Disinfectants and Plumbing Materials: Effects on Sensory and Chemical Characteristics of Drinking Water

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ABSTRACT

The distribution system is the primary cause of taste and odor complaints in drinking water. This research examined the ability of small diameter pipes used in home plumbing to affect drinking water quality. The properties of the materials were investigated in the absence of disinfectant and the presence of either chlorine or chloramines. A panel was trained in flavor profile analysis (FPA) according to Standard Methods 2170B and used to assess the sensory properties of all samples. Chemical analyses were performed to determine disinfectants, total organic carbon (TOC), pH and specific organic contaminants.

The first part of this study investigated PEX pipes manufactured by the silane (PEX-b) and peroxide (PEX-a) cross-linking technology, using the utility quick test (UQT) method. Silane PEX-b had a greater effect on water quality properties such as odor, TOC and residual disinfectant demand than peroxide-linked PEX-a. Chemical analysis revealed that PEX pipes can contribute fuel oxygenates such as ETBE (PEX-b) and possibly MTBE (PEX-a) to drinking water. PEX pipes did not contribute any significant trihalomethanes to drinking water. This study showed that the type of PEX used in homes will determine the extent to which drinking water quality is affected.

The second part of this study used simulated plumbing rigs to investigate seven different materials under low flow and stagnant conditions; chlorinated polyvinyl chloride, cross-linked polyethylene, polyethylene, epoxy-lined copper, copper, stainless steel, galvanized iron and glass (control). Results showed that these plumbing materials have the potential to affect water quality characteristics such as TOC concentrations, residual disinfectant and odor when newly installed in homes. A high TOC concentration was consistent with the presence of a distinct odor or a high FPA intensity rating. Galvanized iron produced the worst odors that were consistently described as "motor oil". Polyethylene generated more intense plumbing associated odors than PEX or cPVC plastic material. cPVC and copper generated the least odors. Both copper pipe and epoxy-lined copper consumed residual chlorine and chloramines.

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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 Taste-and-Odor in the distribution system highlighting both case studies and laboratory experiments. Chapters II and III examine the ability of a commonly used in-home plumbing material, cross-linked polyethylene (PEX) to affect the characteristics of drinking water. Chapter IV provides a detailed analysis of several plumbing materials using a rig system that simulated their use in homes. The ability of these materials to affect drinking water quality is highlighted. This work was prepared for and supported by the National Science Foundation (NSF). Additional support was provided by the Edna Bailey Sussman Foundation. Chapter II entitled "PEX Plumbing Material Can Contribute Chemical/Solvent Odor to Drinking Water" has been presented at the 7th IWA Symposium on Off-Flavors in the Aquatic Environment and submitted to the Water Science and Technology conference for publication.

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CHAPTER I

LITERATURE REVIEW

INTRODUCTION

Aesthetics play a critical role in the evaluation of drinking water quality by both utility personnel and consumers. Some utilities even view consumers as valuable sentinels that provide feedback on water quality delivered at the tap (Whelton, 2003). This is especially significant as people are growing more concerned about water security issues in the United States. In this era of heightened terrorism understanding all potential sources of Taste and Odor (T&O) to drinking water is an important aspect of the Nation's security.

Consumers usually infer that if their water tastes and smells different it may not be safe. The presence of off-flavors or odors undermines consumer confidence in the drinking water industry resulting in increased consumption of bottled water or other alternative sources of water. Jardine *et al*. (1999) reported a study by Auslander and Langlois (1993) which found that only 49% of Toronto residents were satisfied with their drinking water. Forty percent of the households surveyed resorted to alternative drinking water sources. A report on a public survey in the Quebec metropolitan area (Levallois *et al*., 1999) revealed that consumer dissatisfaction with tap water was not perceived based solely on health risks but also included organoleptic quality. The results showed that 14% of consumers were dissatisfied with the odor and 30.6% with the taste or flavor of their drinking water. This dissatisfaction resulted in major rejections of tap water in the Quebec metropolitan area.

This survey is also reflective of the United States where there has been an increased trend towards consumption of bottled water based on customer perceptions. Consumer discontentment during T&O episodes is evident by the use of phrases such as "afraid that some dangerous chemical has been added to the water", "bleachy smell", "foul-smelling tap water" (McGuire, 1995). The water industry is continuously challenged with providing safe and aesthetically

acceptable water to consumers. This entails producing drinking water that complies with primary regulatory standards for health and is free of all off-odors and flavors (McGuire, 1995).

CASE STUDIES OF DISTRIBUTION SYSTEM GENERATED TASTE AND ODOR

In some instances drinking water flowing from a consumer's tap may have substandard aesthetic qualities compared to the water when it left the treatment plant. In order for utilities to advise on and deal with T&O issues, they must understand problems in both the public distribution systems and in domestic plumbing infrastructure. The results of a nationwide survey, conducted by the American Water Works Association, identified the public distribution system as the primary cause of T&O issues associated with drinking water (Suffet *et al.,* 1993). Domestic plumbing, or the private distribution system, was also identified as a contributing factor. Existing data, though limited, indicates that the distribution system can cause many T&O problems, such as rancid, medicinal, chemical, and earthy/musty (Rigal *et al*., 1999; Khiari *et al*., 1999). The sources of T&O in the distribution system and domestic plumbing infrastructure are varied. These include biological sources (fungi and bacteria), chemical sources, system design (dead ends) and system operation (blending chloraminated water with chlorinated).

T&O problems encountered in distribution and plumbing systems occur mostly as a result of (1) pipe or reservoir lining materials leaching into water and (2) reactions of leached compounds in the water with the disinfectant residual within the distribution system (Khiari *et al*., 1999). The type of disinfectant (chlorine, chloramines or chlorine dioxide) used will influence reactions that take place within the distribution system resulting in additional tastes and odors

Khiari *et al.* (1999) presented case studies which portrayed these phenomena. The sensory method employed was flavor profile analysis (FPA) and the chemical methods were closed loop stripping analysis or liquid-liquid extraction coupled with gas chromatography and mass spectrometry. In one case which occurred in eastern France in May 1994, phenol leached from an acrylic coating used to line a water storage reservoir and resulted in "phenol/styrene" type odors. This case study further illustrated the production of medicinal smelling bromophenols and bromodichloro-iodomethane as a result of the reaction of phenol with chlorine in bromide

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containing water. Another medicinal odor was reported in Barcelona Spain in 1995. It was suspected that the odors were produced when residual disinfectant reacted with natural organic matter forming branched aldehydes such as 2-methyl propanal and 3-methyl propanal. In yet another case, installation of a new main in the distribution system resulted in "oil-base paint" and "paint/putty" type of taste and odor. Chemical analysis of water samples revealed substituted benzenes and naphthalene suspected to be leached from bituminous coating on the inside of the pipes.

Similar case studies were reported by Rigal *et al.* (1999) that depicted T&O episodes resulting from the use of synthetic materials. In one case, a newly refurbished water tower leached styrene at 230μg/L which resulted in a "chemical" odor in drinking water. The problem was attributed to the rehabilitation of the water tower with a composite coating made of fiber glass reinforced polyester resin. In another instance solvent and petroleum odors were detected in cheese and butter. The chemicals contributing to these odors were leached from a vinyl-based coating applied to the dairy's water tower. Several chemicals such as styrene, acetone and methyl isobutylketone were identified. Another case involved a taste episode that occurred following the rehabilitation of a reservoir in Rennes. Consumers complained of a very strong "medicinal" taste in the water. Investigation revealed that a vinyl polychloride net added to the cement used to renew the reservoir leached triphenylphosphate which is a known plasticizer. Triphenylphosphate hydrolyzed in the presence of chlorine and formed mono-, di- and trichlorophenols that contributed the medicinal taste.

Identifying the source of a T&O episode is a challenging task. The outlined case studies demonstrate the diverse possibilities for T&O episodes in drinking water distribution systems. Steps taken to rectify the T&O episodes consisted mainly of replacing the component that contributed to the problem. It is important to note that in every instance customer complaints were the first indicator that there was a problem with the quality of the water. The importance of aesthetics as a monitoring tool for water quality should not be overlooked.

Distribution and plumbing materials such as pipes and mains, home plumbing, tanks and reservoirs, ancillaries, linings, sealing systems, are all materials that contact drinking water

before reaching the consumer. Knowledge of the potential for these materials to impact the properties of water will aid in prevention and control and ultimately in providing the consumer with high quality water. Many organic and some inorganic chemicals are known to leach from drinking water system components during standard leaching testing (ANSI/NSF Standard 61) but the sensory properties of leached chemicals are not typically evaluated in the USA. A literature-based evaluation of the potential sensory properties of these leached chemicals revealed that system materials had the potential to cause undesirable T&O characteristics in drinking water (Tomboulian *et al.*, 2004). This study complied information on the characteristics of the potential chemical contaminants. In addition, sensory analysis of system components was used to provide T&O descriptors which can then be subsequently matched with the Taste-and-Odor-Wheel descriptors. Qualitative analysis of taste and odors encountered in the distribution system are summarized in the T&O wheel (Suffet *et al.*, 1999). The wheel compiles the relationship between known taste and odor problems and their causes. This work is a great advancement in understanding, categorizing and ultimately mitigating potential T&O episodes in drinking water distribution systems. A need for more extensive categorizing of tastes and odors produced when distribution and plumbing materials come in contact with drinking water has resulted in a growing trend towards the use of Flavor Profile Analysis.

SYNTHETIC HOME PLUMBING MATERIALS T&O POTENTIAL

The type of materials, plastics versus metals, used in domestic plumbing systems will significantly affect the extent and type of the T&O problems encountered in drinking water. Although secondary maximum contaminant levels exist for several metals and VOCs in drinking water (USEPA, 1979) and copper is known to cause taste problems in drinking water (Dietrich *et al.*,2004; Cuppett *et al.*,2005), studies have shown that organic materials such as plastics possess a greater potential of impacting the organoleptic qualities of drinking water. The contribution from organic compounds leached from materials is two-fold. The organic chemicals can directly or indirectly result in T&O in drinking water. According to recent Norwegian research and experience, performed by the Aquateam and the Norwegian Food Control Authority, it has been shown that biodegradable matter leached from plastic pipes and tanks promote microbiological growth whereas copper pipes inhibit growth due to its toxic

nature (Hem *et al.*, 2002). Biological activity can result in off-flavors and odors in drinking water (Malleret *et al.*, 2002).

Several studies have revealed the potential of VOCs to leach from pipes and linings (Skjevrak *et al.*, 2003; Marchesan *et al.,* 2004) and directly contribute tastes and odors to drinking water. Plasticizers, antioxidants and application solvents used in association with synthetic materials can contribute to off-flavors and odors in drinking water. Antioxidants are sacrificial coatings that protect the underlying polymer material from oxidation reactions. The dissolution of antioxidant as a mechanism that destroys the quality of drinking water has been studied in France as early as 1985.

Using FPA and Threshold Taste Number (TTN), Anselme *et al.* (1985) reported a case study which identified a burnt plastic taste and odor during the passage of drinking water through a 300 meter polyethylene pipe. The burnt taste and odor was present after four months of water use. The main compounds identified using closed loop stripping and simultaneous distillation extraction, 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 hydroxyl toluene. Oxidation of the internal surface of the pipe during the extrusion process also accounted for leaching of polar oxidation by-products that affect T&O properties. Extrusion is the process that molds plastic into a form with a constant cross section, such as a pipe (Meola *et al.*, 2004).

As in similar cases, the problem was solved by replacing the pipe used in the system. Studies done by the Centre de Recherche et de Controlle des Eaux in collaboration with the polyethylene pipe manufacturers showed that good extrusion conditions are needed to prevent pipe oxidation. Insufficiently controlled conditions result in the formation of oxidation products such as aldehdyes, ketones or quinones which convey a burned-oil or sweet flavor to drinking water (Rigal, 1992).

Villberg *et al.,* (1997) investigated the off-flavor and off-odor compounds in high density polyethylene resin (HD-PE) used for pipe manufacturing. The volatile organic compounds from

polyethylene were identified using gas chromatography-mass spectrometry-sniffing system and gas chromatography-fourier transform infrared spectroscopy-sniffing system. Two experimental conditions were analyzed in an attempt to identify volatile organic compounds from HD-PE; pure samples of high density polyethylene granule and odor free water in which granules had been shaken for 4h. Further characterization of the odors was carried out by a trained panel. Panel members analyzed 5ml of leachate water for T&O using individual descriptors. GC work identified several organic compounds that contributed T&O in samples analyzed. These include: 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 .

A similar study by Brocca *et al.* (2002) made impressive advancements in detecting 20 to 30 organic chemicals that could potentially be released by polyethylene pipe materials (PEX, PEM, PEL, cross-linked, medium density and low density respectively). The pipe materials used were all available on the Danish market for use in drinking water distribution systems. For analysis the pipe samples were filled with test water for 24 hours, flushed with tap water for 60 min and finally rinsed with test water for 2 min. Liquid-liquid extractions followed by GC-MS were the methods employed for chemical analysis. This work added needed data to understanding leaching of PE materials.

The complexity of this process was evident in that chemical structures were attributed to only ten (10) compounds with eight being positively confirmed using commercially or synthesized standards. The basic structure of the identified compounds was characterized by a phenolic ring typically substituted with hindered alkyl groups in positions 2 and 6 on the aromatic ring. In this study it was demonstrated that the compounds originated from 1) alteration or degradation products, produced from original additives during the extrusion step (200-250°C) in the pipe manufacturing process and 2) compounds were by-products or impurities resulting from synthesis of pure phenolic additives.

Further confirmation of the lab study was made by investigating the occurrence of similar compounds in water collected in situ from a newly installed pipeline distribution system made of PEX materials. The three common compounds, 3, 5-di-*tert*-butyl-4-hydroxy benzaldehyde, 3,5-di-*tert*-butyl-4-hydroxy acetophenone and cyclo hexa 1,4,dien,1,5-bis (tert-butyl),6-one,4-(2-carboxy-ethylidene) found in the lab samples were found in the in situ samples. The common polymer additives investigated in this study include Irganox 1010, Irganox 1035, Irganox 1076 and 2,6-di-*tert*-butyl-4-methyl phenol.

More recent studies done in Norway (Skjevral *et al.*, 2003), using the leaching protocol EN 1420, showed that HD-PE leached 2,4-di-tert-butyl-phenol (2,4-DTBP), and 2,6-di-tert-butyl benzoquinone (2,6-DTBQ), known degradation products of the antioxidant Irgafos 168® and Irganox 1010® and Irganox 1076® respectively. In addition several esters, aldehydes, ketones, aromatics and terpenoids were detected. Cross-bonded polyethylene (PEX) leached methyl-tert butyl ether (MTBE), tert-butanol, 4-butoxy phenol while polyvinyl chloride (PVC) leached hexanal, octanal, nonanal, decanal. The T&O identified in leachate samples were quantified using the threshold flavor number (TFN) and the threshold odor number (TON). TFN/TON represents the highest dilution of a sample in which a perceptible flavor or odor is detected by the panelists. A TON >3 represents an undesirable odor.

The possibility of increasing the persistence of antioxidants within a pipe structure has been explored. Two approaches to increase the persistence are to 1) produce antioxidants of high molecular weight and therefore low volatility and extractability and 2) chemically bind the antioxidant to the polymer, guaranteeing its permanence in the polymer matrix. A study by Romanian researchers explored the melt grafting of monomeric antioxidants onto low molecular weight polyethylene and high density polyethylene as a feasible industrial application to produce polymer-bound antioxidants. The study successfully showed that antioxidant moieties chemically linked to the polyethylene chains preserved their antioxidant action (Munteanu *et al.,* 1991). Studies have also examined the synthesis of high molecular weight stabilizers using sterically hindered phenols and sterically hindered amines (Kósa *et al.,* 2004). This area of research is novel and certainly warrants further studies. A comprehensive review by Al-Malaika (2003) on the oxidative degradation and stabilization of polymers summarizes in length the

techniques and advantages involved with these approaches. The ability to limit antioxidant and stabilizer leaching would significantly reduce the VOCs in drinking water, hence the T&O episodes associated with these compounds.

Permeation of organic chemicals through pipe walls is another mechanism by which plastic pipes can lead to contamination of drinking water and produce T&O problems. Polyethylene pipes are more highly susceptible to permeation than PVC pipes. The type of PE, method of production, pipe diameter and rate of flow of water are factors that affect the permeation of PE. Many laboratory studies and field experiences have indicated that BTEX compounds (benzene, toluene, ethylbenzene and xylenes), which are found in petroleum, readily permeate PE pipes. There are several reported incidents of permeation affecting drinking water quality (T&O) (Goodfellow *et al.,* 2002). One such reported event involved a 1998 spill of solvents onto land at an industrial site leading to permeation of plastic water pipes. The consumers complained of a strong smell and unpleasant taste. Precautions should be taken when installing plastic pipe materials for transport of potable water through distribution systems. It is not a wise decision to use plastic materials in areas that are prone to contamination from organic chemicals. In the case of a reported T&O incident the utility and consumer should be aware of the potential for plastic pipe materials to permeate organic chemicals from the surroundings.

The potential of plastic materials such as HD-PE, PEX and PVC to contribute odors to drinking water by leaching VOCs has been clearly delineated. The presence of a high VOC was directly related to a high TON for several tested materials (Skjevrak *et al.*, 2003). The rate of migration of VOCs was shown to accelerate in the presence of chlorine disinfectant (Marchesan *et al.,* 2004). These studies confirm the importance of performing leaching tests in all types of water. The studies further demonstrates that pre-testing of materials using an organoleptic assessment is essential as part of a complete material evaluation.

STANDARD TESTING METHODS FOR DISTRIBUTION SYSTEM MATERIALS

T&O episodes related to distribution and plumbing materials can be lessened if standard protocols are implemented which assess the potential of these materials to contribute to T&O in drinking water. Historically, the Europeans, Australians and New Zealanders, have pursued T&O issues more aggressively than in the United States. This is accurately illustrated by the low levels of chlorine that can be tolerated in drinking water in these countries (Piriou *et al.,* 2004).

The AFNOR XP P41 250, EN 1420-1 and BS 6920-2.2.1 are migration/leaching testing standards used in France, Europe, and Britain respectively. These standards are used to prevent inappropriate materials from being used in water distribution systems. All products used for the transport of water intended for human consumption are subject to these testing standards. These standards address water quality problems that would directly or indirectly affect human health. Tests performed include cytotoxicity, extraction of metals, growth of aquatic microorganisms, migration of specific and unknown chemicals, TOCs, and more significantly organoloeptic tests (odor, taste, color and turbidity). These tests are all regulated by appropriate governing bodies. It has been generally accepted that an organoleptic assessment is the first step in material approval for use in potable water in France and all other European countries (Rigal *et al*., 1999). The Netherlands Waterworks Testing and Research Institute (Kiwa) in accordance with EC Directive 80/778 successfully explored a strategy for localizing the causes of T&O in drinking water so as to protect consumers against potential health risk (Hans van der Jagt, 1999).

In the United States no standardized testing protocol exists that assess the potential of distribution and plumbing materials on the organoleptic properties of water. In the quest to better understand and to develop a working protocol for the United States, existing standards (British Standard 6920-2.2.1:2000, French AFNOR Standard XP P41 250, European harmonized: NF-EN 1622, PrEN 1420-1, PrEN Ed.C. draft(2001) N299, prEN 12873-1, and ANSI/NSF 61) were studied and based on findings a standard operating procedure for the analysis of organic drinking water system components was established for the utilities in the United States - Utility Quick Test (Atasi *et al*., 2003; Schweitzer *et al.,* 2004). An official test

standard has not yet been developed. Previous to this formulation only health effects were being assessed for distribution and plumbing materials through ANSI/NSF Standard 61.

Most recently the Australia/New Zealand Standard (AS/NZ 4020) has been revised. AS/NZ 4020 has several testing protocols one of which assesses materials on their ability to impact the organoleptic properties of drinking water. Unlike the other established standards, the AS/NZ 4020 assesses the impact of both plastics and metal materials on water quality. Failure rate due to T&O problems of materials assessed using the AS/NZ 4020 was significant. At least 8.5% of materials failed the organoleptic assessment despite passing previous chemical or microbiological assessments (Marchesan *et al.*, 2004). Pre-testing and certification of materials does not always guarantee that T&O problems caused by leaching of organic compounds will not occur. Significant problems may also arise from improper installation of approved materials. It is therefore imperative that materials be tested under realistic conditions and the materials used only as directed by the manufacturer.

