Critical Reviews in Environmental Science and Technology, 43:679–751, 2013
ISSN: 1064-3389 print / 1547-6537 online
DOI: 10.1080/10643389.2011.627005

Contaminant Migration From Polymeric Pipes Used in Buried Potable Water Distribution Systems: A Review

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Polymeric pipes are increasingly being installed in water distribution systems because of their many advantages. Contaminant migration from polymer pipes into drinking water is a growing concern in the United States and environmental engineers are evaluating the role of these materials on water quality, system operation, and regulatory compliance. To aid these efforts and serve as a source of background information, the authors critically review available literature on polymeric potable water pipes in use, known contaminants released from in-service and new piping, and their perceived sources, and outline future challenges in the United States and abroad.

KEY WORDS: contaminants, leaching, migration, pipe, polymer, plastics, water

INTRODUCTION

Polymer pipes are lightweight, inexpensive, easy to install, and do not have corrosion problems like their metallic and concrete counterparts. Due to these advantageous attributes, polymer pipes are increasingly being installed for potable water distribution globally. This increase is expected to continue because, according to an estimate, the United States will spend between $20 and $22 billion over the next 20 years to repair and replace its buried

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infrastructure (U.S. Environmental Protection Agency, 2002). Polymer pipe is thus progressively becoming the important link between safe drinking water that leaves the water treatment facility and the customer's tap. One critical concern facing polymer potable water pipe systems is contaminant migration from the polymer, and this problem has strong implications on material selection, system operation, and regulatory compliance. Although generally stable, several types of polymer water pipe are known to release inorganic and organic contaminants into water during service. To maintain high quality drinking water, water utilities must be certain that pipes do not liberate contaminants that compromise drinking water safety, aesthetic quality, or regulatory compliance.

Historically, problems occurred in the United States with unplasticized poly(vinyl chloride) (uPVC) by the discovery of vinyl chloride monomer (VCM) migration into drinking water, which led to the passage of a 2 μg/l VCM maximum contaminant level (MCL). In response, some water utilities removed and replaced previously installed uPVC pipes to lessen its impact on drinking water quality, while others increased system flushing frequency (Flournoy et al., 1999). The proposed drinking water regulation of methyl-*tert*-butyl ether (MTBE) in the U.S. Environmental Protection Agency's (USEPA) 2009 Contaminant Candidate List 3 (CCL3) and existing MTBE drinking water regulations in the states of California and New Hampshire also underscores the need to understand contaminant migration from polymer pipes (U.S. Federal Register [USFR], 2009). MTBE was primarily listed on the CCL3 and regulated in California and New Hampshire due to its popular use as a gasoline octane booster, high water solubility, and its wide occurrence as an environmental contaminant. However, MTBE was recently discovered to have been released from several new crosslinked poly(ethylene) (PEX) potable water pipes in Denmark, Germany, Norway, and the United States that were not previously exposed to gasoline (EDAW, 2009; Koch, 2004; Nielsen et al., 2007; Skjevrak et al., 2003). PEX pipe has historically been used for building plumbing and heating in the United States, but is increasingly being installed for buried water system since its approval in 2006 (American Water Works Association [AWWA], 2006).

Because of these problems, it is possible that polymer pipe could be an additional source of regulated and unregulated drinking water contaminants. This will likely complicate regulations, restrict its widespread use, and increase cost of intensive research. Because of the enormous importance of chemical leaching water quality and safety, some extensive research has been carried out worldwide to address this issue. However, no review article was found specifically pertaining to transport of chemical contaminants from polymer potable water pipes. Here we critically review available literature on contaminant migration for in-service and new polymer pipes used in North American water distribution systems. To better understand contaminant sources, their chemical nature, and the pathways by which they leave

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the host matrix, a brief summary is presented for polymers in use, known additives, and pipe production methods. Comparisons between published test methods and between water quality testing data for in-service and new polymer materials are also described to recognize the migration potential of these materials and outline future challenges in the United States and abroad.

TYPES OF POLYMERIC WATER PIPES

Poly(vinyl chloride)

PVC pipe has been installed since the 1970s, and is the most popular polymer pipe for buried water distribution in North America (Burn et al., 2005). In 1999, PVC pipes comprised 66% of the total buried potable water distribution pipe network worldwide (Rahman, 2002). In the United States, 95% of all small diameter pipes and 60% of pipes with diameters greater than 152 mm were PVC (Rahman, 2002). PVC is an amorphous thermoplastic with a glass transition temperature (T_g) of 82°C. Because its T_g is above room temperature, PVC is a glassy, rigid plastic. At present, there are four types of PVC pipe available: unplasticized PVC (uPVC or PVC-U), modified PVC (mPVC or PVC-M), oriented PVC (oPVC or PVC-O), and fusible PVC (fPVC). uPVC pipes up to 1200 mm diameter have been installed in North America (AWWA, 2007, 2010), while mPVC and oPVC are recent advances being increasingly used in Australia and Europe. mPVC pipes contain modifiers intended to improve the pipe's fracture characteristics. oPVC pipes contain polymer chains oriented in the hoop and along longitudinal direction for improved mechanical strength (Uni-Bell, 2001). oPVC pipes have been approved for use in North America up to 600 mm diameter (AWWA, 2009). Fusible PVC is a relatively new product, and its specific formulation, manufacturing methods, extent of use, and the American Water Works Association (AWWA) standards are not available. According to Marti (2005), fPVC formulations meet the requirements for PVC pipe as described in Plastic Pipe Institute Technical Report #2 (Plastic Pipe Institute [PPI], 2010). fPVC has been installed throughout the United States (Tanzi and Andreasen, 2011; Underground Solutions 2010a, 2010b).

Poly(ethylene)

Poly(ethylene) (PE) pipe is the second most commonly used polymer pipe in North America, and has been installed since the 1950s (Davis et al., 2007). There are many types of PE pipe that differ in chemical composition and operating conditions, but these materials have historically been generically classified as PE. All PE pipes have a subzero T_g, thus the material is flexible at room temperature and below ground temperature. All PE pipes are manufactured from PE resins having different densities, crystallinities, and T_g values: low-density (LDPE; 0.910 g/cm^3 $< \rho <$ 0.925 g/cm^3, $T_g = -20$°C),

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medium-density (MDPE; 0.926 g/cm^3 < ρ < 0.940 g/cm^3, $T_g = -70°C$), and high-density (HDPE; $\rho \geq 0.941$ g/cm^3, $T_g = -140°C$; PPI, 2010). LDPE, MDPE, and HDPE are thermoplastic materials. In the United States, HDPE pipes with diameter up to 1575 mm have been used for buried water transport (AWWA, 1999), while LDPE, MDPE, and HDPE pipes have been installed in Europe.

PEX pipes up to 76 mm in diameter are also used for buried water service (AWWA, 2006). PEX pipes are created from LDPE, MDPE, and HDPE polymers by chemically bonding polymer chains to one another during manufacture. These thermoset materials have improved resistance to mechanical failure under pressure. Before buried potable water usage, PEX pipes were most frequently installed for hot water transport in buildings and radiant floor heating. Three types of PEX are available, PEX type A (PEX-A), type B (PEX-B), and type C (PEX-C). Material and chemical permeation differences between six brands of HDPE and PEX-A and PEX-B pipes used in the United States can be found in Whelton et al. (2010).

Most recently, other PE alternatives have become available. Traditionally, HDPE pipes installed in North America were unimodal, containing only one polymer type or one molecular weight, but bimodal PE pipes are now offered. Bimodal PE pipes are a mixture of two different resins with distinctly different molecular weights. The lower molecular weight resin improves pipe flexibility, while the higher molecular weight resin provides material strength. Multilayer PE pipes are also used for buried water service. AWWA has approved multilayer PE pipes containing an aluminum barrier, which had previously been used for hot water plumbing. Aluminum barrier pipes are referred to as PEX-AL-PEX (or AL/PEX), PE-AL-PE (or AL/PE), and PE-AL-PEX. Only two reports were found that described contaminant migration from multilayer PE pipes in our literature review, and both were conducted outside the United States. One study documented the type of PEX used for multilayer pipe (e.g., PEX-C-AL-PEX-B; Nielsen et al., 2007), and the other report examined chemical migration from generically described PE multilayer materials (Koch, 2004).

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Poly(1-butene)

The most infamous polymer pipe event in North America involves the widespread premature failure of poly(1-butene) (PB) pipe. PB has a T_g of –35°C, and its pipe is also known as poly pipe, gray pipe, or polybutylene pipe. From 1978 to 1995 PB pipe was installed across the United States for buried water service connections and building plumbing. In as little as five years of service, PB pipe cracking, leaking, and bursting incidents occurred, which was caused by its vulnerability to chlorinated water attack. From 1995 to 2009, the $1.1 billion dollar PB Pipe Settlement Fund established by court order facilitated the replacement of more than 330,000 PB building plumbing systems. Since the 1980s, PB pipe installation has curtailed in North America,

though some buried water distribution systems still have this polymer pipe installed (Dietrich et al., 2010). Chemical migration from PB pipe will not be reviewed because this pipe is no longer commonly installed.

Fiber Reinforced

Fiber reinforced pipe (FRP) is a polymer composite material and typically used for large diameter (>200 mm) water mains, up to 4000 mm diameter (AWWA, 2007). FRP comprises an epoxy or polyester resin, reinforcement fibers such as glass or carbon based, sand, and other fillers. In the United States, this material is generically referred to as plastic pipe or fiberglass pipe (Tomboulian et al., 2004). In England, FRP is primarily polyester based (Carthorne et al., 1990). FRP consists of three layers: a liner in direct contact with the drinking water; a polymer layer impregnated with wound glass filaments, chopped glass, sand aggregate, or glass mat reinforcements to provide mechanical resistance; and a gel coat or external layer comprising polymer without glass reinforcement. Depending on pipe composition, these materials are also referred to as glass reinforced epoxy (GRE) pipe, glass reinforced pipe (GRP), glass fiber reinforced pipe (GFRP), and glass reinforced plastic (GRP) pipe. Notably, the same acronyms are used for different words in relation to fiber reinforced materials. No compositional or usage information was found for fiber reinforced water pipes in the United States or other countries.

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MATERIALS AND PIPE PRODUCTION

To understand the origin of contaminants detected in drinking waters, polymer manufacturing methods are briefly reviewed here. PVC and PE pipe production practices are readily available in the literature, but such information for multilayer and FRP materials are sparse. Past studies have demonstrated that processing conditions used in polymer and pipe manufacturing can degrade polymer chains and additives, which generates low molecular mass compounds that remain in the pipes after manufacturing. Table 1 lists chemical compounds and their functions in water pipe manufacturing.

Thermoplastic Pipes

While PVC and PE are chemically and morphologically different materials, they both use ethylene monomer as a base molecule. To create PVC, ethylene is combined with chlorine to form ethylene dichloride. At high temperature, this compound is converted to VCM and is subsequently polymerized to form PVC resin. Resin and other additives are then mixed and extruded into pipes. After molded pipe exits the extruder, vacuum cooling occurs followed

TABLE 1. Compounds Used for Polymeric Potable Water Pipe Production

Component	Purpose
Monomer	Base compound used to create the resin.
Antioxidant	Protects the polymer from oxidation during processing, storage, and use. Antioxidants can act locally or migrate through a polymer to intercept and eliminate oxidants. Common antioxidants include alkylphenols, Irganox 1010, 1330, 1076, and Irgafos 168, and 4-methyl-2,6-di-*tert*-butylphenol (BHT).
Accelerant, Retarder	Accelerators increase and retarders decrease reaction rates (e.g., vulcanization, crosslinking) and can include nitrogen- and sulfur-containing compounds.
Catalysts	Initiate chemical reactions between monomer units and/or between monomer and additives. Catalysts can include metals.
Colorant	Provide color, including iron oxide, chromium oxide, or titanium dioxide.
Crosslinker, Photoinitiator	Initiate chemical reactions between monomer units and/or between monomer and additives. PEX-A pipes are created using di-*tert*-butyl peroxide, *tert*-butyl perbenzoate, dibenzoyl peroxide, diacetyl peroxide, dicumyl peroxide, and 2,5-dimethyl-2,5-di-(*tert*-butylperoxy) hexyne-3, di-(*tert*-butyl peroxy isopropyl) benzene, and 1,1-di-(*tert*-butyl-peroxy)-3,5,5-trimethylcyclohexane. PEX-B pipe is created with silanes such as vinyltriethoxysilane, vinyltris(2-methoxyethoxy)silane, and 3-methacryloxypropyltrimethoxysilane. Photoinitiators include benzophenone, 4-chlorobenzophenone, and sulfuryl chloride triallyl cyanurate, and triallyl isocyanurate.
Reticulating agent	Improve crosslink density. Examples include styrene, dimethyldioctadecylammonium bromide, tetradecyltrimethyl ammonium bromide (TTAB).
Curing Agent	Promote or control curing reactions. Examples include isophorone diamine, 2,2,4-trimethyl hexamethylenediamine (TMHD), *p*-toluenesulphonic acid (PTSA), diethylenetriamine, and triethylenetetramine.
Solvent	Used to dilute mixture, improve processing. Examples include methyl isobutyl ketone (MIBK), methyl isoamyl ketone (MIAK), toluene, and xylenes.
Filler	Lessen the amount of resin needed to reduce cost. Fillers can also improve properties such as strength. $CaCO_3$ is commonly applied.
Reinforcement	Improve material strength properties. Glass fibers are used for GFPs.
Impact Modifier	Improve material resistance to impact. Examples include acrylonitrile butadiene styrene, chlorinated poly(ethylene), and acrylic copolymers and are added to mPVC pipe. One study reported PVC water pipe contained PEX as a modifier (Ong et al., 2008), though this claim was not supported in the literature.
Flame Retardant	Decrease flammability.
Lubricant	Increases polymer slippage during processing. Examples include palmitoleic acid, palmitic acid, lauric acid, calcium stearate, magnesium stearate, and dimethyldiheptadecylammonium bromide.

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TABLE 1. Compounds Used for Polymeric Potable Water Pipe Production *(Continued)*

Component	Purpose
Plasticizer	Increase polymer flexibility and pliability. Examples include dialkyl phthalates, adiptaes, sebacates, ricinoleats, and aryl phosphates.
Resin	Solid or liquid that consists of polymer chains after some degree of chemical reaction. Typically an intermediary product after synthesis and before commercial product manufacture. Resin is also referred to as an ingredient in epoxy synthesis. Epoxy resin can include a copolymer of bisphenol A diglycidyl ether (BADGE) and epichlorohydrin.
Stabilizer	Protects polymer chains from thermal or photolytic degradation during the manufacturing or post-manufacturing storage and transport. Carbon black is a common UV stabilizer and other stabilizers include 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 4-butoxyphenol, Ionol 220, metal laureates, octoates, stearates, cadmium-barium pherates, alkyltin dilaurate and maleate, epoxidized linseed and soybean oils.

