

SPME/GC-MS Analysis. Solid phase microextraction holder and 75 μm Carboxen^{TM}-PDMS coating fibers were purchased from Supelco (Bellfonte, PA, USA) for analysis of VOCs. The SPME conditions were optimized by the addition of 2 g of NaCl to 20 mL of sample water placed in a 40 mL VOA vial. The sample was stirred using Teflon coated magnetic stir bars at 45 °C for 20 minutes during which time the fiber was injected into the 10 mL sample headspace for sorption. Samples were allowed to desorb for 3 mins. An Agilent 6890 Series GC system connected to Agilent 5973 network mass selective detector was operated in splitless mode with a 0.75 mm i.d. injection sleeve (Supelco), total helium flow of 24 mL/min, inlet temperature of 220 °C, and 80 kPa pressure. J&W DB-5 capillary column (30 m x 250 µm, 30 µm thickness) was used for all analysis. The temperature program was: 60 °C hold for 7mins then increased from 60 °C to 120 °C at a rate of 10 °C/min and finally from 120 °C to 260 °C at a rate of 20 °C/min. All samples were analyzed within 2 days of collection.

Statistics. Statistical analysis was performed using SAS statistical software. A type I error ( ) of 0.05 was utilized for all tests. The unequal variance t-test was used if the data were found to be normally distributed but the variances were found to be not equal.

RESULTS AND DISCUSSION

Odor Assessment by trained panelists

Panelists assessed the water for odors using standard FPA techniques, giving odor descriptors and intensity ratings. Each UQT consisted of three flushes and the UQT was replicated for each type of pipe material. The cPVC pipes did not contribute significant odor different from the glass controls. Panelists detected only a weak background odor of FPA intensity 0-2 that was described as “sweet” or “musty.” When a “chlorinous” odor was detected in both controls and cPVC samples, it coincided with the presence of disinfectant in the UQT water, with more intense odors attributed to the presence of chlorine than chloramine (FPA ≤ 2).

In contrast, HDPE pipe was found to contribute substantial odor. The data indicate a strong correlation between water stored in the HDPE pipes and a “waxy/plastic/citrus” odor, as described by panelists (Figure II-1). This odor is comparable with the “plastic/sweet/glue/solvent” odor detected from HDPE (Villberg et al., 1998) which was attributed to one more of the alkylphenols, esters, aldehydes and ketones found in other studies (Brocca *et al.*, 2002, Skjevrak *et al.*, 2003). The water samples from the HDPE pipe also demonstrated higher reduction in disinfectant levels than did those from cPVC. The increased disinfectant demand in the water stored in the HDPE pipes is evidenced by reduced value of chlorinous odor descriptors in the pipe water when compared to the water stored in the cPVC pipe and the controls.

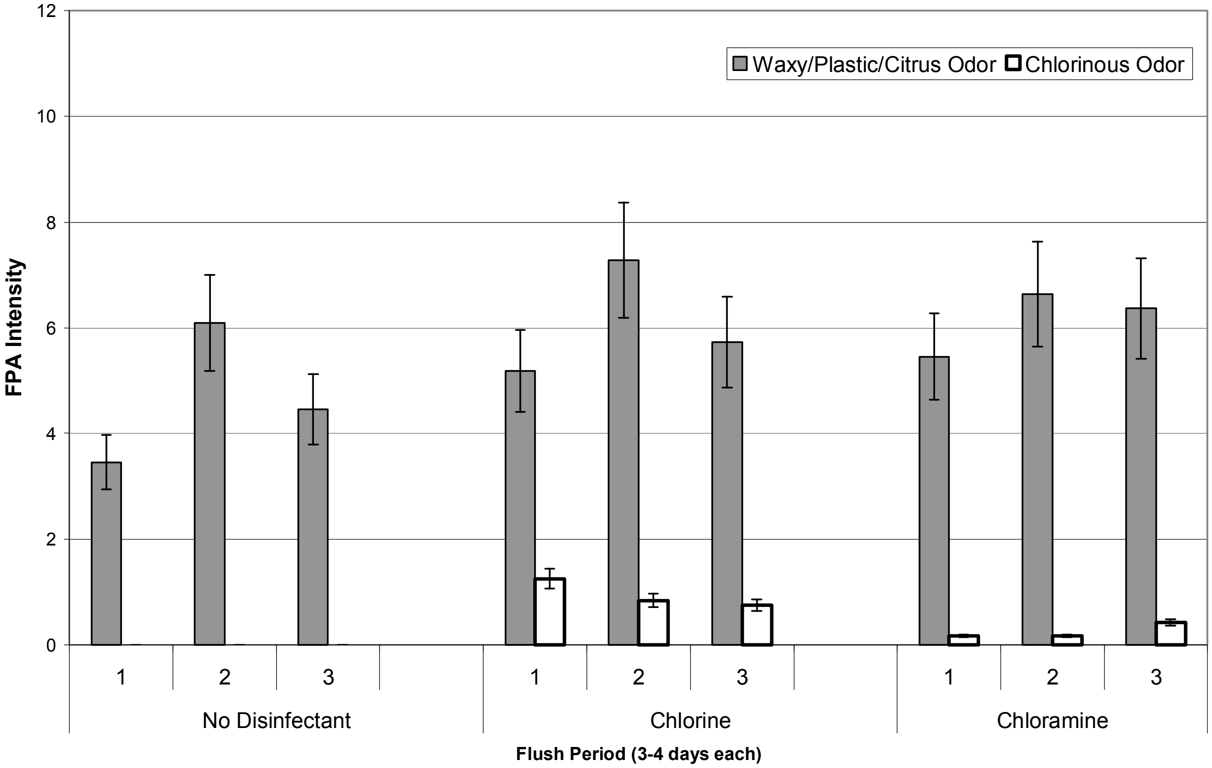


Figure II-1 Average FPA intensity for two replicate UQT experiments utilizing HDPE in the absence of disinfectant and the presence of 2 mg/L free Cl_2 and 4 mg/L chloramines as Cl_2. The standard error of FPA intensity between replicates is shown.

When the UQT was replicated, odor intensity remained relatively constant for each flush and the three types of water tested for the HDPE pipe. (Figure II-1) The descriptors given by the panelists varied slightly with disinfectant type, with “chemical/plastic” given as the descriptor for water with chlorine and “waxy-crayon/plastic” given as the descriptor for water with chloramines. The presence of disinfectant did not appear to affect the intensity of the odor.

Total Organic Carbon

Leaching of organic compounds reported as TOC occurred in the water exposed to both types of pipe. TOC detected in the samples exposed to cPVC pipe was significantly higher than in water exposed to glass controls (Figure II-2), indicated by a Wilcoxon non-parametric t-test performed on the data which generated a p-value of < 0.001. An even greater degree of leaching as evidenced by TOC concentration occurred from the HDPE pipe (Figure II-3). A T-test performed on the data assuming equal variances obtained a p-value of <0.001, showing that the increase in TOC when compared to the control was statistically significant.

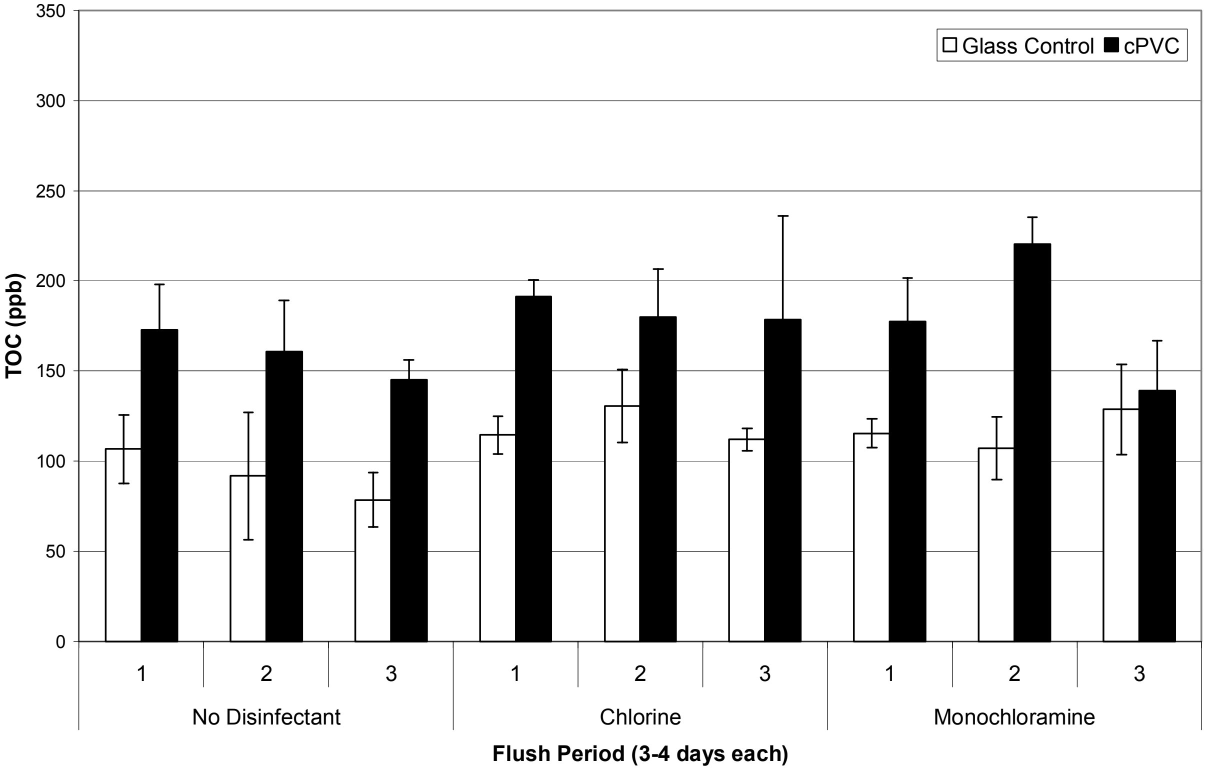


Figure II-2 Average TOC concentrations for two replicate UQT experiments utilizing cPVC in the absence of disinfectant and the presence of 2 mg/L free Cl_2 and 4 mg/L chloramines as Cl_2. The standard deviation of TOC concentrations between replicates is shown.

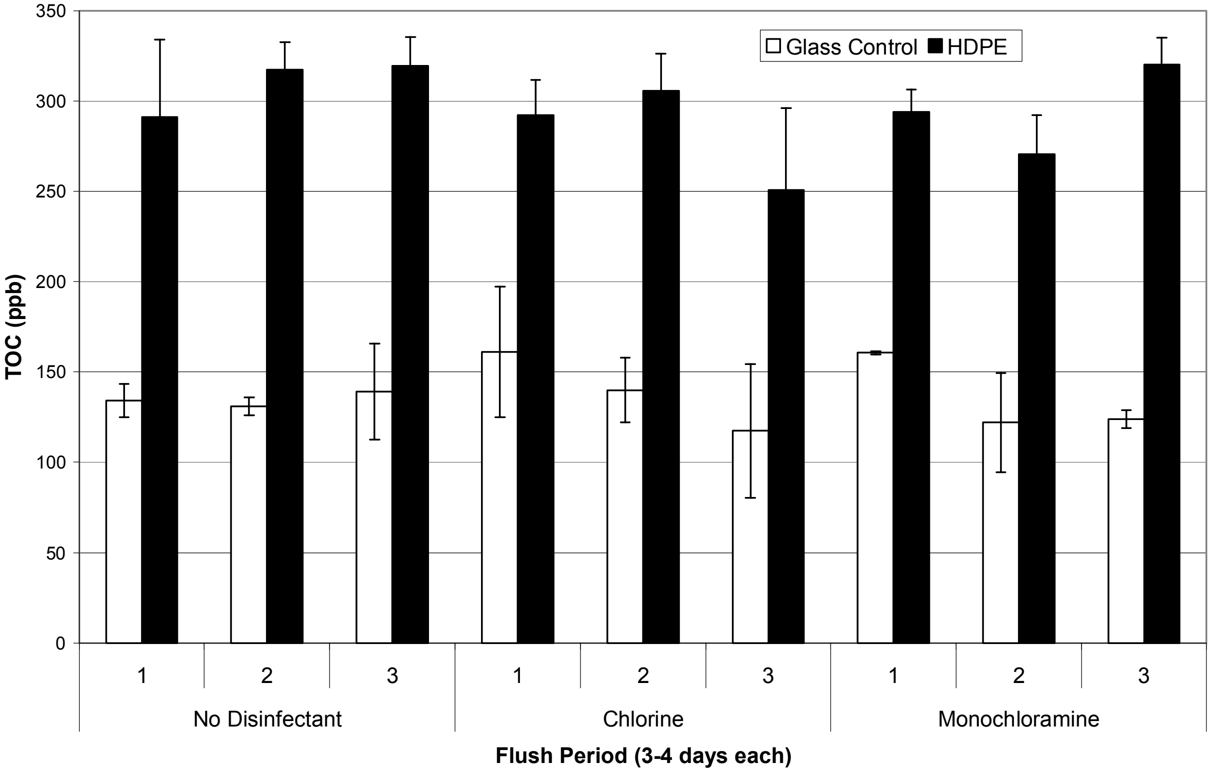


Figure II-3 Average TOC concentrations for two replicate UQT experiments utilizing HDPE in the absence of disinfectant and the presence of 2 mg/L free Cl_2 and 4 mg/L chloramines as Cl_2. The standard deviation of TOC concentrations between replicates is shown.

Organic compounds measured as TOC leached from both the HDPE and cPVC pipes and the concentration of material leached did not change with subsequent flushes (Figure II-2, Figure II-3). As odors were detected in the water exposed to the HDPE pipe, but not the cPVC pipe, the compounds leaching from the cPVC did not cause detectable odor.

Disinfectant Residual

Water exposed to both HDPE and cPVC pipes demonstrated a significantly lower disinfectant residual than did the controls. Lower residual existed for both the water containing chlorine disinfectant (initially present at 2 mg/L), and chloramine disinfectant (initially present at 4 mg/L).

Statistical analysis for chlorine residual (Figure II-4, II-5) was performed using a paired t-test generated p-values of < .05 for both HDPE and. Both HDPE and cPVC differed significantly from control. The graphs represent average demand for both UQT replicates.