A limitation of most of the existing standard testing protocols is the evaluation of materials in only one type of water: chlorinated or non-chlorinated. In the United States this could pose a greater problem as more utilities are moving from chlorine to chloramines as a residual disinfectant and to control disinfection by-products. For acceptable results, testing standards must encompass tests using waters of varying qualities and in the presence of different disinfectants (chlorine, chloramines). Water qualities such as pH, temperature, NOM and type of disinfectant were shown to significantly influence the type and intensity of a T&O event (Heitz *et al.*, 2002; Worley *et al.,* 2003; Whelton and Dietrich, 2004; Khiari *et al.*, 2004). This directly relates to the migration of organic compounds as outlined in a study done by Al-Malack *et al.,* (1999), when they performed experiments to investigate the effects of water quality on the migration of vinyl chloride from unplasticized PVC pipes. The parameters studied included temperature, pH, total dissolved solids and exposure time. The results showed that the unplasticized PVC pipes released more than 2.5 ppb of vinyl chloride monomer into the contact water. Variations in pH and total dissolved solids concentration had the greatest effect on the release of vinyl chloride from the PVC pipe. Increased migration of organic compounds is directly related to increase TON and TTN in drinking water (Skjevrak *et al.,* 2003).

Very little research has been done to study the effects of chloramines on distribution and plumbing materials. In comparison, research shows that chlorine can affect degradation of pipe material increasing the possibility of introducing compounds that can affect the organoleptic properties of water (Heitz *et al.*, 2002). Swedish work done by Hassinen *et al.*, (2004) presented data from a comprehensive study of the effect of chlorinated water on high-density polyethylene pipe stabilized with a combination of phenolic and phosphate antioxidants (Irganox[®] 1010 and Irgafos[®] 168). The results showed that the stabilizing system was rapidly and chemically consumed by the action of chlorinated water. The extent of degradation, studied using size exclusion chromatography and differential scanning colorimeter, was confined to the surface of the unprotected inner wall material.

An earlier detailed study by Dear and Mason (2001) provided the groundwork for this study. Dear and Mason outlined the effects of chlorine depletion of antioxidants in polyethylene pipe material. The experiments were carried out at elevated temperature, pressure and chlorine doses. The results of the study showed that the presence of chlorine in water accelerates the embrittlement process of the pipe. Chlorine diffuses through the pipe wall and consumes antioxidant leading to subsequent oxidation of the pipe material. These conclusions were made using data from a modeling study. The severity of the degradation by chlorine of the pipe depends on its end use, varying from severe in pipes used in water treatment plants to less severe in distribution systems. Further work is needed in the US to assess the properties of materials when exposed to chloramines disinfectant. This would ultimately provide valuable information to manufacturers and utilities and minimize T&O episodes that may result from leaching materials.

The utility quick test incorporates most of its criteria from the European Standard (EN 1420-1) but, allows materials to be tested in varying water qualities and disinfectants. This test follows a defined procedure of flushing, stagnation in the presence of chlorine disinfectant, and rinsing with chlorine free water (Schweitzer *et al.*, 2004). The material is tested under conditions that simulate its function in drinking water systems. Sensory analysis comprises the triangle test and FPA. Trained panelists provide descriptors that give insight into the chemical (s) present which is a useful tool for manufacturers, utilities and consumers. The utility quick test does not address

the effects of materials on the inhibition or promotion of microbial growth or the long-term chlorine demand of materials.

ROLE OF CHLORINE AND CHLORAMINES ON T&O

Chlorination and chloramination are the most widely used disinfection methods worldwide. Disinfection is mandated by the Surface Water Treatment Rule (SWTR) as a necessary process for producing drinking water suitable for human consumption. Free chlorine exists as hypochlorous acid or hypochlorite ion in water ($HOCl$, OCl^-). Chloramines are the products of reaction between free chlorine and ammonia (NH_2Cl, $NHCl_2$, and NCl_3). Chlorine has been used to eradicate most waterborne diseases and many countries require a minimal residual concentration at all times. In the United States the Safe Drinking Water Act requires a residual chorine concentration of 0.2 - 4mg/L.

Studies have shown that chlorine and chloramines may interact synergistically or antagonistically with contaminants in drinking water to increase or decrease the intensity of odors. In extreme cases the presence of disinfectants can completely eliminate odorous compounds from drinking water sources. Chlorine and chloramines have been shown to remove sulphide odors such as hydrogen sulphide and dimethyltrisulphide and cucumber odors such as trans,2-cis,6-nonadienal (Burlingame *et al.,* 1992). One study determined the sensory effects of chlorine and chloramines on geosmin and MIB (earthy/musty) odor intensities (Oestman *et al.*, 2004). The results of a Freidman test performed during the study concluded that trained panelists could effectively evaluate geosmin and MIB by sensory analysis in the presence of chlorine. At low concentrations of geosmin and MIB a slight masking of chlorine was noticed through antagonistic effects during FPA analysis. Varying concentrations of MIB and geosmin (5 to 120 ng/L) were evaluated in the presence of chlorine (0.5 to 20 mg/L) and chloramines (3 to 24 mg/L). The intensity of the earthy/musty odor decreased as the concentration of free chlorine increased. Previous work by Burlingame *et al.,* (1986) stated that water utilities used chlorine/chloramines as a mechanism to reduce or control odors from geosmin and MIB. FPA

results showed a slight trend that chlorine have may synergistic effects. The impact of chloramines on the panelist's ability to detect geosmin or MIB was less confounding.

A similar study by Worley *et al.,* (2003) showed clearly the masking effect of chlorine on the perceived odor intensity of geosmin and 2-MIB. Panelists were presented with unknown samples which included 30 ng/L geosmin and 30 ng/L geosmin in the presence of 1 mg/L chlorine. In the absence of chlorine geosmin was rated an FPA intensity of 4.1. In the presence of chlorine geosmin was rated an FPA intensity of 0.5. This work clearly showed that the presence of chlorine reduced the perceived geosmin intensity. The effect of chlorine and chloramines on the type and intensity of odors generated from VOCs present in drinking water has not been as extensively studied.

In evaluating T&O from chlorine and chloramines disinfectant it should be noted that the disinfectant themselves impart chlorinous type odors that can be detected at very low concentrations (Bruchet *et al.,* 2004). Krasner and Barrett (1984) published descriptors and odor thresholds for the different forms of chlorine and inorganic chlorine. A few of these include hypochlorous acid described as chlorine with an odor threshold of 0.28 mg/L as chlorine and monochloramine described as swimming pool with an odor threshold of 0.48 mg/L as chlorine. Odor thresholds and descriptors were also given for hypochlorite ion, dichloramine and trichloramine.

Water quality characteristics such as pH will affect the odors formed in the presence of disinfectants. Studies have shown that di and trichloramines species which form at pH 6.5 have greater odor potential than monochloramine which forms at pH 8.3 (Kajino *et al.,* 1999). Monochloramine contributes least to the chlorinous properties of drinking water. The negative and positive impacts of a type of disinfectant should be fully assessed to prevent unnecessary T&O in drinking water.

The use of chloramines as a residual disinfectant can result in free ammonia residual. Suffet *et al.,* (1995) reported an odor threshold concentration of 0.037mg/L for ammonia. Odor

descriptors for ammonia include, ammonia, rubbery, plastic, cardboard and reedy (AwwaRF, 2002).

CROSS-LINKED POLYETHYLENE – PEX

Cross linked polyethylene (PEX) developed in the 1950s in Germany has been used extensively in many parts of Europe. PEX was introduced to the US in the 1980s and has since emerged during the 1990s as one of the #1 replacements in plumbing material used for potable water systems. Several advantages such as flexibility, durability, corrosion, electrolysis and chemical resistance, low scale build up, thermal stability, high tensile strength and relatively low installation costs make PEX a very attractive material for hot and cold home plumbing systems (PPI, 2001). PEX also finds useful application in hydronic radiant heating systems, low temperature heat transfer applications, snow melting applications, ice rinks, convectors and radiators. PEX is essentially polyethylene (PE), a thermoplastic that consists of a series of ethylene hydrocarbon chains, that has undergone a chemical or physical reaction that causes the molecular structure of the polyethylene chains to link together (Peacock, 2001). The method and degree of cross-linking of the polyethylene molecules defines the characteristics of the final product. Chemical cross-linking may be subdivided into reactions that take place between the carbon backbone atoms of polyethylene chains and those that involve reactions of side groups onto the backbone.

PEX is manufactured and tested according to stringent national consensus standards: ASTM F876 and F877, PPI TR3, ANSI/NSF Standard 61. Both the product manufacturer and independent third party testing agencies conduct routine quality control and quality assurance evaluations to insure that the product meets ASTM and National Sanitation Foundation Standards. The PEX tubing or fitting once approved will bear the marking of the testing agency. Compliance with the standards ensures the end user of safety and quality. Additionally, PEX is included in all of the major model plumbing codes used in the United States and Canada; Canadian Standards Association (CSA), International Association of Plumbing and Mechanical Officials (IAPMO), Southern Building Code Congress International (SBCCI), Building Officials

and Code Administrators (BOCA), International Plumbing Code (IPC) and National Standard Plumbing Code (NSPC), and approved by the department of Housing and Urban Development (HUD) for hot and cold potable water plumbing use.

The three most common technologies utilized to make PEX are:

1)   Engel (peroxide) process produces PEX-a and which uses peroxide free radicals for cross-linking. Peroxides are heat-activated chemicals that generate free radicals (initiation reaction). Radicals are carbon based entities which possess a free electron. The radical abstracts a hydrogen atom from one of the carbon atoms in the PE chain, leaving a localized PE radical. This reactive species can then form a cross linking bond with another PE radical or abstract hydrogen from another PE strand creating another free radical.

The most common peroxide used is [2,5-dimethyl-2, 5-di-(t-butylperoxy)hexane].   At high temperatures typically between 180°C and 220°C, the peroxide decomposes and forms free radicals. Peroxide is either adsorbed onto PE flakes or pellets. The mixture is usually processed in a chamber containing a reciprocating piston to quickly melt the PE (Engel process) (Jee *et al.,* 1997).

As it requires the reaction of two unpaired electrons on adjacent chains to form a cross-link, theoretically each peroxide group can generate one cross-link.   One drawback of peroxide-initiated cross-linking is the presence of residual by-products in the final product. Many of these products are ketones that impart a strong odor to fabricated items (Peacock*, 2001*).

2)   Dow Chemical developed moisture-cured cross-linking in the late sixties. Two major variants, the Monosil process and the Sioplas process, have emerged and produce PEX-b. The Monosil technique introduces vinylsilane into the polyethylene during conventional extrusion of polyethylene pipe. In the Sioplas technique, however, PE resin first compounded with vinylsilane and a peroxide. This compound combines with a catalyst master batch, which is then fed into the extruder for conversion into pipe. In both cases, the object is to graft a reactive silane molecule to the backbone of the polyethylene. This is accomplished by a radical reaction

that grafts vinyl siloxane onto polyethylene molecules. The radical initiator is typically an organic peroxide—often dicumyl peroxide— with vinyl trimethoxysilane being the siloxane of choice. In the presence of moisture, trimethoxysilane groups attached to adjacent chains undergo hydrolysis, eliminating methanol to form siloxane bridges. Each silane group can react with up to three others, generating a complex bridging group that may link several polyethylene chains. Under ambient conditions the cross-linking reaction occurs slowly, limited by diffusion of water into the sample and a low reaction rate (Jee *et al*, 1997; Peacock, 2001).

The pipe then cures in a high-temperature water bath for several hours, or goes into a steam sauna so the material can be cross-linked. The important difference between the variants is that the Monosil process is a one-step reaction and the Sioplas process has two steps.

3)   Radiation process which subjects the polyethylene to high-energy electrons. For optimum efficiency, ultraviolet radiation initiated cross-linking requires the presence of a photoinitiator (sensitizer) and a bridging agent (cross-linker, cross-linking agent). Examples of photoinitiators include benzophenone, 4-chlorobenzophenone, and sulfuryl chloride triallyl cyanurate and triallyl isocyanurate are effective bridging agents (Peacock, 2001).

In European standards these three methods are referred to as PEX-a, PEX-b and PEX-c respectively. Despite the variations in mechanisms of cross-linking all PEX material is subjected to standard testing protocols for durability and strength as outlined by the plastic pipe institute (PPI). There is however no standardized testing protocol in the US for evaluating the T&O properties of the PEX materials prior to installation in home plumbing systems.

METYL-*tert*-BUTYL ETHER AND ETHYL-*tert*-BUTYL ETHER

A study by Skjevrak *et al*., (2003) assessed the odor from PEX material using the quantitative standard threshold odor number (TON) concept. TON $\geq$ 5 were observed for PEX materials tested. This research study detected several oxygenated components and identified MTBE as a major contributor to taste and odor and thus the high TON values. The Environmental Protection Agency in 1997, recommended that MTBE concentrations in drinking water should not exceed

20-40 µg/L. There is the possibility that materials used during the PEX manufacture and cross-linking process may contribute the compounds that resulted in the presence of MTBE in the drinking water samples.

MTBE is a colorless, liquid hydrocarbon that has been used as an octane booster in gasoline since the 1970s. The two major concerns regarding MTBE from a public health standpoint are (1) Risks to human health, and (2) consumer acceptance of drinking water containing MTBE in terms of odor and taste. Due to its chemical properties, MTBE can be both smelled and tasted by many people at levels below both the federal and state health advisory levels. Therefore, to address the potential adverse affect of MTBE on the aesthetic quality of water, it was determined that a secondary MCL should be established. Adoption of a secondary MCL for MTBE would ensure that consumers are not exposed to drinking water with objectionable taste and odor related to MTBE contamination and would also ensure that MTBE levels are below current, and presumably future, health-based advisory levels.

According to the Environmental Protection Agency (EPA), there is a growing need to characterize the potential risks of oxygenates in drinking water. Only limited information exists on the health impact of MTBE on humans and regulators are still struggling with deciding on levels that would be acceptable or unacceptable from the standpoint of public health or consumer acceptability. The uncertainties in assessing the health risks of MTBE are reflected somewhat in the various guidance values (e.g., advisories, action levels, standards) that have been issued by individual states, ranging at one time from 35 µg/L in California to 230 µg/L in Illinois .

Literature shows that only two MTBE taste and odor studies have been conducted. A study done in Great Britain by Young *et al.,* (1996) evaluated the taste and odor of a number of drinking water contaminants including MTBE. The results of this study showed that the thresholds for odor and taste of 15 and 40 µg/L, respectively, were detected by a sizable proportion of the assessment panel (33 and 44 percent). The second reported study was carried out by the Orange County Water District in California. The results of the study by Shen *et al.,* (1997) showed that MTBE odor may be detected at levels as low as 2.5 µg/L. Based on these studies an MCL of 5 µg/L was considered adequate.

Because of the relative scarcity of future low priced, domestically produced methanol for MTBE and the likely trend toward lower volatility gasoline, ETBE has emerged as a best fuel blending candidate for the future. Therefore due to its less widespread use ETBE has not been extensively monitored in drinking water. There are no reported taste and odors studies evaluating the effects of ETBE on consumer acceptance of drinking water. However it is expected that interest in ETBE will increase significantly in the future (Title 22, California Code of regulations).

SIGNIFICANCE OF RESEARCH

This research project is geared towards enhancing the understanding of the behavior of materials in affecting T&O of drinking water when exposed to varying water qualities in the United States. In evaluating the distribution system work has focused mainly on materials contacted before the water enters the consumers home drinking water infrastructure such as water mains, service pipes, storage towers, and (Rigal *et al.,* 1999). The sustainability of materials for home plumbing systems use as relates to T&O properties has not been widely explored. The growing need for more detailed studies of common household plumbing materials is evident based on limited data. The applicability of the Utility Quick Test to assess materials for potential T&O properties is highlighted.

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CHAPTER II

PEX PLUMBING MATERIAL CAN CONTRIBUTE CHEMICAL/SOLVENT ODOR TO DRINKING WATER

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Abstract

A commonly used residential and commercial plastic plumbing material, cross-bonded polyethylene (PEX-b) produced by the Silane process, was investigated using the principles outlined by the Utility Quick Test (UQT). The UQT is a migration/leaching protocol recommended for use by utilities when evaluating T&O properties of materials prior to installation in distribution systems. Its objective is to assess the type of odors generated when synthetic plumbing material is repeatedly exposed to residual disinfectant chlorine or chloramines under static conditions.

After exposure of the new PEX material to chlorine, chloramines or no disinfectant, a trained panel described the odors in the leachate as "chlorinous" if chlorine or chloramines were present and "chemical–like" with descriptors of sweet, bitter, chemical, solvent, plastic, burnt and mechanical. The presence of disinfectant, chlorine or chloramines, did not appear to significantly alter the odor characteristics or intensity of the PEX odor. The results showed that the "chemical-like" odors persisted even after multiple flushing periods. 2-Ethoxy-2-methylpropane, commonly called ETBE, was identified as a major contributor to the described odor from the PEX material. SPME/GC-MS concentrations of ETBE from pipe samples ranged from a low of 23 μg/L to > 100 μg/L. The concentrations decreased with increased flushing. Panelists were able to smell ETBE at a concentration of 5 μg/L and rated this sample an FPA of 2.5. This research demonstrates that water quality affects the type and intensity of odors being formed in distribution systems. The need for taste and odor testing of plumbing materials prior to installation in residential housing systems or the need to flush to remove odors prior to use is necessary.

Keywords

Chlorine; chloramines; ETBE; odor; PEX; utility quick test; volatile organic compounds.

INTRODUCTION

The distribution system, including home plumbing materials, has been identified as a major contributor to deteriorated water quality and taste and odor (T&O) in drinking water (Khiari *et al.,* 2004, Hem *et al*., 2002, Dietrich *et al.,* 2004, Durand *et al.,* 2004). In evaluating the distribution system, work has focused mainly on materials contacted before the water enters the consumers home drinking water infrastructure such as water mains, service pipes and storage tanks (Rigal *et al.,* 1999 and Tomboulian *et al.,* 2004). The sustainability of materials for home plumbing systems, as relates to T&O properties, has not been widely explored. Studies have shown that many T&O episodes result after installation of new material (Khiari *et al.,* 1999). A lack of understanding of the possibility of these materials to contribute odor could result in dissatisfied consumers or unnecessary panic in a community. In this era of heightened terrorism understanding all potential sources of T&O to drinking water is an important aspect of our security.

Historically, home plumbing systems have utilized galvanized steel, copper and cPVC. Several complexities have resulted in a decline in usage of these materials. Cross linked polyethylene (PEX) emerged during the 1990s as one of the replacements in plumbing material for potable water systems. Several advantages such as flexibility, durability, corrosion resistance, low scale build up, thermal stability and high tensile strength makes PEX a very attractive material for home plumbing systems. PEX is essentially polyethylene (PE), a thermoplastic that consists of a series of ethylene hydrocarbon chains, that has undergone a chemical or physical reaction that causes the molecular structure of the polyethylene chains to link together (Peacock, 2001). The method and degree of cross-linking of the PE molecules defines the characteristics of the final product. Despite the variations in mechanisms of cross-linking all PEX material is subjected to standard testing protocols for strength and durability as outlined by the plastic pipe institute (PPI). There is, however, no standardized testing protocol for evaluating the T&O properties of the PEX materials prior to installation in home plumbing systems.

Research has shown that the synthetic materials such as PE and PEX are capable of leaching volatile organic compounds (VOCs) (Broccas *et al*, 2002, Skjevrak *et al*., 2003). These polymer

materials are usually coated with plasticizers, antioxidants and application solvents that serve as radical scavengers that inhibit oxidation of the plastic pipe. These additions to the polymer material can directly or indirectly result in T&O issues in drinking water. One study assessed the odor from PEX material using the quantitative standard threshold odor number (TON) concept. TON ≥ 5, which exceed the Flavor Profile Analysis (FPA) secondary MCL of TON=3, were observed for PEX material tested (Skjevrak *et al.*, 2003).

In addition there is the possibility that materials used during the PEX manufacture and cross-linking process may contribute compounds that cause T&O episodes when exposed to drinking water. Chemical Accident Reconstruction Services, Inc (Chemaxx) in 2001 investigated an incident of water contamination from cross-linked polyethylene tubing installed in newly constructed homes in California. Consumers complained of a "gasoline" type T&O in their drinking water. The investigation identified the presence of *t*-butanol and MTBE, breakdown products of the cross-linking catalyst, *t*-butyl peroxide. This negative implication of PEX usage is the cause of ongoing debates in California surrounding the use of PEX as a household plumbing material.

However, few studies have attempted to use FPA to characterize the odors generated when VOCs leach from PEX materials. Qualitative descriptors and quantitative intensities are inherent in the standard FPA method. To date the work done has not successfully linked a specific compound to a described odor, although it has been shown that odors in PEX do occur. Additionally, little has been done to evaluate the role of disinfectants in affecting the odors generated from PEX material. Water quality parameters such as pH, temperature, NOM and type of disinfectant have all been shown to significantly influence the type and intensity of T&O compounds and events (Heitz *et al.*, 2002; Worley *et al.*, 2003; Whelton and Dietrich, 2004; Khiari *et al.*, 2004). Knowledge of the effects of type of disinfectant on water quality is becoming more critical as more utilities are switching to chloramines for disinfection and DBP control.