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by water spray cooling. For mPVC pipe, modifiers are incorporated during extrusion. For oPVC pipe, polymer chains are oriented radially around the pipe circumference. No fPVC production methods were found.

To obtain PE resin, ethylene molecules are directly polymerized into PE. Free-radical polymerization and Ziegler-Natta catalyst are used for producing PE polymer of different density/crystallinity (e.g., LDPE, MDPE, HDPE). A unique difference between PE and PVC polymers is that PE is a semicrystalline material, where crystalline and amorphous polymer chain packing regions coexist. PVC is a completely amorphous material. This morphology difference has a strong effect on transport behaviors of these polymers. Molecular transport is greatly reduced in crystalline regions of a polymer. When PE crystallizes from the melt, the degree of crystallization is determined by cooling conditions as well as the degree of short- and long-chain branching of the resin. Resins with many side branches are less crystalline and less dense than those with fewer branches (e.g., LDPE vs. HDPE). After PE resin synthesis, additives are compounded into resin, which are then extruded into a pipe. Resin composition and relative quantities used for bimodal PE pipe were not found.

Thermoset Pipes

PEX

PEX-based pipes are produced from the same resins used to create LDPE, MDPE, and HDPE pipes. Thermoplastic resins are crosslinked by chemical or radiation processes that transform them into thermosets. Three different

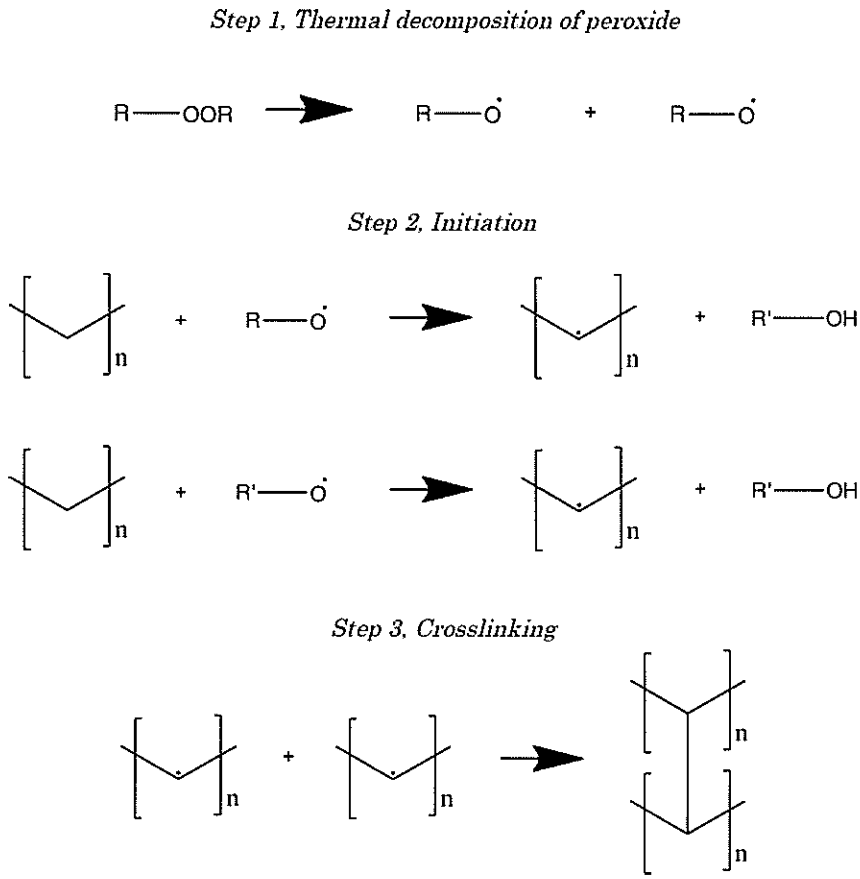

FIGURE 1. Chemical reactions for peroxide-crosslinked PEX manufacturing.

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types of PEX are used for potable water pipe, PEX-A, PEX-B, and PEX-C, and their chemistry and manufacture methods differ quite substantially (Jee et al., 1997; Loan, 1972; Murphy, 1996; Peacock, 2001).

PEX-A pipe is manufactured using the Engel method, also known as the peroxide method. Heat-activated peroxide compounds are incorporated into the polymer below the peroxide decomposition temperature to limit pre-curing in the extruder. Generally, 1.4–6.6 g of peroxide compound is added per 100 g of polymer (Murphy, 1996). Upon heating, the peroxides decompose into free radicals that subsequently extract hydrogen atoms from the PE polymer chain enabling crosslinking (Figure 1).

PEX-B pipe is created using either the Monosil or Sioplas process. The Monosil approach grafts vinylsilane onto polymer chains during extrusion. The Sioplas technique involves the use of PE resin compounded with vinylsilane and an organic peroxide compound late in the pipe extrusion process. For both manufacturing approaches, silane molecules are first grafted

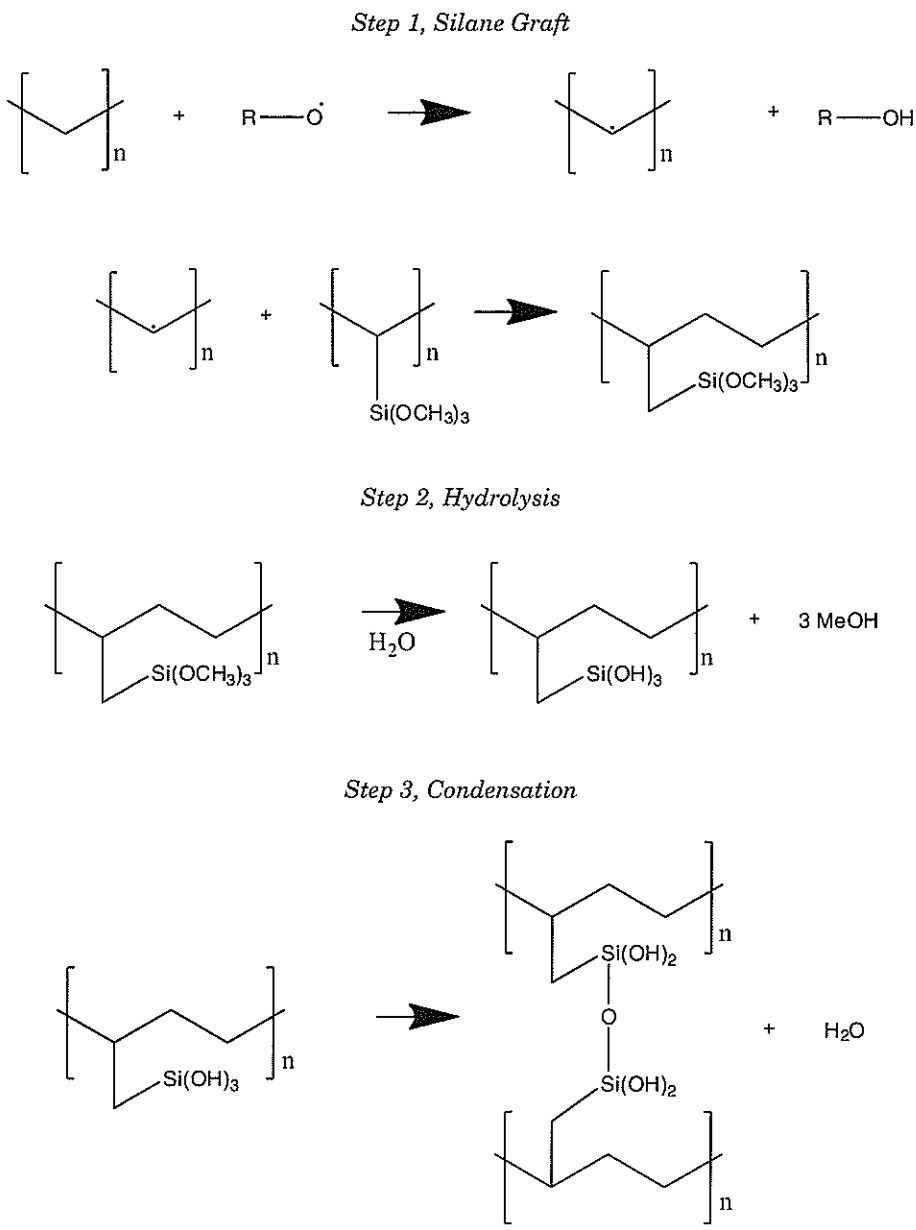

FIGURE 2. Chemical reactions for silane PEX manufacturing.

to the PE chains (Figure 2). Hydrolysis follows and the radical initiator attaches neighboring polymer chains, and methanol is typically a byproduct. During extrusion, silane and peroxide compounds are mixed into the resin. Crosslinking is facilitated by either immersing PEX-B pipe in a high-temperature water bath or steam chamber for several hours.

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PEX-C pipe manufacturing is commonly referred to as the beta irradiation method or clean method since no crosslinking agents are required. PEX-C pipe is produced by applying a high-energy beam to the material below its melting temperature during extrusion. Hydrogen atoms are removed and alkyl radicals are created, which subsequently crosslink the polymer. Beam exposure is accomplished by passing the pipe through a linear accelerator multiple times. Unlike PEX-A and PEX-B pipe methods, PEX-C manufacturing is carried out when the PE is in solid state and does not involve any solvents. No data were found for methods used to produce multilayer PE pipes.

FRP

FRPs are three-layer composites and their manufacturing involves three phases using a filament winding process and mandrel (Demir, 2010). The mandrel is externally lined with steel band and a Mylar film. This interface enables the pipe to detach from the mandrel after production. Reinforcement impregnated with liquid resin of a predetermined thickness is applied to the mandrel. The external layer consists of 70% resin and 30% chopped glass, and its thickness and composition depend on the desired pipe mechanical characteristics. All percentages for concentration used in this paper are based on material mass. Type E or C glass is added, which is comprised of mainly SiO_2 (>50%) and some fractions (<25%) of Al_2O_3, B_2O_3, CaO, MgO, Na_2O, F_2O_3, ZnO, and TiO_2 (Murphy, 1996). The resin used can contain curing agents. In Great Britain, polyester resin has been used for FRPs (Carthorne et al., 1990), while in the United States, epoxy resin has been more common. Polyester pipes are heated to accelerate crosslinking with organic peroxides, while epoxy is formed by reacting diglycidyl ether of bisphenol A (DGEBA) with an amine.

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Additives

Additives such as antioxidants, stabilizers, lubricants, and fillers are commonly incorporated into polymers to improve their properties such as mechanical strength, resistance to degradation, flexibility, color, and processing ease (Table 1; Murphy, 1996). Degradation products of those additives may also exist in polymer pipes (Brocca et al., 2002). With the exception of uPVC pipe, ingredients used to manufacture other types of PVC and polymer pipes were not well documented. PVC pipes generally contain 70–90% resin and 10–30% additives (Burn et al., 2007). As Table 2 demonstrates, formulation varies between and within countries and potentially between products. Discussions with pipe industry experts confirmed that formulation data for PE pipes and FRPs is not publically available, and some general additives are known for PVC pipes (Table 2; Burn et al., 2005; PPI, 2010). Next generation

TABLE 2. Comparison of an American and Australian PVC Pipe Formulation

Purpose	Compound description	U.S. formulation, phr	Australia formulation, phr
Resin	PVC Pipe Resin (K67)	100.0	100.0
Stabilizer	6% Tin pipe stabilizer	0.40	—
Stabilizer	Calcium stearate	0.60	0.65
Lubricant	Oxidized poly(ethylene) wax [unspecified]	0.20	—
Lubricant	165 parrafin wax	1.75	—
Filler	Calcium carbonate	4.00	—
Pigment	Titanium dioxide	1.50	2.00
Stabilizer	Thermolite 178-Atofina (Butyltin mixed thio complexes; 4-nonylphenol[branched]; alkylmercaptoester; Petroleum distillates)	—	0.70
Filler	Filler 1T-Omya (Calcium carbonate)	—	2.70
Lubricant	Metablen P700 (Acrylic processing aid)	—	0.75
Lubricant	Loxiol G60 (Palmityl stearyl phthalate)	—	0.15
Lubricant	Paraflint H1-Schuman Sasol (Paraffin wax)	—	0.50
Lubricant	H12-Clariant Licolub (Oxidized MDPE wax)	—	0.15
Lubricant	AC617 Wax (LDPE homopolymer wax)	—	0.15
Lubricant	AC307A (Oxidized HDPE homopolymer)	—	0.10

Note. Table expanded from Burn et al. (2005). Chemical composition of Australian pipe compounds was obtained from Material Safety Data Sheets. phr = parts per hundred parts of resin.

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polymer pipes containing nanosize additives are being increasingly developed and will likely be commercialized in the next 20 years (Whelton et al., 2011a). Since the potential hazard of nanomaterials is not known, nanomaterials incorporation will likely present further challenges in regulation, environment, health, and safety (EHS) of polymer potable water pipes.

Byproducts Produced During Pipe Manufacturing

PVC and PE pipe processing involves high mechanical stress, temperature, irradiation, and chemical transformations that can cause chain scission in polymers and degradation of additives. In addition, PEX pipes undergo further processing with crosslinking or irradiation. This chemical reaction step will likely result in unreacted initiators and initiator degradation products to remain in the pipes after manufacturing. Irradiation can also directly cause polymer chain scission, producing low molecular mass molecules. While FRP pipe production also involves high temperature, little data on manufacturing byproducts are available for this polymer pipe.

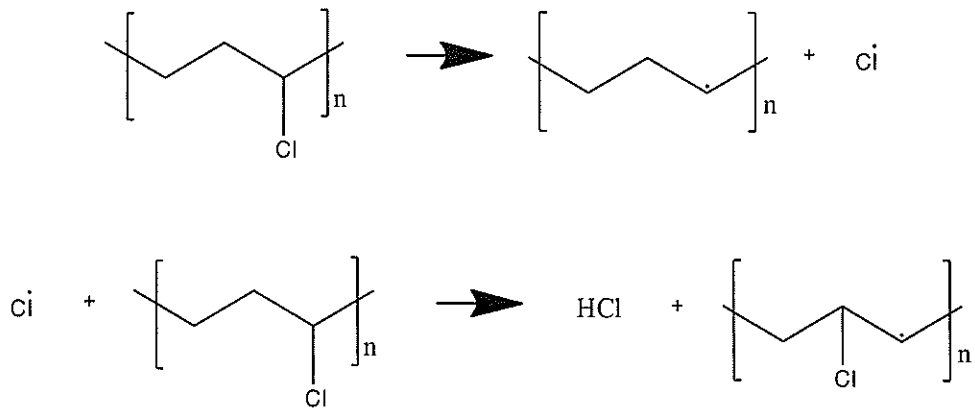

FIGURE 3. Chemical reactions for PVC dehalogenation.