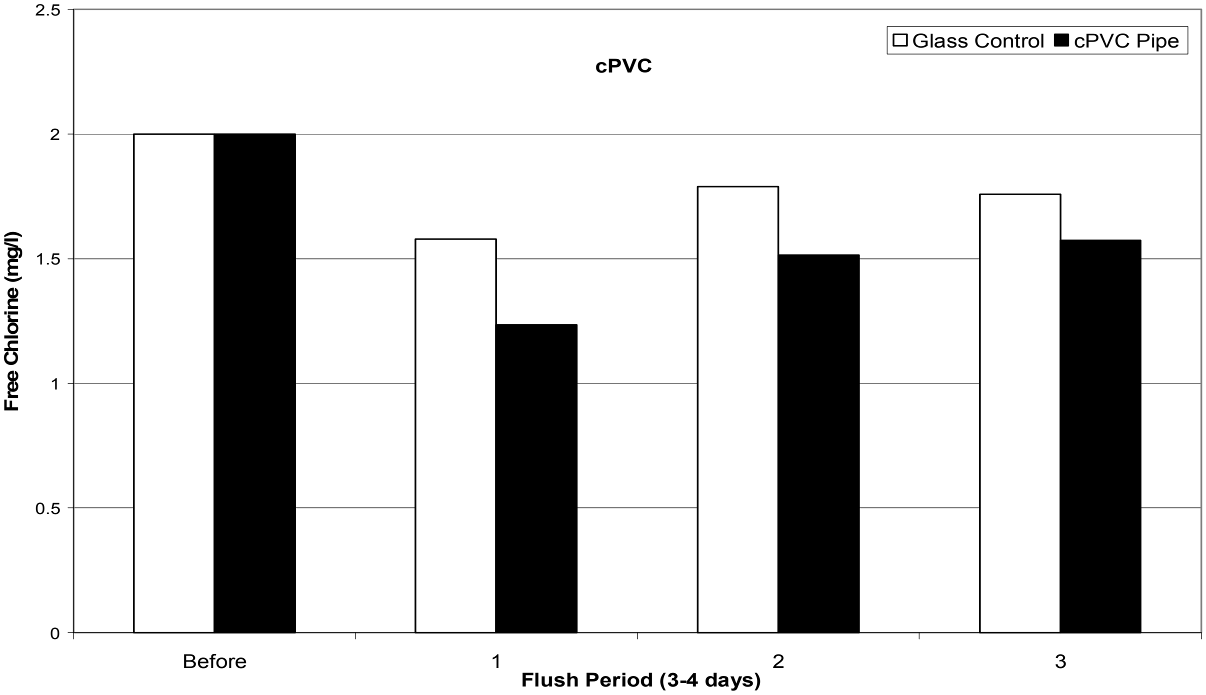


Figure II-4 Average disinfectant residual (as free chlorine) remaining at the end of the 72 hour contact time for two UQT replicates. Chlorine at 2 mg/l as disinfectant shown for sample and control. "Before" represents the water before it was used to fill the controls and pipes.

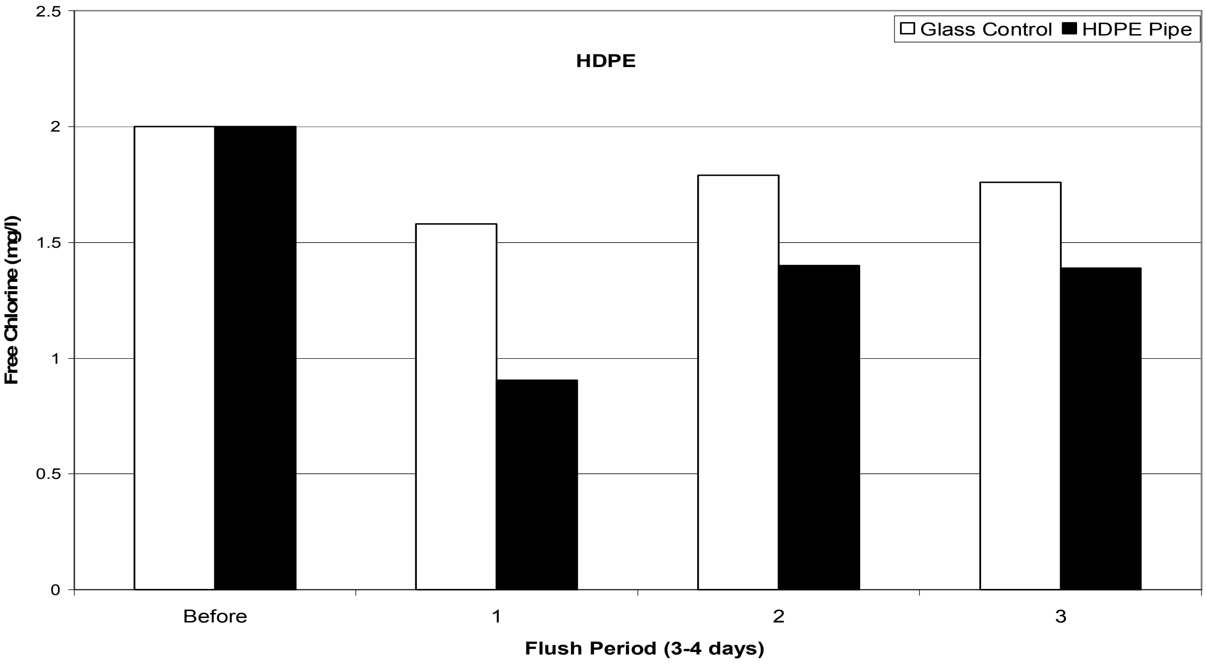


Figure II-5 Average disinfectant residual (as free chlorine) remaining at the end of the 72 hour contact time for two UQT replicates. Chlorine at 2 mg/l as disinfectant shown for sample and control. "Before" represents the water before it was used to fill the controls and pipes.

Statistical analysis for chloramine residual (Figure II-6, II-7) was performed using a paired t-test and generated p-values of < 0.05 for both HDPE and cPVC. Both HDPE and cPVC differed significantly from control.

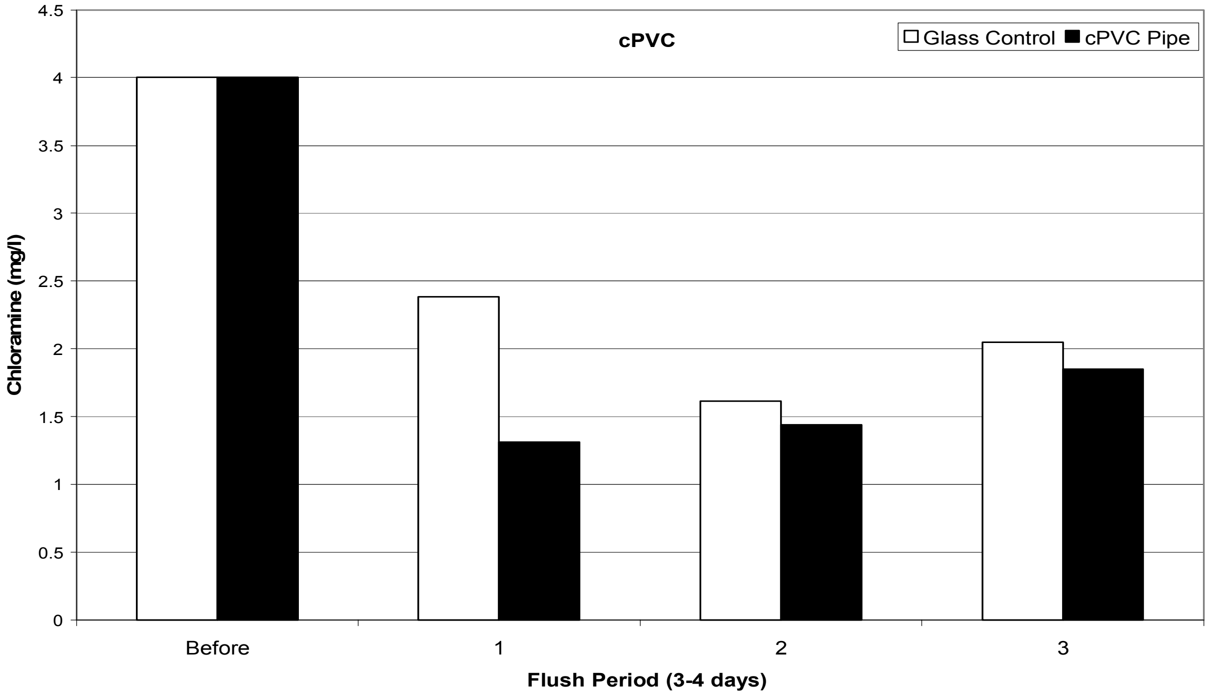


Figure II-6 Average disinfectant residual (as chloramine) remaining at the end of the 72 hour contact time for two UQT replicates. Chloramine at 4mg/l as disinfectant shown for sample and control. "Before" represents the water before it was used to fill the controls and pipes.

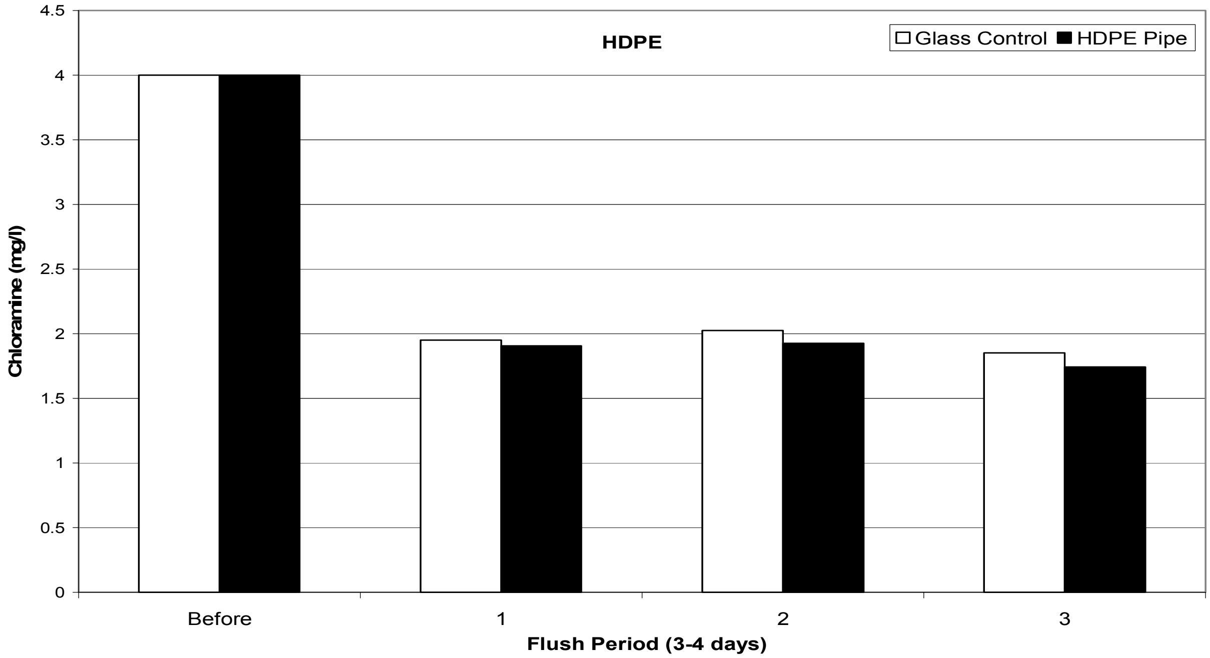


Figure II-7 Average disinfectant residual (as chloramine) remaining at the end of the 72 hour contact time for two UQT replicates. Chloramine at 4mg/l as disinfectant shown for sample and control. "Before" represents the water before it was used to fill the controls and pipes.

Sorption and Formation of Trihalomethanes

Following the UQT, THM values in water exposed to HDPE pipe had a mean value of 0.71 ppb (n = 18), compared to a mean control value of 0.92 ppb (n = 18). There was no significant difference between THM concentrations in the HDPE and control, ($p > 0.71$). Values in water exposed to cPVC pipe had a mean value of 0.48 ppb (n = 18), compared to a mean control value of 0.23 ppb (n = 18), values were not statistically different ($p > 0.47$). The leached organic compounds from either pipe material failed to form THMs.

To determine if the TOC from the HDPE was capable of forming THMS, and the THMs were capable of sorbing back into the HDPE, another series of experiments performed. Reference water with no disinfectant was exposed to the HDPE pipe for 72 hours, drained, chlorinated and then analyzed at varying times for TOC and THM formation. Results showed the leached organic matter did not form THMs. THM concentrations for all controls and HDPE samples were less than 1 ppb. TOC analysis (Figure II-8) showed increased levels of TOC emanating from the pipes which tended to decrease with time. THM analysis failed to show a significant difference between pipe and glass control samples in THM concentration over time after the chlorine was added. Although trihalomethanes did not form from the leached TOC, other disinfection by-products are possible but were not measured.