The goal of this research was to assess the type and intensity of odors generated when PEX plumbing material was exposed to tap water under static conditions. Specific objectives were to:

determine the odor characteristics and intensities of any leached odorants when drinking water contacted with PEX material; examine the role of chlorine and chloramines in the leaching of odorous chemicals; attempt to identify and link a specific compound to the odor generated in drinking water from PEX exposure. To achieve these objectives, the PEX material was exposed to different water qualities using the utility quick test (UQT), a standard operating leaching/migration protocol established for utilities in the United States (Khiari *et al.*, 2004).

MATERIAL AND METHODS

Cross-linked polyethylene -10 feet Lengths of PEX ¾ inch pipe were purchased at a local home department store. The PEX material was certified according to NSF-61 standards, based on health effects, for use in hot/cold potable water systems. The PEX material utilized was manufactured using the silane cross linking procedure (PEX-b according to European standards).

Migration Protocol - 8 feet lengths of PEX pipe were used to accommodate sample volume for analysis. Each pipe length was flushed for three hours, disinfected with 50 mg/L free chlorine and rinsed according to the leaching protocol of the UQT. Separate experiments consisted of dosing the experimental water with no disinfectant (control), 2 mg/L free chlorine or 4 mg/L chloramines as chlorine. All experiments were performed at room temperature and pressure. For each experiment synthetic tap water was made up using nanopure water and salt concentrations typical of drinking water in the Eastern United States. The following concentrations of ions were generated; 8 mg/L Mg^{2+}, 46 mg/L SO^{2-}_4, 20 mg/L Na^+, 0.05 mg/L Al^{3+}, 11 mg/L Ca^{2+}, 2.6 g/L Si,, 4 mg/L K^+, 1.4 mg/L NO_3^- as N, 10.0 mg/L Cl^-, 0.002 mg/L PO_4^- as P. No additional TOC was added to the water resulting in water of very low TOC concentrations (0.1 - 0.2 mg/L); alkalinity 34 mg/L as $CaCO_3$, and pH range 7.8-8.0. The PEX pipe material was filled completely with experimental water and sealed using Teflon lined VOA vial stoppers and parafilm "M" paper and left under static conditions for three consecutive periods. A fresh batch of experimental water was used to refill the pipe section after each stagnation period. The exposure time per flush varied between 96 hours (4 days) and 72 hours (3 days). Controls for each experiment were performed by placing experimental water in standard

500 mL glass Erlenmeyer flasks that were wrapped with aluminum foil paper to prevent exposure to light, and then sealed with glass stoppers.

Flavor Profile Analysis -Ten (10) research students and faculty at Virginia Tech were recruited and trained for several weeks in FPA. This training and research protocol was approved according to the standards of the Virginia Tech Institutional Review Board for human subjects. For FPA analysis of samples, 4-6 members were present at all times. The procedure for FPA analysis was followed from standard methods 2170 (AWWA, 1993). Test sample (200 mL) placed in 500 mL Erlenmeyer flasks was analyzed by panelists at temperature of $45^{\circ}C$.

SPME/GC-MS Analysis - Solid phase microextraction holder and 75 μm Carboxen™-PDMS coating fibers were purchased from Supelco (Bellfonte, PA, USA) for analysis of VOCs. The SPME conditions were optimized by the addition of 6 g of NaCl to 30 mL of sample water placed in a 40 mL VOA vial. The sample was stirred using Teflon coated magnetic stir bars at $50\ ^{\circ}C$ for 20 minutes during which time the fiber was injected into the 10 mL sample headspace for sorption. 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 $^{\circ}C$ hold for 7mins then ramped from 60 $^{\circ}C$ to 120 $^{\circ}C$ at a rate of 10 $^{\circ}C$/min and finally from 120 $^{\circ}C$ to 260 $^{\circ}C$ at a rate of 20 $^{\circ}C$/min. Samples were allowed to desorb for 3 mins. All samples were analyzed within 2 days of collection.

Quantification of ETBE -100 µg/mL in Methanol stock tert-Butyl-ethyl ether (ETBE) (CAS#637-92-3) was purchased at Chem Service, Inc (West Chester, Pa). The GC/MS was operated at the set temperature program and monitored for previously identified ions m/z 57, 59, 87 in ion selective mode (59 being the major peak). ETBE eluted at approximately 2.83 mins. To quantify the concentration of ETBE in the samples, a standard curve was prepared using the same experimental SPME conditions as the samples. The standard curve for ETBE was determined by preparing different liquid-phase concentrations in synthetic water with no disinfectant; 5, 50, 100 and 150 µg/L. The amount of compound that was sorbed onto the fiber

was analyzed by GC/MS, and a linear curve was obtained. The calibration curve was used to obtain the concentrations of ETBE in the experimental pipe samples analyzed.

RESULTS AND DISCUSSION
FPA analysis of PEX leachate

Analysis of the samples after exposure to the PEX material clearly demonstrated the presence of a distinct odor as summarized in Table 2-1. Although the descriptors used varied among panelists the overall odor can be summarized under the general category of "chemical/solvent". This odor was perceived as being either "sweet" or "bitter" by the panelists. The descriptors used to characterize the odor were consistent between flushes and within a panelist.

Table 2-1. **Descriptors used to describe the PEX odor generated after each exposure period (1st flush - 4 days; 2nd flush 3 days; 3rd flush 3 days)**

Flush Period	No Disinfectant	Chlorine Disinfectant	Chloramines Disinfectant
First flush	alcohol	alcohol/sweet chemical	alcohol/chemical
	sweet chemical	plastic	bitter mechanical
	burning/ plastic	glue	glue
Second flush	spicy sweet chemical	spicy sweet chemical	spicy chemical solvent
	bitter mechanical	chemical	bitter chemical
	sweet chemical/fruity	sweet chemical fruity	sweet chemical fruity
Third flush	sweet chemical fruity	sweet chemical fruity	sweet chemical fruit
	almond	burning plastic pipe	almond
	rotten swampy	plastic pipe	plastic

The overall average intensities of the odor are shown in Figure 2-1. FPA intensities ranged from a low of 2 to a high of 6 in some cases. Odor intensities were rated using the FPA intensity scale adapted from the food and beverage industry. This scale ranges from 0 (odor free) – 12 (strong). However it was observed during analysis of the water samples that panelists rarely utilized the higher end of the scale. Strong odors were rated with intensities ranging from 3 - 6 depending on the sensitivity of the panel member. In Figure 2-1 an odor rated FPA 3 was considered

undesirable. The presence of the residual disinfectant chlorine or chloramines did not alter the "chemical/solvent" odor intensity rating of the PEX pipe samples to any great extent. After each flush period there was a decline in residual chlorine and chloramines concentration. The decreasing trend in disinfectant concentration was similar to the trend noticed in the control samples. The data does not show a clear overall trend of antagonism or synergism of chlorine or chloramines on the PEX odor although some panelists referred to the chlorine odor as chemical and vice versa. Results also showed that both in the presence and absence of disinfectant the panel sometimes described a "burning" sensation in addition to the "chemical/solvent" characteristic odor. The results show that the "chemical-like" odors persisted even after the third flush period for each disinfectant. Previous work has described a burning plastic odor from polyethylene pipes used in distribution systems (Anselme *et al.,* 1985)
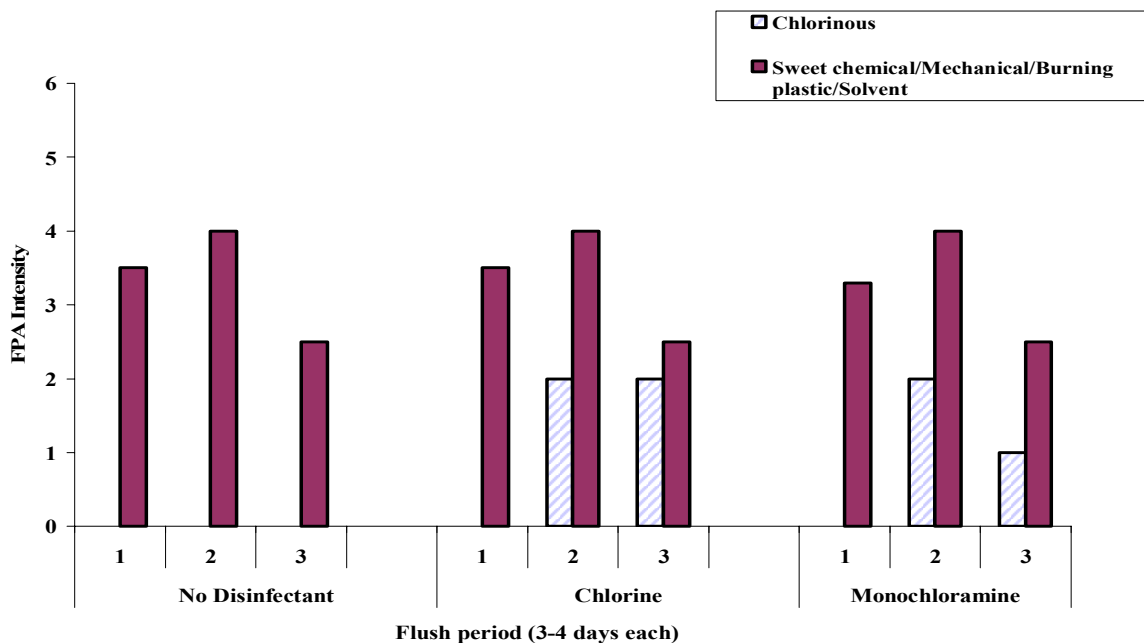
Figure 2-1.   Average FPA intensities of odor generated by PEX material exposed to water containing no disinfectant, 2 mg/L free chlorine and 4 mg/L chloramines as chlorine

Identification of odor compounds

Further work was done to identify potential odorous compounds in the PEX leachate samples using SPME/GC-MS. Analysis of the results showed the repeated presence of the oxygenate 2-ethoxy-2-methylpropane, commonly known as ETBE (ethyl-t-butyl ether). MTBE, which has

been reported to be in PEX pipes, was clearly not present in the PEX used for this research. Further confirmation of the lab study was made by identifying the occurrence of ETBE in water collected in situ from newly installed domestic pipeline distribution system made of PEX materials. SPME/GC-MS response for ETBE is shown in Figure 2-2. Several other organic compounds were also identified similar to Skjevrak *et al*., (2003). Aqueous ETBE concentrations ranged from a low of 23 µg/L to > than 100 µg/L in the flush water. As seen in Figure 2-3 the concentration of ETBE decreased with continued exposure of the pipe material to experimental conditions. Higher concentrations were obtained in the absence of disinfectant. This could be explained using previous work which showed that the presence of chlorine lowers the measured concentrations of organics when using SPME for analysis (Lin *et al.,* 2003). It could also mean that ETBE is being degraded by the presence of chlorine or chloramines. These data was generated via one UQT therefore repeatability of this trend is not known. Further studies are needed to verify the applicability of these assumptions to ETBE.
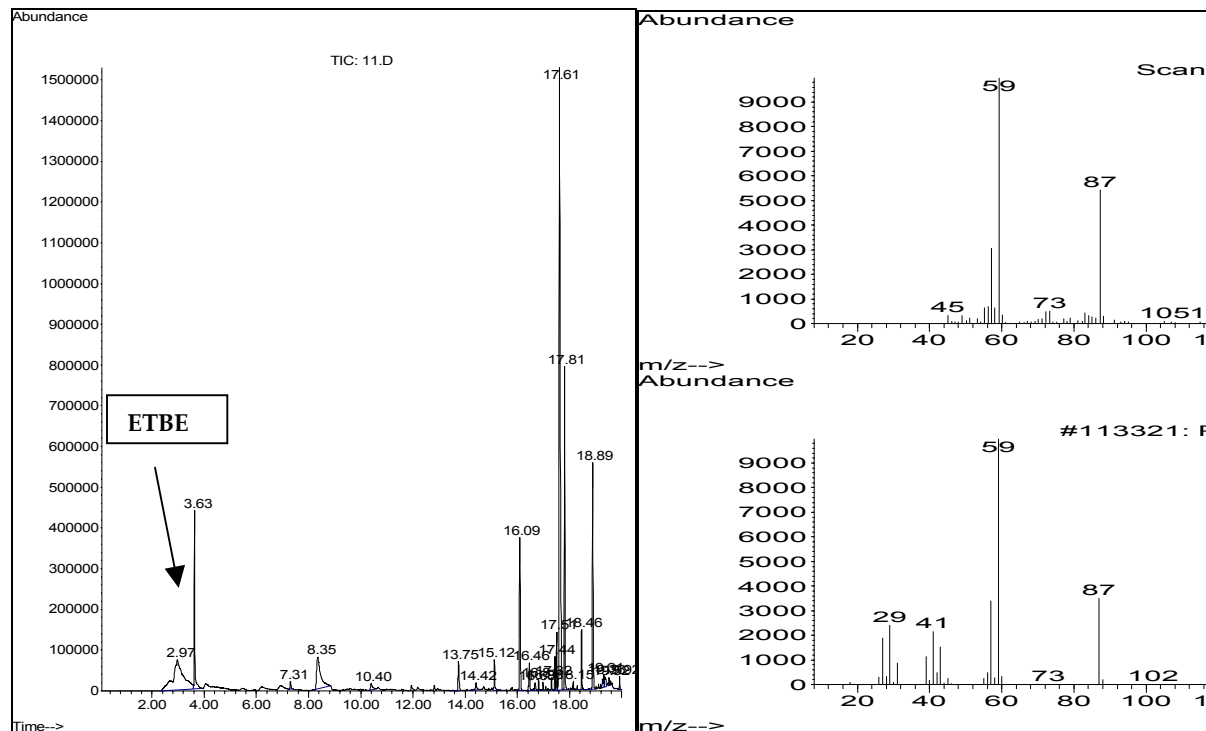
Figure 2-2.   SPME GC/MS response for 2-ethyl-t-butylether (MW 102) in PEX pipe samples and corresponding mass spectrum

ETBE Concentrations
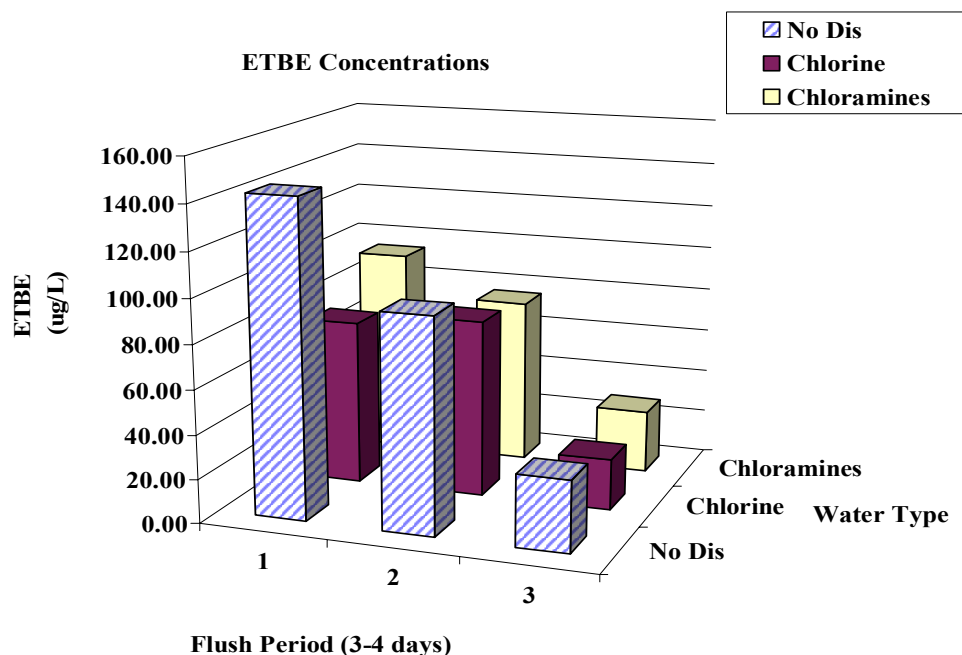
Figure 2-3.   **Concentration of ETBE in the no disinfectant, chlorine and chloramines samples after each flush period**

Odor Characteristics of ETBE

Once ETBE was identified as a consistent contaminant in the water samples from PEX pipe, the next step was to determine whether it could be a potential source of the chemical/solvent odor. Panelists were given known concentrations (5 to 50 µg/L) of the ETBE standard solutions in synthetic tap water alone or with 2 mg/L Cl_2 and 4 mg/L NH_2Cl as Cl_2 and asked to describe the odor and rate its intensity. Similar "solvent/chemical" descriptors as summarized in Table 2-1 were used to describe the odor of the standard ETBE solutions.   The lowest concentration analyzed (5 µg/L) was rated an FPA of 2.5. A previous study by Young *et al.,* (1996) resulted in a proposed secondary MCL for a similar oxygenate, MTBE, of 5 µg/L in California. Similar to the PEX pipe samples, panelists recorded a burning sensation during FPA analysis of ETBE samples. This burning sensation was experienced by most panelists and occurred in the absence or presence of disinfectant. It is of interest to compare the odor descriptor and intensity of ETBE in synthetic tap water alone or with disinfectant.

The effect of low and high residual chlorine and chloramines disinfectant concentrations on the FPA odor intensity of a 50 µg/L ETBE standard solution was examined.

Table 2-2. Average FPA intensities for 50 µg /L ETBE in synthetic water

Synthetic Tap Water Solution	FPA Intensity	
	Chemical/Solvent* Odor	Chlorinous Odor
No Disinfectant	3.4 ± 1.5	Not Detected
Free Chlorine		
0.7 mg/L	2.5 ± 1.3	3.7 ± 0.58
2.0 mg/L	1.5 ± 0	3.8 ± 1.3
MonoChloramine		
2.0 mg/L	4.6 ± 2.6	Not detected
4.0 mg/L	3.2 ± 0.8	Not detected

* Chemical odor = sweet, bitter, burning

The results recorded in Table 2-2 show that the ability of panel members to detect the ETBE odor was reduced in the presence of chlorinous odor from free chlorine. These results do not correspond directly with those of the PEX pipe sample (Figure 2-1) where it was observed that FPA intensities remained constant despite the presence of disinfectant. In understanding this it is important to note that several other organic compounds were detected in the PEX leachate and may be contributing to the overall chemical odor intensity of the PEX samples. Interestingly, some panelists were able to single out a separate strong chlorine odor in the presence of chlorine disinfectant. For others it was difficult to dissociate the solvent and the chlorine odor. This chemical/solvent odor was rated higher when the chlorine concentration was low. No chlorinous odor was detected when chloramines disinfectant was used, even though chemical analysis showed chloramines present. The chloramines odor therefore did not mask the ETBE odor. An average FPA intensity of 3.4 for the chemical odor was reported in the absence of disinfectant.

CONCLUSION

The results of this study show the potential of a type of silane PEX material to contribute a "chemical/solvent" odor, perceived as "sweet" or "bitter", with a strong burning sensation, to drinking water both in the presence and absence of disinfectant. This work supports the growing need for T&O testing of household plumbing materials prior to installation. Evaluating and understanding the potential of home plumbing materials to impair the T&O properties of drinking water will collectively benefit material manufacturers, utilities and most importantly, the consumers. Plastic pipe manufacturers must carefully consider the compatibility of the additives and other chemicals used in pipe processing with various drinking water qualities. This is especially important with PEX material since several methods of processing exists. All PEX materials will not display identical characteristics under similar conditions. The current solution to these odor problems is extensive flushing prior to use, which is not economical and does not adhere to the principles of water conservation and environmental sustainability. This area of research warrants further studies.

ACKNOWLEDGEMENTS

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CHAPTER III

CROSS-LINKED POLYETHYLENE PIPE: A COMPARISON OF MANUFACTURING PROCESSES ON DISINFECTANT DEMAND, ODORS AND LEACHING OF ORGANIC CHEMICALS

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Abstract
Cross-linked polyethylene (PEX) pipe is used for the transport of potable water in home plumbing systems. PEX pipes manufactured by the silane (PEX-b) and peroxide (PEX-a) cross-linking technology were investigated using the principles of the utility quick test (UQT). The silane manufactured PEX pipe contributed more intense odors to drinking water in the absence of chlorine and chloramines disinfectant than peroxide manufactured PEX. 2-Ethoxy-2-methylpropane (ETBE) was found to contribute significantly to the odor characteristics for PEX-b. Overall silane PEX-b had a greater effect on water quality properties such as odor, TOC and residual disinfectant demand than peroxide linked PEX-a. PEX pipes did not contribute any significant trihalomethanes (THMs) in drinking water. This study showed that the type of PEX material used in home systems will directly determine the effects on drinking water quality.