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During PVC extrusion, dehydrochlorination is the primary polymer degradation mechanism and can initiate at temperatures greater than 150°C (Sombatsompop et al., 2004; Zheng et al., 2003). Dehydrochlorination results in conjugated double bonds, HCl, and chloride radical ($Cl^{\bullet}$) formation (Figure 3). This reaction is accelerated in the presence of oxygen, which facilitates carbonyl formation in the polymer (>C=O). Conjugated double bonds are vulnerable to crosslinking and scission reactions (Sombatsompop et al., 2004). To scavenge HCl during extrusion, metal-based thermal stabilizers are commonly added to PVC.

For PE materials, auto-oxidation is common during extrusion. Specifically, auto-oxidation fractures polymer chains, thereby producing low molecular mass ketones, aldehydes, alcohols, and carboxylic acids (Andersson et al., 2004; Anselme et al., 1986; Iring and Tudos, 1990). Auto-oxidation is a three-step autocatalytic process that occurs in the presence of oxygen and begins once free radicals are produced (Figure 4). Auto-oxidation involves hydrogen atom abstraction from polymer chains (R) by free radicals (alkyl radical [$R^{\bullet}$], peroxy radical [$ROO^{\bullet}$], hydroxyl radical [$HO^{\bullet}$], hydrogen radical [$H^{\bullet}$]). This process continues until free radicals are either bound with additives (e.g., antioxidants) or themselves. Primary auto-oxidation products include water, CO, and CO_2 and nonvolatile and volatile organic compounds to a lesser degree (Iring and Tudos, 1990). Product types and quantities depend on a variety of material-related factors such as resin type, purity, initiators, degree of thermal stabilization, residence time, and temperature. During PEX pipe manufacture, auto-oxidation is intentionally initiated with organic peroxide compounds to create crosslinks (Iring et al., 1979; Peacock, 2001). The polar, oxidized products have a strong affinity for water and can be hydrolyzed, chemically transformed, or dissolved in aqueous solution and in the presence of other contaminants.

Step 1, Initiation Reactions

$$RH + O_2 \rightarrow R^{\bullet} + HOO^{\bullet}$$

$$ROOH \rightarrow RO^{\bullet} + HO^{\bullet}$$

$$ROOH + RH \rightarrow RO^{\bullet} + H_2O + R^{\bullet}$$

Step 2, Propagation Reactions

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + RH \rightarrow R^{\bullet} + ROOH$$

$$RO^{\bullet} + ROH \rightarrow R^{\bullet} + ROOH$$

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$

$$ROOH \rightarrow ROO^{\bullet} + H^{\bullet}$$

Step 3, Termination Reactions

$$R^{\bullet} + R^{\bullet} \rightarrow RR$$

$$ROO^{\bullet} + ROO^{\bullet} \rightarrow ROOR + O_2$$

$$ROO^{\bullet} + R^{\bullet} \rightarrow ROOR$$

$$RO^{\bullet} + R^{\bullet} \rightarrow ROR$$

$$RO^{\bullet} + RO^{\bullet} \rightarrow ROOR$$

$$RO^{\bullet} + H^{\bullet} \rightarrow ROH$$

$$R^{\bullet} + H^{\bullet} \rightarrow RH$$

FIGURE 4. Chemical reactions for PE auto-oxidation. The following symbols are defined for clarification: Polymer chains [R], alkyl radical [$R^{\bullet}$], peroxy radical [$ROO^{\bullet}$], hydroxyl radical [$HO^{\bullet}$], hydrogen radical [$H^{\bullet}$].

Additive degradation is another source of manufacturing byproducts. Additives such as antioxidants, stabilizers, crosslink initiators, and processing aides can decompose during processing. To prevent PE oxidation, additives such as Irganox®[1] 1076 and Irganox® 1010 and Irgafos® 168 are used during extrusion (Ciba Specialty Chemicals, Inc., Tarrytown, NY, USA). Antioxidant degradation products can remain in the polymer after manufacturing (Piringer and Baner, 2000).

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Organic peroxides are commonly used for PEX-A and PEX-B pipe manufacturing and peroxide decomposition during processing is intentionally facilitated to create radicals, which are required for crosslinking reactions. When one common radical initiator di-*tert*-butyl peroxide is present, byproducts MTBE, TBA, and ether-*tert*-butyl ether (ETBE) can be produced and remained in the polymer. A proposed reaction scheme for byproduct production of this initiator during high-temperature pipe extrusion includes (a) degradation of di-*tert*-butyl peroxide into TBA, (b) dehydrogenation of TBA to isobutylene, and (c) isobutylene reaction with ethanol or methanol to form ETBE or MTBE, respectively (Figure 5). Ethanol and methanol could be formed due to vinylsiloxane hydrolysis or hydrogen reduction of other reaction byproducts (Iring and Tudos, 1990; Peacock, 2001). EDAW (2009) recently documented MTBE migration from PEX pipes (types not identified)

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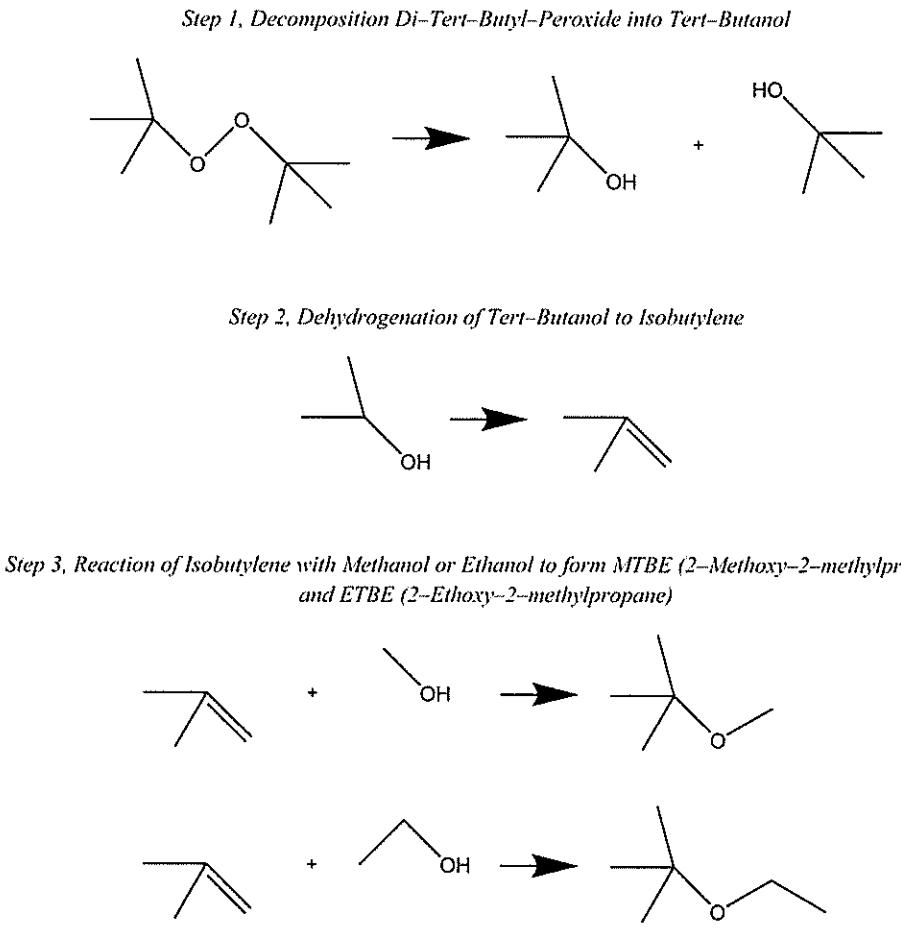

FIGURE 5. Chemical reactions for MTBE, ETBE, and TBA production during PEX manufacturing. Scheme is based on Baur et al. (1990).

purchased in the United States, and their report is discussed later in this article.

FACTORS AFFECTING CONTAMINANT MIGRATION AND INDIRECT AND DIRECT MIGRATION INDICATORS

Past investigators have primarily detected (and sometimes quantified) contaminants that migrated from polymer pipes into drinking water, but few have identified the principal factors that affect contaminant migration. Fundamentally, the rate of migration is described as molecular diffusion of a substance through a polymer material having certain thickness into water. Diffusion, commonly expressed by the diffusion coefficient (D), occurs in response to a concentration gradient expressed as the change in concentration due to a change in position. Diffusion will occur until an equilibrium concentration of the contaminant between the polymer and water is established.

Diffusion in polymers is a function of both contaminant and polymer properties (Comyn, 1985; Crank, 1975). Generally, small molar volume contaminants diffuse faster through polymers than larger, bulkier compounds. Diffusion through amorphous or low crystalline materials is typically faster than that in higher crystalline materials of the same type (e.g., LDPE vs. HDPE). Crosslinks restrict contaminant transport and contaminants can diffuse through less crosslinked materials faster due to the less tortuous path. Because the free volume in a polymer is greater above its glass transition temperature, diffusion at a temperature above T_g is much faster than diffusion below it. Therefore, if the water temperature exceeds the polymer's T_g, diffusion through the polymer is greater as compared to water temperature below T_g. Increased water temperature generally increases the rate of contaminant release, and elevated temperature is commonly used in the laboratory to accelerate migration (sometimes without regard for the effect of temperature on material properties). Contaminant and polymer polarity can also affect transport. For example, polar contaminants such as those that contain alcohol, aldehyde, and ketone functional groups generally diffuse out of nonpolar polymers faster than nonpolar contaminants of equal size and shape. Whelton and coworkers recently discovered that polar organic contaminants diffused much faster into oxidized PE pipe surfaces and much slower out of these same oxidized materials than through new PE pipes (Dietrich et al., 2011; Whelton et al., 2010, 2011b). These findings are particularly important because no previous study examined the role of chlorinated water exposure on contaminant migration from polymer pipe.

Environmental conditions and water quality can also affect diffusion rate. Specific research on polymer pipe has shown that low water pH, greater water hardness, greater total dissolved solids (TDS) concentration, and larger chloride-to-sulfate ratios increase metal stabilizer release from PVC pipe

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TABLE 3. Surface Area-to-Water Volume Ratios for 3-m-Long HDPE Pipes

Pipe outer dimension, cm	Nominal inner diameter, cm	SA/V ratio, cm^2/ml
2.5	0.939	4.26
5.0	1.697	2.36
10	3.214	1.24
20	6.161	0.65
30	9.108	0.44
40	11.43	0.35

Note. Calculations based on a SDR-9 HDPE pipe 10 ft (3.048 m) length with nominal inner pipe diameter according to ASTM 3350 (ASTM 2010).

(Al-Malack, 2001; Al-Malack et al., 2000; Burn and Sullivan, 1993; Lasheen et al., 2008; Packham 1971c). Migration has also been found to be faster under turbulent flow compared to laminar flow conditions (Denberg et al., 2007), where the aqueous concentration is near zero at all times. This finding is consistent with Fick's first law of diffusion where the rate of transfer of a diffusing substance through unit area is proportional to the concentration gradient (Crank, 1975).

Aqueous contaminant concentration is also influenced by the total surface area of the polymer in contact with water (surface area-to-water volume ratio [SA/V]), retention time, and polymer's conditioning history. Generally, a large SA/V ratio is indicative of a small diameter pipe (Table 3). Longer retention times (exposure periods) typically result in a greater mass of contaminant accumulated in the water. A polymer pipe's water exposure history (e.g., rinsing, flushing, stagnation) also influences aqueous contaminant concentration. Pipes that have been prerinsed before migration testing will likely have less contaminant to release than those that are examined as is. Another factor that complicates the migration testing of PVC pipe networks is that adhesive used to join PVC pipes can increase contaminant migration from the joints (Jones-Lepp et al., 2001; Rhodes et al., 1980).

Historically, contaminant migration has been investigated by applying indirect and direct methods. Indirect methods involve monitoring a water's total organic carbon (TOC) concentration, pH, disinfectant level, and taste and odor attributes. TOC and water pH have been used as relative indicators of contaminants that enter the water. Drinking water disinfectant, such as free available chlorine, is added to potable water to keep the water free of microbiological health risks. But in the laboratory, a decrease in disinfectant concentration implies either that this chemical compound migrated from the polymer into the water and reacted with the disinfectant, and/or disinfectant interacted with the polymer surface (Colin et al., 2009; Whelton and Dietrich, 2009; Whelton et al., 2011b). The most direct detection and quantification methods involve chromatographic and spectroscopic separation of organic compounds in the water itself, and these methods have been reviewed elsewhere (U.S. National Research Council,

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1999). Since contaminants can sometimes impart detectable tastes or odors at part per trillion concentrations, water organoleptic characteristics are sometimes monitored.

CONTAMINANTS DETECTED IN WATER DISTRIBUTION SYSTEMS

Few studies have described contaminant migration data for North American in-service or new polymer potable water pipes. Most of the openly available literature originates from Europe and has focused on contaminant migration from uPVC pipe, with some effort toward PE materials (Table 4). Unfortunately, only a few pipe networks have been tested in each country. Such limited data makes it difficult to compare migration results of pipes used/tested in different countries. Further complicating direct comparison between available data include (a) many different formulations and pipe production conditions are used, (b) not all published studies screened water for the same contaminants even when the same type of material was analyzed, and (c) certain types of pipe have been tested more frequently than others. Globally, no field or laboratory study was conducted for contaminant migration from mPVC, oPVC, fPVC, bimodal PE pipes, or FRP-epoxy. Other knowledge gaps are included in the subsequent discussions.

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Poly(vinyl chloride)

METAL STABILIZERS

Metal stabilizers, such as lead and tin, are used in uPVC pipe manufacturing and can be released from pipes in drinking water distribution systems. In the United States, no more than 10% of the tap water samples can exceed

TABLE 4. Vinyl Chloride Monomer Water Distribution System Sampling Results from a 1990s Study of U.S. Water Systems

State	No. of systems sampled	No. of sample VCM detects	No. samples above VCM MCL
Arkansas	81	3	1
Kansas	125	32	11
Louisiana	—	—	—
Missouri	167	NR	2
Nebraska	17	3	NR
New Mexico	15	0	0
Oklahoma	12	HT	HT
Texas	18	NR	2

Note. Results from Flournoy et al. (1999). Louisiana declined VCM testing; NR = data not reported; HT = Oklahoma sampled water systems, but sample holding time was exceeded so analyses were not completed.

a 15 μg/l lead concentration. Above this level, water systems must take additional steps to reduce lead in drinking water. Today, there are no U.S. MCLs for other metal-related stabilizers.

From the 1950s to 1970s, lead released from uPVC water pipes was reported throughout Europe. Aqueous lead concentrations associated with uPVC pipe installed for less than one month to 6 years were 0–10 μg/l in the Netherlands (Boelens, 1960), 10 μg/l concentration in Italy (Visintin and Monteriolo, 1965), 0–50 μg/l in England (Packham, 1971b). Sadiq et al. (1997) reported lead release from PVC pipes installed in a Dhahran, Saudi Arabia, drinking water distribution system where lead concentration ranged from 0.03 to 0.12 μg/l. Because of toxicity, lead stabilizers were banned for PVC pipe production in Sweden, Japan, Denmark, and the Netherlands, and replaced with more expensive calcium/zinc stabilizers (Burn et al., 2005; Nielsen et al., 2005).