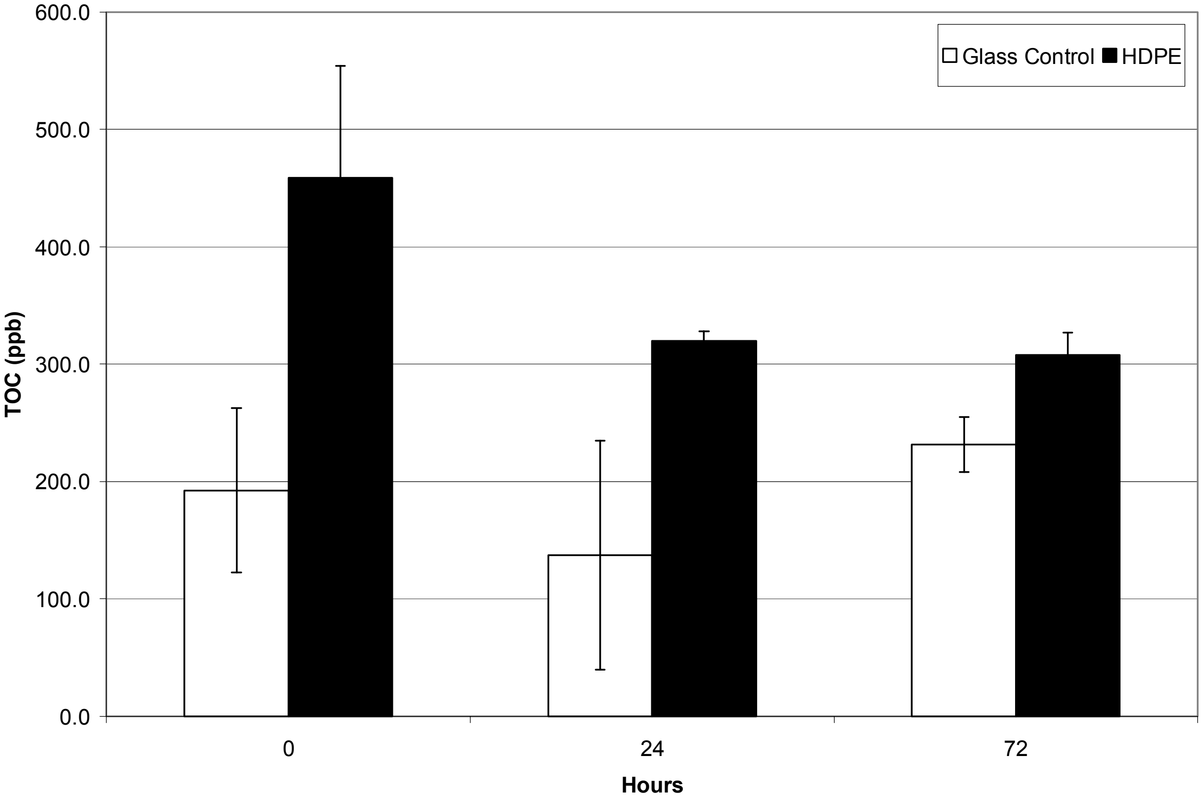


Figure II-8 Average TOC concentrations in water drained from pipes and controls after 0, 24 and 72 hours. Error bars represent standard deviation of sample replicates.

Although THMs were not detected in the UQT flushes, or from reaction of the leached TOC, the potential of trichloromethane to sorb to the pipes was investigated. To test this, sorption of trichloromethane was specifically evaluated. The trichloromethane concentration in the water exposed to the HDPE for 72 hours had a concentration of 33.5 ppb, compared to a concentration of 49 ppb for the control. The data were subjected to a t-test (assuming equal variances), which generated a p-value of less than 0.01. This suggests that HDPE polymer had the ability to sorb trichloromethane.

Volatile Organic Compounds (VOCs) detected by SPME/GC-MS analysis

SPME followed by GC-MS analysis detected several organic compounds with the potential to cause odor. Some of the compounds were identified in previous studies of synthetic plumbing materials and their interaction with drinking water, including alkanes (Villberg et al., 1998), ketones(Skjevrak *et al.*, 2003, Villberg *et al.*, 1998), and phenolic compounds (Brocca *et al.*, 2002, Skjevrak *et al.*, 2003). These compounds are listed below. Likely candidates for the “waxy/plastic/citrus” attributed by panelists to HDPE include some combination of higher weight alkanes (related to paraffin), phenolic compounds and ketones.

Table II-1. Compounds and their associated odors detected by SPME-GC/MS analysis in water in contact with cPVC or HDPE but not detected in controls with odor descriptors (Merck, 2001).

cPVC			**HDPE**	
Compound	**Odor Descriptor**		**Compound**	**Odor Descriptor**
1-3 butadiene	"gasoline like"		benzene	"pleasant-sweet"
titanium dioxide	none		phenol	"sweet-tarry"
			bisphenol	"phenol-like"
			cyclotetradecane	"hydorcarbon"
			tetradecane	"hydrocarbon"
			cyclohexadiene	"gasoline/terpentine"
			cyclohexanone	"solvent-acetone"
			cyclopentanone	"solvent-acetone"

Table II-1 lists compounds detected in the water exposed to pipe material and not in the water exposed to glass controls along with corresponding odor descriptors. The results show a higher number of organic compounds leached from the HDPE pipes when compared to the cPVC pipes. This correlates to the increased odor detected from HDPE by FPA panelists who analyzed the water, and demonstrates a link between increased leaching of VOCs and potential odor problems. The titanium dioxide detected in the cPVC is likely added to give the pipe its bright white color.

CONCLUSIONS

Sensory data indicated that the HDPE pipe leached compounds that contributed a “waxy/plastic/citrus” odor to drinking water. The odor was present in water exposed to the pipe material, and its intensity did not diminish during subsequent flushing and stagnation periods within the approximately 10 day timeframe of the utility quick test. Panelists tended to describe the odor as “chemical/plastic” in the presence of chlorine, and “waxy-crayon/plastic” in water with chloramines. The presence of disinfectants did not alter the intensity of the odors, which is unlike previous studies where these disinfectants masked odors (Worley *et al.*, 2003, Durand and Dietrich, 2005b). Several odorous ketones, alkanes and phenols were detected in headspace and likely contributed to the perceived odor. In contrast, cPVC pipe did not leach compounds and did not cause a detectable odor to be present. This demonstrates the impact that different types of plumbing materials can have on water quality aesthetics. This is important knowledge for utilities and consumers as associating the presence and intensity of the odor and linking it with a specific plumbing material can help identify problems and suggest solutions.

Water exposed to the both the HDPE and cPVC pipe for 72-96 hour stagnation times also showed increases in TOC of 0.1 to 0.2 mg/L, and a marked decrease in disinfectant residual. These conditions could promote biofilm growth. The chemical structure of the leached TOC included specific ketones, phenols and hydrocarbons detectable by solid phase micro extraction. The disinfectant consumption can likely be attributed to the interaction of oxidizing disinfectant species with either antioxidants from the manufacturing process or the polymer itself. More research is needed to further determine the nature of the leached TOC and understand the decay of chlorine and chloramines when in contact with the polymer pipe material. Additionally, the role of disinfectant consumption and TOC release are of concern for the formation of biofilms and colonization of the pipe surfaces by microbes. This research confirms the ability of synthetic plumbing materials to affect water quality and reinforces the value of sensory testing to determine the effects of new materials on consumer perception of water quality.

ACKNOWLEDGMENTS:

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CHAPTER III

SENSORY ASPECTS OF DRINKING WATER IN CONTACT WITH EPOXY-LINED COPPER PIPE

T. H. Heim and A. M. Dietrich
Civil and Environmental Engineering, Virginia Polytechnic Institute and State University,
418 Durham Hall, Blacksburg, VA, 24061-0246 USA
(E-mail: *heimt@vt.edu; andread@vt.edu*)

Abstract

Pipe relining via *in situ* epoxy lining is a solution to remediating corroded copper, lead and iron pipes in distribution systems. In this investigation, the effects on odor, TOC, and disinfectant demand in water exposed to epoxy lined copper pipes were examined. The study was conducted in accordance with the Utility Quick Test (UQT), a method for utilities to conduct sensory analysis of materials in contact with drinking water. Repairing corroded pipes with epoxy's leak sealing ability may have the undesirable consequence of impacting drinking water aesthetics.

A migration test was performed using water with no disinfectant and levels of chlorine and monochloramines representative of those found in the distribution system. Panelists repeatedly and consistently described a "plastic/adhesive/putty" odor in the water from the pipes. The odor intensity remained relatively constant for each of two subsequent pipe flushes. Water samples stored in the pipes showed a significant increase in the leaching of organic compounds (as TOC). Water stored in the pipes also showed a marked increase in disinfectant demand relative to the water stored in glass control flasks. A study conducted at a full scale installation at an apartment demonstrated that after installation and flushing, the epoxy lining did not yield detectable differences in water quality under field conditions.

Keywords
Chlorine; chloramine; drinking water; epoxy; Flavor Profile Analysis; leaching; odor;

INTRODUCTION

Distribution system corrosion is a serious problem in drinking water systems. Repair costs related to corrosion for public utilities in the United States are estimated at 22 billion US dollars per year (Brongers, 2002). Estimates for private infrastructure are even higher; with the potential cost of 1 Trillion US dollars to replumb every household in the US (Edwards, 2004). One solution to the corrosion problem is to repair leaking pipes by means of *in situ* remediation. This generally involves scouring the pipes via grit blasting, followed by the application of epoxy paint liners injected at high pressure to coat and seal pipe surfaces from further corrosion (Engineers, 2001). One of the most popular and effective of such liners is epoxy based coatings, which have become a popular solution to residential copper pinhole leak problems.

Epoxy was first used as a lining material over 40 years ago to prevent corrosion in Japanese industrial processes, and spread quickly to other applications. Epoxy is essentially a combination of two compounds. The first is a low-molecular-weight polymer with *epoxy* groups at each end, the second is diamine (Dekker, 1988). The two groups of molecules combine to form a cross-linked network which is extremely strong and durable (Center, 2002). Epoxy lining is now used in a variety of applications. These include water main and reservoir linings, and *in situ* remediation of home plumbing systems with pinhole leaks. It has also been used extensively by the navy for shipboard pipe remediation (Brady and Adkins, 1994, Engineers, 2001). The liner used for these applications is certified by the National Sanitation Foundation under protocol NSF-61 for use as a plumbing material, and is capable of carrying hot and cold water.

As corrosion problems continue to increase, so does the use of relining techniques such as epoxy liner. The introduction of a new synthetic material to a distribution system can have immediate ramifications on water quality, as evidenced by an increase in consumer complaints. Leaching of organic compounds has repeatedly been determined to be a cause of many of these complaints (Dietrich *et al.*, 2004, Tomboulian *et al.*, 2004, Hem and Skjevrak, 2002). Aesthetic problems reported by households generally occur immediately following installation and trail off with time and subsequent continued flushing of the pipes. Polymer based liners have been found to be the cause of these complaints in several instances (Rigal, 1992, Tomboulian *et al.*, 2004).

Consumer awareness of water quality is heavily influenced by taste and odor perception at the tap (McGuire, 1995, Whelton, 2003). Aging water distribution systems are continuously updated with new materials and treatment techniques, usually with the goal of reducing corrosion. It is critical to consider the effects on taste and odor, and thus consumer perception, that these changes will have (Dietrich, 2006). The effects of materials present in the distribution system cannot be understated. In a survey of water utilities, 65% pointed to the distribution system as the source of their taste and odor problems (Suffet et al., 1995). If materials added to the distribution system cause water to be unpalatable to the consumer, their effectiveness as corrosion reducers is of little use.

To date, no study has been done to determine the aesthetic effects of water exposed to epoxy-lined pipes via sensory analysis. The intent of this research was to use the Utility Quick Test (UQT) in conjunction with Flavor Profile Analysis (FPA) to examine the effects on water quality imparted by exposure to epoxy-lined copper pipe and representative levels of chlorine and monochloramines. The UQT provides a protocol for water utility personnel to determine how the properties of the water in their utility will affect a specific plumbing material (Schweitzer *et al*., 2004). Specific objectives were to determine if epoxy lining imparted odor to the water and to examine the effects of epoxy liner on TOC, THMs, free copper and disinfectant residual.

MATERIALS AND METHODS

Epoxy Lined Copper Pipe

7 foot (2.1m) lengths of ¾ inch (19.05mm) epoxy lined copper pipe were acquired from ACE Duraflow®, and shipped in wooded packaging secured with nails to assure no cross contamination of volatile organics (i.e. from adhesives, plastics) would occur.

Utility Quick Test

2.1m lengths of epoxy-lined copper pipe were flushed using distilled water for 1 hour, filled with water containing 50mg/L free chlorine for 3 hours, and flushed again with distilled water to eliminate any chlorine residual. “Reference” water was then prepared to simulate tap water typically found in the Eastern US. The reference water was synthesized using Nanopure water 125combined with salts equaling 8 mg/L Mg^{2+}, 46 mg/L SO_4^{2-}, 20 mg/L Na^+, 0.05 mg/L Al^{3+}, 11 mg/L Ca^{2+}, 2.6 mg/L SiO_3^{2-}, 4 mg/L K^+, 1.4 mg/L NO_3^- as N, 0.002 mg/L PO_4^- as P. Three separate batches of the water were then prepared, one containing 2 mg/L free chlorine, one containing 4 mg/l as monochloramine, and one containing no disinfectant. pH in the waters was adjusted to between 7.7-7.9 and the pipe lengths were filled to their entire volume to eliminate headspace and capped with Teflon lined VOA vile caps. The pipes were stored undisturbed at room temperature for 72-96 hours (3-4 days), after which the leachate water was removed for analysis. The fill and drain process was repeated 2 additional times for each UQT. Controls were prepared with the 3 types of water being stored separately in 500 ml glass Erlenmeyer flasks with ground glass stoppers and stored in the dark covered in aluminum foil for identical time periods as the pipes (72-96 hours).

Flavor Profile Analysis

FPA was conducted in accordance with the procedures found in Standard Methods 2170. Odor free water was obtained from a Barnstead® Nanopure filter. All samples were prepared in 500mL Erlenmeyer flasks with ground-glass stoppers and heated to 45° C in a water bath for 15 minutes prior to testing. Five to seven panelists from a trained group of ten were presented with the flasks in random order at two minute intervals. Prior to sampling, and between each subsequent sample, panelists sniffed flasks filled with odor free water to calibrate themselves and clear their noses. Panelists were asked to give a descriptor and intensity rating (0-12) of the odor of the water in the flasks in accordance with their FPA training. Training and research was approved according to the standards of the Virginia Tech Institutional Review Board for human subjects.

TOC Analysis

Analysis of total organic carbon (TOC) concentration content of water samples from the UQT was performed using a Sievers® 800 Portable TOC analyzer, and the parameters described in Standard Methods 5310C.

Disinfectant Residual

Residual for free chlorine, total chlorine and monochloramine was determined by measuring the concentration of these species before and after they were stored in the pipes and control flasks. Concentrations of the disinfectant species were determined using appropriate powder pillows and a HACH® Pocket Colorimeter II and HACH® DR/2400 Portable Spectrophotometer.