Key Words
Silane-PEX; peroxide-PEX; utility quick test; flavor profile analysis; TOC; chlorine; chloramines

INTRODUCTION

The use of plastic pipe in commercial and residential applications for potable water transport systems has seen incredible growth during the past years. Cross-linked polyethylene (PEX) is the most recent material incorporated into the US market (> 10 years). Although new to the USA, PEX has been used in Europe for several decades. Currently it is estimated that 12% of residential homes in the USA use PEX plumbing material. The advent of increase PEX usage in the USA has been somewhat due to the problems associated with pinhole leaks from copper

corrosion and leaching of lead from lead containing materials. PEX is highly resistant to corrosion and scale build-up therefore suitable in areas with aggressive water types providing a great alternative to materials such as copper (Jee *et al.,* 1997). It is expected that PEX application in residential and commercial plumbing systems will show rapid continued growth in future years.

Very few studies have examined the sustainability of PEX material when used in drinking water infrastructure. Researchers in Norway were the first to extensively investigate the ability of PEX pipes, used in in-house installations, to leach volatile organic compounds (VOCs) and subsequently impart taste and odor (T&O) to drinking water (Skjevrak *et al.,* 2003). This study utilized an existing standard protocol (EN 1420-1) to test various PEX materials. Results showed that PEX contributes an odor of Threshold Odor Number (TON) ≥ 5. According to standards in the United States this is unacceptable based on a secondary Maximum Contaminant Level of TON = 3 (USEPA, 1979a). Chemical analysis identified the oxygenate methyl t*ert*-butyl ether (MTBE) as the major VOC component in water exposed to the PEX pipes. These findings in Norway prompted the need to investigate the potential of newly installed PEX material to alter drinking water characteristics under varying water quality conditions.

Additionally, the need for extensive evaluation of PEX material was confirmed by the recent findings of MTBE in drinking water obtained from newly constructed homes using PEX plumbing in California (Chemaxx, 2001). After extensive evaluations PEX material was identified as the most likely source of the MTBE contamination. However the issue of uncertainty as to whether the correct source was identified arises. Data collected by regional water quality control boards and drinking water utilities indicate that ground and surface water contamination of MTBE occurs in the Northeast and mid-Atlantic regions as well as California and has been detected in community water systems (Zogorski *et al.,* 2002). The findings of MTBE in drinking water and the possible connection to PEX pipes, sparked heated debates over the environmental and public health implications of using PEX materials in potable water systems (DeRosa, 2004). In November 2004, the first ever appellate ruling applying the California Environmental Quality Act was ordered for building materials, such as PEX. Recent

rulings have allowed the use of PEX material in Californian homes, however the negative stigma surrounding its application still lingers.

The implication of PEX as a viable source of MTBE in drinking water warrants investigation considering that historically MTBE in drinking water has been attributed mainly to fuel spills, leaking underground storage tanks and the release of unburned fuel directly into the atmosphere or surface waters. MTBE imparts T&O to drinking water at concentrations as low as 2.5 µg/L (Shen *et al.,* 1997). This value is well below US Environmental Protection drinking water consumer advisory concentrations of 20 to 40 µg/L, which is based on taste and odor thresholds (USEPA, 1997). Another important factor to be considered in regards to MTBE is the possible human health effects. The EPA classifies MTBE as a potential carcinogen. However, due to insufficient toxicity data no health advisory standards have been finalized.

Considering that there are fundamental differences between each PEX manufacturing technology it would be expected that the ability of PEX pipe to affect drinking water quality would vary based on manufacturing type. Three characteristic technologies exist for manufacturing PEX. These include (Peacock*,* 2001; Jee *et al.,* 1997):

(1)   Engel (Peroxide) process which requires an initiator in the compound, generally an organic peroxide that generates free radicals for cross-linking. Peroxides are incorporated during the extrusion process and cross-linking is achieved by heating the polyethylene (PE) above the decomposition temperature of the peroxides to create the 'free radicals'. The radical abstracts a hydrogen atom from one of the carbon atoms in the PE chain, leaving a localized PE radical. This reactive species can then form a crosslinking bond with another PE radical or abstract hydrogen from another PE strand creating another free radical. Cross-linking process occurs while the material is in its amorphic or 'hot' state.

(2)   Silane process, involves grafting a reactive vinyl silane molecule to the backbone of polyethylene. There are two major variants, the Monosil process and the Sioplas process. The Monosil technique introduces vinylsilane into the polyethylene during conventional extrusion of polyethylene pipe. In the Sioplas technique PE resin is first compounded with vinylsilane and a

peroxide. This compound combines with a catalyst master batch, which is then fed into the extruder for conversion into pipe. The materials crosslink or cure on exposure of the pipe to water. This process uses HDPE resin with additives that react when the pipe is exposed to heat and moisture after extrusion.

(3)   Radiation process, which involves β, γ or electron-beam irradiation to liberate free radicals for cross-linking. First PE is extruded into pipe. After the extrusion process, cross-linking of the PE is achieved by bombarding the pipe with electromagnetic radiation (gamma) or high energy electrons (beta).

The polymer material generated by these technologies are termed PEX-a, PEX-b and PEX-c respectively according to European Standards. Similar technologies incorporate unique chemicals and conditions into the manufacturing process, knowledge of which is proprietary to the specific PEX pipe manufacturer. Most chemicals used during the manufacture of plastic pipes have the potential to be introduced into drinking water once the pipes are in use (Brocca *et al.,* 2002; Anselme *et al.,* 1985). Oxidation of the internal surface of the pipe during the extrusion process can also result in the leaching of polar oxidation by-products such as aldehdyes, ketones or quinones which convey odors to drinking water (Rigal 1992).

The early study of the sustainability of different PEX materials will help avoid future catastrophic failures of piping systems such as occurred with polybutylene (Zhou *et al.,* 1996) or leaching of lead from materials after conversion to chloramines (Edwards *et al.,* 2004). The focus of this study was to highlight any differences between the ability of peroxide and silane PEX to alter water quality characteristics such as odor, type of leached organics, total organic carbon (TOC) concentrations, disinfectant demand and the formation of disinfection by-products. Celina *et al.* (1995) performed characterization and degradation studies of peroxide and silane PEX that showed that silane PEX-b is less uniformly cross-linked and more sensitive to degradation than peroxide PEX-a. This paper investigates whether this difference in degradation potential can be applied to the odor characteristics of each PEX material. A specific objective was to investigate the occurrences of the fuel oxygenates MTBE and ETBE and identify possible sources from each PEX type.

MATERIALS AND METHODS

Cross-linked polyethylene used for testing

Two different types of PEX material were used. Peroxide PEX (PEX-a) was purchased from a PEX pipe manufacturer and silane PEX (PEX-b) from a local home building Supply Company. All PEX materials used for this study were manufactured in the United States. The internal diameter of the pipes was 3/4". Seven feet lengths of PEX-b and 5 feet lengths of PEX-a pipe were used to accommodate sample volume for analysis. The surface area to volume ratio corresponds to 502 cm^2 / 608 mL for PEX-b and 359 cm^2 / 434 mL for PEX-a and equals 0.83:1 ratio. 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.

Characteristics of the Synthetic Water

For each experiment synthetic tap water was prepared using nanopure water (Barnstead® Nanopure Filter) and mineral concentrations typical of drinking water in the Eastern United States. The following concentrations of ions were generated: 8 mg/L Mg^{2+}, 46 mg/L SO^{2-}_4, 20 mg/L Na^+, 0.05 mg/L Al^{3+}, 11 mg/L Ca^{2+}, 2.6 mg/L Si, 4 mg/L K^+, 1.4 mg/L NO_3^- as N, 10.0 mg/L Cl^-, 0.002 mg/L PO_4^- as P. The alkalinity of the experimental water was 34 mg/L as $CaCO_3$, and pH range 7.8-8.0. Separate experiments consisted of dosing the experimental water with no disinfectant, 2 mg/L free chlorine or 4 mg/L monochloramine as chlorine. No additional natural organic matter was added to the water. Initial TOC concentrations in base synthetic water of 0.1 - 0.2 mg/L were recorded. All experiments were performed at room temperature and pressure.

Migration/Leaching Protocol

Each pipe length (PEX-a, PEX-b) was flushed for three hours, disinfected with 50 mg/L free chlorine and rinsed according to the leaching protocol of the utility quick test (UQT). The UQT is a leaching/migration protocol recommended for use by utilities when evaluating T&O properties of materials prior to installation in distribution systems (Schweitzer *et al.,* 2004). The PEX pipe material was filled completely with experimental water and sealed using Teflon lined VOA vial stoppers and parafilm "M" paper and left under static conditions for three consecutive

periods. A fresh batch of experimental water was used to refill the pipe section after each stagnation period. The exposure time per flush varied between 72 hours (3 days) and 96 hours (4 days)

Experimental Controls

Controls for each experiment were performed by placing synthetic water in standard 500 mL glass Erlenmeyer flasks that were wrapped with aluminum foil paper to prevent exposure to light, and then sealed with glass stoppers. The water was stored in the flask headspace free. The flasks were further protected by sealing the glass stoppers with parafilm paper. An individual control was set up for each experimental condition investigated.

Flavor Profile Analysis (FPA)

Ten (10) research students and faculty at Virginia Tech were recruited and trained for 40-45 hours for the duration of 10-12 weeks in FPA according to Standard Method 2170B (AWWA, 1993). The training protocol utilized taste and odor standards to train panelists to recognize a variety of odors. This training and research protocol was approved according to the standards of the Virginia Tech Institutional Review Board for human subjects. The trained panel members would convene biweekly to evaluate test samples. Test samples (200 mL) were placed in stoppered 500 mL Erlenmeyer flasks and were heated to 45 ^{o}C in a water bath. For analysis a sample was first removed from the water bath and swirled for five sec. The stopper was then removed and the sample was vented for 2-4 sec after which the stopper was replaced and the sample swirled for another 10 sec. The sample was then analyzed by short sniffs over a 10 sec period. FPA descriptors and intensity rating were recorded by each panelist individually. The samples were rated based on an FPA scale ranging from 0 to 12, where 0 represented an odor free sample and 12 the strongest intensity, for example, the intensity associated with a 15 (wt/vol) glucose concentration. After each sample a flask containing odor free water was sniffed and a 2 min waiting period between samples enforced. Odor free water was taken from the Barnstead® Nanopure Filter. After the samples had been analyzed individually by the panelists a group discussion was initiated during which time panelists would come to consensus on an overall descriptor and FPA intensity. The FPA analysis was organized such that a panel member

only analyzed 4-5 samples at any one time and that each sample was analyzed by at least 4 panel members. The samples were also presented to panelists in a randomized manner.

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 6 g of NaCl to 30 mL of sample water placed in a 40 mL volatile organic analysis (VOA) vial. The sample was stirred using Teflon coated magnetic stir bars at 50 ^{o}C for 20 min with the fiber exposed in the 10 mL sample headspace for sorption. 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 ramped 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. Samples were allowed to desorb for 3 mins. All samples were analyzed within 2 days of collection. Identification of compounds was based on library matching to the NIST98 library. The identification of 2-ethoxy-2-methylpropane (ETBE) was confirmed with a standard.

TOC Analysis

Sample preparation and analysis was followed according to Standard Methods for the *Examination of Water and Wastewater* Method 5310A (Clesceri *et al.,* 1998). TOC concentrations were measured using an automated Sievers ®800 Portable TOC Analyzer.

Residual Disinfectant Analysis

Residual disinfectant concentrations, free chlorine, total chlorine, monochloramine and free ammonia were measured using Hach® Pocket colorimeter II and Hach® DR/2400 Portable Spectrophotometer. Free chlorine and total chlorine measurements were based on the DPD Method (Standard Method 8021), Monochloramine measurements were based on Indophenol Method (Standard Method 10171) and free ammonia measurements on Salicylate Method (Standard Method 8155) (DR/2400 Procedure manual, 2002).

pH Analysis

pH was measured 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.

Trihalomethane (THM) Analysis

Total THMs analyses were performed according to USEPA Method 502.2 (USEPA 1995) using a Tremetrics (Austin, TX) 9001 gas chromatograph (GC) with a Tracer (Austin, TX) 1000 Hall detector, Tekmar (Cincinnati, OH) 3000 Purge Trap Concentrator and Tekmar 2016 Purge Trap autosampler. The trap purchased was a Supelco (Bellefonte, PA) VOCARB 300 Purge Trap K. A column 3, which is a J&W Scientific DB-624 (30 m long x 0.53 mm ID, 3 µm film thickness), was chosen. The temperature program was an initial temperature of $45^{o}C$ held for 3 minutes, ramped to $200^{o}C$ at $11^{o}C/min$, and then stopped at $200^{o}C$.

RESULTS AND DISCUSSION

PEX pipe was investigated under three conditions. The material was analyzed in the absence of disinfectant and the presence of residual chlorine or chloramines. Each experimental condition was studied over three flush periods (1, 2 and 3). Each flush period varied between 3-4 days which indicates the length of time that the PEX pipe was exposed to the experimental water. The data did not indicate that the length of exposure time (3 days or 4 days) to PEX pipe affected the intensity of the odor to any great extent. The standard error for each experimental condition was calculated using the overall FPA intensity agreed upon by the FPA panelists.

Odor Analysis – Peroxide PEX (PEX-a) verus Silane PEX (PEX-b)

Panelists identified a "bitter plastic/oily" odor in water exposed to PEX-a. From Figure 3-1 it is seen that FPA analysis of samples from two replicate UQT experiments was highly variable. This is indicated by the large standard error for many of the experimental conditions. From the results however, it is clear that an odor was present in all the samples analyzed. This distinct odor was absent in experimental water exposed to glass (control). The control samples were described as "threshold" or "odor free" in the absence of disinfectant and "chlorinous" in the

presence of residual chlorine or chloramines. The results from a third replicate experiment generated significantly different results. Samples were described as "odor free", "threshold" or "septic" although the pipes used had been subjected to the same water quality conditions as the previous experiments. The variation in overall FPA intensity between similar experimental conditions over three UQT shows that differences between separate lengths of pipe can exist despite being manufactured through similar processes. New PEX pipe was used to set up each individual utility quick test experiment. The results highlight the vulnerability of the manufacturing process of PEX pipe and the need to adhere to strict conditions to maintain consistency of the PEX product.
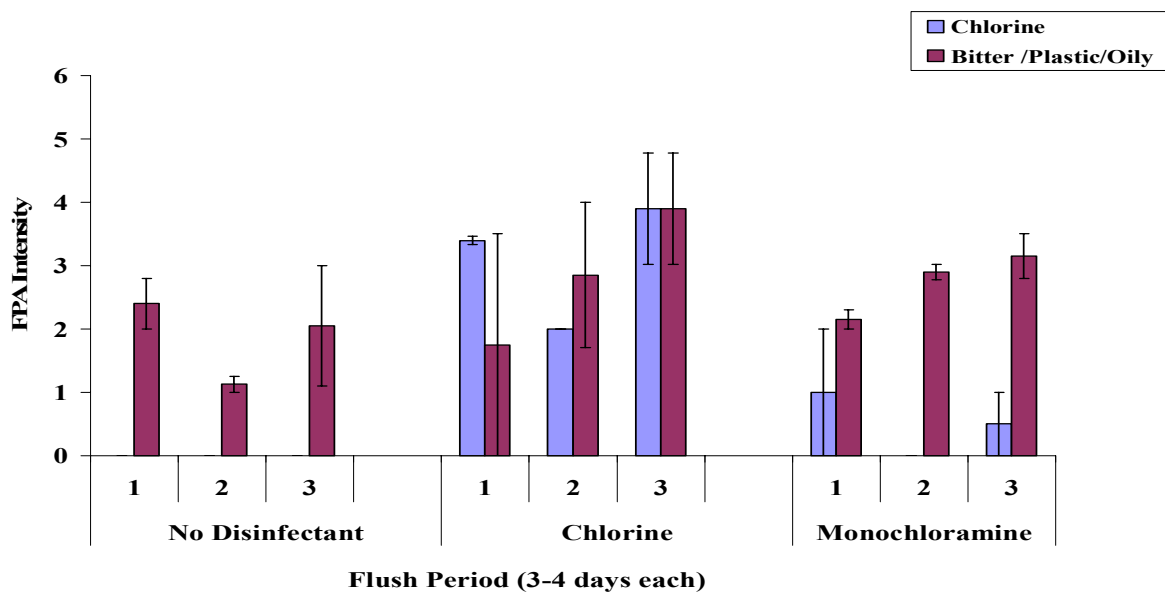

Figure 3-1. **Average FPA intensity for two replicate UQT experiments utilizing peroxide PEX (PEX-a) in the absence of disinfectant and the presence of 2 mg/L free Cl_2 and 4 mg/L chloramines as Cl_2. The standard error of FPA intensity between replicates is shown.**

A more intense and complex odor was described in water that had been exposed to PEX-b. When compared to the FPA analysis of the PEX-a leachate, the overall intensity of this odor was fairly consistent both in the presence and absence of residual disinfectant. A wider range of descriptors were used by panelists to describe this odor; "sweet chemical", "mechanical", "burning", "plastic", "solvent", "bitter". Although this odor was present in all replicate experiments, the variability in rated intensity was significant especially for the "chlorinous" type

odor. For many panelists it was very difficult to separate the "chemical" odor from the "chlorinous" odor and they would tend to use the descriptors interchangeably. The ability to identify and rate a "chlorinous" odor was dependant upon the sensitivity of the panelists being used. Similar to PEX-a there were no distinct odors in the control samples.
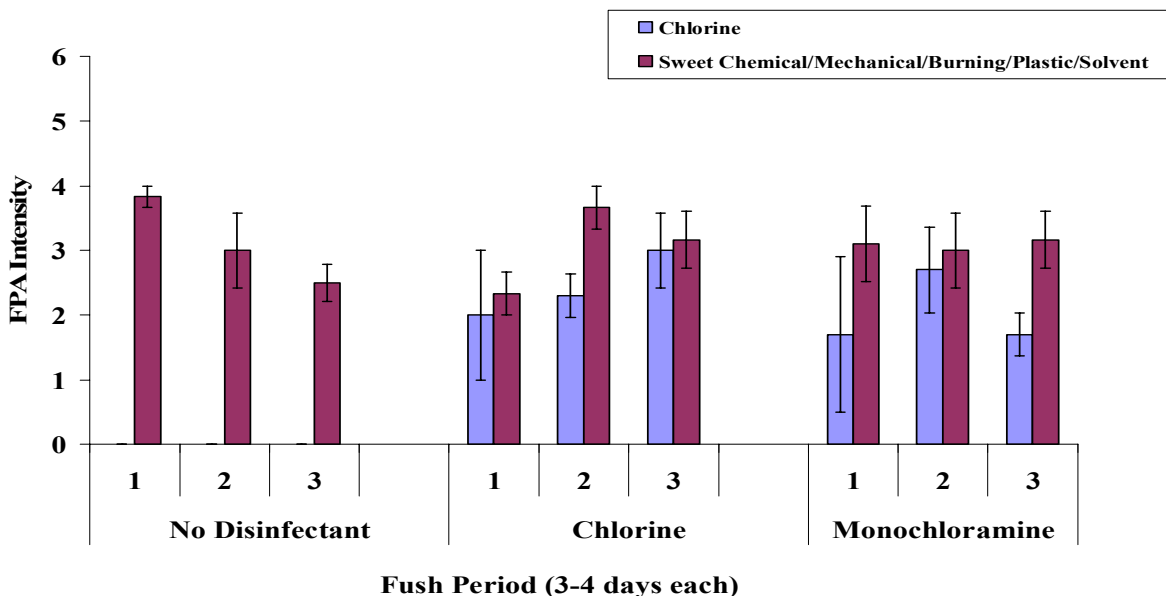

Figure 3-2. **Average FPA intensity for three replicate UQT experiments utilizing silane PEX (PEX-b) in the absence of disinfectant and the presence of 2 mg/L free Cl_2 and 4 mg/L chloramines as Cl_2. The standard error of FPA intensity between replicates is shown.**

In summary the results showed that in the absence of disinfectant, peroxide PEX-a contributed less odors to the drinking water. Figures 3-1 and 3-2 support this. Making a comparison using the FPA intensities in the presence of residual disinfectant was less valid since the presence of residual disinfectant chlorine or chloramines could have synergistic effects enhancing odor intensity for water exposed to both PEX types. The occurrence of a distinct odor both in the presence and absence of residual disinfectant eliminates any possibility of attributing the odors entirely to pipe degradation by chlorine or chloramines. Alternative explanations include: 1) leaching or dissolution of antioxidants and stabilizers and 2) leaching of by-products of the manufacturing processes. Chemical analysis was therefore necessary to identify the VOCs in the leachate waters.

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

SPME followed by GC-MS analysis detected several aldehydes, ketones, esters, aromatics and acids, many of which have been identified in previous studies as degradation products of various antioxidants and stabilizers (Table 3-1) (Anselme *et al.,*1985; Villberg *et al.,*1997; Brocca *et al.,*2002; Skjevral *et al.*, 2003). Many of these compounds are known to impart characteristic T&O to drinking water even at nanogram per liter concentrations and may contribute to the overall odor detected. For example the compounds decanal and nonanal can contribute a citrus, floral or sweet odor to drinking water (Rashash *et al.,* 1997). A "mild, oily, sweet, slightly rose" odor is ascribed to 2-ethyl-2-hexanol, and the butyric ester of butanoic acid has a "fruity, pineapple" odor (Sigma-Aldrich, 2003) while m-xylene is described as having a sweet solvent odor in water and butanol as "alcohol, solventy" odors (AWWA, 1993). A few of these compounds were commonly detected in water samples exposed to peroxide PEX-a and silane PEX-b material. There were also compounds that were unique to a particular PEX material. Table 3-1 gives a summarized list of the compounds that were frequently detected in most samples.