Tin release, in the form of alkyltin compounds (also referred to as organotins), from in-service PVC pipes has also been reported. Tin compounds are reportedly in PVC at 0.5–2.0 mass fraction (Hoch, 2001). Tin does not have a regulated U.S. drinking water concentration, but efforts are underway worldwide to characterize health risks posed by tin in drinking water. According to the World Health Organization (WHO), data are insufficient to permit guideline values for individual dialkyltins or the mono derivatives, and drinking water concentrations are several orders of magnitude lower than the doses that cause developmental effects in rats and mice (World Health Organization [WHO], 2004). Several laboratory studies discussed later in this review describe laboratory test results and modeling of tin release from PVC pipe available in the United States. Nielsen et al. (2005) analyzed water samples from three PVC water distribution pipelines in Denmark where retention time was roughly 7 hr. These PVC pipes (type unspecified) had various diameters, lengths, and time in-service (5 and 15) years. Dibutyltin (DBT) was detected at 0.031 μg/l concentration and lead was detected at 0.82 μg/l concentration. Recently, Richardson and Edwards (2009) detected different organic tin compounds in three New York drinking water systems: 0.060 μg/l (dimethyltin [DMT]), 0.028 μg/l (monomethyltin [MMT]), and 0.176 μg/l (monobutyltin [MBT]).

No studies were found reporting the migration of other stabilizers, such as cadmium, barium, calcium, or zinc stabilizers, from in-service PVC pipes. One report was identified where tin loading in PVC potable water pipe purchased in Canada was quantified after organic solvent extraction. Forsyth et al. (1993) found that methylene chloride was the most effective organic solvent compared to tetrahydrofuran and chloroform. These researchers also reported that butyltin loading for one PVC pipe varied from <0.9 μg butyltin/g PVC pipe to 5,985 μg butyltin/g PVC pipe, depending on the extraction solvent selected.

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Two studies that examined lead release from PVC pipe referenced by Wong et al. (1988) were not summarized here because they were only available in German (Nikals and Meyer, 1961) and Romanian (Cosoveanu, 1967). A PVC tin leaching study (Mazaev and Slepnina, 1973) referenced by the WHO (2004) was also not evaluated here because that work was only available in Russian. A unifying conclusion of metal migration studies was that contaminant release was greatest immediately after installation and decreased over a several week period.

VCM

VCM can migrate from in-service PVC pipes, and a 2 μg/l drinking water MCL exists for this contaminant in tap water samples. In the 1970s, frequent detections of VCM in drinking water coupled with the discovery of this compound's negative health effects resulted in an allowable loading of VCM in U.S. uPVC pipes at 2.2 mg VCM/kg final product and Europe at 1.0 mg/kg (American National Standards Institute/National Sanitation Foundation International [ANSI/NSFI], 2007; AWWA, 1988; Neilsen et al., 2005). From early investigations, the greatest U.S. VCM drinking water concentration found was 10 μg/l (Fishbein, 1979). Dressman and McFarren (1978) detected VCM at 0.03–1.4 μg/l concentration from three PVC pipelines installed in Arizona, California, and Texas. VCM was detected in the tap water from a small number of the 100 cities surveyed in Germany with the greatest concentration of 1.7 μg/l, but the exact small number was not reported (Bauer, 1981).

In the 1990s, VCM testing was conducted on buried water distribution systems located in the mid- and southwestern United States (Flournoy et al., 1999; Uni-Bell, 1994). In Kansas, VCM was found to have migrated from PVC pipes installed in 1996 and was detected at concentration as high as 8.9 μg/l, four times greater than the MCL. In 1998, Kansas testing was expanded and revealed one of 24 Kansas water systems had VCM levels above the MCL. In summer 1998, two of 167 public drinking water systems in Missouri had VCM concentrations above the MCL. A third round of testing in Kansas found 32 public drinking water systems with VCM 0.5–1.9 μg/l, 11 systems at or above the MCL 2–13.6 μg/l, and no detectable VCM at 82 systems. VCM test results from other states were not as descriptive (Table 5). Beardsley and Adams (2003) reported VCM concentrations 0–11.6 μg/l in a Missouri water distribution system. Richardson and Edwards (2009) also analyzed tap water at four locations in New York and did not detect VCM.

Poly(ethylene)

Field testing to confirm chemical migration from installed PE-based pipes has not been conducted in the United States, but field testing has been carried out in several European countries. European testing of PE-based pipelines did

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TABLE 5. Publicly Available Contaminant Migration Results for Installed or New Polymer Potable Water Pipes Worldwide

		Country															
Pipe class	Description	AUS	CAN	DEU	DNK	EGY	FRA	GBR	ITA	JPN	NLD	NOR	ROM	RUS	SAU	SGP	USA
Poly(ethylene)	LDPE	—	—	—	L	—	—	F	—	—	—	—	—	—	—	—	—
	MDPE	—	—	—	L	—	L, F	L,F	—	—	—	—	—	—	—	—	—
	HDPE	—	—	—	—	—	—	—	—	—	—	L, F	—	—	—	—	L
	Bimodal PE	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	PEX-A	—	—	—	L, F	—	—	—	—	—	—	—	—	—	—	—	L
	PEX-B	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	L
	PEX-C	—	—	—	L, F	—	—	—	—	—	—	—	—	—	—	—	—
Multilayer	PEX-AL-PEX	—	—	L	L	—	—	—	—	—	—	—	—	—	—	—	—
	PE-AL-PE	—	—	L	—	—	—	—	—	—	—	—	—	—	—	—	—
	PE-AL-PEX	—	—	L	—	—	—	—	—	—	—	—	—	—	—	—	—
Poly(vinyl chloride)	uPVC	L, F	L, F	F	-	L	-	L	F	L	F	L	F	L	L, F	L	L, F
	mPVC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	oPVC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	fPVC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Composite	FRP-Poly(ester)	—	—	—	—	—	—	L	—	—	—	—	—	—	—	—	—
	FRP-Epoxy	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Note. L = laboratory investigation of new pipe; F = field investigation of pipe installed in a water distribution system; Hyphen (-) indicates no tests were found. The following information was not reported above because necessary pipe data were unreported: Neilsen et al. (2005) did not report the type of laboratory or field tested PE in Denmark, Skjevrak et al. (2003) did not report the type of laboratory PEX tested in Norway, Brocca et al. (2002) did not report the type of laboratory or field tested PEX in Denmark. The type of PEX or PE used for multilayer pipes in Germany was not reported (Koch, 2004). The aluminum multilayer PEX examined in Denmark was (PEX-C)-AL-(PEX-B) (Neilsen et al., 2007). AUS = Australia; CAN = Canada; DEU = Germany; DNK = Denmark; EGY = Egypt; FRA = France; GBR = United Kingdom; ITA = Italy; JPN = Japan; NLD = The Netherlands; NOR = Norway; ROM = Romania; RUS = Russia; SAU = Kingdom of Saudi Arabia; SGP = Singapore; USA = United States.

not detect any regulated contaminants but many unregulated contaminants were uncovered. These contaminants were associated with MDPE, HDPE, and PEX (type not identified) pipelines. In contrast to PVC pipe, there is no consensus as to which contaminants are most common in PE pipe networks. This lack of consensus is likely due to the limited data available and experimental design deficiencies mentioned in the laboratory testing section of this review. Unregulated contaminants detected in European buried distribution systems include antioxidants, their degradation products, a pipe colorant, and several aliphatic and aromatic compounds of unknown origin.

European in-service PE pipes have been found to release a number of aliphatic and aromatic polar and nonpolar organic compounds into drinking water. Work in France has been the most commonly cited PE pipe field case study, and represents the first laboratory or field investigation that confirmed contaminants can migrate from PE pipes into drinking water (Anselme et al., 1986; Anselme et al., 1985a). These investigators examined a 300 m in-service HDPE pipe because customers had complained over a three-month period about water flavor problems. Removal and subsequent laboratory testing of HDPE pipe sections uncovered the antioxidant BHT (0.70–4.3 μg/l), several polymer pipe antioxidant degradation products: alkyl thiophene (0.35–0.90 μg/l), 2,4-di-*tert*-butylphenol (DTBP; 0.7–0.12 μg/l), 2,6-di-*tert*-butylbenzoquinone (DTBQ; 0.5–3.0 μg/l), and one contaminant of unknown origin, alkyl naphthalene (0.90–1.80 μg/l). Short-chain aldehydes (0.5–0.6 μg/l) were also detected and could likely be low molecular mass byproducts/resin impurities produced by the polymer extrusion process.

In the United Kingdom, migration has been examined from MDPE pipes at dead-end locations in a buried water distribution system (Carthorne et al., 1990). Several compounds were detected in water from two locations where pipes had been installed for one and two days and six months. Considerable variability was found for the two antioxidants Irganox® 1010 (0–0.46 μg/l) and Irganox® 1076 (0–0.39 μg/l), antioxidant degradation product 2,4-DTBP (0.07–1.69 μg/l), and UV light stabilizer Cyasorb® UV 531 (0–0.065 μg/l) (Cytec Industries, West Patterson, NJ, USA). Water testing conducted six months later on formerly one- to two-day old pipes did not detect any of the previously detected contaminants (Carthorne et al., 1990). These researchers also studied the formation/migration of phthalimide from 12 MDPE pipes that were one week to three years old. In the laboratory, phthalimide was found to be formed by chlorine reaction with copper phthalocyanine, an MDPE pipe colorant. Testing of the three-year-old in-service MDPE pipe determined that phthalimide concentration varied between 0.12 and 0.38 μg/l.

The role of a polymer pipe inner wall biofilm on contaminant release was evaluated by Skjevrak et al. (2005) in Norway. These authors examined contaminant migration from an in-service HDPE pipe into the same pipe that was covered with biofilm, and detected 2,4-DTBP in the biofilm in 22 weeks.

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From 22 to 52 weeks, the antioxidant degradation product 2,4-DTBP was not detected. The authors suggested that biofilm may be capable of metabolizing 2,4-DTBP or migration may have reduced with time. Unfortunately, 2,4-DTBP concentration was not quantified.

In Denmark, Brocca et al. (2002) and Nielsen and coworkers (2005, 2007) examined contaminant migration from in-service PE pipe systems. Brocca et al. (2002) analyzed water samples from newly installed PEX pipe (unspecified) after 60 hr at 20°C exposure period. Three organic compounds were detected: 3,5-di-*tert*-butyl-4-hydroxyl benzaldehyde, 3,5-di-*tert*-butyl-4-hydroxyl acetophenone, cyclohexa-1,4-diene-1,5-bis(*tert*-butyl), 6-on, 4-(2-carboxy-ethylidene), but their amounts were not given.

Nielsen et al. (2005) analyzed water samples from existing PE-based pipelines from three water distribution systems. Seven pipe sections were examined that had various diameters, lengths, and time in-service from one year to three years. Differences in the presence/absence of antioxidant degradation products and their concentrations across all pipe sections were detected. Seven antioxidant degradation products were detected ranging from 0 to 3.0 μg/l concentration: 2,6-DTBQ, 2,4-DTBP, 3,5-di-*tert*-butyl-4-hydroxystyrene, 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 3,5-di-*tert*-butyl-4-hydroxyacetophenone, 7,9-di-*tert*-butyl-1-oxaspiro[4,5]-deca-6,9 dien-2,8-dione, and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) methylpropanoate. The specific type of PE pipes analyzed (e.g., HDPE vs. MDPE vs. PEX-A) was not reported, so results cannot be directly compared to other PE pipe studies. A follow-up study examined contaminant migration from PEX pipe installed at six different sites (residential and institutions; Neilsen et al., 2007). Three antioxidant degradation products were detected at four locations ranging from 0.05 to 2.9 μg/l concentration: 2,6-DTBQ was detected at four sites; 7,9-di-*tert*-butyl-1-oxaspiro (4,5) deca-6,9-diene-2,8-dione detected at three sites; and 2,4-DTBP was detected at one location. Again, the type of in-service PEX was not described.

While other investigators have characterized contaminant migration from PE pipes in European buried water distribution systems, original source documents could not be obtained. Extensive searching was conducted by several academic and government research institutions through interlibrary loan service. Rogers et al. (2004) referenced Crane (1994) who reported the release of a stabilizer in PE pipe that contained recycled material [6,6-di-*tert*-butyl-4,4'-thio-di-*m*-cresol]. Crathorne et al. (1990) also noted work conducted by the UK Water Research Centre that identified the antioxidant Sanatox [6,6-di-*tert*-butyl-4,4'-thio-di-*m*-cresol] and/or its degradation product in tap water [2-tert-butyl-5-methyl-(1,4)-benzoquinone] migrated from PE pipes. The type of pipes (in-service vs. new) and the aqueous concentration detected could not be determined due to lack of references in the Rogers et al. and Carthorne et al. studies.

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Fiber Reinforced

No studies were found that characterized migration from in-service FRP, while one study examined migration from a poly(ester)-based FRP in the laboratory. Literature on FRP pipe has primarily focused on mechanical failure testing (Farshad and Necola, 2004; Stocchi et al., 2006). If contaminants do migrate from FRP into water, the types of contaminants released would likely be similar to those of epoxy or poly(ester) coatings used to line pipes. Epoxy coatings are generally prepared by reacting a resin, commonly DGEBA, and an amine or anhydride curing agent. Poly(ester) coatings are created using a resin that either includes a DGEBA vinyl ester resin, or isophthalic terephthalic poly(ester) resin. Due to late stage curing high viscosity, which restricts the movement of both polymer molecules and curing agent, the curing process of these coatings is not fully complete. That is, unreacted monomer, partially reacted low molecular resins, and curing agents still remain in the coatings. During service, these small, polar molecules, as well as residual solvents, likely migrate from the coatings or FRP into drinking water. It is also possible that impurities and sizing compounds on the FRP reinforcement material (e.g., oxides on glass) could also migrate into drinking water.

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LABORATORY TESTING: STANDARD METHODOLOGIES, PUBLISHED TEST CONDITIONS, AND RESULTS

Methodologies Used for Evaluating Migration

There are many different testing methodologies used worldwide to directly or indirectly evaluate contaminant migration. These methodologies are typically endorsed by a regulatory agency or independent, non-profit agency. These procedures focus on determining the effect of a polymer on water quality such as taste and odor, TOC concentration, and microbiological growth. Burn et al. (2005) summarized test methodologies used in Australia, New Zealand, and the United States for evaluating the impact of polymeric potable water materials on water quality. Rogers et al. (2004) summarized testing requirements of 19 countries including those in Australia, Europe, and North America. According to Rogers and coworkers (2004), the most common test methods were: organoleptic testing (16 of 18 countries), TOC concentration (14 of 18), and specific contaminant detection (18 of 18). However, only method abbreviations were provided and complete test method names, conditions, and references were not enumerated.