Trihalomethane Analysis

Trihalomethane (THM) content of water samples used in FPA was performed according to USEPA Method 502.2 (USEPA 1995). The instrument was a Tremetrics 9001 gas chromatograph with a 1000 Hall detector, Tekmar 3000 purge trap and concentrator and Tekmar 2016 Purge Trap autosampler.

Formation and Sorption of Trihalomethanes

The fate of THM's in water exposed to epoxy-copper pipe was investigated by examining whether or not THMs were formed from leached TOC and chlorine during the UQT and then sorbed into the polymer before analysis had taken place. To investigate THM formation from leached TOC, reference water with no disinfectant was used to fill sections of pipe as well as glass control flasks and allowed to remain under static conditions for 72-96 hours. The water was then drained from the pipes and controls into 40ml amber vials with Teflon lined caps. Chlorine was added at 2 mg/l as HOCl. Sodium thiosulfate was subsequently added to quench the THM formation reaction at 0, 24 and 72 hours. The samples were then analyzed for concentration of THMs and TOCs.

An investigation into the sorption of THMs into the epoxy polymer itself was conducted by filling one foot lengths of epoxy lined copper pipe and amber glass vials with "reference" water containing 60 μg/L or 19 μg/L trichloromethane diluted from a stock solution. The vials and pipes were filled to eliminate headspace and sealed with PTFE caps and Parafilm® and allowed to rest horizontally for 72 hours. Following the contact period, pipes and vials were sampled through the PTFE caps using 5ml glass single-use hypodermic needles to prevent exposure to air. Following needle extraction, samples were injected into purge trap samples ports for analysis conducted by correlation with a five point standard curve.

pH Analysis

pH was determined using the Accumet® (cat# 13-620-287) electrode and the Accumet® pH Meter 910 purchased from Fisher Scientific. pH values were measured and recorded prior to exposure to pipe samples and after each subsequent flush period.

SPME/GC-MS Analysis

Solid phase microextraction holder and 75 μm Carboxen^{TM}-PDMS coating fibers were purchased from Supelco (Bellfonte, PA, USA) for analysis of VOCs. The SPME conditions were optimized by the addition of 2 g of NaCl to 20 mL of sample water placed in a 40 mL VOA vial. The sample was stirred using Teflon coated magnetic stir bars at 45 ^{o}C for 20 minutes during which time the fiber was injected into the 10 mL sample headspace for sorption. Samples were allowed to desorb for 3 mins. An Agilent 6890 Series GC system connected to Agilent 5973 network mass selective detector was operated in splitless mode with a 0.75 mm i.d. injection sleeve (Supelco), total helium flow of 24 mL/min, inlet temperature of 220 °C, and 80 kPa pressure. J&W DB-5 capillary column (30 m x 250 µm, 30 µm thickness) was used for all analysis. The temperature program was: 60 ^{o}C hold for 7mins then increased from 60 ^{o}C to 120 ^{o}C at a rate of 10 ^{o}C/min and finally from 120 ^{o}C to 260 ^{o}C at a rate of 20 ^{o}C/min. All samples were analyzed within 2 days of collection.

Field Application

A field study was undertaken in order to record data associated with epoxy liner in copper pipes at a full scale installation. The site was a small apartment complex in Maryland which suffered from extensive pinhole leaks in its copper plumbing. Water samples were taken prior to epoxy installation and following initial and subsequent flushing. Samples were analyzed for water quality and subjected to FPA analysis. Additionally, FPA was performed on tap water stored under stagnant conditions in epoxy lined copper pipes for seventy-two hours, two hours, one hour, and thirty minutes to determine the effect of stagnation time on odor intensity.

Statistics

Statistical analysis was performed using SAS statistical software. A type I error ( ) of 0.05 was utilized for all tests. The unequal variance t-test was used if the data were found to be normally distributed but the variances were found to be not equal. An Analysis of Variance (ANOVA) was performed to detect differences between more than three locations for determined parameters. In case normality or homogeneity of variances was violated, the Kruskal Wallis nonparametric ANOVA was used.

RESULTS AND DISCUSSION

Odor Assessment by trained panelists

Panelists assessed the water for odors using standard FPA techniques, giving odor descriptors and intensity ratings (Table III-1). Each UQT consisted of three flushes and the UQT was replicated 3 times over a period of several months. The data indicate a strong correlation between water stored in the pipes and a "plastic/adhesive/putty" (also frequently described as "PVC-soft plastic") odor. The increased disinfectant demand present in the water stored in the pipes is also evidenced by the lack of chlorine descriptors in the pipe water when compared to the water stored in the controls.

Table III-1 Odor descriptors and intensities averaged for 3 flushes (mean ± s.d.) within a replicate of samples from Utility Quick Test performed on epoxy lined copper pipes

Water	**Descriptor(s) and Intensity**		
	Replicate 1	**Replicate 2**	**Replicate 3**
No Disinfectant Control	Earthy/Rotten/Musty 2.3 ± 0.6	Odor Free	Odor Free
Pipe + No Disinfectant	Plastic/Glue/Putty 4.7 ± 0.6	Plastic/Glue 4.3 ± o.1	Plastic/Adhesive/Chemical 4.7 ± 0.6
Chlorine Control	Chlorinous 5.7 ± 0.6	Chlorinous 2.7 ± 1.2	Chlorinous 5.7 ± 0.6
Pipe + Chlorine	Plastic/Glue/Putty 5.7 ± 0.6	Plastic/Glue/Adhesive 4.5 ± 0.5	Plastic/Putty/Chemical 5.0 ± 1.0
Chloramine Control	Chlorinous 4.0 ± 1.0	Chlorinous 2.3 ± 0.6	Chlorinous 2.7 ± 0.6
Pipe + Chloramine	Plastic/Glue/Putty/Musty 4.7 ± 1.5	Plastic/Glue 4.3 ± 0.6	Plastic/Adhesive/Putty 4.8 ± 1.3
Odor Free	Sweet/Odor Free 0.7 ± 1.2	Threshold	Odor Free

When the UQT was replicated three times, odor intensity remained in the 3 – 6 range for each flush and the three types of water tested (Figure III-1). Odor descriptors remained relatively constant throughout. Type or presence of disinfectant did not appear to affect "plastic/adhesive/putty" odor intensity.

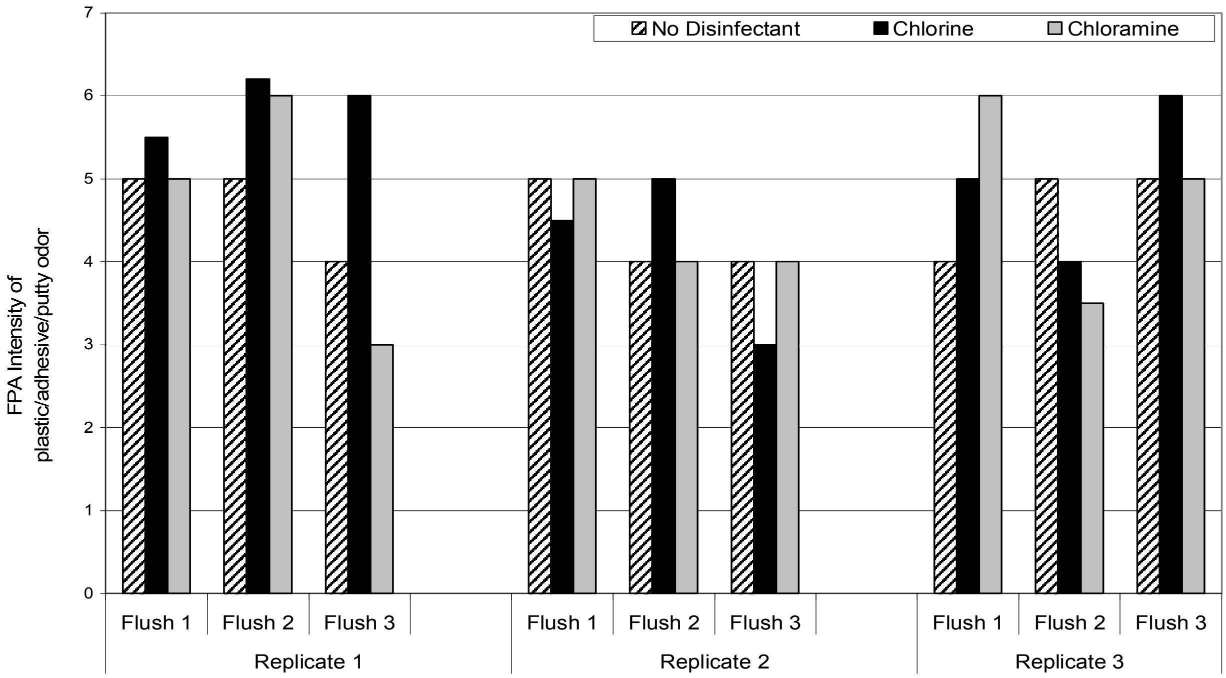

Figure III-1 FPA average intensities of odor generated by epoxy lined copper pipe exposed to water containing no disinfectant, 2 mg/L free chlorine or 4 mg/L chloramines as chlorine

Total Organic Carbon

Leaching of TOC from the pipes occurred and the data showed a positive correlation between water stored in the pipes and an increase in TOC concentrations when compared to the controls (Figure III-2). A one-way ANOVA yielded a p-value of < 0.001, indicating that the TOC increase was significant.

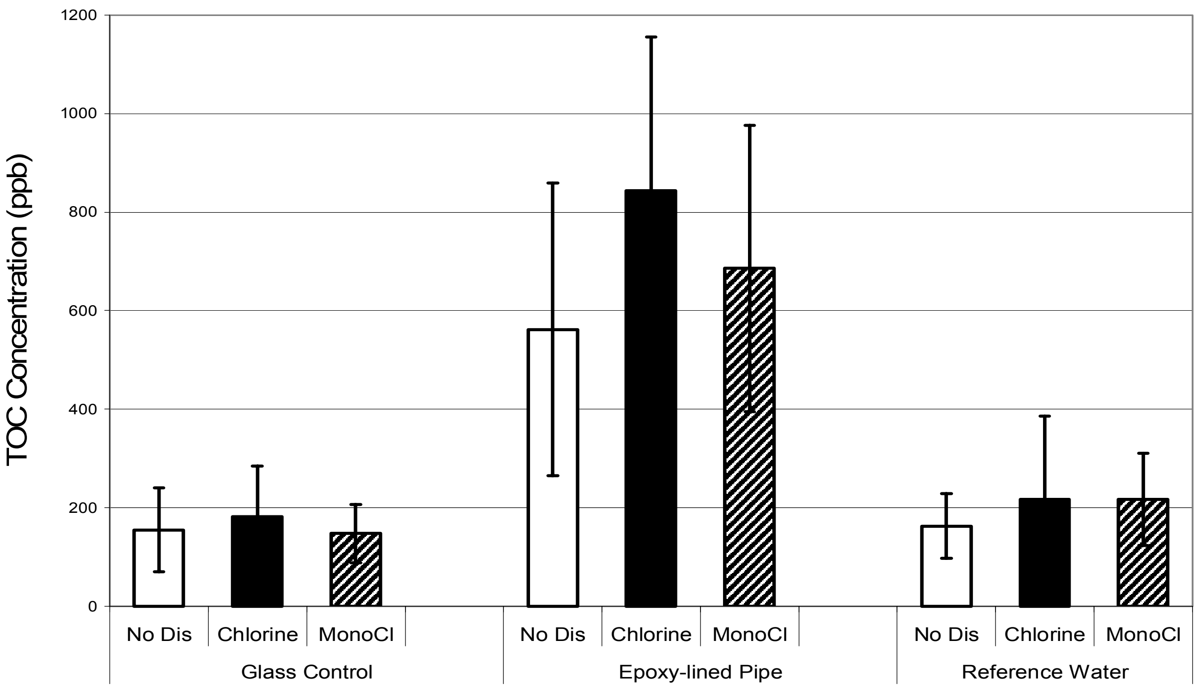

Figure III-2 Average TOC concentrations over three flushes generated from three replicates of UQT performed on epoxy lined copper pipe and water containing no disinfectant, 2 mg/L free chlorine or 4 mg/L chloramines as chlorine, standard error between flushes shown. "No Dis" means no disinfectant.

Trihalomethanes

THM values ranged between 0 and 2.3 ppb for any flush or replicate. Analysis of THMs showed a statistically significant but negligible increase in THM concentrations for the water exposed to the epoxy liner in the pipes during the UQT. A Nonparametric Wilcox T-test, yielded a p-value of 0.0141.

Sorption and Formation of Trihalomethanes

TOC analysis (Figure III-3) showed increased levels of TOC emanating from the pipes which tended to decrease with time. THM analysis detected only trichloromethane (Figure III-4) showed an increase in THM concentration over time when chlorine was added to reference water containing TOC leached from epoxy lined pipe. The data suggest that the TOC leached from the pipes readily forms THMs in the presence of chlorine, with concentration increasing with the passage of time. As no significant amount of THMs were detected after the pre-chlorinated reference water was stored in the pipe, it is reasonable to suggest that THMs are forming during the UQT and being sorbed into the pipe wall before the water is drained and subjected to THM analysis.