Table 3-1.   **Compounds frequently detected by SPME-GC/MS analysis in leachate samples from each PEX manufacturing technology[1].**

Peroxide Only (PEX-a)	Silane Only (PEX-b)	Compounds in Both (PEX-a and PEX-b)
di-*tert*-butyl peroxide	**propane, 2-ethoxy-2-methyl (ETBE)[2]**	decanal
t-butanol	propane, 2,2-diethoxy	nonanal
	hydroperoxide, 1-ethyl propyl	Butanoic acid-butyl ester
	p-xylene	1-hexanol, 2-ethyl
		2,5-hexanediol,2,5-dimethyl

[1] compounds in this table were detected in at least 50% of the leachate samples from the utility quick tests
[2] Confirmed with chemical standard

The compounds listed in Table 3-1 were all detected in the water exposed to pipe material and not in the control samples. From the results we see that ETBE was detected in PEX-b leachate. The occurrence of ETBE was consistent. It was detected in over 95% of the samples analyzed

after exposure to PEX-b. Further analysis comparing retention time and mass spectrum of an ETBE standard confirmed the presence of ETBE in the leachate samples (Durand and Dietrich, 2005). Experiments to quantify the ETBE in pipe samples measured concentrations ranging from a high of 100 µg/L after the first 72 hours of exposure to a low of 23 µg/L after the third 72 hours exposure. Interestingly, di-*tert*-butyl peroxide and *t*-butanol were detected in 95% of the leachate samples of PEX-a. MTBE was also detected but only occasionally (<10%) and was not quantified.

ETBE is known to have a sweet, burning, bitter chemical odor with an intensity of 2 (very weak on the FPA scale) at a concentration of 5 µg/L (Durand and Dietrich, 2005). ETBE is a likely contributor to the overall plastic/chemical odor and burning sensation of PEX-b. Previous studies have described MTBE as "sweet" or "bitter" chemical odor at concentrations as low as 5 µg/L (Young *et al.,* 1996) and therefore possibly contribute to the overall PEX-a associated odor.

Known reaction pathways for the formation of MTBE and ETBE were examined in an attempt to understand the origin of these two compounds in the PEX leachate waters. Figure 3-3 summarizes the possible pathways that are used to commercially manufacture ETBE and MTBE (Baur *et al.,* 1990).

MTBE and ETBE reaction pathways

isomerization		Dehydrogenation

(1)   n-butane   →   isobutane   →   isobutylene + ethanol →→ETBE

Dehydrogenation

(2)   tert-butanol   →   isobutylene + ethanol →→ETBE

isomerization		Dehydrogenation

(3)   n-butane   →   isobutane   →   isobutylene + methanol →→MTBE

Dehydrogenation

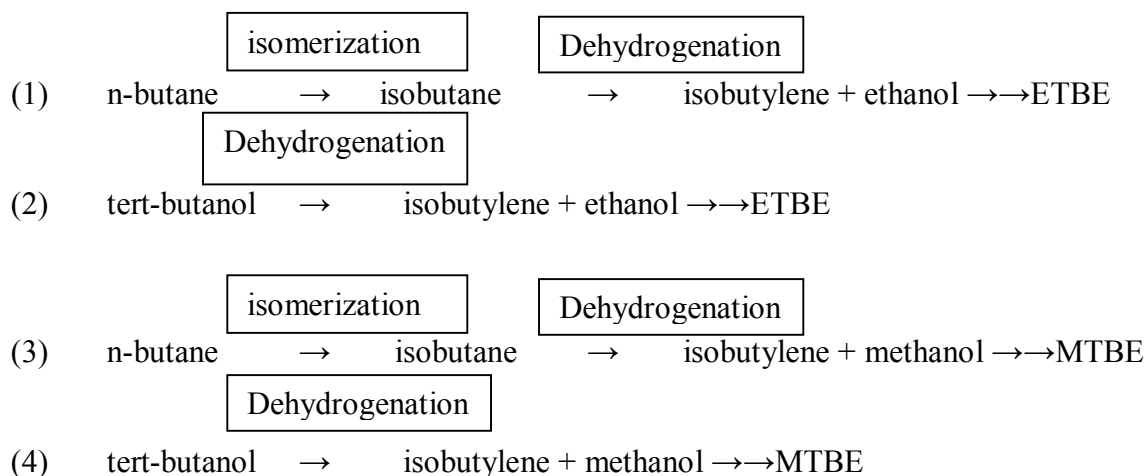(4)   tert-butanol   →   isobutylene + methanol →→MTBE

Figure 3-3.   Reaction pathways for the commercial synthesis of the fuel oxygenates MTBE and ETBE.

To explain the occurrence of MTBE and ETBE we considered the degradation of one of the commonly used initiator and cross-linking catalysts in polymer pipe manufacture, di-*tert*-butyl peroxide, which was detected in PEX-a leachate. Other commonly used organic peroxide cross-linking initiators include *t*-butyl perbenzoate, benzoyl peroxide, acetyl peroxide, dicumyl peroxide and 2,5-dimethyl-2,5-di-(t-butylperoxy) hexyne-3. Peroxide initiators are used during the manufacture of both PEX-a and PEX-b material. The degradation products vary based on the peroxide initiator used and reaction conditions.

In the high temperature environment needed for cross-linking several separate and undesirable reactions may occur. Degradation of *t*-butyl peroxide followed by hydrogen abstraction by radicals, β scission and intramolecular displacement and rearrangement can lead to the formation of acetone, ethane, methane, *t*-butanol and isobutylene oxide (Pryor, 1966). Isobutylene, methanol, and *t*-butanol have all been identified as chemicals that leach from PEX material (Tomboulian *et al.,* 2004). The degradation product *t*-butanol can also undergo dehydrogenation to form isobutylene. In the presence of ethanol or methanol isobutylene can react to form ETBE or MTBE. Therefore the most feasible reaction pathway for the formation of oxygenates (ETBE and MTBE) in the pipes samples corresponds to pathways 2 and 4 in Figure 3-3 and are contingent upon the presence of isobutylene, methanol and ethanol.

 The source of ethanol or methanol is highly variable. These compounds can be formed from the hydrolysis of vinylsiloxanes such as vinyl trimethoxysilane (used in PEX-b manufacture) to liberate methanol (Peacock, 2001) or the hydrogen reduction of oxidation by-products of the manufacturing process such as ketones (Peacock 2001; Ouellette, 1994). Although the exact chemicals utilized in the manufacture of the PEX-a and PEX-b pipes for this research were not known, the analysis explained is reasonable and feasible. It is evident that the occurrence of ETBE or possibly MTBE is directly related to the conditions and chemicals used during the manufacturing process of the PEX pipes, since they were similarly leached in water under conditions of no disinfectant, chlorine and monochloramines containing water.

To prevent the production of organic compounds that could ultimately be introduced into drinking water and contribute to T&O issues, conditions should be optimized during the pipe

manufacturing process. Timing is crucial during the manufacturing process and good quality control is necessary. The decomposition of organic peroxides is an approximately first-order reaction and increases exponentially as a function of temperature. For example the half-life of di-*t*-butyl peroxide decreases from 160 mins at 140°C to 0.35 mins at 200°C (Peacock, 2001). Initiator molecules used during the cross-linking of polyethylene using different PEX technologies should be selected with respect to the final temperature at which the resin must be processed. The ultimate goal during the process should be to homogenize and mold the resin into the desired shape below the temperature at which the peroxide decomposition becomes significant. This is necessary since at high temperatures the ratio of scission to cross-linking reactions increases, resulting in the formation of several degradation products that could subsequently lead to taste and odor problems.

TOC analysis of PEX-a and PEX-b

The difference in measured TOC from water exposed to PEX-a and PEX-b was substantial. Figures 3-4 and 3-5 show the increase in measured TOC after each flush period for PEX-a and PEX-b respectively. There was an overall decline in measured TOC for PEX-b but no clear trend for PEX-a, concentrations were fairly consistent between flushes. The maximum increase in TOC for water exposed to PEX-a both in the presence and absence of disinfectant, was 0.4 mg/L and for PEX-b 1.4 mg/L as compared to 0.1 mg/L for the control water (glass). This difference shows a direct correlation to the more intense odor that was observed for PEX-b leachate. It also corresponds to the higher degradation properties of silane PEX-b (Celina *et al.,* 1995).
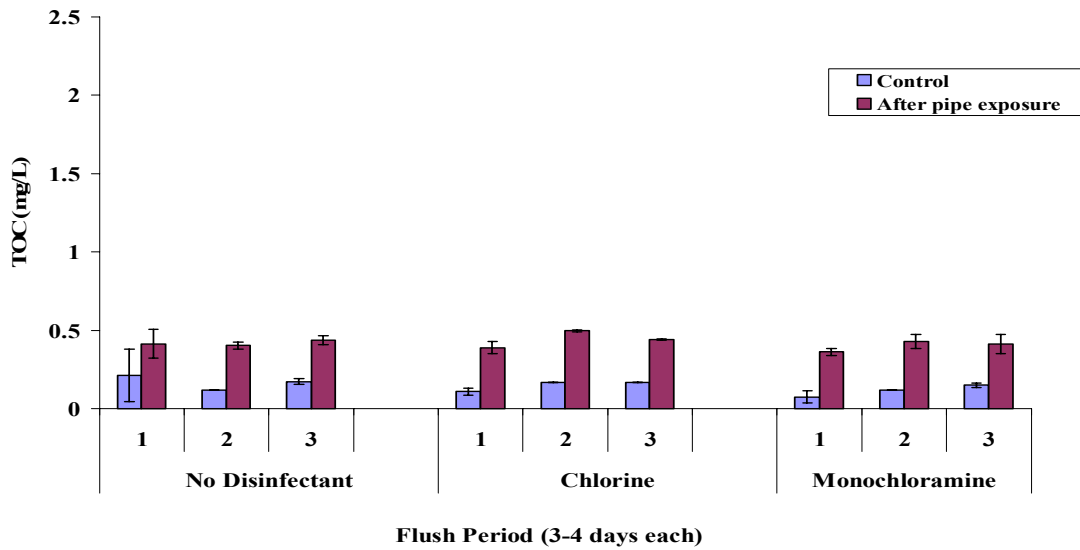
Figure 3-4. Variation in TOC of peroxide PEX (PEX-a) after exposure to water containing no disinfectant, 2 mg/L as Cl_2 and 4 mg/L monochloramine as Cl_2. The standard error of the value is shown.
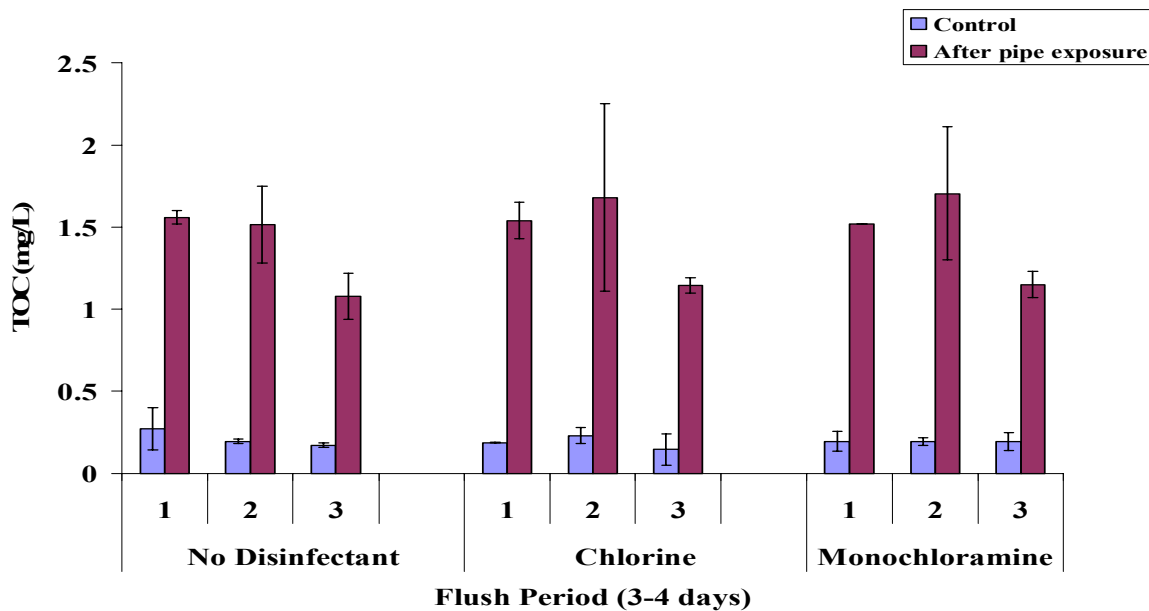

Figure 3-5. Variation in TOC after exposure of silane PEX (PEX-b) to water containing no disinfectant, 2 mg/L Cl_2 and 4 mg/L monochloramine as Cl_2. The standard error of the value is shown.

Overall the residual disinfectant demand was minimal for both PEX types. There was no measurable demand on monochloramines by the PEX materials used in this study. Figures 3-6 and 3-7 represent the monochloramines demand for PEX-a and PEX-b respectively. For chlorine however, a slightly higher demand was noticed for PEX-b when compared to PEX-a as shown in Figure 3-8 and 3-9 respectively. The change in concentration between the control and the pipe sample depicts the chlorine demand of the pipe material. This is most likely due to the presence of more organic compounds (high TOC) which increase the chance of reaction and formation of chlorinated organic compounds. Interestingly, however, was the fact that despite the high TOC and residual chlorine present there was no significant disinfection byproducts (THMs) measured in the water exposed to the PEX pipe material. Further studies are needed to characterize the TOC and subsequently explain the effects of the high TOC in the leachate. The question remains as to whether the TOC could potentially act as substrate for the growth of microorganisms on the pipe surface leading to additional odor in the drinking water.
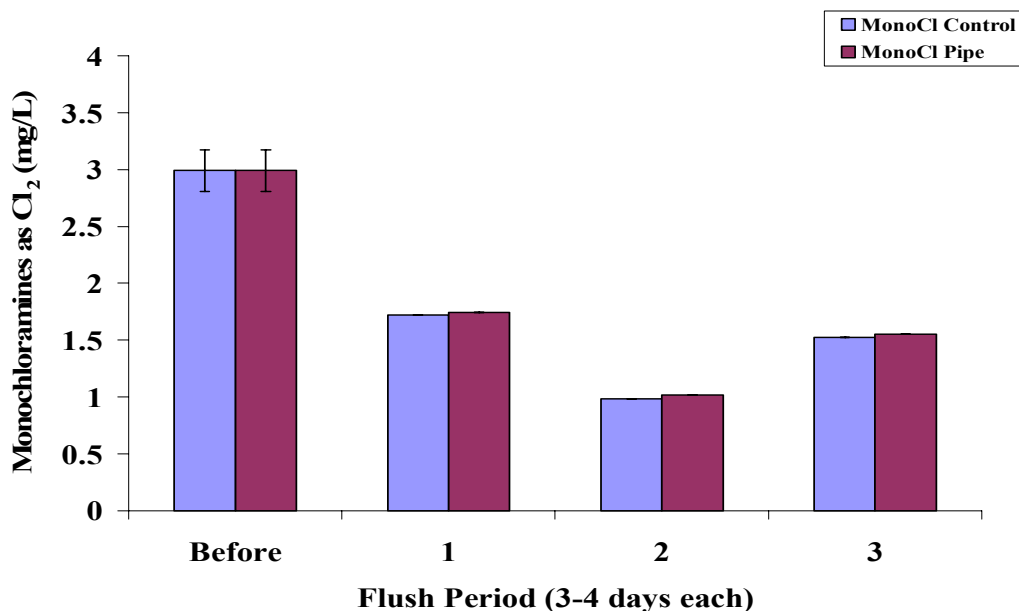

Figure 3-6   Residual monochloramine for PEX-a compared to the controls. Standard error between initial measured monochloramine for each flush period is shown.
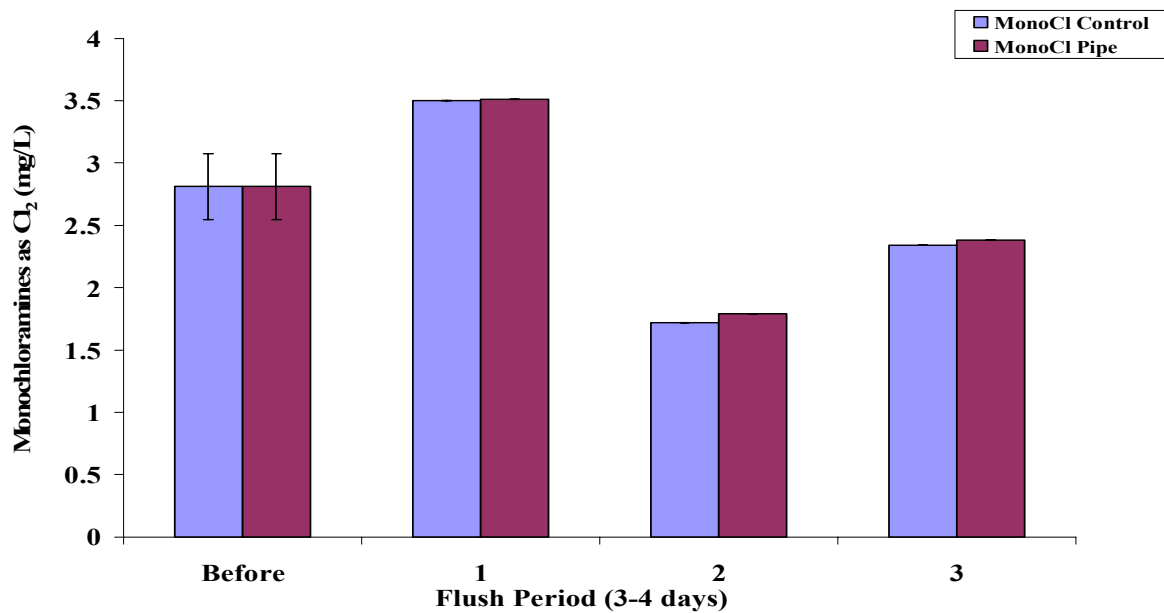
Figure 3-7. **Residual monochloramine concentration for PEX-b compared to the control. Standard error between initial measured monochloramine for each flush period is shown.**
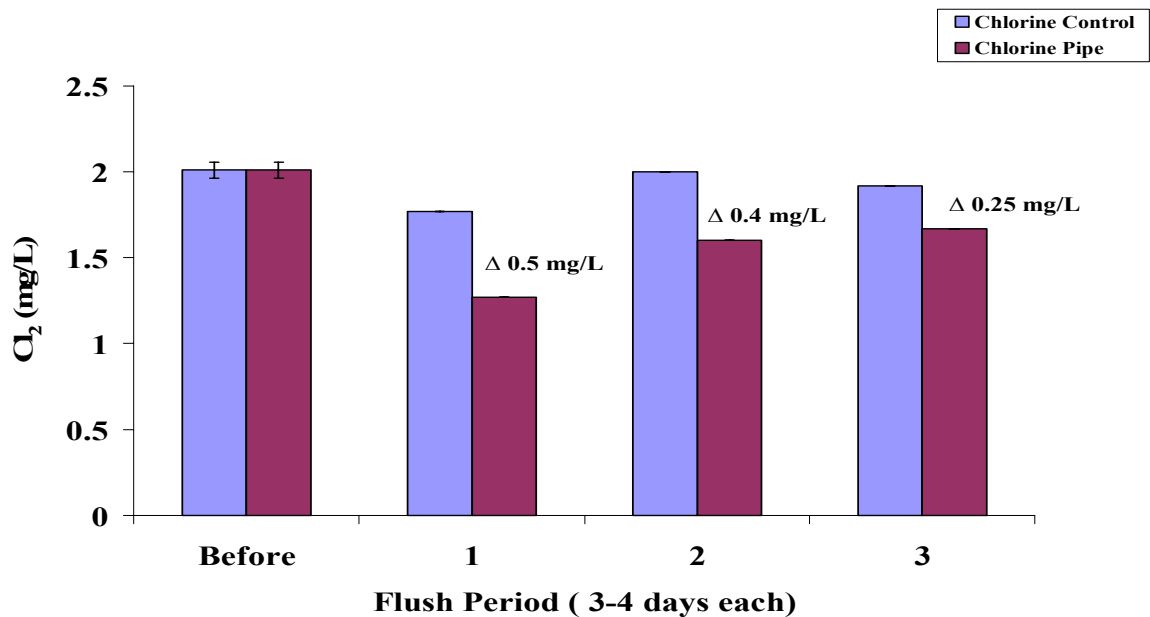