In the United States, the American National Standards Institute/National Sanitation Foundation International (ANSI/NSFI) Standard 61 is used to evaluate contaminants imparted to a drinking water by polymer pipes (ANSI/NSFI,

2007). A description of this method in the present work is not an endorsement by us or our institutions. This protocol is voluntary and many North American water utilities require that polymer pipes receive ANSI/NSFI certification before being considered for installation. To achieve certification, pipe manufacturers submit their product to the NSFI for analysis along with a list of material ingredients, manufacturing methods, known impurities, typical material use conditions, and estimated service life. Over a 20 or more day period, polymer pipes are filled with extraction water and the water is subsequently sampled for formulation-dependent analytes including inorganic and organic compounds. Extractant water is typically either: (a) pH 5, with 2 mg/l free chlorine and 100 mg/l hardness; (b) pH 6.5, with 2 mg/l free chlorine and 100 mg/l hardness; (c) pH 8, with 0 mg/l free chlorine and 100 mg/l hardness; and (d) pH 10, with 2 mg/l free chlorine. Resulting data is compared to U.S. and Canadian regulated and unregulated contaminant levels. Materials are either deemed compliant or noncomplaint with ANSI/NSFI Standard 61. Unfortunately, NSFI water quality test data is not publically disclosed. As a result, North American water utilities and regulators must rely on the same publicly available studies reviewed in this work for evaluating migration from polymer pipe.

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Published Test Conditions

A wide range of test conditions has been reported. The three most popular procedures that have been used are (a) static immersion testing (cutting of the material into small pieces and immersing cut pieces in an aqueous solution), (b) static pipe coupons (filling a pipe section with test solution and capping both ends), and (c) water flowing intermittently or continuously through a pipe. In all cases, water has been sampled and analyzed to detect contaminants and in most experiments, the extractant water was completely removed and replaced with a freshly made aqueous solution. Quantification of contaminant concentration was sometimes but not always conducted. Quantification involves obtaining chemical standards and development of a calibration curve for comparing the spectroscopically detected compound against a known chemical standard. Not all studies applied the same analytical and extraction methods. Because of this variability, some investigators could only detect certain chemicals and not others (e.g., tin vs. VCM). Greater than 95% of the papers reported migration data for new polymer pipes under static conditions.

Lack of consistent methods used to report material characteristics and conduct experiments makes interpretation of available data challenging. Not all investigators described the type of material examined (e.g., the type of PVC, PE, or PEX) and no studies were found that examined formulation variability across commercially available polymer pipe. It is estimated that

pipes manufactured from 1970 to 2007 have been tested, but the pipe manufacture date was not always reported. This omission is noteworthy from a data interpretation standpoint because formulations have changed over time. For example, the 3.2 g/kg maximum allowable loading of VCM in uPVC pipe instituted post-1977 due to health concerns implies VCM migrating from uPVC installed after 1977 would be less than before that year. With the development of next generation polymer potable water pipes that contain nanomaterials (Whelton et al., 2011a), understanding pipe age and what these materials contain will become even more important.

Test conditions also varied significantly. We calculated pipe SA/V ratios when adequate data were available (pipe inner dimensions and length), SA/V ratios ranged from not reported to 15.9 cm^2/ml, with most between 2 and 4 cm^2/ml. Several calculations could not be conducted because investigators did not report pipe lengths or inner diameter. Contaminant flux comparisons across studies cannot be conducted unless the SA/V ratio and exact exposure duration is reported. Pipes have been tested as is, after a series of rinses, and sometimes after half-day to four-day disinfection with free chlorine or combined chlorine disinfectant. Contaminant migration was commonly examined without preconditioning. Since newly installed pipes are typically flushed and disinfected before use, as is testing results alone do not provide a realistic assessment of long-term contaminant migration in an actual water distribution system.

Extractant water exposure duration ranged from 1 hr to two years, where most investigators conducted multiple short duration experiments (e.g., three days). Extractant water was either distilled, tap, or a synthetic tap water. Initial water pH and disinfectant levels (if present) were typically noted. However, when tap water was used, its organic and ion compositions were rarely described even though ion levels have shown to influence metal stabilizer migration from uPVC pipe. Only a few reports were found where migration was monitored under flowing water conditions (Boettner et al., 1982; Forsyth et al., 1993; Rhodes et al., 1980; Richardson and Edwards, 2009), and these only focused on PVC pipe release for VCM and tin. Most laboratory investigations applied static conditions. Experimental design and analytical detection limits were often not reported.

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Results

Poly(Vinyl Chloride) Pipes and Deficiencies in These Pipe Data

Appendix Table A-1 summarizes laboratory and field studies that reported aqueous compounds detected in contact with PVC pipe. Table A-1 results do not differentiate PVC pipe types (uPVC, mPVC, oPVC, fPVC) because researchers frequently omitted the type of PVC examined. Notable findings of laboratory PVC studies are described below.

Metal Stabilizers and Other Metal Compounds: Lead and Cadmium

Gross et al. (1974) examined the influence of certain PVC additives as well as temperature, pH, and extraction time on lead release. Three tests were performed: (a) immersion of PVC pipe pieces in water (pH 5) at 35°C for 72 hr, (b) immersion of PVC pipe pieces in water (pH 7.8) at 23°C for three consecutive 24-hr extractions followed by one 72-hr extraction, and (c) rinse pipe sections with tap water for 6 hr, fill pipe with extractant water (pH 4.8), and let sit for 48 hr at 20°C. While no SA/V ratios could be calculated, results showed that as the amount of $CaCO_3$ filler increased, the amount of lead extracted decreased and this reduction was attributed to better dispersion of the tribasic lead sulfate stabilizer. Unfortunately, the degree of stabilizer dispersion was not reported. Gross et al. (1974) also concluded that the order of modifiers that reduced lead release were acrylonitrile butadiene styrene (ABS) > chlorinated poly(ethylene) (CPE) > acrylic = control, but no explanation was provided for this finding. It is possible that stabilizer migration was limited due to modifiers increasing contaminant path tortuosity.

Lead migration from uPVC pipe in tropical climates has also been studied. Wong et al. (1988) evaluated the impact of extrusion temperature, water types, and water temperature on contaminant release. Pipes extruded from uPVC resin in the lab were rinsed with detergent, and extractant water was sealed in pipe sections for 48-hr intervals (15 days total). Tap water, bicarbonate buffered distilled water, and phosphate buffered distilled water were used at 5, 27, and 45°C and the SA/V ratio was 4 cm^2/ml. A greater extrusion temperature was reported to decrease lead release from uPVC pipe, but no postulated reason was provided for this finding. When tap and bicarbonate buffered solution temperature increased, lead migration increased, but lead migration into phosphate buffer solutions decreased at elevated water temperature. No reason for the unexpected phosphate buffered water result was provided and pH values were not reported for any water. Thus, results of this work have limited application to other laboratory and real world environments.

The influence of certain dissolved ions and water temperature on uPVC pipe lead release has also been studied (Wong et al., 1990). Pipe sections extruded in the laboratory were filled with distilled water (SA/V ratio 4 cm^2/ml) containing water with either NO_3^-, SO_4^{-2}, ethylenediaminetetraacetic acid (EDTA), or HCO_3^-. Water was changed and sampled every two days for 30 days. Lead leaching was greatest during the first eight to 10 days of exposure and decreased as temperature decreased: 45°C > 25°C > 5°C. Lead leaching was least for pipe extruded at 190°C compared to pipes extruded at 170 and 180°C. A problem with interpreting these results, however, is the absence of statistical comparisons and water pH measurements. Koh et al. (1991) reported much of the same data from Wong et al. (1990) with the addition of extruded uPVC pipe microscopic examination. Based on scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX)

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results, Koh et al. (1991) reported that lead was more evenly distributed in 190°C extruded pipe than the pipe processed at 170°C. While not mentioned by the researchers, this technique by definition could only characterize 1 μm depth into the PVC surface and their pipe had a reported 1,800 μm wall thickness. Approximately 0.06% of the total pipe wall thickness was examined. During polymer extrusion, cooling through the pipe wall can sometimes be nonuniform and additive level can vary down the length of the pipe (Dernberg, 2009). An important, unmentioned limitation of both experiments is that short duration experiments do not represent long-term uPVC pipe lead leaching or different water quality.

In the 1990s, Danish researchers examined water quality impacts of seven brands of PVC pipe (type unspecified; Forslund, 1991). This team filled pipes with distilled water (no buffer or pH values reported) and evaluated aqueous TOC, lead, and cadmium concentrations as well as taste and odor quality every three days for nine days at 23°C. After the first 72 hr of immersion, TOC concentration was generally <0.1–0.6 mg/l, but lead and cadmium levels varied between 10 and 320 μg/l and <0.1 and 0.22 μg/l, respectively. After three successive 72-hr exposure periods for the same pipes, lesser contaminant levels were detected: <0.1–0.1 mg TOC/l, 4–20 μg lead/l, and <0.04–0.2 μg cadmium/l. PVC pipes had minimal impact on water taste and odor quality during the entire test period. Like previous studies, this work pertains to short duration water exposure (nine days). Pipe dimensions were not provided so contaminant flux could not be calculated and pH values were also not reported. Absence of pipe surface area and water quality characteristics inhibits relating these results to other pipes/conditions.

In 2008, investigators documented lead release from new Egyptian PVC pipes by carrying-out static pipe testing with five different water compositions (Lasheen et al., 2008). Waters all comprised the local tap water with adjusted pH 6, 7.5, and 8 at 124 and 250 mg/l as $CaCO_3$ alkalinity concentrations, two chloride/sulfate ratios (0.83 and 3), with and without EDTA concentration. Water was sampled and changed every two days to three days for five months. These investigators found lead release was greatest at low pH, greatest chloride/sulfate ratios, and in the presence of EDTA, but because temperature was not reported, their results cannot be easily compared to other PVC studies. No effort was conducted to determine the initial or final contaminant mass in the PVC pipe.

Metal Stabilizers

Some research has been conducted to document tin release from PVC pipes, while only one study has focused on calcium, magnesium, and titanium release. Most work quantified aqueous contaminant concentration, but did not characterize pipe stabilizer loading before or after testing. Rhodes et al.

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(1980) examined tin stabilizer leaching from small-scale static and intermittent flowing PVC pipe networks (7.62 m) into tap and river waters. Pipe loops having 25.4 mm and 50.8 mm inner diameter (ID) with 2–3-week water contact time, and water was sampled more frequently during the first 144 hr. Alkyltin compounds migrated into pH 5 water at 37°C and tin concentration was greatest during the first 24-hr period (35 μg/l). Migration decreased as validated by the 3 μg/l concentration after two-day exposure and 0.25 μg/l concentration after 22-day exposure.

In 1982, the USEPA measured organic tin compound migration from PVC pipe (type unspecified) using several approaches: (a) dissolution of PVC pipe in solvent, (b) PVC pipe-water contact, and (c) a flowing water-PVC pipe loop (Boettner et al., 1982). Their method involved water sampling from a PVC pipe loop (surface area = 0.71 m^2) operated for 22 days. Buffered as well as distilled pH 5 water solutions with and without free chlorine were used, and water changes occurred at 48- and 96-hr intervals. These investigators, however, used 37°C for their experiment, which is greater than 5–25°C typical of North American buried water distribution systems. Boettner et al. discovered that organotin compounds migrated into the water during the 22-day period at a concentration of 35 μg/l detected after the first 24 hr of exposure, which decreased to 0.07 μg/l after 22 days. During the first 24 hr, the greatest organotin flux was detected (0.8239–2.218 ng/cm^2-day) while subsequent fluxes varied from 0.003 to 0.053 ng/cm^2-day. Organic compounds detected include DMT, trimethyltin (TMT), DBT, and tributyltin (TBT). Poels and Dibbets (1982) investigated lead migration from uPVC pipes in Germany. Over a 30-day period these researchers sampled water every three days. Distilled water (buffer not specified) having pH 4.6 was used for extractions. Generally, aqueous lead concentration decreased from a peak value (0.04 mg/l) during the first week to a lower level (0.01 mg/l) in the final week of testing. Water pH values before and after testing were not quantified.

Jirackova-Audouin and Verdu (1985) examined the solubility and diffusion of 10 organotin stabilizers in uPVC sheets manufactured in their laboratory. Solubility was determined by immersing one uPVC sheet in each stabilizer for 100 hr and was analyzed by infrared spectroscopy for stabilizer sorption. Though, stabilizers are thought to be solids and thus an undisclosed solvent was likely used for this work. Organotin diffusion into uPVC was monitored by absorbance measurements for three separate uPVC films sandwiched between one source plate and one uPVC sheet on the latter side. Experiments were conducted at 100 degrees, but neither Fahrenheit nor Celsius units were provided. Since the T_g of PVC is roughly 85°C and melting temperature is near 100°C, we must assume units were degrees Fahrenheit. Replicate measurements were not described (nor were mean or standard deviation values), thus readers are left to assume that results represent only one measurement. Researchers reported that three of the 10 organotin

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compounds dissolved completely in the polymer due to the lack of spectroscopic signal, while seven other compounds had reported 5–88 ml^{-1} solubility. First, ml^{-1} units for solubility and ms^{-2} for diffusion coefficients do not follow general solubility (mass/volume) and diffusion (area/time) rules. Diffusion values were reported for all ten organotin compounds, even those that were not soluble in uPVC. Variability in solubility and diffusion values also was not reported and it is possible any numerical differences between solubility and diffusion coefficient values are artifacts of analytical techniques, not true differences between organotin compounds. Also, no statistics were applied to support researcher claims. While not conducted, a simple uPVC stabilizer extraction and quantification would have helped describe the results. In conclusion, the researchers reported that molar volume did not control diffusion through uPVC, but contaminant-polymer interactions did control chemical transport. This study was novel, but lacked necessary replicates, controls, analytical confirmatory techniques and results presented cannot be directly applied to other uPVC materials and contaminants.

Wu et al. (1989) documented total organotin release from one brand of schedule-40 and one brand of schedule-80 PVC pipe using a recirculating pipe loop (46 m), laboratory conditioned water, and two flow rates. Unfortunately, test water characteristics (e.g., pH, ion content) and temperature were not described. Over a 40-day period, concentrations ranged from 0 to 5 μg/l. Wu et al. (1989) predicted initial tin surface concentration using a mathematical model and aqueous tin concentration. Similar to previous researchers, a reduction in mass of tin released was observed as exposure time increased. Researchers concluded that in a water distribution system flowing through several hundred meters of pipe length, aqueous tin concentration would exceed a Mavaev and Shelepnina (1973) recommended 20 mg/m^3 (20 μg/l) maximum allowable tin drinking water concentration. Wu and coworkers recommended that PVC pipe should be initially water rinsed for 4 hr (water flow representative of a Reynolds number of 6000 or greater) to reduce the amount of tin available to migrate below 20 μg/l. J. Lee (personal communication, 2011) reported that Reynolds number of 6000 or greater is quite common in water distribution systems and represents turbulent flow. Because water pH and temperature were not reported, results of this experiment cannot be directly compared to other conditions. Also, initial PVC pipe tin loading was not quantified to validate investigator predictions.