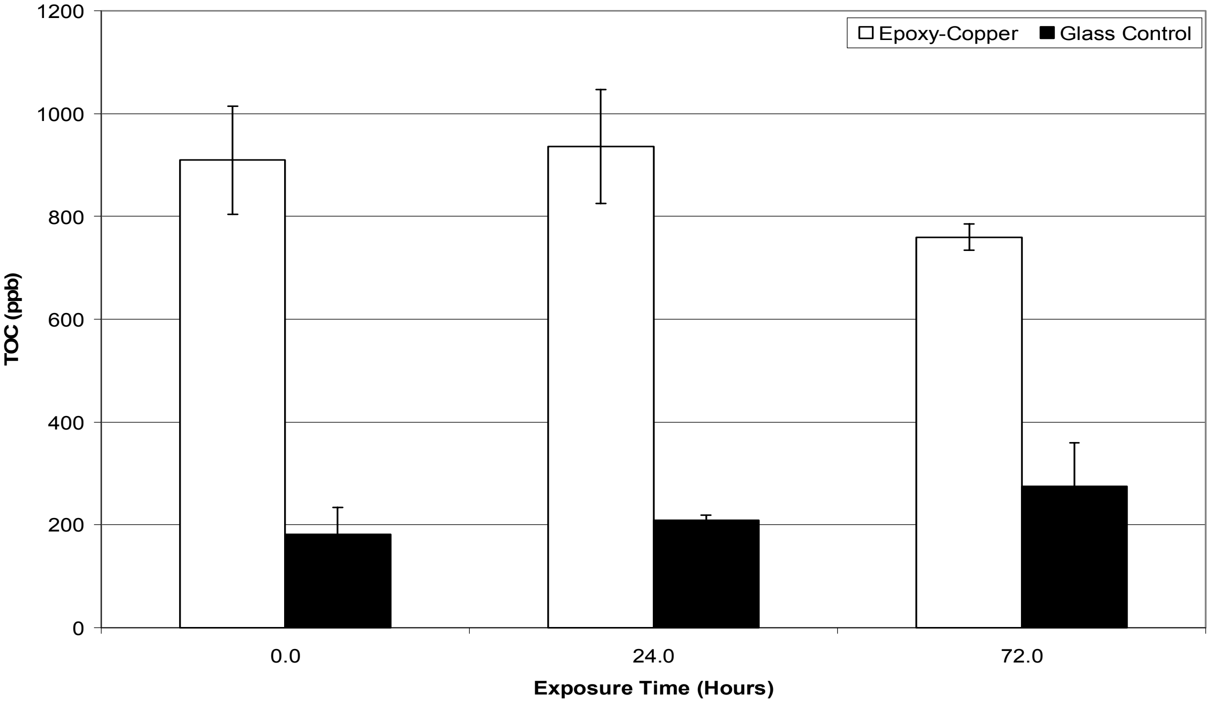

Figure III-3 Average TOC concentrations in water drained from pipes and controls after 0, 24 and 72 hours. Error bars represent standard deviation of sample replicates.

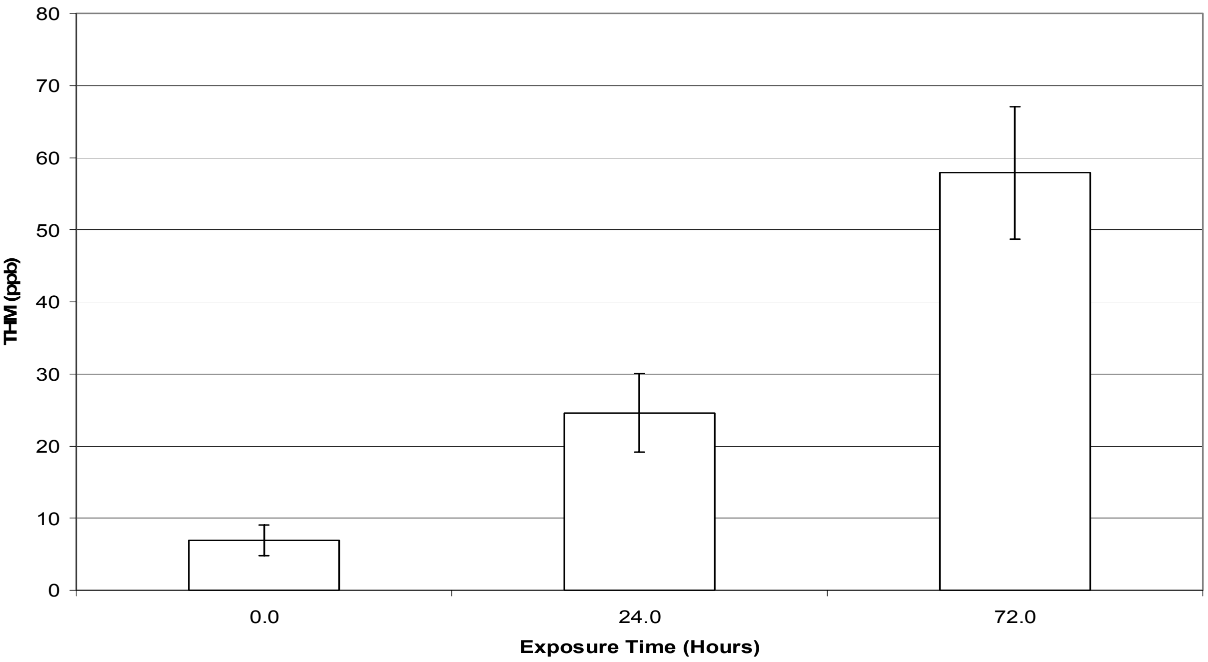

Figure III-4 Average THM concentrations (only trichloromethane present) formed from the reaction of free chlorine and leached TOC. THM concentration in controls at 0, 24 and 72 hours showed THMs did not exceed 1.5 ppb. Error bars represent standard deviation of sample replicates.

Investigation into the sorption of trichloromethane into the epoxy pipe liner showed a 25% decrease which was not significantly different ($p = 0.1$), when the epoxy lined copper pipe was exposed to water containing 60 μg/L trichloromethane for 72 hours. When the experiment was performed with a contact time of 7.5 days and a starting concentration of 17 μg/l, trichloromethane concentrations in the water exposed to the epoxy copper pipe was decreased by nearly half, which was a statistically significant decrease ($p < 0.05$).

Free Copper

No copper was detected during analysis by the ion specific electrode. The data were subjected to Kruskal-Wallis Non-Parametric ANOVA, which generated a p-value of 0.36 thus there was no statistical difference detected between reference water, water exposed to epoxy lined copper pipe, and the control water for dissolved copper.

Disinfectant Residual

Water exposed to epoxy lined pipes demonstrated a significantly lower disinfectant residual than the controls. Disinfection residual was higher however, than in unlined epoxy pipes. This is likely due to oxidation of the epoxy polymer by free chlorine and chloramines. Lower residual existed for both the water containing chlorine disinfectant (initially present at 2 mg/L), and chloramine disinfectant (initially present at 4 mg/L). Statistical analysis was performed using a nonparametric t-test with p-values of < 0.05 for chlorine and monochloramines respectively. The graphs represent average demand for all 3 UQTs performed.

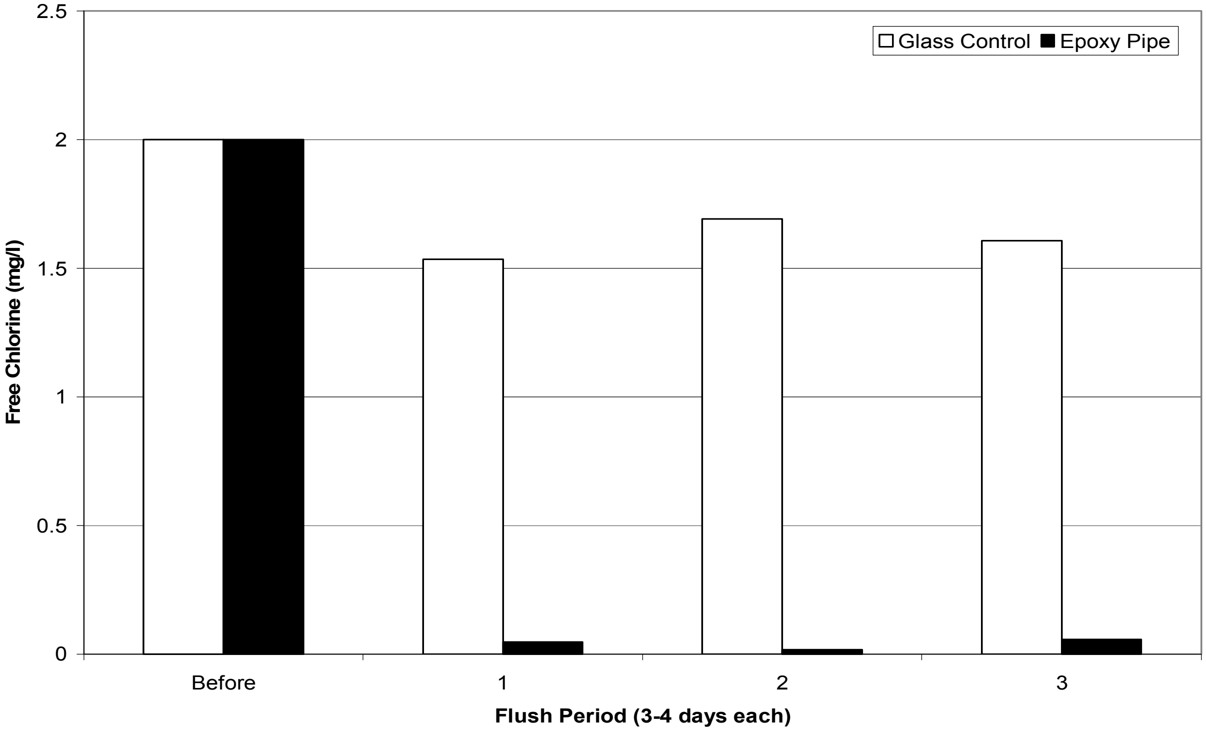

Figure III-5 Average disinfectant residual (as total chlorine) remaining at the end of the 72 hour contact time for UQT replicates and flushes. Chlorine as disinfectant shown for sample and control.

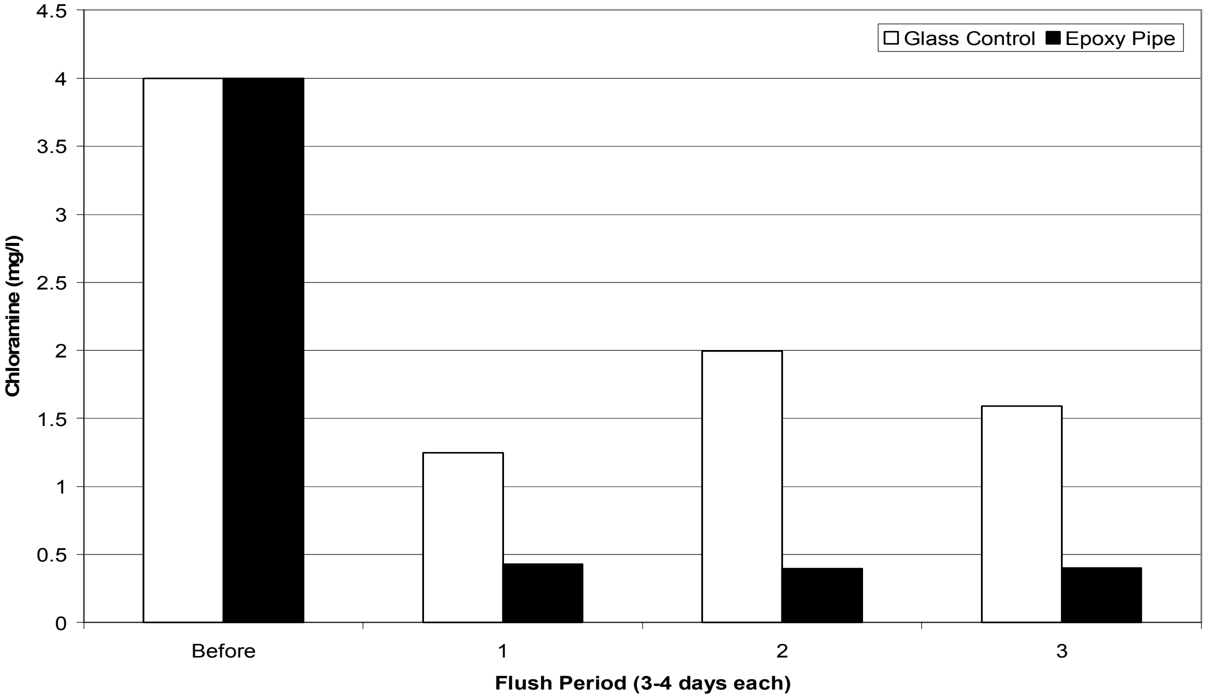

Figure III-6 Average disinfectant residual (as chloramine) remaining at the end of the 72 hour contact time for UQT replicates and flushes. Chloramine as disinfectant shown for sample and control.

Volatile Organic Compounds (VOCs) detected by SPME/GC-MS analysis

SPME followed by GC-MS analysis detected alkenes, aldehydes, and aromatics. Bisphenol A is one of the key components used in making epoxy resin (Dekker, 1988). It has also been shown to be toxic to fish when leached from a epoxy lined water tank (Yeo and Kang, 2006). These compounds are listed below. Several of these compounds are known to have aesthetic impacts on drinking water, and a combination of them is most likely responsible for the "plastic/adhesive/putty" odor reported by FPA panelists.

Table III-2 Compounds detected by SPME-GC/MS analysis that were specific to Epoxy-lined copper and not detected in controls and their odor descriptors (Merck, 2001).

Compound	Odor Descriptor
phenol	"sweet-tarry"
nonyl-phenol	"phenol-like"
stryene	"sweet"
bisphenol A	"phenol-like"
toluene	"sweet-solvent"
benzaldehyde	"almond"

Table III-2 lists compounds detected in the water exposed to pipe material and not in the water exposed to glass controls. The results show a significantly higher number of organic compounds detected in the water exposed to the epoxy liner when compared to controls. This correlates to the increased odor intensity and number of descriptors detected by FPA panelists who analyzed the water, and demonstrates a link between increased leaching of VOCs and potential odor problems.

Field Study

A study was conducted at an epoxy-lining installation site. A group of small apartment buildings had experienced serious pinhole leaks and pipe relining with epoxy was being carried out. Water samples taken prior to epoxy installation, 30 minutes after initial flushing, and 1 week after initial post installation flushing and regular water use by consumers were analyzed for pH, TOC, free and total chlorine, and odor. The samples showed no significant difference in any of the above water quality parameters prior to and after installation of epoxy liner. This confirms reports from consumers that odor causing compounds are not present in significant quantities in epoxy-lined pipes under conditions of normal use. The "plastic/adhesive/putty" odor as described by panelists in the UQT was detected in the air during application and curing of the epoxy resin. This confirms the association of the odor causing compound with the epoxy lining process.