Figure 3-8 **Residual chlorine in PEX-b pipe sample compared to controls. Standard error between initial measured chlorine for each flush period is shown.**
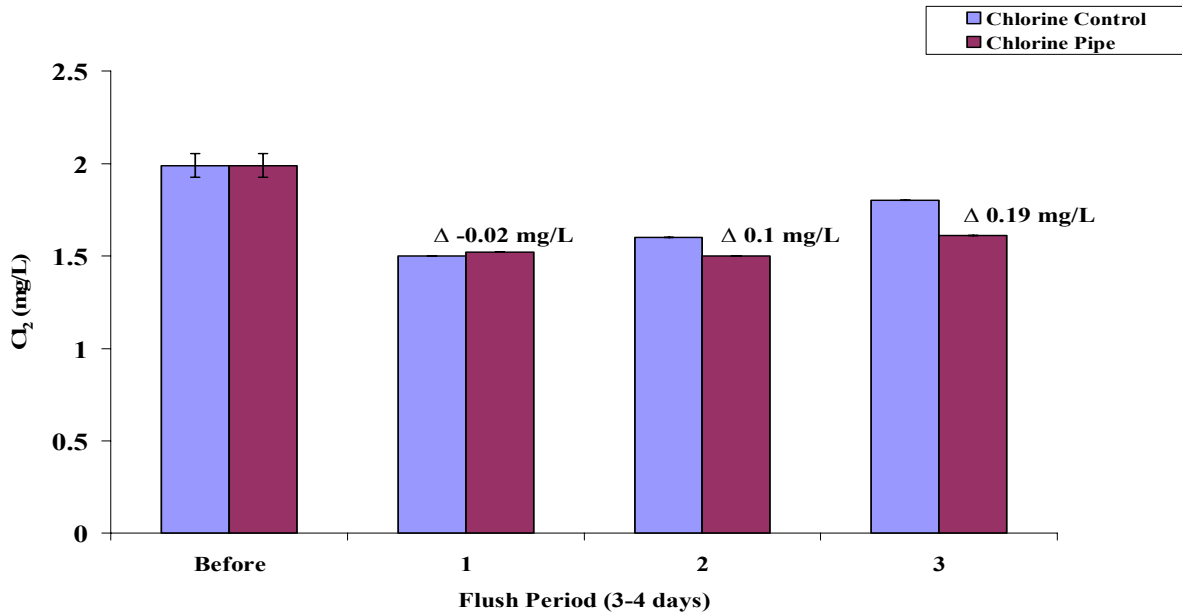
Figure 3-9. **Residual chlorine for PEX-a pipe samples compared to controls. Standard error between initial measured chlorine for each flush period is shown.**

CONCLUSIONS

Cross-linked polyethylene (PEX) offers several advantages such as high strength and endurance, resistance to corrosion and flexibility to homeowners and homebuilders. This study highlights potential negative impacts of PEX pipe usage. PEX can contribute both odors and TOC to drinking water. The study showed that not all PEX materials have the same effect on drinking water. It is imperative that PEX pipe manufacturers consider the organoleptic impacts of various additives used during the PEX pipe manufacturing process. Additional studies using PEX from different manufacturers in different water qualities is needed to fully understand the impact of PEX pipe on drinking water quality.

ACKNOWLEDGEMENTS

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CHAPTER IV

IMPACT OF PIPE MATERIALS ON THE ODOR, DISINFECTANT RESIDUAL AND TOC – LEVELS OF DRINKING WATER

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Abstract

Three individual replicate plumbing rigs simulated the use of small diameter pipes in residential and commercial systems for potable water transport. These rigs were used to investigate seven different materials under low flow and stagnant conditions; chlorinated polyvinyl chloride (cPVC), cross-linked polyethylene (PEX-a), polyethylene, epoxy-lined copper, copper, stainless steel, galvanized iron and glass (control) under consistent water quality and operational conditions. The specific objectives were (1) to examine the role of chlorine and chloramines disinfectant in affecting the odors generated from new plastic and metallic pipes; (2) categorize the odor descriptors and intensity of odors from water exposed to each material in the presence and absence of disinfectant; and (3) evaluate changes in water quality (TOC, pH, disinfectant residual) based on type of material and disinfectant present.

Domestic plumbing materials have the potential to affect water quality characteristics such as TOC concentrations, residual disinfectant and odor when newly installed in homes, especially during the first weeks of service. Aqueous TOC concentrations increased as much as 1 mg/L for some materials. The increased TOC observed for many plumbing materials was consistent with the presence of a distinct odor or a high FPA intensity rating. The descriptors most consistently used to describe odors from both plastic and metallic pipes are, "plastic", "oily", "chemical" and "solvent". Galvanized iron produced the worst odors that were consistently described as "motor oil" with FPA intensity ranging from 4-6. This material generated the most intense odors. Polyethylene generated more intense plumbing associated odors than PEX or cPVC plastic material. The least odorous materials were chlorinated polyvinyl chloride and copper. Both copper pipe and epoxy-lined copper consumed residual chlorine and chloramines. Understanding the interaction of materials and water quality is a complex task.

Key Words

Domestic plumbing materials; odors; TOC; chlorine; chloramines

INTRODUCTION

Taste and odor (T&O) issues arise from the source water, within the treatment plant, in distribution systems, and in consumer home plumbing (Dietrich, 2005). Interestingly, however, utilities and regulatory agencies usually do not extend regulations beyond the point where public water transmission lines end and private lines begin. In the United States, unlike countries such as France, it is not mandatory that manufacturers of pipes and other components used in distribution systems (main and domestic) conduct T&O testing of materials with relevant water qualities and disinfectants as part of their approval process. This poses a possible problem because pipe structures and associated gadgets (tanks, reservoirs, ancillaries, linings, sealing systems) are the final materials that contact drinking water before reaching the consumer and, have the potential to severely impact drinking water quality such as odor-production (Tomboulian *et al.,* 2004) or lead leaching (Edwards *et al.,* 2004). Consumers often detect changes in aesthetic water qualities and report concerns and complaints to their utilities. Knowledge of the potential for materials to impair the properties of drinking water will aid the utility in swiftly identifying the source of T&O complaints and ultimately in providing the consumer with high quality water. Further, consumers need to be aware of plumbing and water quality issues in order to make informed decisions regarding material selection that will guarantee the highest quality drinking water.

Aesthetic qualities of drinking water reaching the consumer's tap can be significantly affected by the type of materials and disinfectant used in the domestic plumbing system. Research has shown that plastics and organic coatings have a greater potential than metals to impart T&O to drinking water (Rigal *et al.,* 1999). T&O problems encountered in distribution and plumbing systems occur mostly as a result of (1) pipe or reservoir lining materials leaching into water and (2) reactions of leached compounds in the water with the disinfectant residual within the distribution system (Khiari *et al.*, 1999). The type of disinfectant (chlorine, chloramines or chlorine dioxide) used will influence reactions that take place within the distribution system resulting in additional tastes and odors. Several studies have shown that the presence of residual disinfectant chlorine can have deleterious effects on some pipe materials and subsequently affect

the T&O properties of drinking water (Marchesan *et al.,* 2004; Heitz *et al.,* 2002; Hassinen *et al.,* 2004).

As more utilities convert to chloramines, there exists the need to evaluate interactions of materials and chloramines (Seidel *et al.,* 2005). Undesirable chemical reactions have occurred that resulted in destruction of rubber gasket materials with odor being generated (Khiari *et al.,* 2002). Conflicting results from another study concluded that degradation of gaskets after exposure to chloramines is application specific and depends on the end-use of the material being contacted (Bonds, 2004). This highlights the need for more complete evaluation of the T&O impacts of chloramines on other materials.

Copper is the most commonly used metallic piping material in domestic plumbing systems in the USA. The presence of free chlorine employed for disinfection increases the corrosion and leaching of copper plumbing materials resulting in an increase in dissolved copper concentration in drinking water (Hong *et al.,* 1998). Studies have shown that copper could affect the taste properties of drinking water (Dietrich *et al.,* 2004; Marchesan *et al.,* 2004; Cuppett, 2005). However there are no reported studies of copper material imparting an odor to drinking water. Stainless steel and galvanized iron are less frequently used in domestic systems in the USA, however, they have been used quite extensively in Japan and European countries such as Germany (BSSA, 2003; Sorg and Bell, 1986). Galvanized iron and stainless steel are considered less prone to corrosion. The potential of stainless steel and galvanized iron when used in domestic plumbing systems to affect T&O of drinking water has not been extensively studied. One of the few studies (Khiari *et al.,* 2002) showed that water exposed to galvanized pipe could obtain a sour taste or astringent mouthfeel due to the presence of zinc and aluminum salts. The aesthetic properties of metals, particularly the odor properties, need further research.

Chlorinated polyvinyl chloride, polyethylene and cross-linked polyethylene are rapidly replacing copper as preferred domestic plumbing materials worldwide. However, a major drawback associated with the use of plastics is the leaching of volatile organic compounds (VOCs) directly from the plastic or from antioxidants and other solvents used to protect the plastic pipe from oxidation (Brocca *et al.,* 2002). Other mechanisms that can add organic compounds to the water include permeation and oxidation of the internal surface of the plastic pipe during the extrusion

process (Goodfellow *et al.,* 2002; Anselme *et al.,* 1985). The contribution from organic compounds leached from materials is two-fold. VOCs have been shown to directly or indirectly affect the organoleptic properties of drinking water (Skjevrak *et al.*, 2003). According to recent Norwegian research and experience, performed by the Aquateam and the Norwegian Food Control Authority, it has been shown that biodegradable matter leached from plastic pipes and tanks promote microbiological growth whereas copper pipes inhibit growth due to its toxic nature (Hem *et al.*, 2002). Biological activity can result in off-flavors and odors in drinking water (Malleret *et al.*, 2002).

In this study various commercial domestic plumbing materials were evaluated simultaneously in a simulated plumbing system to determine their effects on the aesthetic properties of drinking water in the presence of chlorine or chloramines disinfectant. Materials were assessed based on their impact after exposure to drinking water under stagnant conditions. Flavor Profile Analysis (FPA) was employed to conduct odor assessment.

The main goal of this study was to clearly define the contribution of newly installed domestic pipe materials to odors in drinking water under controlled conditions that simulated domestic use. The more specific objectives were (1) to examine the role of chlorine and chloramines disinfectants in affecting the odors generated from new plastic and metallic pipes; (2) categorize the odor descriptors and intensity of odors from water exposed to each material in the presence and absence of disinfectant; and (3) evaluate changes in water quality (TOC, pH, disinfectant residual) based on type of material and disinfectant present.

MATERIALS AND METHODS

Plumbing Rigs

Three individual replicate plumbing rigs were constructed of the same plumbing materials but differed in water circulating through the rig. The water consisted of typical minerals (see below) but one had no disinfectant, one had chlorine and the other had chloramines. Eight different types of pipes were assessed in each rig: chlorinated polyvinyl chloride (cPVC), polyethylene (PE), peroxy-catalyzed cross linked polyethylene (PEX-a), epoxy-lined copper (E. copper),

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copper, stainless steel (SS), galvanized iron and glass which served as the control material. The glass pipes were covered with aluminum foil to limit the penetration of light into the water matrix.

Figure 4-1.   Simulated plumbing rig systems.

All materials were approved for use in potable water systems by the National Sanitation Foundation (NSF 61) and purchased at a local home building Supply Company or ordered directly from the manufacturers. The diameter of the pipes ranged from 3/4″ to 3/8″ and lengths were 8 feet. The pipes were exposed to experimental water for eight (8) hour stagnation periods, three times each day. Between each stagnation period the pipes were flushed for two minutes and refilled with a fresh batch of experimental water. Experimental water for each plumbing rig was stored in individual 189 liter (50 gallons) glass-lined hot water heater tank purchased from a

local home department store. Water flowed from the storage tanks into the pipes solely under the influence of gravity. There were no pumps in this system. The rigs were operated at room temperature, $20 - 25^oC$.

Experimental Water

Local tap water was treated with commercial, house scale granular activated carbon and ion exchange systems to produce deionized and carbon filtered water. Minerals were added to the experimental water in a composition similar to water in the Eastern United States. The following concentrations of ions were generated in deionized and carbon filtered water; 8 mg/L Mg^{2+}, 46 mg/L SO^{2-}_4, 20 mg/L Na^+, 0.05 mg/L Al^{3+}, 11 mg/L Ca^{2+}, 2.6 mg/L Si, 4 mg/L K^+, 1.4 mg/L NO_3^- as N, 10.0 mg/L Cl^-, 0.002 mg/L PO_4^- as P. Humic Aldrich natural organic matter (NOM) that was prechlorinated for approximately 24 hours was added resulting in an initial water of very low TOC concentrations (0.5 - 0.6 mg/L) and no residual disinfectant demand; alkalinity was 34 mg/L as $CaCO_3$, and the pH range was 7.8-8.3. Sodium hypochlorite (4-6 % strength) was dosed to obtain residual chlorine concentrations of $0.5 - 2$ mg/L. Ammonium hydroxide solution (14.8 N) and 4-6 % sodium hypochlorite solution (1 mole Cl_2:1.15 mole N) was dosed to give monochloramine concentrations of 1-4 mg/L as Cl_2. A variation in residual disinfectant concentration was made after the first four months in operation to facilitate the use of the plumbing rig for bacterial and corrosion studies that were occurring simultaneously. Residual chlorine was changed from 2 mg/L to 0.5 mg/L. Residual monochloramine was changed from 4 mg/L as Cl_2 to 1 mg/L as Cl_2.

Sampling

After an eight (8) hour stagnation period water was drawn from each pipe material and collected in clean two (2) liter glass bottles. Water was collected from the storage tank to coincide with every rig sampling. One rig was sampled per day. During the first month of operation of each rig, samples were collected every two weeks and then tapered to once every month then once every three months. Data were collected over a six month period.

FPA Analysis

Ten (10) research students and faculty at Virginia Tech were recruited and trained for several weeks in FPA. This training and research protocol was approved according to the standards of the Virginia Tech Institutional Review Board for human subjects. For FPA analysis of samples, 4-6 members were present at all times. FPA analysis was followed from Standard Methods 2170.

Ten (10) samples comprising 8 pipe samples, 1 tank sample and an odor free sample, were analyzed during an FPA session. Sample volume (200 mL) was placed in 500 mL wide mouthed glass-stoppered Erlenmeyer flasks and analyzed by panelists at a temperature of $45^{\circ}C$ maintained by a constant temperature water bath. The order of the samples was randomized among panelists. Samples were arranged such that each panel member analyzed no more than seven samples while at the same time ensuring that each sample was analyzed at least four times.

A sniffing protocol was designed to maintain consistency among panelists. The steps included; Remove flask labeled "odor free" from the water bath; Swirl 5 times, remove stopper and then sniff; remove first sample from water bath based on the order presented in table given; swirl for 5 seconds, remove stopper for 1-2 seconds then quickly replace stopper (VENTING); swirl flask again for 5 seconds; remove stopper and analyze sample for 10 seconds. Analysis should be done in 2-3 short sniffs; replace stopper and place sample flask into water bath; wait 2 minutes then analyze the next sample. After sample analysis the panelists discussed the results deciding on a final descriptor and intensity for the identified odors.

Total Organic Carbon Analysis

Sample preparation and analysis was followed according to Standard Methods for the *Examination of Water and Wastewater* Method 5310. TOC concentrations were measured using an automated Sievers ®800 Portable TOC Analyzer.

pH Analysis

pH was measured using the Accumet® (cat# 13-620-287) electrode and the Accumet® pH Meter 910 purchased from Fisher Scientific.

Residual Disinfectant

Residual free chlorine and monochloramine in water sampled from the plumbing rigs were determined by measuring the concentration of these species after exposure of experimental water to the pipe material. The residual disinfectant concentration in each tank was also measured for comparison. Concentrations of the disinfectant species were determined by the DPD colorimetric method using a HACH® Pocket Colorimeter II and HACH® DR/2400 Portable Spectrophotometer. Free chlorine measurement was based on the DPD Method (Standard Method 8021), and monochloramine measurement was based on Indophenol Method (Standard Method 10171)

RESULTS AND DISCUSSION

The FPA panel identified a consistent background odor in the experimental water with a very low intensity rated no higher than 2 (very weak based on FPA intensity scale). This background odor was identified in samples from each rig and was characteristic to samples taken from the storage tank containing water with no disinfectant. Panelists were trained to isolate and separate this odor from other characteristic odors that might originate from exposure to pipe material. After repeated FPA sessions many panelists simply used the general word "background" to describe this odor. Results summarized in Table 4-1, 4-2 and 4-3 are reported for plumbing material analyzed after approximately 2 days, 1 month, 3 months and 6 months of exposure of pipe material to experimental waters with and without residual disinfectant.

Water quality parameters such as pH and temperature showed no significant variations for the duration of this study.

Plumbing Rig with No Disinfectant

For most materials tested, with the exception of galvanized iron, the panel used similar odor descriptors to characterize water samples when no disinfectant was present. Descriptors such as "musty", "solvent", "earthy" and "almond" were used interchangeably between panelists for different materials. In many instances an odor was discerned but the intensity was so low that it

could not be identified and described fully, thus it was rated as "Threshold". This rating was given an FPA intensity of 1.0. Samples in which absolutely no odor was detected was described as odor free and given an FPA intensity of zero. Table 4-1 summarizes the FPA results of water after exposure to pipe materials in the absence of residual disinfectant.

Table 4-1   Overall FPA descriptors for water samples contacted for 8 hours with different pipe materials in a simulated plumbing rig in the absence of residual disinfectant.

	Time of Rig Operation (days)			
Pipe Materials	2	32	102	177
Glass	Threshold	Threshold[1]	Odor Free	Threshold
Chlorinated polyvinyl chloride (cPVC)	Chemical	Threshold	Background	Threshold
Cross-linked polyethylene (PEX-a)	Solvent	Threshold	Background	Threshold
Polyethylene (PE)	Plastic	Threshold	Threshold	Musty/Grassy
Epoxy-lined copper (E. Copper)	Oily	Threshold	Threshold	Sweet Almond
Copper	Chlorine	Threshold	Threshold	Background
Stainless Steel	Septic	Threshold	Background	Threshold
Galvanized Iron	Motor Oil	Motor Oil	Motor Oil	Motor Oil

[1]Threshold = Barely discernible odor

Galvanized iron displayed a unique odor which was characterized as "Motor Oil" or "Mechanical Oil". This described odor was very unpleasant and easily detectable in water samples. The odor persisted at a very high intensity throughout the duration of this study. As shown in Figure 4-1, FPA intensities as high as 5.3 were recorded for water in contact with galvanized iron pipe in the absence of disinfectant. The overall trend for each material depicted in Figure 4-1 is a decrease in odor intensity over time of operation of the rig. PE and E. copper,

showed a slight increase in intensity after 177 days (approx. 6 months). The results further showed that materials displayed the most intense odors during the first month of exposure. Overall a consistent background odor was detected for all materials in the absence of residual disinfectant with the exception of galvanized iron.
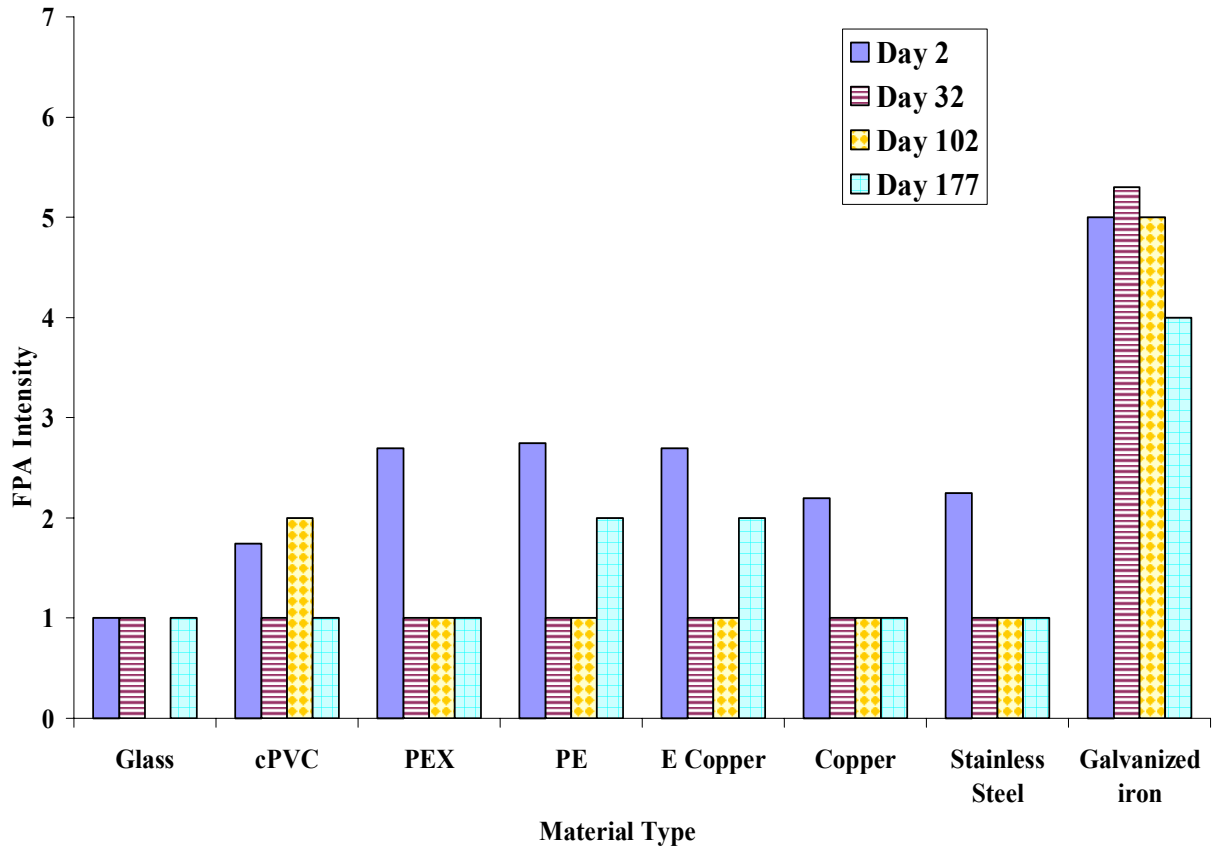

Figure 4-2.   FPA intensity determined over a 6 month period for pipe materials in contact with water containing no residual disinfectant over 8 hour stagnation periods.