Quevauviller et al. (1991) examined tin migration from five different PVC materials (type unspecified) at room temperature by immersing 15 g of PVC pieces in 500 ml tap water for 33 days. Results showed that 80% of the total aqueous tin quantified for the 33-day period was liberated during the first two days. The drastic difference between tin leaching for the five materials tested was attributed to differences between material formulations. Unfortunately, water pH and formulation differences were not described.

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Release of tin stabilizers and other metal containing additives (calcium, magnesium, titanium) from laboratory extruded PVC pipe has also been documented (Dietz et al., 1995). Laboratory extruded pipes that contained titanium dioxide (1.0 part of ingredient per hundred parts of resin [phr]), calcium stearate (1.5 phr), magnesium stearate (0.25 phr), and tin stabilizer (1.2 phr) were immersed in water for two months (SA/V ratio 1.61 cm^2/ml) at 25 and 50°C. Water was sampled once every two weeks for metal content. Water pH was not reported. The greatest concentrations of methyl, butyl, and octyl tin compounds were detected in 50°C waters and increasing organic chain length decreased the amount of organic tin detected in the waters. This is likely due to smaller molecules can diffuse more easily through polymers than larger molecules. Calcium and magnesium stabilizers also migrated from PVC pipe into water. Elevated temperature increased magnesium migration, but did not affect calcium migration. It is interesting to note that calcium was present at six times the magnesium loading of PVC, and calcium release was unaffected by elevated water temperature conditions. These results imply metal-based lubricants used for PVC manufacture can remain in PVC after extrusion and enter water when pipes are placed in service. Titanium was not detected in water despite the fact that titanium was present at four times the magnesium loading. A better understanding of the interaction between these ingredients with PVC material and with water is needed.

Richardson and Edwards (2009) investigated organotin migration from new PVC pipes by immersion, static pipe coupon, and pipe loop test methods. Experiments were one day to two years in duration. Water pH was 6.9 and water temperature, flow rate (for pipe loop), and the presence/absence of a biofilm were varied. A weak temperature dependence on tin release was observed between 4 and 52°C, but a stark contrast was found for MMT and DBT levels at 22 and 52°C. Organic tin aqueous concentrations were MMT 0.310 μg/l (22°C) and 0.700 μg/l (52°C), and DBT was 820 μg/l (22°C) and 2840 μg/l (52°C). Follow-up work to extract and quantify tin compounds in PVC pipes would likely have provided the information needed to explain the aqueous DBT and MMT relationship and possibly identify what percent of the total tin was released during their experiment. The authors did report that the presence of a biofilm reduced the organic tin leaching rate compared to pipes without a biofilm coating.

A study conducted by Al-Malack (2001) stands out from all other PVC projects and deserves mention because of the limited PVC data set available. The author used static and circulatory pipe loop experiments to investigate the effect of immersion time on metal stabilizer release from two brands of Saudi Arabian uPVC pipes. Water temperatures were 35 and 45°C, and experiments were conducted for 8, 24, and 48 hr. TDS levels were 2, 160, and 2670 mg/l, and pH was varied from 5 to 9. Five metals (lead, tin, calcium, cadmium, and barium) were found to migrate from PVC pipe into extractant waters, and migration was generally greatest at low pH, high TDS

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concentration, and long exposure time. However, Al-Malack did not reveal the limits of detection for his methods nor did he provide a reason why all of these metals would be present in one PVC pipe, or if this practice was common in Saudi Arabia. This is the only study found in the literature where the use of and detection of more than four different heavy metals was found migrating from one PVC pipe.

Johnson and Clark (2006) of Rohm and Haas Company more recently described tin release from 60 PVC pipes that were tested by the NSFI as well as two examined during their own laboratory study. NSFI provided these researchers data from 60 PVC pipe tests and these materials were created with either methyltin or butyltin stabilizers. Unfortunately, NSFI data (and almost all other data alluded to in their paper) were not provided for reader review. The Rohm and Haas Company team also monitored aqueous tin concentration over a 21-day test period for a PVC pipe that was over 40 years old and another pipe with 22 years in-service. The SA/V ratio was 3.15 cm^2/ml; however, water quality and temperature were not reported. Aqueous data showed tin concentration decreased during the entire experiment from 39 to 0.4 $\mu g/l$ for three replicates for one pipe specimen. However, individual replicate measures were input into their first-order decay model, not mean values. A difference between rate constants led the researchers to conclude that formulation and/or processing conditions were responsible for differences in leaching characteristics. However, the three columns of data presented are three replicate measurements of the same pipe and actually describe within pipe variability. Also notable is that their first-order model predicted significantly different day 0 tin concentrations for the same pipe (67, 85, 105 mg/l). The substantial differences in these predictions imply that the experimental approach applied is not appropriate. Further, since a very short leaching experiment was conducted (21 days) compared to the expected service life of the material (40+ years) and the final tin concentration at 21 days was not zero (only seven sampling events), slight differences in final concentration likely greatly skewed the fitted curve and equation used to predict tin concentrations. Also notable, water analysis frequency was not consistent (varied between one and six days) and this inconsistent sampling approach agrees with the ANSI/NSFI Standard 61 protocol (ASNI/NSFI, 2007). The 40-year-old PVC pipe was chemically determined to contain 0.22 and 0.30 mass fraction tin using elemental analysis methods and tin loading through the pipe was equal, no gradient was discovered. Overall, results from Johnson and Clark (2006) are not supported by the data presented in their work and cannot be independently interpreted.

In 2007, the USEPA and Argonne National Laboratory published results of a study to quantify organotin release from three PVC pipe brands (Impellitteri et al., 2007). This team quantified aqueous tin compound concentration for deionized water in contact with two PVC pipes. Two PVC pipe brands were examined for 180 days and one brand was monitored

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for 339 days, SA/V 1.57 cm^2/ml (temperature not reported). Tin compound concentrations were the greatest during the first 1–5 days (and organotin species and concentration leached varied by pipe type). Five different tin compounds were detected: MMT, DMT, MBT, DBT, and TBT and exposure to one PVC brand increased water pH from 5 to 9. Moreover, some aqueous tin concentrations differed from others by a factor of 2000. X-ray absorption spectroscopy was used to identify different organotin compounds in PVC pipe and validated that MMT was the dominant tin compound in the three PVC brands tested.

In 2009, the research team of Fristach et al. (2009) concluded that the long-term organotin concentration in drinking water would be significantly less than the WHO safe limit of 150 $\mu g/l$ for DBT. This conclusion was based on mathematical models applied to estimate organotin leaching from PVC pipe as a function of both surface area and time. DBT leaching rates were estimated during the first year of pipe use and drinking water concentrations of 0.895 and 28.88 $\mu g/l$ were predicted. Notably, the authors acknowledged that PVC pipe properties and metal stabilizer loadings are poorly understood and frequently not reported. In the future, organotin diffusion rates must be better characterized for model optimization. The diffusion coefficient used by Fristach et al. (2009; $1.56 \times 10^{-10} \pm 1.42 \times 10^{-10}$ cm^2/s) was back-calculated from two studies who did not measure diffusion coefficients. These studies were relied on however because they were the only studies that contained data whereby a diffusion coefficient could be estimated.

VCM

Laboratory testing of PVC pipes for VCM migration was first reported by Banzer (1979) and Rhodes et al. (1980). Banzer (1979) used distilled water and did not report pH. Under static and circulating pipe loop conditions, Banzer discovered that lesser initial VCM loadings in the pipe (mg/kg) decreased the amount of VCM detected in the water (Table 6). Test results revealed that aqueous VCM concentration increased three fold when samples were in a pipe loop, and there was a negligible difference between the static and pipe loop methods. No aqueous VCM was detected when initial VCM loading in the pipe was 2.5 or 1 mg/kg. Rhodes et al. (1980) did not detect VCM migrating from a small-scale PVC pipe loop with tap water (detection limit was 0.1 $\mu g/l$).

Ando and Sayato (1984) investigated conditions that promote VCM migration into water and chemical reactions between VCM and free chlorine disinfectant. These researchers sealed deionized phosphate buffered water in PVC pipe sections (1 m length × 20 mm ID, SA/V ratio of 0.8 cm^2/ml) at pH 5, 7, and 9 and also immersed PVC pipe pieces in water bottles (SA/V ratio 8.8 cm^2/ml) at pH 1–9. All experiments were conducted for (1, 2, and 3) day periods at 20°C. While no VCM was detected in the pipe sections, VCM was found in water that contained completely immersed PVC samples, and

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TABLE 6. VCM Concentration in New uPVC Pipe Influences Flux Into Water During Static and Pipe Loop Experiments

Initial VCM in pipe, mg/kg	Calculated Compound flux, ng/cm^2-day
<1	BDL, BDL, BDL, BDL
2.5	BDL, BDL, BDL, BDL
14.8	634, 634, 952, 952, 1904
28	BDL
34.8	1270, 1904, 2221, 2221, 4126
179	4444
283	13331

Note. Data from Banzer (1979) was used to calculate flux reported in this table. BDL = VCM below analytical detection limit of 0.002 mg/kg in water. Experiment duration varied among 1, 2, 3, 150, and 180 days; each reported test result is shown.

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calculated fluxes ranged from 4.5 to 7.4 μg/cm^2-day (based on reported mg TOC/l and SA/V ratio). In a separate experiment, these authors also reported that free chlorine reacted with VCM to form disinfectant byproducts chloroacetaldehyde and chloroacetic acid ($pK_a = 2.86$), and this reaction proceeded more rapidly as pH decreased. While no reaction mechanism was provided, the VCM reaction likely occurred when HOCl was present as this chemical species increases in concentration at pH less than 7.54. Because Ando and Sayato (1984) did not determine the fate of these disinfection byproducts, it is possible these compounds could diffuse into PVC pipe after production, remain in the water, or decompose in water.

Al-Malack et al. (2000) evaluated the influence of water pH, temperature, TDS concentration, and exposure time on VCM migration from PVC pipes. Schedule-80 uPVC pipes manufactured in 1994 (tested in 1996) were examined (SA/V 3.08 cm^2/ml). Each pipe section was filled with double distilled water and experiments were conducted at various pH (4, 5, 7, 9), temperature (5, 22, 35, 45°C), and TDS (2, 160, 2670 mg/l) conditions over a 30-day exposure period. Water was analyzed for VCM at different time intervals. Results showed that 2.5 μg/l VCM was only detected in 45°C water samples. After 3 and 30 days at 45°C and pH 5, VCM concentrations were 1 and 2.5 μg/l, respectively. Al-Malack et al. concluded that an increase in water pH from 4 to 9 increased the VCM diffusion coefficient. However, this phenomenon has not been described elsewhere. Also, Al-Malack et al. (2000) provided several conclusions about pipe initial VCM loading based on empirical calculations using equations developed by Berens and Daniels (1976). There are several concerns with this approach. First, initial VCM loading in the Saudi Arabian pipe was estimated by quantifying aqueous VCM concentration then back calculating the initial VCM loading in the pipe using an empirical equation. Next, a VCM diffusion coefficient was calculated at each temperature using an equation derived by Berens and Daniels (1978), $D = 3.7e^{-17000/RT}$,

where R is the usual gas constant (1.987 cal mol^{-1} $degree^{-1}$) and T is degrees Kelvin. Thus, the diffusion coefficients reported by Al-Malack et al. (2000) were not based on their experimental testing. The calculated diffusion coefficients were subsequently used to calculate the maximum VCM fractions that migrated from the PVC pipe after 30 days at 45°C. This approach is suspect because Berens and Daniels (1976) reported that the VCM concentration in pipe walls is uniform immediately after manufacturing (where the above-mentioned equation applies). However, over time VCM diffuses out of pipe walls during storage, and its distribution in the pipe is not likely to be uniform. That is, the concentration of VCM near the pipe surface is likely to be lower than that in the pipe center. Therefore, diffusion is nonuniform at long storage times. Al-Malack et al. (2000) analyzed their PVC pipe two years after its manufacture, and thus the application of the diffusion coefficient equation is questionable. Moreover, no work was carried out to directly quantify VCM distribution or loading in the Saudi Arabian PVC pipes for validation purposes. It should be mentioned that the Al-Malack team noted that their experimental VCM diffusivity values were 180 times less than their empirically calculated diffusion coefficients. This finding underscores the fact that their assumptions were problematic. Al-Malack and coworkers also reported that VCM release was greater for tap waters than distilled water. Lack of replicates, statistical comparisons, and other independent measurements inhibit broad interpretation of these results. Aside from Berens (1974) and Berens and Daniels (1976), Al-Malack et al. (2000) is the only another study that has reported contaminant diffusivity values for polymer potable water pipe.

The role of direct sunlight exposure on VCM release from uPVC pipes into drinking water has also been investigated, and comments about these two studies will be discussed after their brief introduction. Al-Malack and Sheikheldin (2001) filled each pipe section with water, exposed them to constant sunlight, and monitored VCM concentration over a 30-day period. Black and gray uPVC pipes tested were both 12.7 cm ID and in 44 ml water volume for a SA/V ratio of 3.15 cm^2/ml. Unfortunately, these researchers did not provide the water's initial characteristics (e.g., pH, ion content). Results showed aqueous VCM concentration was greater for sunlight exposure pipes 1.5 and 2.5 mg/l than those stored in shade 0.5 and <0.25 μg/l. Based on their results, these authors estimated the VCM loadings in black and gray uPVC pipes were 355,000 and 170 μg/kg, respectively. No confirmatory experiment was conducted to validate this loading estimation.

Al-Malack (2005) followed up with a study to assess the effect of artificial ultraviolet (UV) light exposure on VCM leaching from uPVC pipe. This researcher found that after 14-day exposure to artificial UV light source to the same water, a VCM concentration of 2.3 μg/l was detected, and the artificial UV radiation intensity used was greater than that of the sun. Aqueous VCM results were used to estimate the initial VCM loading in the pipe (3 μg/kg), and calculate a VCM diffusion coefficient of 3.19×10^{-12} cm^2/s at 35°C. In

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the United States, polymer pipe exposure to UV light is expected to occur only during pipe storage and transport since polymer pipes are installed in underground and building applications. It is important to note that VCM diffusivity should increase with temperature, but the VCM diffusion coefficient calculated by Al-Malack and Sheikheldin (2001) for their UV study at 35°C (10^{-12} cm^2/s) was substantially less than the diffusion coefficients obtained by Al-Malack et al. (2000) for 5°C (10^{-10} cm^2/s) and 45°C (10^{-9} cm^2/s). VCM diffusion coefficient values reported for the UV effect study are of suspect because of several reasons. The extractant water temperature likely fluctuated (but was not reported) during day and night hours under sunlight and water temperature is likely substantially raised under artificial UV irradiation. Further, the diffusion equation used by Berens and Daniels (1976) to predict diffusion through a flat sheet was indiscriminately applied to VCM migration from a PVC pipe. These results underscore the need for improvement of data quality, interpretation, and reporting in the literature.