In a follow up laboratory study, FPA was performed on tap water stored under stagnant conditions in epoxy lined copper pipes for seventy-two hours, two hours, one hour and after thirty minutes of flushing (Figure III-7). The results indicate that odor intensity is directly affected by stagnation time, and flushing removed the odor in the same way demonstrated by the field data.

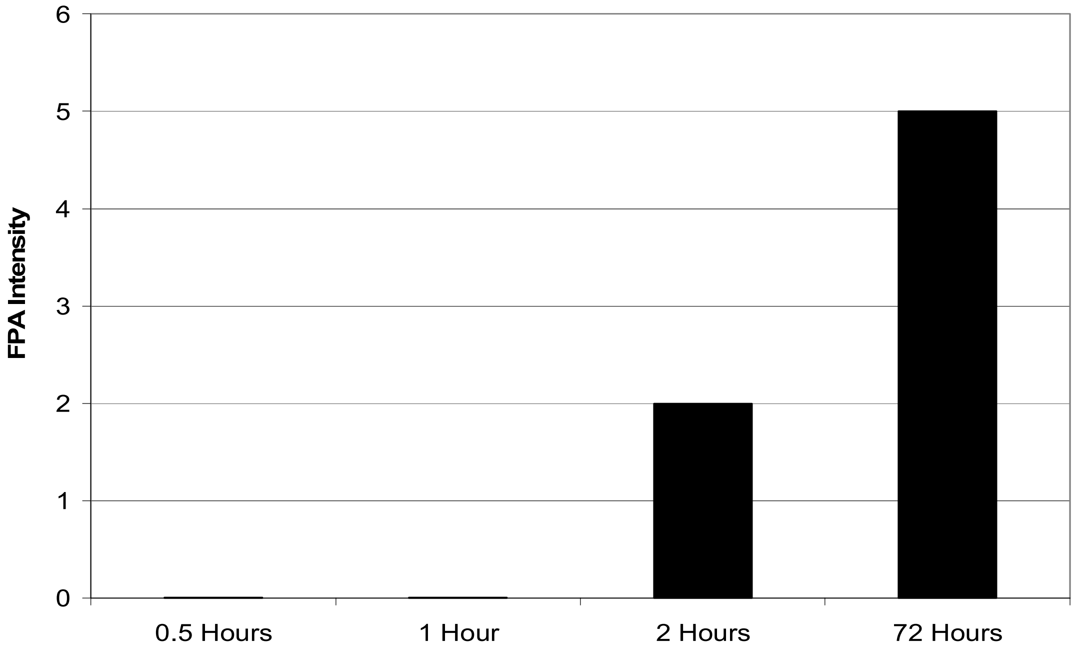

Figure III-7. FPA intensity of plastic/adhesive/putty odor resulting from differing stagnation times of tap water stored in epoxy lined copper pipe.

CONCLUSIONS

Sensory data indicated that the epoxy liner leached compounds that contributed a "plastic/adhesive/putty" odor to drinking water. The odor was present in water exposed to the pipe material, and its intensity did not diminish during subsequent flushing and stagnation periods within the time frame of the utility quick test. While significant odor occurred after 72 hours of leaching, short-term laboratory tests demonstrated that the odor imparted was proportional to stagnation time and was not detectable after only 1 hour of leaching. Field tests with flowing water after full-scale installation of the epoxy liner in an apartment building showed no detectable odor, indicating that water usage determined the extent of the odor. The presence of chlorine or chloramines did not change either the intensity or descriptors for the "plastic/adhesive/putty" odor, which is unlike previous studies where these disinfectants masked odors (Durand and Dietrich, 2005b, Worley *et al.*, 2003). This is important knowledge for utilities and consumers as associating the presence and intensity of the epoxy-related odor with water usage can help identify problems and suggest solutions.

Water exposed to the epoxy liner for 72-96 hour stagnation times also showed a significant increase in TOC (0.4-0.6 mg/L) and a severe decrease in disinfectant residual. The chemical structure of the leached TOC and the cause of disinfectant consumption were not identified, but formation of THM or other disinfectant byproducts in a possibility. More research is needed to determine the nature of the leached TOC and understand the decay of chlorine and chloramines when in contact with the epoxy material, as well as the possible sorption of THM into the pipe material itself. This research confirms the ability of synthetic plumbing materials to affect water quality and reinforces the value of sensory testing to determine the effects of new materials prior to installation.

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CHAPTER IV

COMPARISON OF FIVE POLYMERIC PLUMBING MATERIALS IMPACT ON WATER QUALITY AND SENSORY CHARACTERISTICS

T. H. Heim and A. M. Dietrich
Civil and Environmental Engineering, Virginia Polytechnic Institute and State University,
418 Durham Hall, Blacksburg, VA, 24061-0246 USA
(E-mail: *heimt@vt.edu; andread@vt.edu*)

Abstract

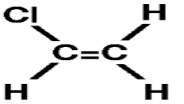
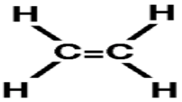
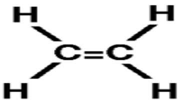
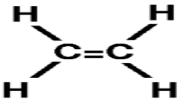
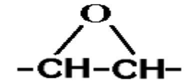
The leaching and migration procedure outlined by the Utility Quick Test (UQT) was used to examine five commonly used types of polymer plumbing material and compare the results. Pipe materials included cPVC, HDPE, PEX-a, PEX-b, and epoxy-lined copper. PEX-a and PEX-b data was previously reported by Durand and Dietrich, 2005. Home plumbing materials may have the ability to impact drinking water aesthetics, specifically in the time immediately following installation. The UQT was developed by drinking water experts for utilities to conduct sensory analysis of materials in contact with drinking water. The UQT allows locally available plumbing materials to be tested against drinking water specific to a region. This investigation compared the effects on odor, TOC, THM formation and disinfectant residual in water exposed to the pipes. A comparison of the results demonstrates the importance of utilizing an organoleptic standard when selecting a pipe material, as well as the effects on other water quality parameters this selection might have. Such data could potentially be used at plumbing supply stores to aid in customer selection of materials for a specific use.

Keywords
cPVC; Drinking water; epoxy; Flavor Profile Analysis; HDPE; odor; PEX; utility quick test

INTRODUCTION

Pipes and pipe fittings constructed of polymers have undergone a continuing trend of increased use in homes and distribution systems across the US and worldwide. A visit to a local building supply store yields a myriad of pipe material choices. Polymers such as High-Density Polyethylene (HDPE), varieties of Cross-Linked Polyethylene (PEX), Polyvinyl Chloride and chlorinated Polyvinyl Chloride (PVC and cPVC) make durable, cost effective replacements to traditional materials such as copper. Synthetic pipes are easier and more cost effective to install due to light weight and increased flexibility, and can be less expensive than copper to manufacture. Other polymer based materials such as epoxy liners have now become a popular alternative to re-piping in the event of corrosion and copper pinhole leaks.

Table IV-1. Commonly Used Polymer Pipes

Name	**Monomer**	**Monomer Structure**	**Common Uses**	**Used In US Since**
cPVC	vinylchloride		hot and cold water distribution systems in home plumbing	1952
HDPE	polyethylene		home plumbing and distribution mains, sewerage and drainage	Early 1970's
PEX-a	polyethylene		hot and cold water plumbing systems, radiant heating systems, snow melting applications	Early 1980's
PEX-b	polyethylene		hot and cold water plumbing systems, radiant heating systems, snow melting applications	Early 1980's
Epoxy-Cu	epoxy		relining copper pipes to treat pinhole leaks, lining for tanks and water towers	Early 1990's

While these new types of plumbing material enjoy significant advantages in terms of cost and installation, their potential to impact drinking water aesthetics and generate taste and odor problems bears further examination. Aesthetic impacts can occur via direct leaching of volatile organic compounds (VOCs) from the polymer itself, or from microbial growth resulting from the available leached polymer acting as a substrate. Numerous studies of the first mechanism show the ability of VOCs to leaching directly from pipe materials and cause odors in drinking water. This was first examined by Anselme in 1985, who demonstrated the occurrence of organoleptic changes caused by defective polyethylene pipe, via both the leaching of polymer additives and oxidation of the surface of the pipe during extrusion (Anselme et al., 1985a). Further studies have confirmed the ability of VOCs to leach from pipes and pipe linings, and effect taste and odor (Skjevrak *et al.*, 2003, Marchesan and Morran, 2004). These VOCs can originate from the pipes themselves, as well as the plasticizers, antioxidants and solvents used in their manufacture.

Drinking water aesthetics play an essential rule in consumers' perception of the quality and purity, and their willingness to accept it over bottled water. As the consumer does not have access to even the most rudimentary water quality analysis equipment, they depend solely on their senses to judge water quality. Any changes detected in the taste or odor of tap water from what the consumer considers normal could result in the perception that the water is unsafe, unpalatable, and generally less fit to drink (Whelton, 2003). Recent research has attempted to link the acceptable level of copper in drinking water regulated by the United States Environmental Protection Agency (USEPA) with consumer detection through taste (Dietrich et al., 2004). Other research has shown an even greater potential for synthetic materials to impact taste and odor. (Rigal and Danjou, 1999, Anselme *et al.*, 1985a, Khiari *et al.*, 1999, Tomboulian *et al.*, 2004)

Water utilities desire to produce a product that consumers will use with confidence, and depend on the consumer to act as a "sentinel" for the quality and consistency of their water (Whelton, 2003). Consumer confidence and water industry knowledge of aesthetic issues is of even greater importance given the heightened state of awareness concerning bioterrorism.

Understanding the interaction of the materials from which the distribution system is comprised with drinking water is inherently important to maintaining a high quality product at the tap, and maintaining high consumer confidence. A 1989 AWWA nationwide study reported 65% of water utilities considered the distribution system responsible for their taste and odor problems (Suffet et al., 1995). The combination of increased concern regarding terrorist threats to the distribution system, coupled with heightened consumer standards in regard to tap water necessitate that water utilities produce a consistent high quality product at the tap. The ability to control and understand off-flavors and odors, including those generated by the distribution system is fundamental to this process.

The effect aesthetic quality of tap water has on consumer confidence and perception necessitates the use of a method to assess the impacts on taste and odor that new plumbing materials may have when introduced into the distribution system. In recent decades, Europe, Australia and New Zealand have developed standard methods to analyze taste and odor impact in new plumbing materials to a greater extent than the United States. Examples of this include the AFNOR XP41, used in France, the BS 6920-2.2.1 used in the United Kingdom, EN 1420-1, which is utilized by other parts of Europe, and most recently, AS/NZ 4020, the standard for Australia and New Zealand. The goal of these methods is to ensure that materials to be used in the distributions system are subjected to a thorough organoleptic assessment prior to their approval for use.

Currently, The United States has no standard method to provide an evaluation of aesthetic effects from synthetic plumbing materials such as those that exist in Europe. Based on the findings of an international workshop of drinking water experts, as well as the opinions of experts in the field, the Utility Quick Test (UQT) was developed in 2001 to constitute the US equivalent of an organoleptic assessment tool for synthetic plumbing materials (Schweitzer et al., 2004). This process seeks to generate sensory data which help to understand the leaching of volatile organics from the plumbing materials being tested, and predict the effects such materials might have on the distribution system. Water used in the test can be varied from highly pure sources like carbon filtered D.I. water to tap water which represents local water quality. The type and concentration of disinfectant utilized can also be varied to examine the effects that this might have on leaching and odors. This allows a utility to customize a test based on a specific pipe material available in their area and test it using their water and a selected type and concentration of disinfectant. The results could also potentially be used to design selection criteria to aid in pipe choice by consumers when purchasing plumbing materials from local plumbing supply retailers.

Even if new plumbing materials successfully complete testing by aesthetic standards noted above, complications may still arise in the field due to installation, interaction between adhesives and fittings, and local water quality characteristics (such as type of disinfectant). This illustrates the importance of testing new materials for specific locations and the respective conditions to which they will expose the pipes.

MATERIALS AND METHODS

Polymer Pipes

7 foot lengths of ¾ inch (internal diameter) epoxy lined copper pipe were acquired from ACE Duraflow®, and shipped in wooded packaging secured with nails to assure no cross contamination of volatile organics (i.e. from adhesives, plastics) would occur. cPVC and HDPE and Silane linked PEX (PEX-b) pipe with internal diameters of ¾ inches were acquired from local building supply companies. ¾ inch Peroxide linked PEX (PEX-a) was purchased from a PEX pipe manufacturer. The HDPE pipe was manufactured by Aquajet Inc. and the cPVC pipe by Nibco Inc; both were purchased at a local home supply store. All pipe materials were certified according to National Sanitation Foundation (NSF-61) standards, based on health effects, for use in hot/cold potable water systems and suitable for use in home plumbing systems in the United States.

Utility Quick Test

2.1m lengths of each type of pipe were flushed using distilled water for 1 hour, filled with water containing 50mg/L free chlorine for 3 hours, and flushed again with distilled water to eliminate any chlorine residual. "Reference" water was then prepared to simulate tap water typically found in the Eastern US. The reference water was synthesized using Nanopure water combined with salts equaling 8 mg/L Mg^{2+}, 46 mg/L SO_4^{2-}, 20 mg/L Na^+, 0.05 mg/L Al^{3+}, 11 mg/L Ca^{2+}, 2.6 mg/L SiO_3^{2-}, 4 mg/L K^+, 1.4 mg/L NO_3^- as N, 0.002 mg/L PO_4^- as P. Three separate batches of the water were then prepared, one containing 2 mg/L free chlorine, one containing 4 mg/l as monochloramine, and one containing no disinfectant. pH in the waters was adjusted to between 7.7-7.9 and the pipe lengths were filled to their entire volume to eliminate headspace and capped with Teflon lined VOA vile caps and sealed with Parafilm®. The pipes were stored undisturbed at room temperature for 72-96 hours (3-4 days), after which the leachate water was removed for analysis. The fill and drain process was repeated 2 additional times for each UQT. Controls were prepared with the 3 types of water being stored separately in 500 ml glass Erlenmeyer flasks, with ground glass stoppers and stored in the dark covered in aluminum foil for identical time periods as the pipes (72-96 hours).