The materials were ranked in descending order (Figure 4-2) based on an average FPA intensity calculated using the intensities recorded in Figure 4-1 for each material. Results showed overall odors in the absence of disinfectant were most intense for galvanized iron and least intense for glass (control) material.
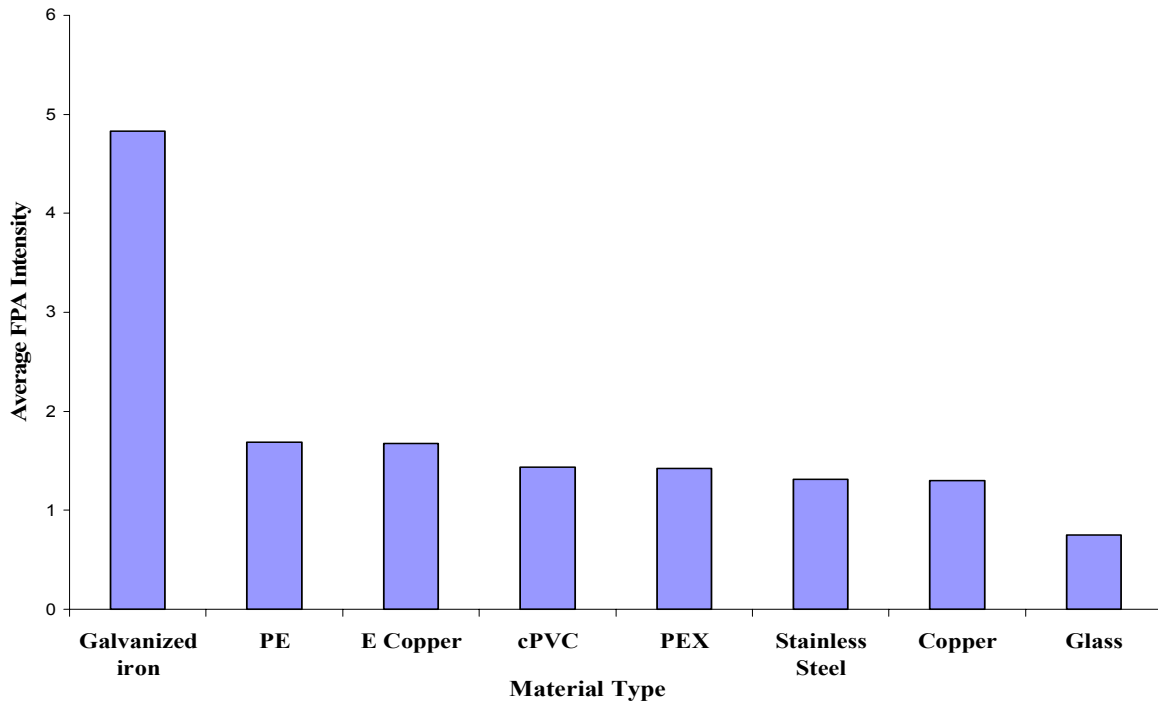
Figure 4-3.   Overall ranking of plumbing materials in order of descending odor intensity in the absence of disinfectant.

Plumbing Rig with Chlorine Disinfectant

Water sampled from pipes exposed to chlorine disinfectant was consistently described as "chlorinous" by the panelists. In some instances the panelists identified a "petroleum", "mechanical" or "almond" odor that somewhat enhanced the chlorine intensity. It proved to be a difficult task for many panelists to isolate a characteristic odor in the presence of chlorine. Table 4-2 summarizes the descriptors that were used to categorize the FPA analysis of pipe samples exposed to water with free chlorine.

Table 4-2   Overall FPA descriptors for water samples contacted for 8 hours with different pipe materials in a plumbing rig in the presence of residual free chlorine.

	Time of Rig Operation (days)			
Pipe Materials	**4**	**30**	**101**	**175**
Glass	Chlorinous	Chlorinous	Chlorinous	Threshold
Chlorinated polyvinyl chloride (cPVC)	Chlorinous	Oily/ Chlorinous	Chlorinous	Chlorinous
Cross-linked polyethylene (PEX-a)	Chlorinous	Chlorinous	Chlorinous	Chlorinous
Polyethylene (PE)	Chemical/ Chlorinous	Chlorinous/Almond	Sweet Mechanical	Chlorinous/Almond
Epoxy-lined copper (E. Copper)	Chlorinous/Oily	Chlorinous/Almond	Chlorinous	Chlorinous/Background
Copper	Chlorinous Plastic	Chlorinous/Almond	Odor Free	Chlorinous
Stainless Steel	Chlorinous	Chlorinous	Chlorinous	Chlorinous
Galvanized Iron	Motor Oil	Motor Oil	Motor Oil	Motor Oil

These data reflect the panelist's inability to clearly decide on a descriptor which resulted in instances of combined descriptors such as "oily/chorine". Similar to the rig with no disinfectant, water exposed to galvanized iron pipe material generated an intense odor and panelists could not identify the presence of any residual chlorine. Chlorine did not appear to have any synergistic effects on the mechanical odor from galvanized iron.
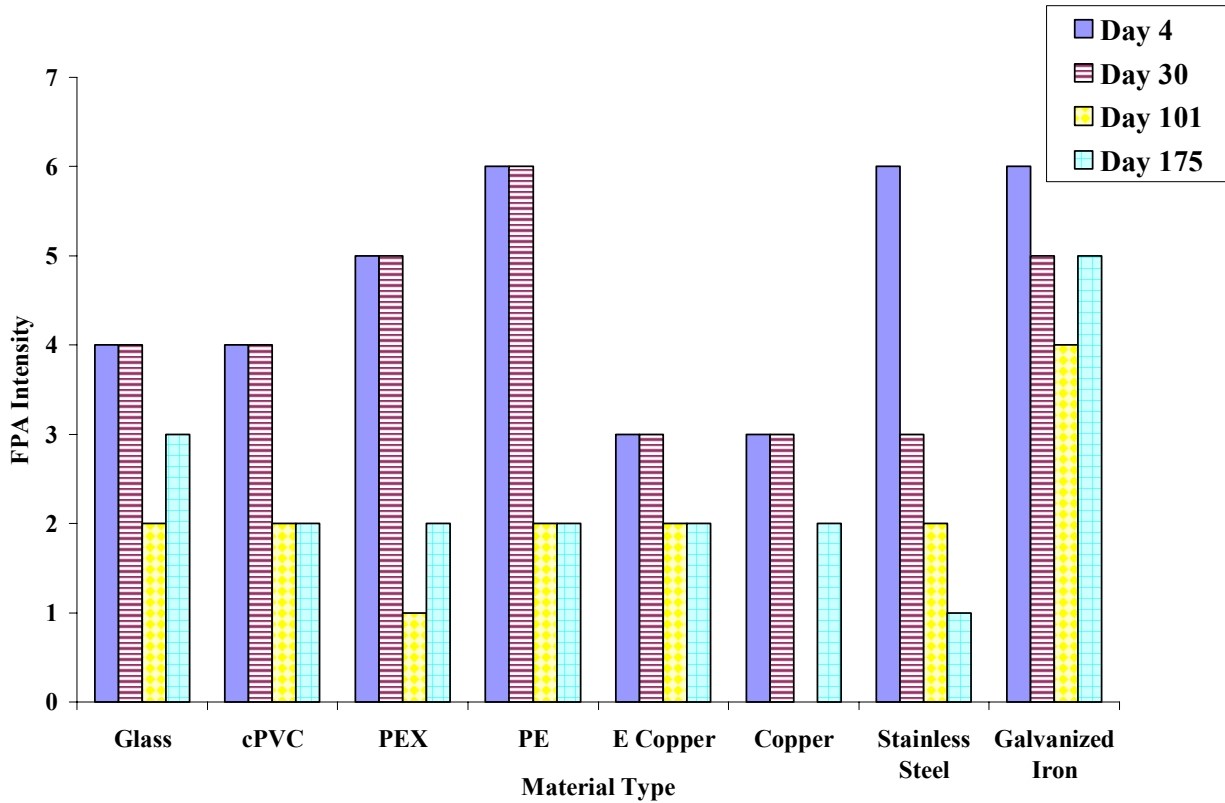
FPA Intensity

Day 4
Day 30
Day 101
Day 175

7

6

5

4

3

2

1

0

Glass cPVC PEX PE E Copper Copper Stainless Steel Galvanized Iron

Material Type

Figure 4-4. **FPA intensity determined over a 6 month period of pipe materials exposed to water with residual free chlorine. Residual free chlorine was 2 mg/L for days 4 and 30 and 0.5 mg/L for days 101 and 175.**

Overall higher FPA intensities were recorded for each material in the presence of chlorine as shown in Figure 4-3. PE contributed more intense odors than PEX or cPVC in the presence of chlorine. It is possible that the interaction of leached organics with free chlorine may be intensifying the chlorinous odor detected in samples after exposure to the plastic materials when compared to the copper and stainless steel. Similar to the trends observed in the absence of disinfectant, odors were more pronounced during the first month of sampling. Also the overall trend was a decline in odor intensity with operational time. Experimental conditions were changed from 2 mg/L to 0.5 mg/L free chlorine after the fourth month and coincide with the lower FPA intensities of "chlorinous" odor recorded. Another reasonable explanation may be simply that the quantity of odor causing compounds being leached from the pipes decreased with time.

An overall ranking of the plumbing materials exposed to residual free chlorine showed that galvanized iron pipe was the most odorous and copper the least (Figure 4-4). These data are based on FPA intensities attributed to both non-chlorinous and chlorinous type odors as previously detailed (Table 4-2; Figure 4-3).
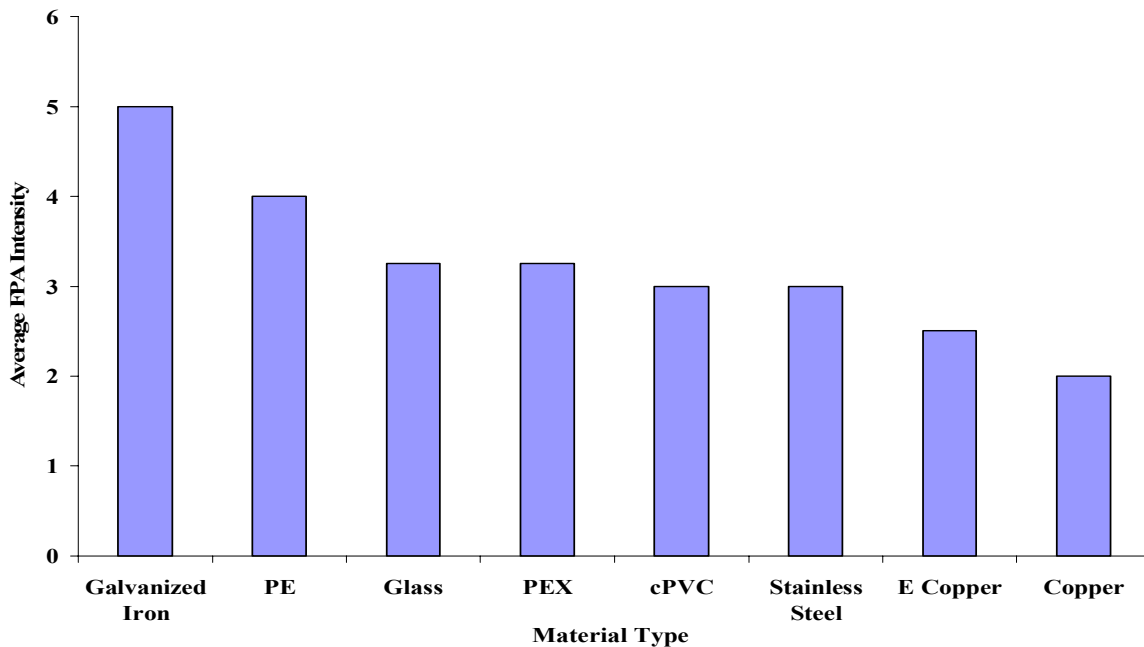

Figure 4-5   Overall ranking of plumbing materials in order of descending odor intensity in the presence of residual free chlorine based on average FPA intensities.

Plumbing Rig with Chloramines Disinfectant

Panelists noted that a "chlorinous" odor was not as potent or consistent in samples obtained from pipes exposed to chloramines disinfectant. Panelists attributed a combined "chlorine/almond" odor to the residual monochloramine present in water samples analyzed. This descriptor aided in differentiating between odors from residual free chlorine ("chlorinous") and monochloramine. The presence of additional odors such as "plastic" and "rubbery" was much more noticeable. Table 4-3 summarizes odors from pipes exposed to water containing chloramines disinfectant.

Table 4-3   Overall FPA descriptors for water samples contacted for 8 hours with different pipes in a plumbing rig in the presence of residual chloramines.

Pipe Materials	Time of Rig Operation (days)			
	4	30	90	160
Glass	Chlorinous	Chlorinous	Threshold[1]	Background
Chlorinated polyvinyl chloride (cPVC)	Chlorinous	Chlorinous	Threshold	Chlorinous
Cross-linked polyethylene (PEX-a)	Chlorinous/Almond	Chlorinous	Sweet Chemical	Background
Polyethylene (PE)	Chlorinous/Rubbery	Chlorinous/Sweet	Background	Sweet/Almond
Epoxy-lined copper (E.Copper)	Rubbery/Plastic	Chlorinated Oil	Chlorinous	Background
Copper	Grassy/Pungent	Oil/Chlorinous	Threshold	Bitter Mechanical
Stainless Steel	Sulfur Charcoal	Chlorinous	Sweet Chemical	Chalky/Cabbage
Galvanized Iron	Motor Oil	Motor Oil	Motor Oil	Motor Oil

[1]Threshold = Barely discernible odor

A few of the materials displayed characteristic odors in the presence of chloramines. Stainless steel leachate was described as "sulphur" and "chalky" but not "chlorinous" when in contact with chloramines containing water but had no previous such odor when contacted with water with no disinfectant or chlorine. Similarly copper metal displayed increased odors in the presence of chloramines disinfectant. PE and Epoxy lined copper also contributed distinct odors such as "rubbery" and "oily". Identical to the other two rigs, the "Motor Oil" odor from galvanized iron persisted at high intensity.

Corresponding FPA intensities for the odors summarized in Table 4-3 are graphed in Figure 4-5. FPA odor intensities declined with increased exposure of the material to chloraminated water. This was parallel with a decrease in residual disinfectant concentration from 4 mg/L to 1 mg/L as Cl_2, providing an explanation for the decline in odor similar to the plumbing rig with residual

free chlorine. A decrease in leached organics could also provide an explanation for the decrease in odor intensity observed, similar to that observed for the rig with no disinfectant.
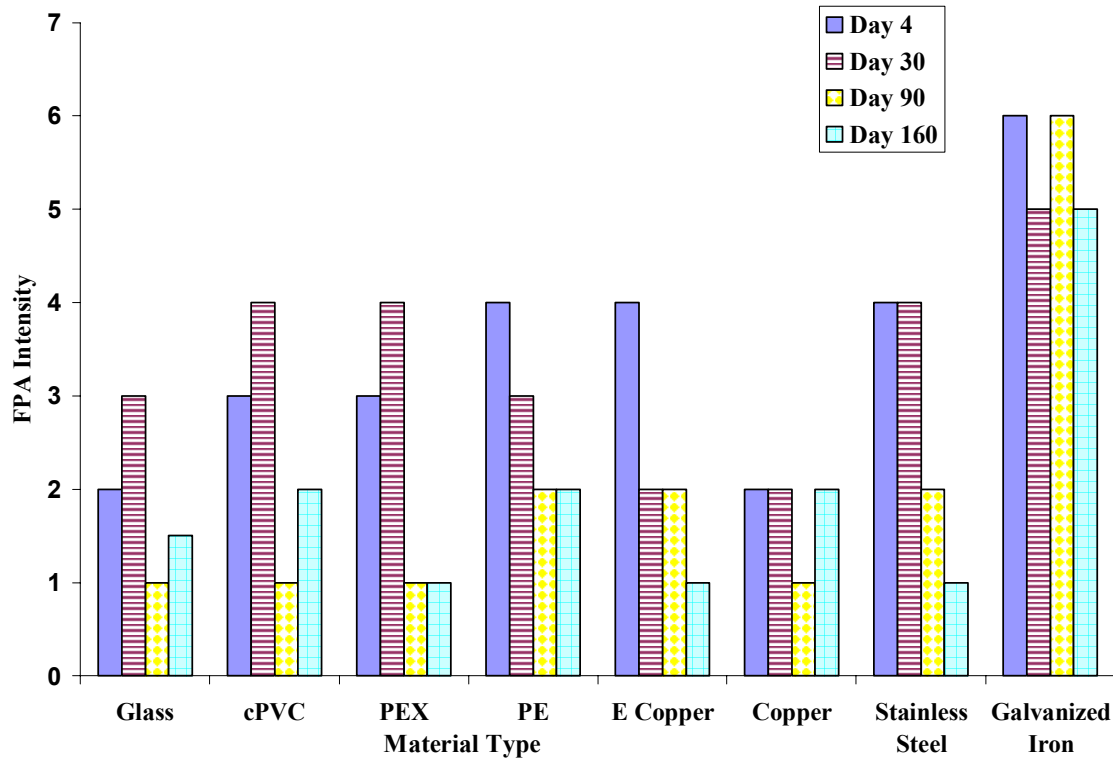

Figure 4-6.   FPA intensity determined over a 6 month period of pipe materials exposed to chloramines disinfectant. Residual monochloramines was 4 mg/L for days 4 and 30 and 1 mg/L for days 90 and 160.

Figure 4-6 depicts the odor ranking of the plumbing materials when used in the presence of residual chloramines. Similar to the results in the presence of residual free chlorine, galvanized iron was the most odorous material and copper metal the least odorous.
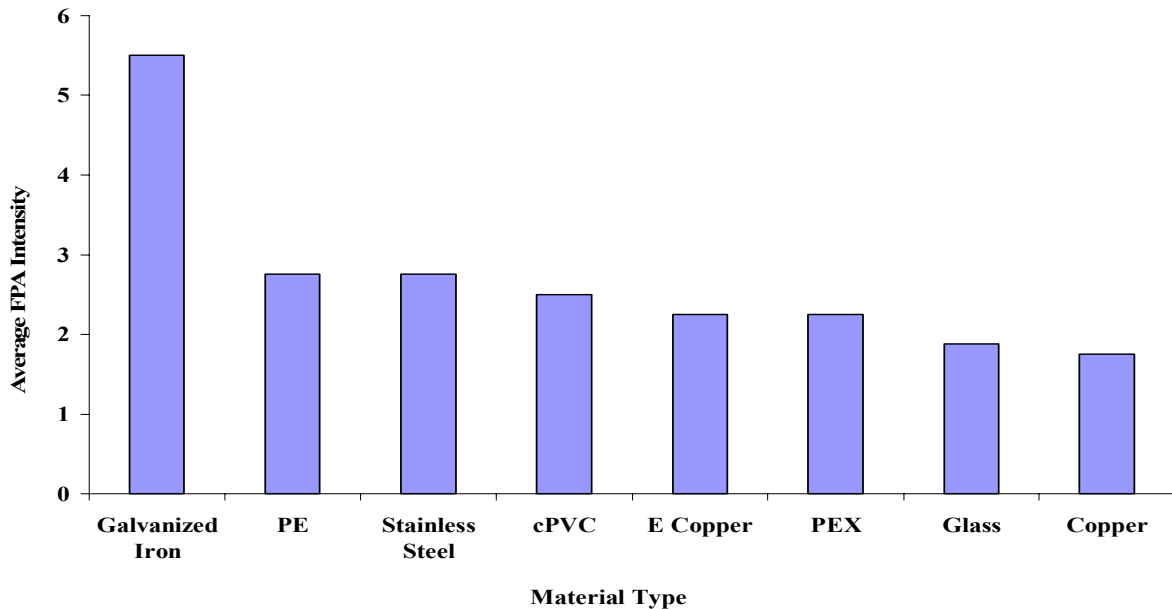
Figure 4-7   Ranking of plumbing materials in order of descending odor intensity in the presence of residual chloramines based on average FPA intensities.