More recently, Richardson and Edwards (2009) examined VCM migration from new PVC pipes by immersion, static pipe coupon, and pipe loop test methods. Like their previously described organotin experiments, VCM migration experiments were one day to two years in duration and water temperature, flow rate (for pipe loop), and the presence/absence of a biofilm were varied. Biofilm was concluded to have a negligible impact on VCM migration from PVC pipe. Walter et al. (2011) also published similar results from Richardson and Edwards (2009).

Other Contaminants and Critical Assessment of PVC Laboratory Work

Several organic contaminants not previously described here have been found migrating from PVC pipe. Several of these contaminants, such as phthalates (type unspecified; Anselme et al., 1985b; Crathorne et al., 1990; Durand, 2005), DBP (plasticizer commonly added during PVC pipe manufacture; Rhodes et al., 1980), DGEBA (Carthorne and Warren, 1986; Crathorne et al., 1990), are of regulatory interest. Other contaminants are likely lubricants used for manufacturing such as lauric, myristic, palmitoleic, palmitic, stearic acids, benzothiazole, and phenylacetaldehyde, and remained in the pipe after production (Crathorne et al., 1990). Low molecular mass degradation products also detected include hexanal, octanal, nonanal, and decanal (Skjevrak et al., 2003). Cyclohexanone was detected by Boettner et al. (1981) and Heim and Dietrich (2007) and is likely residual solvent from the PVC resin. Benzothiazole and tris-chloroethylphosphate (TCEP) were reported by Crathorne et al. (1990), but the source of these compounds was not identified in the literature.

Organic compound release reported as TOC concentration has also been detected by Koch (2007; two German PVC pipes, nine day exposure, <0.1 mg/m^2-day, 23°C and 60°C), and this TOC contribution was calculated

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based on reported TOC results and the SA/V ratio. Khiari et al. (2002) concluded that TOC concentration was not affected by PVC white and PVC gray pipes after a short-exposure period. Water odor, taste, and flavor were not affected by two German (Koch, 2007) and two U.S. (Khiari et al., 2002), and 21 Australian/New Zealand (Marchesan and Morran, 2004) PVC pipes.

Based on the current body of science for contaminant migration on PVC pipe, several major deficiencies have been identified. First, some researchers did not report water pH values and omitting this basic water quality characteristic is problematic for data interpretation. Water pH controls metal complexation, hydrolysis, and some researchers have suggested that contaminant migration from PVC is also influenced by water pH. Second, PVC pipe dimensions were many times not reported and lack of this information prevents contaminant flux calculation (mass/area-time). While researchers sometimes report aqueous concentration, contaminant flux values cannot be calculated and compared to other larger/smaller diameter pipes without knowing the pipe inner diameter and length to calculate the SA/V ratio. For almost all PVC pipes, researchers did not characterize contaminant loading in the pipe before or after testing. Absence of this information prevents utilities, public health officials, regulators, and pipe manufacturers from understanding how the experimental results relate to actual buried water pipes and their service conditions. For example, a three-day, 30-day, or two-year study can yield good aqueous contaminant data, but without knowing initial contaminant loading in the pipe, predicting the amount of metal released during the service life of the pipe or how different water chemistries affect release cannot be determined.

Also reported were that certain modifiers could prevent contaminant release or their components (e.g., calcium and magnesium) could migrate into water. While these discoveries are important, no justification of these phenomena was provided. We suspect divalent cations originated from lubricants used during PVC manufacturing. It is likely that lubricants remained in the pipe after extrusion and variations between PVC formulations/ingredients could result in varying amounts of contaminant released into drinking water. Finally, replicate variability (mean and standard deviation) as well as statistical comparisons are not commonly carried out. Claims that aqueous contaminant concentrations were different (and varied by only a few μg/l representing one or two samples) should be supported by statistical testing, as numerical differences may be artifacts of analytical methods and/or internal replicate variability. Much of the existing PVC migration data cannot be easily translated to other PVC pipes or water quality/operating conditions.

Poly(Ethylene) Pipes and Deficiencies with Existing Contaminant Migration Data

Appendix Tables A-2, A-3, and A-4 were created based on the global literature review and represent a compiled list of contaminants detected in waters

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in contact with PE pipes. These tables compare multiple pipe types and include both laboratory and field testing results. Notable laboratory studies and deficiencies in existing data of contamination migration are described below.

In France, Anselme et al. (1985a; 1985b; 1986) investigated chemical migration from new HDPE pipes. Testing included 2 m section prerinsed with tap water (700 l/hr) for 12 hr, filled with water, capped, and exposed for 12 hr. Investigators discovered that the water's UV_{260} absorbance increased along with an increased abundance of ketones, aldehydes, alkyl phenols, naphthalene, and quinone compounds. No justification for selecting the 260 nm wavelength was provided and UV_{254} is most common for characterizing dissolved organic content of natural and treated waters (American Public Health Association, American Water Works Association, Water Environment Federation, 2010). Nucleic acids such as DNA and RNA have a maximum absorbance at 260 nm, and absorbance at 260 nm could represent the shoulder of the 254 nm peak. HDPE granule soaking for 48 hr in mineral water also confirmed the release of additives and additive degradation products. Another important study component included estimation of the expected contaminant release duration. A PE pipe was repeatedly flushed with water, sealed, and allowed to soak for 48 hr with a SA/V ratio of 1.54 cm^2/ml. After water exposure, TOC, phenol concentration, UV_{260} absorbance, and flavor quality of the water were measured. Results showed that after 48 hr, TOC concentration was approximately 14 mg/l, but decreased to a value between 1 and 2 mg/l during subsequent flushes. The amount of phenol imparted to the water was also lowered by water flushing 8 μg/l after 24 hr and 5 μg/l at end of experiment.

In Denmark, Forslund (1991) also determined that LDPE (7 brands), HDPE (7 brands), and PEX (5 brands) pipes affected water quality. Pipe dimensions were not provided so contaminant flux could not be calculated. All pipe sections were filled with distilled water and were left static for nine days. LDPE and HDPE pipes were stored at 23°C while PEX pipes were placed in a 60°C atmosphere. After three days, water TOC levels for LDPE and HDPE pipes were found to be <0.1–0.2 mg/l and <0.1–0.6 mg/l, respectively. With the exception of two HDPE and LDPE pipes, after nine days all TOC concentrations were <0.1 mg/l. After three days, water taste was statistically stronger in LDPE pipes than for control water. TOC concentrations were also substantially greater in PEX pipe waters compared to LDPE and HDPE pipes after three days (0.4–101 mg/l) and nine days (0.2–44 mg/l). Water odor and taste values for HDPE and LDPE waters were also significantly greater than control waters. Three of the five PEX brands had statistically significant greater taste values than control waters. The aqueous phenolic compound concentration was also quantified in PEX pipe water as a surrogate for antioxidant and antioxidant degradation products. Phenolic concentration ranged from <2 to 290 μg/l. Since temperature is known to accelerate contaminant

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migration from polymers into water, and elevated temperatures can promote compound decomposition. Because different water temperatures were used for testing different pipes, the increased concentration of TOC, taste, odor values, however, cannot be compared directly between LDPE, HDPE, and PEX. The type of PEX pipe examined (PEX-A, -B, or -C) was not described.

In Finland, Villberg et al. (1998) identified compounds that migrated from HDPE granules (32 g) into 250 ml water after 4 hr at room temperature. Results showed that 91 compounds, primarily hydrocarbons and polar organics (aldehydes and ketones), with molecular mass of 46 g/mol to 184 g/mol migrated from granules into water. Several manufacturing byproducts such as octanal (30–130 μg/l), nonanal (40–270 μg/l), and decanal (36 μg/l) as well as other small ketone compounds were detected, methylbutanone (1–2 μg/l), dimethylbutanone (3–8 μg/l), methyl isobutyl ketone (1.2–2 μg/l), methylheptadienone (1–3 μg/l), heptanal (10–50 μg/l), dimethylhexanone (1–2 μg/l), dimethylheptenone (4–9 μg/l), and isopropylhexanone (3–10 μg/l). While important, these data represent HDPE granules as opposed to drinking water pipes and are not included in the Appendix tables. It is possible, compounds detected here may thermally degrade under extrusion conditions (described previously in this review) and do not exist in finished pipe. It is also possible, the addition of processing additives might influence compound stability (e.g., antioxidants could prevent them from degrading) and contaminant in granules could remain in the pipe after extrusion. Further, HDPE pipe microstructure may differ from the granule form and microstructure differences may strongly influence contaminant transport and release from polymers into water.

The next three studies described evaluated migration from PE-based pipes but many did not specify the type of PE examined or quantify contaminant concentration. While investigators who carried out these projects designed their studies well, absence of this information inhibits direct comparison of their results to pipes already installed by utilities, regulatory limits under consideration, or the literature. In Denmark, Brocca et al. (2002) examined organic compound migration from one PEX (unspecified), two brands of MDPE, and one LDPE water pipe. Pipe sections were filled with water at 23°C and water was analyzed after a seven-day exposure period. Ten phenolic and hindered alkyl compounds were detected, but not quantified in the extractant water. Suspected antioxidant degradation products formed likely during pipe manufacture include 4-ethylphenol, 4-*tert*-butyl phenol, 2,6-DTBQ, 2,4-DTBP, 3,5-di-*tert*-butyl-4-hydroxystyrene, 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 3,5-di-*tert*-butyl-4-hydroxyacetophenone, 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) methylpropanoate, and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) methylpropionic acid. However, cyclohexa 1,4-diene, 1,5-bis(*Tert*-butyl), 6-on, 4-(2-carboxy-ethylidene) was later correctly named the antioxidant degradation product 7,9-di-*tert*-butyl-1-oxaspiro[4,5]-deca-6,9 dien-2,8-dione by Nielsen et al. (2005).

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In Norway, Skjevrak et al. (2003) examined the impact of new HDPE, PEX, and PVC drinking water pipes on water quality. Pipe sections were first rinsed, then filled with distilled water and left for three days at room temperature. Water odor was quantified and contaminants were spectroscopically identified and grouped into six classes: antioxidants, esters, aldehydes, ketones, terpenoids, and aromatic hydrocarbons. Thirty-eight contaminants were found in water in contact with HDPE pipe. Similar to Brocca et al. (2002), 2,4-DTBP was detected in all samples and is a known degradation product from the antioxidant Irgafos® 168. Water odor quality was found greater than or equal to a threshold odor number (TON) value of four for five of seven brands of HDPE pipes. Eight compounds were identified in PEX pipe waters and their presence and concentration varied significantly between the two PEX pipe brands tested. The total VOC quantity released to water during three successive test periods was fairly constant for the HDPE and PEX pipes. VOC consisted mainly of oxygenates, though several VOC contributing compounds were not identified. MTBE was identified in test water from PEX pipes.

Nielsen et al. (2005; 2007) analyzed chemical migration from multiple brands of PE and PEX water pipes available in Denmark. Unfortunately, the specific type of the PE pipes analyzed (e.g., HDPE vs. MDPE, PEX-A vs. PEX-B vs. PEX-C) was not reported so results only have general value. Three brands of new PE pipes were examined at room temperature over a nine day period using distilled water (Nielsen et al., 2005). Every three days, water was removed and replaced. At the end of each exposure period, five antioxidant degradation compounds at concentration between 0.05 and 1.5 μg/l were detected, with levels generally decreasing during subsequent exposures: 2,6-DTBQ, 2,4-DTBP, 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 3,5-di-*tert*-butyl-4-hydroxyacetophenone, and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) methylpropanoate. Chemical concentration varied based on the brand of pipe. Researchers suspected these compounds were antioxidant degradation products. 2,6-DTBQ (1.5 μg/l) and 2,4-DTBP (1.4 μg/l) had the greatest concentrations after three days, decreasing after nine days.

Nielsen et al. (2007) also investigated chemical migration from seven new PEX-A and PEX-C pipes into water at room temperature over a nine-day period and one pipe was a multilayer PEX. Compounds detected were 2,6-DTBQ, 2,4-DTBP, 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 3,5-di-*tert*-butyl-4-hydroxyacetophenone, 7,9-di-*tert*-butyl-1-oxaspiro[4,5]-deca-6,9 dien-2,8-dione, 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) methylpropanoate. Concentrations detected after each three-day exposure period ranged from 0 to 33 μg/l, and large variation was found across PEX brands. After nine days, contaminants were detected in waters in contact with four of the seven PEX pipes. 2,6-DTBQ concentration was greatest for one pipe at 16 μg/l after three days, but did not decrease below 12 μg/l after nine days. After nine days, water from three other pipes had 2,6-DTBQ concentrations ranging from 5

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to 7 μg/l. Differences in chemical migration from PEX pipes likely relate to pipe ingredients and manufacturing methods.

As described previously, Koch (2007) quantified TOC release and impact on water odor for several new polymer pipes used in Germany. Five types of PE pipes (total of nine pipes) were examined: Multilayer pipes PEX-AL-PEX, PE-AL-PE, and PEX-AL-PE along with standard PEX-A and PEX-C pipes. Unfortunately, the type of PE and PEX polymers present in the multilayer materials were not reported. Multilayer pipes could be one of three types of thermoplastic pipes or one of three types of thermoset pipes (see literature review). Pipes were rinsed with demineralized water then filled with extractant water at three different conditions for 72 hr duration: (a) at 23°C no disinfectant, (b) at 23°C with 1 mg/l free chlorine concentration, and (c) at 60°C no disinfectant. At the end of each 72-hr exposure period, water was removed and analyzed for TOC concentration, GC/MS detection of contaminants, and water odor assessment. Fifty-nine contaminants were detected in water due to polymer pipe exposure and are listed in the Appendix tables, but no individual contaminant concentrations were quantified. After a nine-day exposure period, a wide range of calculated TOC release (0.01–0.32 ng/dm^2-day) was found at 23°C and a number of compounds were detected. Several notable contaminants detected include a crosslink initiator (di-*tert*-butyl peroxide), crosslink initiator degradation products (MTBE, ETBE), antioxidant degradation product (2,4-DTBP, 7,9-di-*tert*-butyl-1-oxaspiro[4,5]-deca-6,9 dien-2,8-dione, 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde), resin/processing aides (toluene, benzene, tetrahydrofuran), manufacturing byproducts, solvents used for processing, and many aromatic and short-chain aliphatic compounds that contained alcohol, aldehyde, and ketone functional groups of unknown origin. Water odor was also significantly affected during the nine-day exposure period and greater odor intensity was generally noticed with waters where more contaminants were detected. Contaminant release for the 60°C testing series was recorded, but these results will not be discussed because 60°C is atypical of buried water distribution systems.