Flavor Profile Analysis

FPA was conducted in accordance with the procedures found in Standard Methods 2170. Odor free water was obtained from a Barnstead® Nanopure filter. All samples were prepared in 500mL Erlenmeyer flasks with ground-glass stoppers and heated to 45° C in a water bath for 15 minutes prior to testing. Five to seven panelists from a trained group of ten were presented with the flasks in random order at two minute intervals. Prior to sampling, and between each subsequent sample, panelists sniffed flasks filled with odor free water to calibrate themselves and clear their noses. Panelists were asked to give a descriptor and intensity rating (0-12) of the odor of the water in the flasks in accordance with their FPA training. Training and research was approved according to the standards of the Virginia Tech Institutional Review Board for human subjects.

TOC Analysis

Analysis of total organic carbon (TOC) concentration content of water samples from the UQT was performed using a Sievers® 800 Portable TOC analyzer, and the parameters described in Standard Methods 5310C.

Disinfectant Residual

Residual for free chlorine, total chlorine and monochloramine was determined by measuring the concentration of these species before and after they were stored in the pipes and control flasks. Concentrations of the disinfectant species were determined using appropriate powder pillows and a HACH® Pocket Colorimeter II and HACH® DR/2400 Portable Spectrophotometer.

Trihalomethane Analysis

Trihalomethane (THM) content of water samples used in FPA was performed according to USEPA Method 502.2 (USEPA 1995). The instrument was a Tremetrics 9001 gas chromatograph with a 1000 Hall detector, Tekmar 3000 purge trap and concentrator and Tekmar 2016 Purge Trap autosampler.

pH Analysis

pH was determined using the Accumet® (cat# 13-620-287) electrode and the Accumet® pH Meter 910 purchased from Fisher Scientific. pH values were measured and recorded prior to exposure to pipe samples and after each subsequent flush period.

SPME/GC-MS Analysis

Solid phase microextraction holder and 75 μm Carboxen^{TM}-PDMS coating fibers were purchased from Supelco (Bellfonte, PA, USA) for analysis of VOCs. The SPME conditions were optimized by the addition of 2 g of NaCl to 20 mL of sample water placed in a 40 mL VOA vial. The sample was stirred using Teflon coated magnetic stir bars at 45 ^{o}C for 20 minutes during which time the fiber was injected into the 10 mL sample headspace for sorption. Samples were allowed to desorb for 3 mins. An Agilent 6890 Series GC system connected to Agilent 5973 network mass selective detector was operated in splitless mode with a 0.75 mm i.d. injection sleeve (Supelco), total helium flow of 24 mL/min, inlet temperature of 220 °C, and 80 kPa pressure. J&W DB-5 capillary column (30 m x 250 μm, 30 μm thickness) was used for all analysis. The temperature program was: 60 ^{o}C hold for 7mins then increased from 60 ^{o}C to 120 ^{o}C at a rate of 10 ^{o}C/min and finally from 120 ^{o}C to 260 ^{o}C at a rate of 20 ^{o}C/min. All samples were analyzed within 2 days of collection.

RESULTS AND DISCUSSION

FPA Analysis

All of the pipes analyzed, with the exception of cPVC, generated significant odor. Water samples exposed to HDPE, PEX-a, PEX-b and epoxy all shared the common descriptor of "plastic," but also displayed a variety of other distinct descriptors. PEX-b had the greatest variety of different descriptors with five, while HDPE, PEX-a and epoxy had three each. PEX-a and PEX-b, while structurally the most similar, had significant differences in both descriptor and intensity, suggesting that the manufacturing process or other factors may have as much to do with aesthetic impact as the polymer itself(Durand and Dietrich, 2005b).

The highest odor intensity was generated by the HDPE pipe, followed by epoxy, PEX-b and PEX-a. All of the odor intensities had a relatively small variance in intensities between flushes.

cPVC was the most inert of all the materials tested, and panelists were unable to detect any difference between samples in contact with it and those in contact with glass controls.

Several trends also became apparent when the results from all pipes types were compared. First, the intensity of the odor descriptors did not decrease significantly between flushes for any of the pipes which generated odors. This highlights what may be one limitation of the UQT, the time span of the leaching and migration protocol is not long enough to provide data on whether or not odors from leached VOCs will decline over time. Second, while in the epoxy and PEX-b samples, the type of disinfectant used did not affect odor descriptors or intensity, presence of disinfectant increased odor intensity in the PEX-a samples and type of disinfectant led to different odor descriptors in the HDPE samples. This data could potentially be useful to utilities considering changing disinfectant types and seeking to evaluate if such a change could impact aesthetics related to leaching of compounds from polymer pipes.

Table IV-2. Odor descriptors, intensity, and trends generated from FPA analysis of polymer pipe materials. Average odor intensity is between subsequent flushes.

	cPVC	HDPE	PEX-a	PEX-b	Epoxy-Cu
Odor Descriptor(s)	None (No difference from control)	“waxy" "plastic" "citrus”	"bitter" "plastic" "oily"	"chemical" "mechanical" "burning" "plastic" "solvent"	“plastic" "adhesive" "putty”
Average Odor Intensity	NA	5.7 +/- 1	2.5 +/- 0.9	3.2 +/- 0.6	4.7 +/- 0.8
Intensity Decrease with flushes?	NA	NO	NO	NO	NO
Descriptor Impacted by Disinfectant Type?	NA	YES	NO	NO	NO
Intensity Impacted by Presence of Disinfectant?	NA	NO	YES	NO	NO

Volatile Organic Compounds (VOCs) detected by SPME/GC-MS analysis

GC-MS analysis utilizing SPME yielded a variety of organic compounds some of which have the potential to impact odors at very low concentrations. Similar findings have been have previously identified in the literature (Anselme *et al.*, 1985b, Villberg *et al.*, 1997, Brocca *et al.*, 2002, Skjevrak *et al.*, 2003). It is notable that cPVC, the most organoleptically unreactive polymer also had the fewest number of identified compounds. Compounds detected in HDPE included benzene and phenol which have sweet and sweet-tar like odors respectively, as well as alkanes and ketones. Compounds in epoxy-copper included phenol, styrene, which tends to have a sweet-chemical smell and toluene which has an odor described as sickeningly sweet and tarry (Merck, 2001) and bisphenol A, shown to be toxic to fish when leached from a epoxy lined water tank (Yeo and Kang, 2006). PEX-b most notably generated the occurrence of 2-ethoxy-2-methyl propane, also known as ethyl-tert-butyl ether (ETBE) a fuel additive known to contribute a sweet, burning, bitter chemical odor when water samples containing it are analyzed via FPA (Durand and Dietrich, 2005b). Table IV-3 gives a summarized list of the compounds that were frequently detected in most samples.

Table IV-3. Compounds detected by SPME-GC/MS analysis that were specific to the pipe materials being analyzed and not detected in controls.

cPVC	**HDPE**	**PEX-a**	**PEX-b**	**Epoxy-Copper**
1-3 butadiene	benzene	di-*tert*-butyl peroxide	propane, 2-ethoxy-2-methyl	phenol
titanium dioxide	phenol	*t*-butanol	propane, 2,2-diethoxy	nonyl-phenol
	bisphenol	decanal	hydroperoxide, 1-ethyl propyl	stryene
	cyclotetradecane	nonanal	*p*-xylene	bisphenol A
	tetradecane	Butanoic acid-butyl ester	decanal	toluene
	cyclohexadiene	1-hexanol, 2-ethyl	nonanal	benzaldehyde
	cyclohexanone	2,5-hexanediol,2,5-dimethyl	Butanoic acid-butyl ester	
	cyclopentanone		1-hexanol, 2-ethyl	
			2,5-hexanediol,2,5-dimethyl	

TOC Analysis

Comparative TOC analysis of pipe materials shows a significant difference in concentration of leached organic carbon between polymer types. Figure IV-1 shows the amount of TOC leached from each material specific to disinfectant types. The materials are arranged from least amount of TOC leached (cPVC) to greatest (PEX-b).

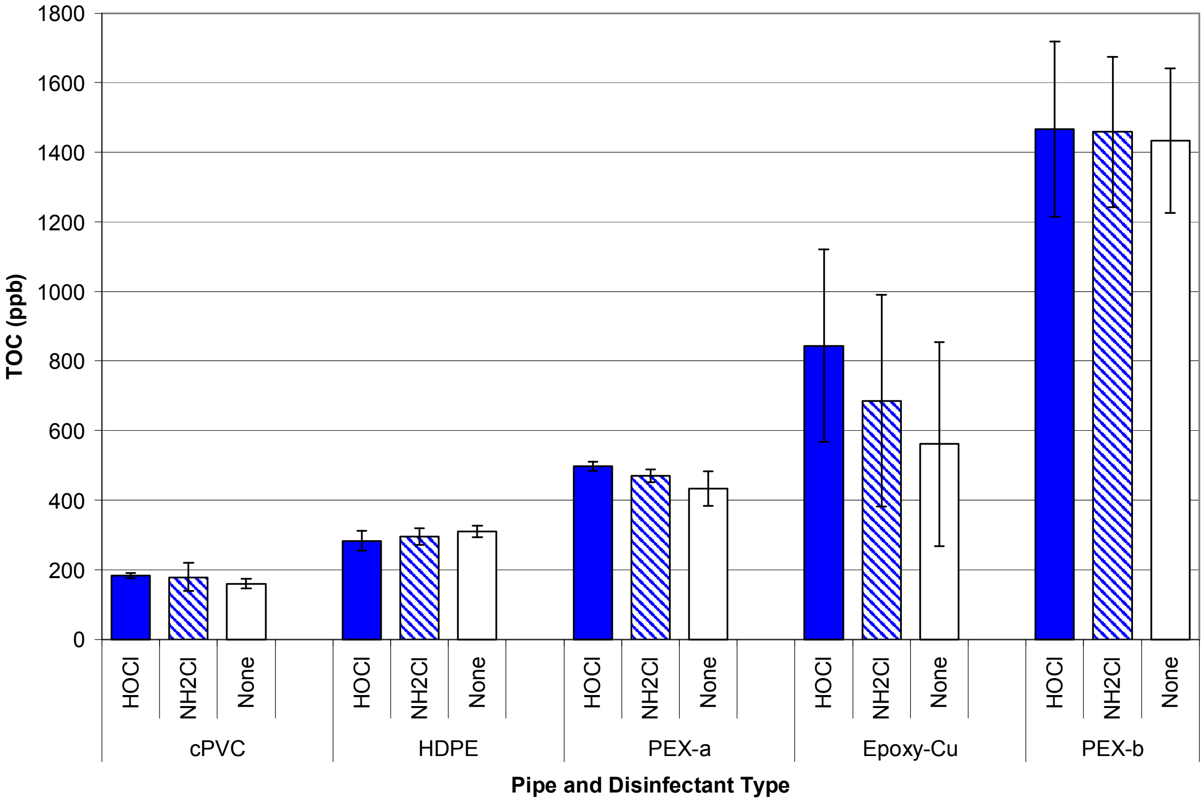


Figure IV-1. Average TOC concentrations for replicate UQT experiments in the absence of disinfectant and the presence of 2 mg/L free Cl_2 and 4 mg/L monochloramines. The standard deviation of TOC concentrations between replicates is shown.

It is notable that PEX-b, which leached the greatest amount of TOC as well as the greatest number of compounds detected by GC-MS analysis, did not contribute the most intense odors as analyzed by FPA it did however, appear to contribute the greatest variability of odors. cPVC, which leached the least amount of TOC and had the fewest number of compounds identified by GC-MS, had the least impact on water aesthetics. This suggests that specific volatile organics themselves and not simply the concentration present in the water may determine odor intensity and aesthetic impact. No correlation between type of disinfectant present and amount of TOC leached is observable. The variability of TOC leached was greatest in the samples with the highest concentrations.

Disinfectant Demand

Average disinfectant residual remaining after 3 subsequent flushes during the UQT was compared for all pipe materials for both chlorine and monochloramine. Results for chlorine (Figure IV-2) showed that exposure to the epoxy-lined copper led to the greatest difference in remaining disinfectant concentration when compared to control, demand was still less however, than that found in unlined copper pipe. All other pipe materials also had less chlorine when compared to the control, but the difference was not as pronounced.

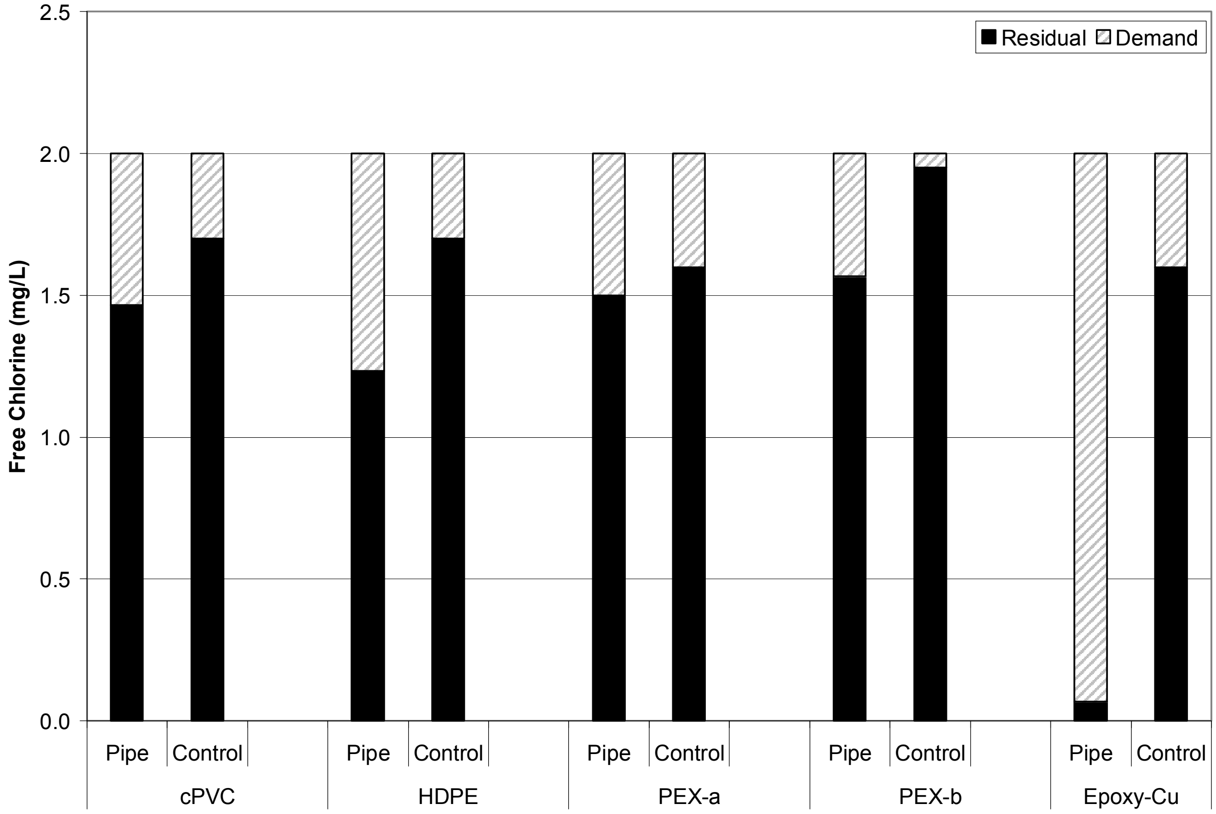


Figure IV-2. Average disinfectant residual (as free chlorine) remaining at the end of the 72 hour contact time for UQT replicates and flushes. Chlorine at 2mg/l as disinfectant shown for pipe and control.