Odors and the Role of Disinfectants

Our data indicate that the perceived intensity of the non-chlorinous plumbing associated odor was greater in the presence of chloramines than chlorine. This could be due to masking of the plumbing associated odor by the disinfectant when at high chlorine concentrations (1-2 mg/L as Cl_2). Previous studies have shown that the odor threshold concentration for chloramines is about two times higher than for chlorine (i.e, 0.15 – 0.65 mg/L monochloramine vs 0.06 – 0.36 mg/L free chlorine) (Krasner and Barnett, 1984; Piriou *et al*, 2004). Thus, chloramines are a poorer masking agent than chlorine and do not conceal the plumbing odor. This has implications for utilities converting to chloramines as their consumers may be better able to detect non-chlorinous odors in the presence of less odorous chloramines. The impact of chlorine and chloramines on the removal, masking and generation of odors in drinking water has been documented in previous work (Bruchet and Duguet, 2004).

The data also showed that of the three plastic pipes studied, polyethylene contributed the highest intensity plumbing material related odors to drinking water and was followed by PEX-a material. Very little odor was detected in water exposed to cPVC pipes. These results are supported by previous studies by Skjevrak *et al*. (2003) that showed that water in contact with high density polyethylene and PEX had TON $\geq$ 4 and 5 respectively, while water exposed to PVC had no significant odors. Epoxy –lined copper also displayed "plastic" odor causing potential during the first weeks of use. The trends for epoxy-lined copper were the same both in the presence and absence of residual disinfectant and similar to those reported in short-term migration tests (Heim and Dietrich, 2005).

TOC Analysis

Figure 4-7, 4-8 and 4-9 show a general increase in TOC concentration which fluctuated during the first 50 days that the rigs were in operation. Thereafter the TOC concentrations gradually leveled off. This directly correlates to the higher intensity odors detected during those first days of rig operation. This trend however was not shown to be true for galvanized iron. For galvanized iron the high odor intensity persisted both in the presence and absence of elevated TOC concentrations. There is a need to identify and characterize the organic compounds that contribute to the measured TOC. This will help in better understanding the odor characteristics of these materials.

Figure 4-7, 4-8 and 4-9 also show that the measured TOC concentrations of the tank were fairly consistent over time. TOC concentrations increased as much as 1 mg/L for some materials such as epoxy-lined copper in the presence of free chlorine and PEX in the presence of residual monochloramine compared to only about 0.4 mg/L for water with no disinfectant. It is reasonable to assume that any large increase in TOC is linked to the pipe material such as sorption, leaching or microbial growth.
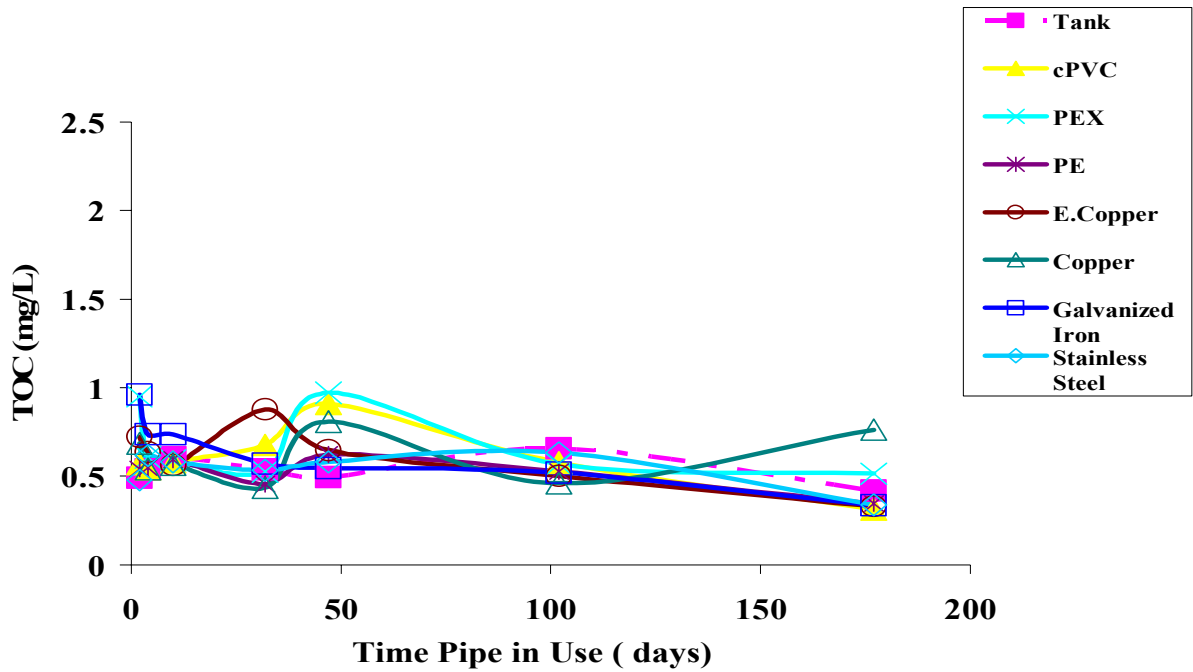
Figure 4-8   TOC variations in leachate samples from pipe material after exposure to synthetic water with an absence of disinfectant for 8 hour stagnation periods.
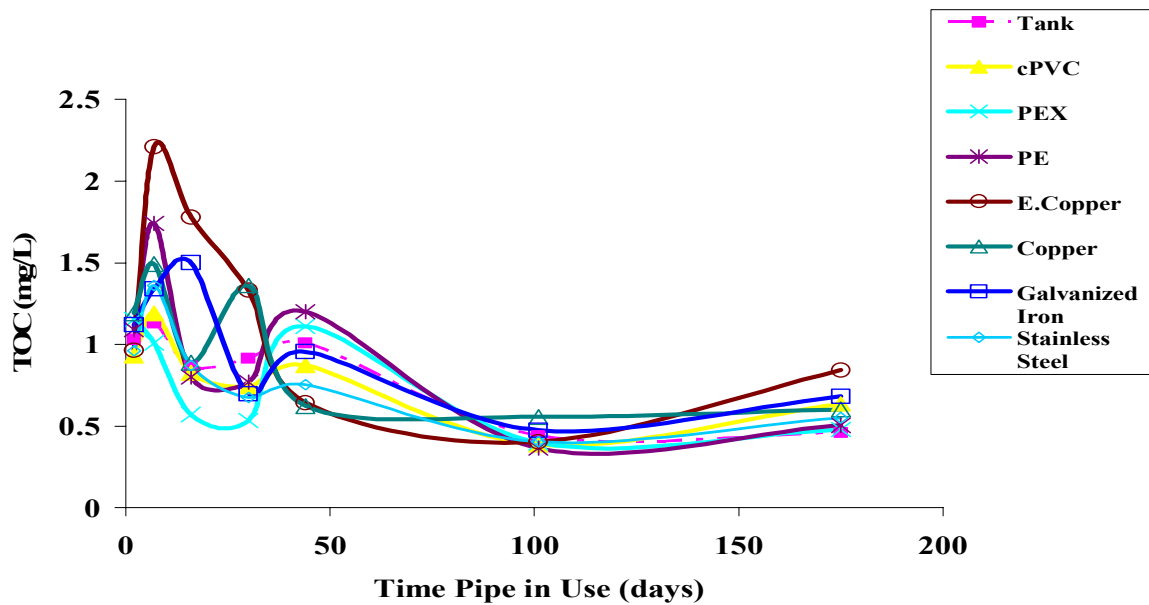

Figure 4-9   TOC variation in leachate samples from pipe materials after exposure to chlorinated synthetic water for 8 hour stagnation periods.
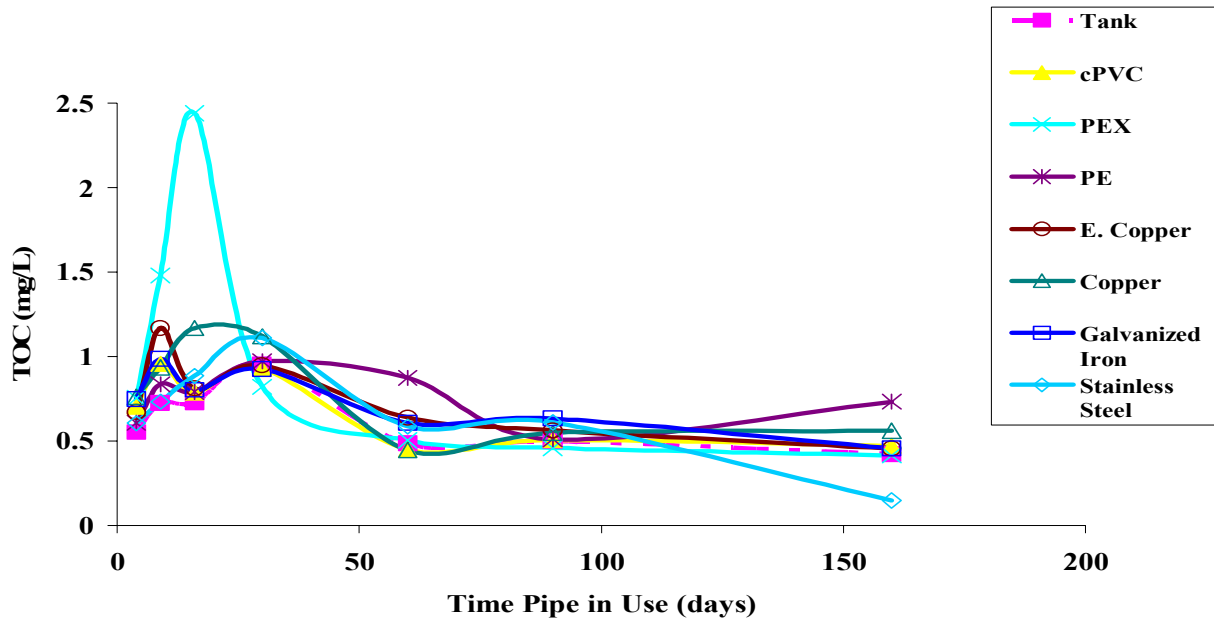
Figure 4-10   TOC variation in leachate samples from pipe materials after exposure to chloraminated synthetic water for 8 hour stagnation periods.

This study did not include analysis for microbial activity in pipe leachate. However, the potential for leached organic compounds to serve as a source of substrate for the growth of microorganisms such *Legionella, Mycobacterium* and *Pseudomonas* exists (Van der Kooij, 1999). The measured TOC concentration is not a good predictor of bacterial growth (Rizet *et al.,* 1982) because the ratio of biodegradable organic nutrients to TOC is not a constant value (Hascoët *et al.,* 1986). Only a small fraction of the measured TOC is susceptible to microbial attack, the rest consists of refractory organic compounds, generally called "humic substances" which are not available for microbial growth. Again the need for further characterization of measured TOC is highlighted. The impact of biofilms on the aesthetic properties (floc formation, turbidity, taste and odor) of drinking water needs further study. Potential deterioration of aesthetic quality can occur both in the storage tank and the distribution system (domestic and public)

Residual Disinfectant Demand

The trend in measured residual chlorine and monochloramine concentration for each sample time are as depicted in Figure 4-10 and 4-11 respectively. The most significant difference was observed for copper metal which consumed disinfectant. Loss of residual disinfectant as much as 1 mg/l free chlorine was observed for copper pipe. The resulting low concentration of residual disinfectant was also reflected in the reduced FPA odor intensities attributed to copper after exposure to experimental water (Figure 4-3).

Epoxy-lined copper also consumed chlorine and monochloramine residual and this occurred with an increase in TOC leached from the pipe and increased "plastic" odors. Similar phenomenon were observed during short term leaching migration test with epoxy-lined pipe and chlorine, chloramines and no disinfectant water where it was observed that increased TOC and decreased residual did not result in trihalomethane formation (Heim and Dietrich, 2005). The highest demand by the pipe material on residual chlorine or monochloramine occurred during the first week that the pipes were in contact with the water. A study by Lu *et al*. (1999), suggests that chlorine demand of synthetic pipes is due to deposits, water and biomass and demand of metallic pipes is due to the material, deposits and then water.
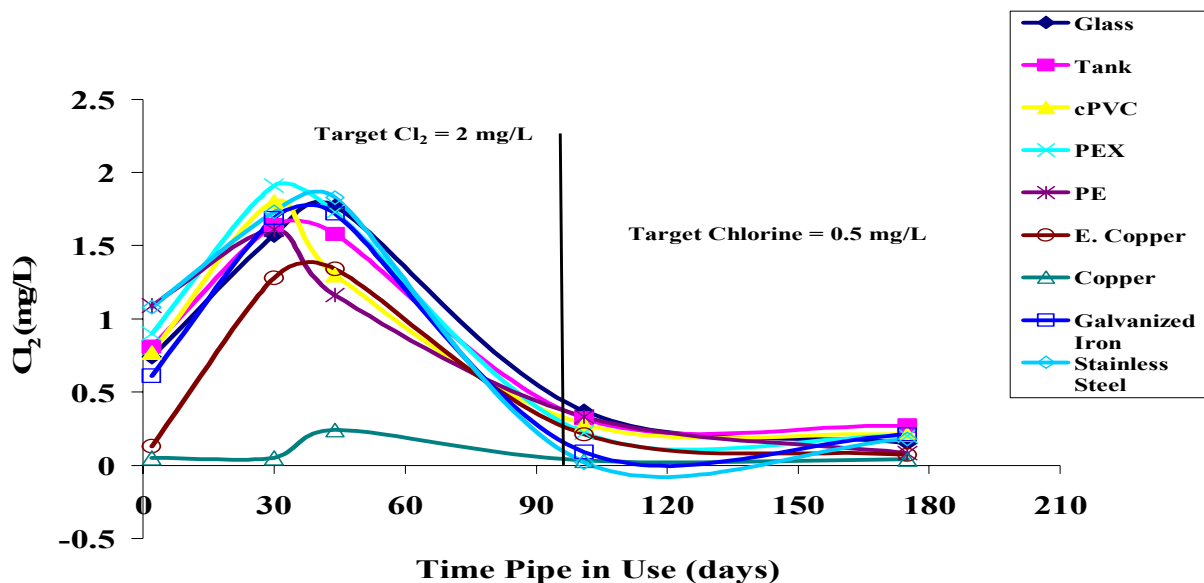

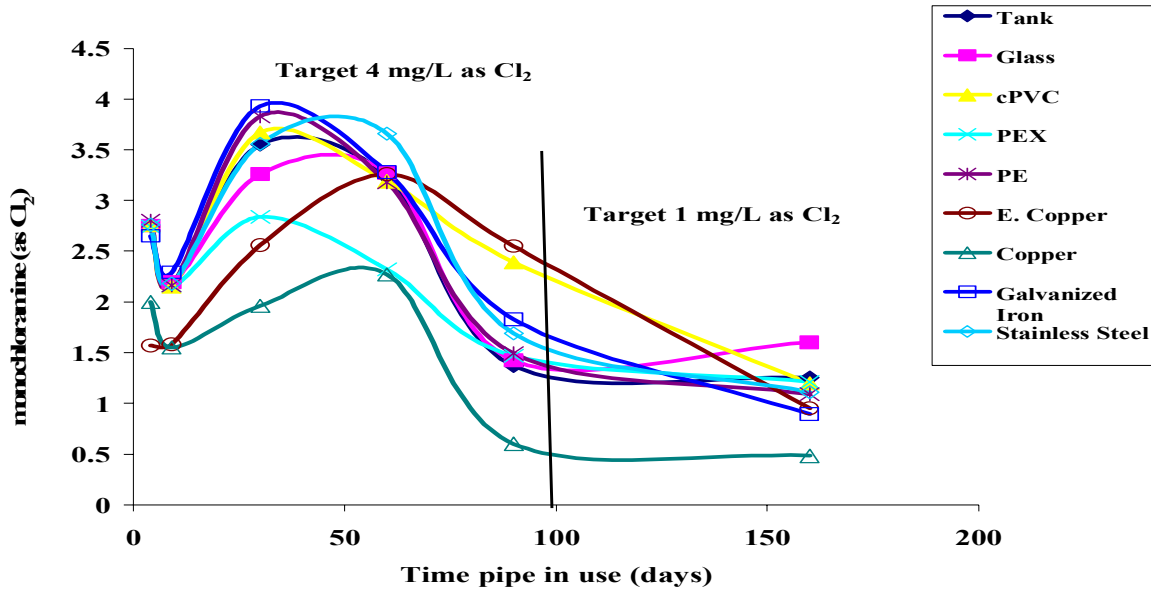**Figure 4-11. Residual free chlorine concentrations in pipe samples**

Figure 4-12.   Residual monochloramine concentration in pipe samples

CONCLUSION

This research showed that domestic plumbing materials have the potential to affect water quality characteristics such as TOC concentrations, residual disinfectant and odor. The increased TOC observed for some plumbing materials was consistent with the presence of a distinct odor or a high FPA intensity rating. There is a need to further study and characterize measured TOC leached from pipe samples. This research demonstrated that:

- New plumbing material generated odors during the first few days in use, but gradually decreased over time, EXCEPT for galvanized iron.
- Polyethylene was the most odorous plastic and galvanized iron the most odorous metal.
- The least odorous materials were chlorinated polyvinyl chloride and copper.
- Chloramines had less impact than free chlorine on masking non-chorinous odors from pipes.
- Free chlorine masked some of the specific odors associated with the pipes.
- Copper pipe consumed chlorine and chloramines.

The dynamism of the drinking water industry warrants innovative discoveries all specifically geared towards maximizing the understanding of complex aesthetic, chemical and microbial problems. Evaluating and understanding the potential of plumbing materials to impair the odor properties of drinking water will collectively benefit distribution and plumbing material manufacturers, utilities and most importantly, the consumers. The limits to research are abounding and need to be continuously explored and challenged.

ACKNOWLEDGEMENTS

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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: June 16, 2004

MEMORANDUM

TO: Andrea M. Dietrich Civil & Environmental Engineering 0246
             Monique Durand

FROM: David Moore

SUBJECT: **IRB Exempt Approval:**   "Taste and Odor Testing of Plumbing Materials" IRB
             # 04-321

I have reviewed your request to the IRB for exemption for the above referenced project. I concur
that the research falls within the exempt status.   Approval is granted effective as of June 16, 2004.

VITA

Monique Lucia Durand was born on December 1st, 1978, in the beautiful island of Dominica, better known as the "Nature Island of the Caribbean". After completing high school in 1995, she attended Clifton Dupingy Community College where she pursued A-level Biology, Mathematics and Chemistry for two years. Upon graduating from this institution Monique became employed at one of the more prestigious high schools in Dominica, the Convent High School. Monique worked as a high school teacher for three years, teaching mathematics and science to students between the ages of 11 and 16 years.

In the year 2000, Monique began her undergraduate degree in Environmental Science at Midwestern State University in Wichita Falls, Texas. While attending Midwestern State University, she participated in a summer undergraduate research program at the University of Arkansas, in Fayetteville, in the summer of 2002. This work was presented at the 225th American Chemical Society National Meeting in New Orleans in March 2003. Monique completed her Bachelors of Science Degree in three years.

Monique then entered Virginia Tech's Environmental Engineering program in the Fall of 2003 to pursue a Master of Science Degree. During the course of her graduate program, Monique attended and participated in several conferences. In November 2004, she presented at the AWWA Water Quality Technology Conference in San Antonio, Texas. In October of 2005, Monique also presented at the 7th IWA Symposium on Off-Flavors in the Aquatic Environment. This work was submitted for publication in the Journal of Water Science and Technology. At the IWA conference, Monique along with other research students assisted Dr. Dietrich, her academic advisor, and Gary Burlingame of the Philadelphia Water Works with a training workshop – "Sensory Analysis of Water: controlling geosmin and 2-methylisoborneol and other odorants".

Following graduation in December 2005, Monique will begin her career with Hazen and Sawyer, P.C., as an Assistant Engineer specializing in water and wastewater design in Hollywood Florida. Monique is excited and greatly anticipating the start of another journey in her life.