When the residual levels of chloramine were measured, only two of the five pipe materials tested, HDPE and epoxy-lined copper, showed a significant difference in chloramine residual when compared to the control. As with chlorine, exposure to epoxy-lined copper resulted in depletion of the majority of the disinfectant present, but this was again less than the demand found in unlined copper pipe.

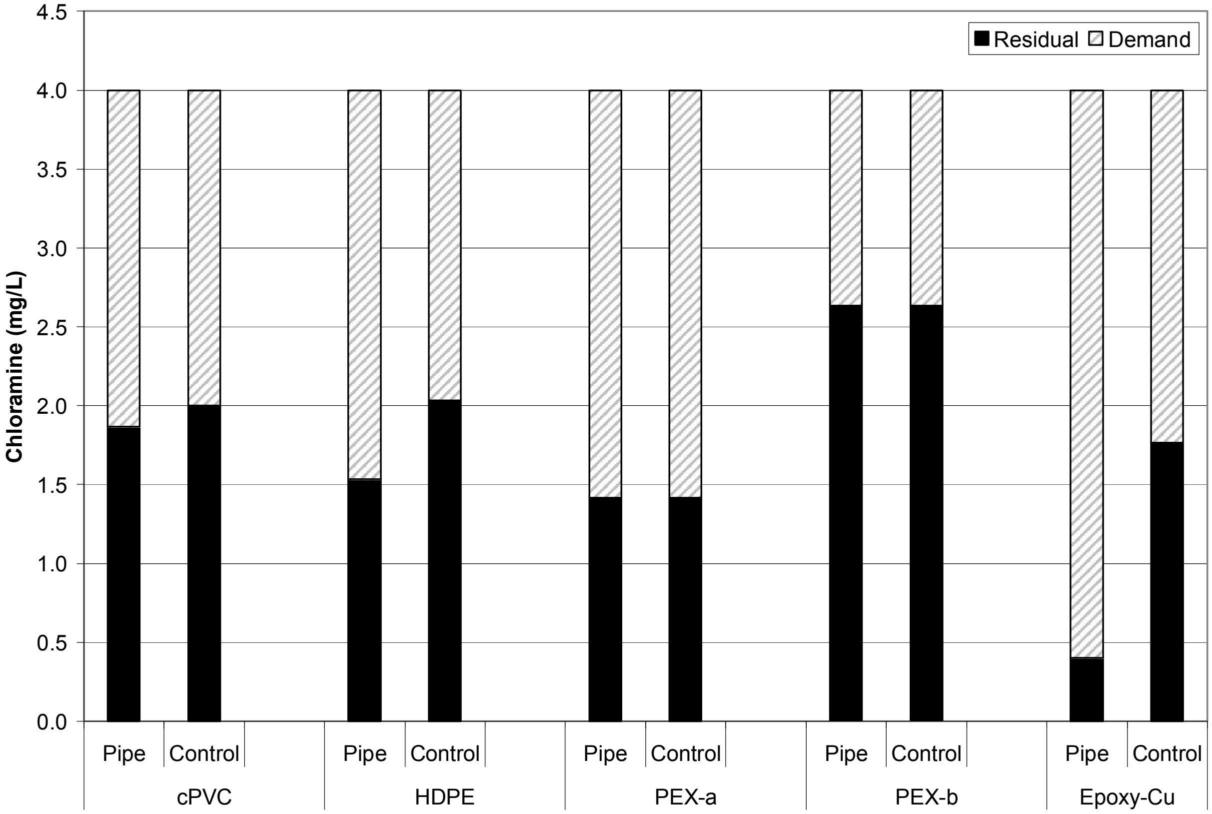


Figure IV-3. Average disinfectant residual (as total chloramine) remaining at the end of the 72 hour contact time for UQT replicates and flushes. Chloramine at 4mg/l as disinfectant shown for pipe and control.

Potential of Newly Installed Pipes to Impact Water Quality and Aesthetics

The water quality parameters mentioned above outline the ability of polymer based plumbing materials to impact water quality immediately following installation. The results can be summarized and compared (Table IV-4) to evaluate this impact and compare and contrast results.

Table IV-4. Evaluation of parameters effecting water quality by newly installed pipe material. 0 indicates least impact to water quality, 5 indicates greatest impact. Rating indicates sum of individual parameters.

	cPVC	HDPE	PEX-a	PEX-b	Epoxy-Cu
Odor	0	5	3	3	5
TOC	1	2	3	3	5
Chlorine Demand	1	2	0	2	5
Chloramine Demand	0	1	0	0	3
Rating	**2**	**10**	**6**	**8**	**18**

Such a table could potentially lead to the development of a set of guidelines for consumers to use when selecting a plumbing materials type from their local building supply retailer or plumbing professional for home installation.

Aesthetic Impact after Extended Time Periods

The same pipe materials evaluated by the Utility Quick Test were also subjected to longer term analysis in a series of three plumbing rigs, which cycled water with chlorine, chloramine and no disinfectant for over a year(Durand and Dietrich, 2005a). Samples were taken regularly and analyzed for the same parameters as those in the UQT. Data from the rigs initially indicate similar odor descriptors for each pipe to those found from the UQT. All odors decreased with the passage of time, however, and after a month, the odors had been reduced to “threshold.” Levels of TOC leaching from the pipes also tended to drop significantly during this initial one month period. These trends, when viewed in correlation with the UQT data, demonstrate the impact that newly installed plumbing materials can have on water quality and aesthetics and how those impacts decrease over time. While the UQT is a good indicator of the immediate impact of newly installed pipes, it does not represent the effects these pipes will have after the passage of any significant amount of time.

CONCLUSIONS

The results of this study indicate the ability of different polymer based pipe materials to significantly effects water quality and aesthetics when analyzed by the Utility Quick Test. Data indicate that the effects can vary depending on material, but with the exception of cPVC, all materials studied had a significant impact on odor and TOC concentration of water exposed to the pipes. Some pipe materials also had an effect on the amount of disinfectant consumed. These findings have implications in regard to the short term impact of newly installed plumbing materials on water quality. This demonstrates the utility of the UQT in studying the interaction between a specific water and pipe material. Such information could potentially be used to aid homeowners in understanding the possible effects on their drinking water immediately following installation and in the selection of a plumbing material which best suites their needs.

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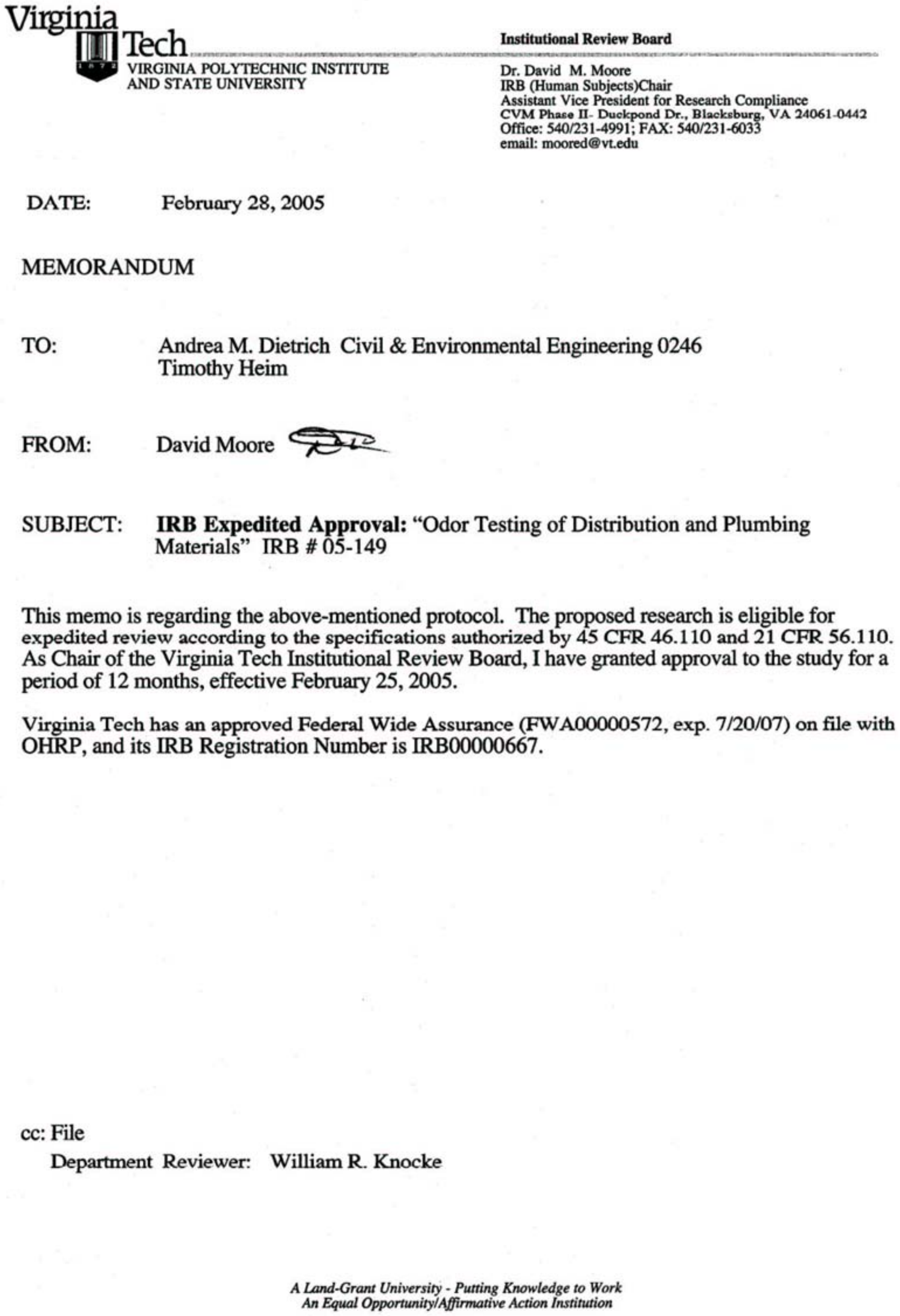
Appendix 1. IRB Approval for Human Subjects



Virginia Tech
VIRGINIA POLYTECHNIC INSTITUTE
AND STATE UNIVERSITY

Institutional Review Board
Dr. David M. Moore
IRB (Human Subjects)Chair
Assistant Vice President for Research Compliance
CVM Phase II- Duckpond Dr., Blacksburg, VA 24061-0442
Office: 540/231-4991; FAX: 540/231-6033
email: moored@vt.edu

DATE: February 28, 2005

MEMORANDUM

TO: Andrea M. Dietrich Civil & Environmental Engineering 0246
Timothy Heim

FROM: David Moore

SUBJECT: **IRB Expedited Approval:** "Odor Testing of Distribution and Plumbing Materials" IRB # 05-149

This memo is regarding the above-mentioned protocol. The proposed research is eligible for expedited review according to the specifications authorized by 45 CFR 46.110 and 21 CFR 56.110. As Chair of the Virginia Tech Institutional Review Board, I have granted approval to the study for a period of 12 months, effective February 25, 2005.

Virginia Tech has an approved Federal Wide Assurance (FWA00000572, exp. 7/20/07) on file with OHRP, and its IRB Registration Number is IRB00000667.

cc: File
Department Reviewer: William R. Knocke

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VITA

Timothy Howard Heim, the son of Howard R. Heim Jr. and Mavourneen Ann Heim was born on June 17th, 1981 in Sayre, Pennsylvania. After high school, he attended The Pennsylvania State University, from which he graduated *Magna Cum Laude* with a BS in Environmental Resource Management in 2003, as well as minors in Environmental Engineering and Watersheds and Water Resources.

Following his graduation from college, Timothy accepted a job with Weston Solutions Inc., working as an associate project scientist in the Emissions Test Practice, allowing him to travel the country and perform environmental monitoring at a great variety of industrial locations. His work with Weston cumulated with his managing a network of perimeter air monitoring stations at an EPA Superfund remediation site. He would later return in a consulting position to assist in the Weston's EPA START contract involving environmental monitoring in New Orleans following Hurricane Katrina.

In the fall of 2004, Timothy entered Virginia Tech's Environmental Engineering program to pursue a Master of Science Degree and perform research in drinking water aesthetics under Dr. Andrea Dietrich. In July 2005, Timothy presented a workshop on the 2-of-5 test to a senior water treatment operator's forum in Charlottesville, VA. In August 2005, He performed field work in collaboration with an industry group addressing the problem of *in situ* pipe remediation in the Washington, DC area. In October of 2005, Tim submitted a paper on the aesthetic impact of epoxy-lined copper pipes at the 7th IWA Symposium on Off-Flavors in the Aquatic Environment in Cornwall, Ontario.