In the United States, Durand (2005) and Durand and Dietrich (2007) studied the type of odors generated when one brand of new PEX-A and one brand of new PEX-B pipe were repeatedly exposed to residual disinfectant chlorine or combined chlorine under static conditions at 23°C, as well as a 175-day experiment analyzing water quality impacts of eight piping materials. Several aldehydes, ketones, esters, aromatic acids were detected migrating from each material, but not all compounds were detected in each extractant water. Notable compounds detected include: di-*tert*-butyl peroxide, 2-ethoxy-2-methyl (ETBE) propane, decanal, TBA, 2,2-diethoxy nonanal propane, 1-ethyl propyl hydroperoxide, butanoic acid-butyl ester, *p*-xylene, 2-ethyl-1-hexanol, and 2,5-dimethyl-2,5-hexanediol. ETBE was the only contaminant that was quantified, having concentrations ranging from 23 μg/l to

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greater than 100 μg/l. ETBE concentration decreased with increased water flushing. TOC levels were found to be 0.5 to 2.5 mg/l concentration for HDPE and PEX pipes, with the greatest TOC concentration detected after exposing pipes to disinfected water. Contaminant flux could not be calculated because pipe ID and length dimensions were not provided.

Heim and Dietrich (2007) examined the impacts of one brand of HDPE pipe used in the United States on water odor, contaminant migration, trihalomethane formation, and disinfectant consumption. Pipe (19 mm ID, 2.13 m length) was flushed with distilled water for 1 hr, filled with water containing 50 mg/l free chlorine for 3 hr, and flushed again with distilled water to eliminate any chlorine residual. A synthetic tap water (pH 7.7–7.9) was then added to pipe sections with and without disinfectant and pipes were stored at 23°C for 72–96 hr. Pipes were filled with synthetic tap water and drained two additional times. Results showed that water was odiferous, which implied contaminants had migrated into water. TOC release was 0.14 μg/cm^2 but the unspecific exposure duration prevents calculation of a contaminant flux (mass/area-time). Notable contaminants detected include: phenol, bisphenol (type unspecified), cyclotetradecane, tetradecane, cyclohexadiene, cyclohexanone, and cyclopentanone. Based on the personal experience of the present authors, monomodal HDPE was the material examined.

The following EDAW (2009) description is abbreviated because only a summary of the results is publicly available. In response to State of California plumbing code concerns, 10 different brands of new PEX pipe were tested in accordance with ANSI/NSFI Standard 61 to determine if MTBE and TBA are released from PEX pipes and at what rate (EDAW, 2009). While testing was conducted for 107 days, the experimental details (surface area, water volume, water change frequency) were not disclosed. Steady declines in aqueous MTBE and TBA concentrations was explained by EDAW (2009) for each PEX pipe, but concentration data (initial, during experiment) was not provided. EDAW (2009) reported that waters in contact with 10 samples were found to be at or below the 13 μg/l State of California primary MCL for MTBE by day 90, and six of 10 samples reached the 5 μg/l State of California secondary MCL for MTBE by day 90. TBA results ranged from nondetection to 62 μg/l for all 10 samples after 90 days. It is noteworthy to recognize that the lack of details in the EDAW (2009) report inhibits an independent review of the data or interpretation of what the data actually imply. For example, the authors did not describe the type of PEX pipes examined (e.g., PEX-A, PEX-B, or PEX-C) or provide chemical concentration results for the entire period. This omission raises concerns regarding the study's completeness and how data were interpreted. As explained in the Introduction of the present work, certain types of PEX pipes are created using initiator compounds that decompose into MTBE, ETBE, and TBA during manufacture while other PEX pipes are not created with those

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compounds. Thus, reporting that an unspecified type of PEX pipe does not contain MTBE, ETBE, or TBA compounds is not a major finding, especially if the investigator does not report what type of PEX he tested. Statistical comparisons and mean and standard deviation aqueous concentration values were also not reported. The EDAW (2009) report underscores the need for researchers to provide a detailed account of the polymer pipe, experimental conditions, and results so that independent validation can be conducted and results can be incorporated into decision making processes by utilities and regulators. While the EDAW study likely required significant financial and equipment resources for completion, the resulting report does not enable utilities or regulators to understand the water quality implications of the PEX pipe.

Work conducted by Pinelli et al. (2010) further underscores the fact that if polymer pipe types are not reported, laboratory results cannot be directly applied to pipes being considered by utilities or evaluated by researchers and regulators. These Italian researchers conducted a well-designed experiment that examined the bulk properties and contaminant migration of 23 different commercial new PE pipe samples at 40°C. For migration testing, 5 cm length pipes were rinsed for 30 min. (water type and quality not described), then immersed in 100 ml of mineral water, and finally incubated at 40°C for 24 hr. Water was analyzed to detect polycyclic aromatic hydrocarbons and VOCs. Contaminants detected in water were reported as μg chemical per kg of water: seven pipes benzene (0.61–0.64 μg/kg), five pipes toluene (0.58–0.68 μg/kg), and seven pipes fluorene (0.06–0.16 μg/kg). The researchers reported that fluorene is a well-known component of carbon black. In the United States, carbon black is frequently present in HDPE water pipes up to 0.02 mass fraction (American Society for Testing and Materials, 2010). Because the PE pipe types were not described, results of this work cannot be directly interpreted by utilities, regulators, or public health officials. Even while pipe density was representative of HDPE material, the pipe described by Pinelli et al. (2010) could be either a thermoplastic or a thermoset because HDPE resin is used to create both materials. Whelton et al. (2010) demonstrated a new monomodal HDPE and HDPE based PEX-B potable water pipes can have similar densities, but different contaminant diffusion characteristics.

Brocca et al. (in press) examined contaminant migration from one brand of LDPE and two brands of MDPE pipes at room temperature. These researchers detected and quantified numerous antioxidant degradation products to include 4-ethylphenol, 4-*tert*-butylphenol, 2,6-DTBQ, 2,4-DQBP, 3,5-di-*tert*-butyl-4-hydroxystyrene, 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 3,5-di-*tert*-butyl-4-hydroxyacetophenone, 7,9-di-*tert*-butyl-1-oxaspiro[4,5]-deca-6,9 dien-2,8-dione, and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) methylpropanoate. Results of their work have been partially published in Nielsen et al. (2005).

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PE pipe water flavor impacts and the compounds inside PE pipes have been examined by several Australian, American, British, and Danish researchers. In comparison to all 23 PVC pipes that passed the Australia/New Zealand drinking water flavor test, Marchesan and Morran (2004) found five of 25 PE pipes failed that same test. Contaminants have been extracted from commercial PE pipes using organic solvent and detected using spectrophotometric identification methods. Carthorne et al. (1990) extracted three PE specimens using dichloromethane including: a black PE, a blue PE, and a blue MDPE. Their results showed that Irganox® 1010 and Irganox® 1076 and 2,6-DTBQ were detected and these researchers proposed Irganox® 1010 and Irganox® 1076 degraded into 2,6-DTBQ. Chloroform extractions conducted by Denberg et al. (2009) for a PEX-A pipe revealed Irganox® 1076, 2,6-DTBQ and 2,4-DTBP were present and their distribution was homogeneous in the radial direction but varied substantially in the longitudinal direction. Within 2 cm of pipe length, antioxidant loading varied from 1.8 to 5 g/kg. Aside from these reported extractions, past researchers have not typically quantified compounds within PE pipes.

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FRP and deficiencies with existing data

Research conducted in Great Britain provided the only experimental evaluation of contaminant migration from a FRP (Carthorne, 1990). Pieces of new poly(ester) GRP (40 cm ID and 0.9 cm wall thickness) were removed and placed in buffered deionized water in the presence of free chlorine at 1 mg/l concentration. Exposure times were 24, 48, and 96 hr, but water temperature was not reported. A number of contaminants were detected in extractant water after 24 hr exposure, and taking into account experiment dilution ratios, the contaminant concentration in water was estimated for a full-scale pipe. Primary components detected after 24 hr and their estimated full-scale pipe concentrations were phthalic acid ester (26 μg/l), dimethyl phthalate (21 μg/l), benzaldehyde (4 μg/l), acetophenone (3 μg/l), styrene (0.7 μg/l), and TCEP (3 μg/l). Other compounds detected but not quantified were dialkoxy phthalate ester, dioctyl phthalate (also called DOP and DEHP), benzoic acid, nonanol, 2-ethyl hexanoic acid, and two unknown isomers with molecular mass of 240 g/mol.

FUTURE CHALLENGES

Source of Contaminants

The more than 100 publicly available sources compiled and reviewed in the present work indicate that little is known regarding contaminant migration from polymer potable water pipe worldwide. Few brands of polymer pipes have been tested and contaminants detected in water are directly related to

TABLE 7. Categories for Compounds Detected in Water

Category	Description of Compounds	Origination
Category I	Unreacted monomer and resin	Compound added to pipe during manufacture
Category II	Additives such as antioxidants, stabilizers, pigments, processing aides, initiators, lubricants, curing agents, crosslinking agents, flame retardants, fillers, plasticizer, accelerants, solvents	Compound added to pipe during manufacture
Category III	Broken polymer chains that in general have oxygen functional groups containing alcohol, ketone, aldehyde, and carboxylic acids	Formed by chemical reactions occurring in the material during manufacture
Category IV	Primary or greater derivative degradation products of ingredients	Formed by chemical reactions during pipe manufacture, in-service, or in water

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the compounds used to create the polymer and the pipes' processing conditions (Table 7). Moreover, aqueous contaminant concentration depends not only on the initial contaminant loading and polymer microstructure in the bulk and near pipe surface. Frequently overlooked in the literature is that contaminant concentration is strongly influenced by migration test conditions (e.g., pH, temperature, static or flow, pre/post water rinse, SA/V ratio, aqueous ion levels, and contaminants water solubility). Future investigators should focus on understanding contaminant loading in the pipe as well as the influence of water quality and environmental factors on migration.

Based on the data covered in this literature review, the Appendix tables describe the similarities and differences between polymer pipe systems. While these tables include lists of contaminant names, their source (pipe types), and country (where the study was conducted), the summarized data do not differentiate between contaminants released from pipes manufactured by different vendors in different countries, or describe the contaminants detected under different water conditions (e.g., temperature, pH). In some countries, only one type of pipe from one vendor produced during a single year has been analyzed to date (e.g., HDPE, PEX-A, PEX-B in the United States). As a result, the Appendix tables only contain data for this single sample even though there are multiple manufacturers in the United States (and world), which use different ingredients and manufacturing processes for their specific pipes. As more information becomes available, Appendix tables should become multidimensional to account for variability within materials, countries, and water qualities.

Most prior research has focused on detecting contaminants in water, while less effort has focused on quantifying contaminant concentration. Contaminant detection is important, but water utilities, public health officials, and regulators cannot understand the context of a detected contaminant without knowing its aqueous concentration. More effort must be made to equip utilities, regulators, and health officials with aqueous concentration results.

Despite the fact that contaminant presence and loading (mg/kg pipe) in the pipe strongly governs the total quantity of contaminant that is available to leach from the material, few researchers have quantified contaminant loading and distribution in the pipe. This lack of prior work may be due to the difficulty and absence of metrology to detect and quantify small quantities of contaminant in solid polymers with good accuracy. The literature clearly demonstrates numerous investigators do not recognize the fundamental differences between polymer pipe properties, ingredients, or how test conditions may influence contaminant migration. Failure to understand these concepts has resulted in the existing miscellany of peer-reviewed data that are informative, but have little comparative value. Existing data cannot be used by utilities, researchers, and regulators to draw comparisons with other tests reported in the literature, or even tests that involve the same type of pipe. Added to this is a lack of a fundamental understanding what are the main factors that control the migration of contaminants from the matrix to the exposed water for each polymer pipe (e.g., water solubility, temperature, contaminant concentration, polymer morphology). Without such essential data, a comprehensive model to contaminant release from each type of pipe cannot be developed.

Reviewed studies also show that several pipe materials and contaminants have been investigated more frequently than others. The number of contaminants associated with each pipe does not indicate that certain materials leach less/more contaminants than others, but more appropriately identifies which pipes have and have not been thoroughly studied, and which contaminants have been detected across multiple pipe types. Tables 5, 8, and 9 and those in the Appendix provide an overview of the published work.

Conceptual Model

Based on the data presented here, we propose a contaminant migration conceptual model for aged polymer pipe (Figure 6). Future work is needed to quantify and mathematically model these phenomena, though the proposed model for aged pipe was not found anywhere in the literature. The model considers the fact that resins used to fabricate pipes generally contain residual monomers and partially reacted molecules. Antioxidants and other additives are often physically blended in the formulation to aid the processing and enhance pipe properties. Some additives and low molecular mass molecules likely undergo thermal oxidative degradation during pipe

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TABLE 8. Contaminant Flux Comparison for PE Pipes (ng/dm^2-day)*

	Type of pipe and number of brands tested							
	Nielsen et al. (2005)	Nielsen et al. (2007)			Brocca et al. (2011)		Skjevrak et al. (2003)	
Compound*	HDPE 3	PEX-A 3	PEX-C 3	PEX-AL-PEX* 1	LDPE 1	MDPE 2	PEX [unspecified] 2	HDPE 7
4-ethylphenol	◊	◊	◊	◊	130.0	◊		
4-*tert*-butylphenol	◊	◊	◊	◊	1.2	16, 62		
2,6-DBTQ	0–72.6	5.4	58.5–130.1	69.4	85.0	4.7, 85		0.9–180.7
2,4-DTBP	12.2–37.0	7	◊	13	◊	40, 1524		
3,5-DTBHS	◊	◊	◊	◊	7.3	2.8, 4.0		
3,5-DTBHB	0–10.6	0.5–7.4	5.4–9.2	16.3	56.0	6.6, 9.0		
3,5-DTBHA	0–13.9	1.4–5.6	0.6–2.6	4.7	39.0	8.0, 39.0		
7,9-DTBODDD	0–32.4	18.4	37.9–357.7	173.4	6539.0	93, 2910		
3-(3,5-DTBHP) methylpropanoate	0–31.0	17.3	◊	11.9	43.0	22, 33		
MTBE							41.7, 279.2	
Tert-butanol							4.3, 9.8	
4-Butoxy phenol							18.8	
5-Methyl-2-hexanone							5.5	
Mesityl oxide							2.1	
Tert-butyl isobutyl ether							0.8	
ETBE*								

Note. *ETBE flux from one brand of PEX-B pipe in the United States was calculated from Durand and Dietrich (2007) reported data to be 564–2164 ng/dm^2-day. PEX-AL-PEX was PEX-B-AL-PEX-C. Diamond (◊) indicates polymer was tested but contaminant was not detected in water in contact with that polymer. All data represent exposure during static conditions (nonflowing). DTBHS = di-*tert*-butyl-4-hydroxystyren; DTBHB = di-*tert*-butyl-4-hydroxybenzaldehyd; DTBHA = di-*tert*-butyl-4-hydroxyacetophenon; DTBODD = di-*tert*-butyl-1-oxaspiro[4,5]-deca-6,9 dien-2,8-dion; DTBHP = di-*tert*-butyl-4-hydroxyphenyl. 4-methyl-2,5-di-*tert*-butyl-phenol (BHT) was not detected in any study.

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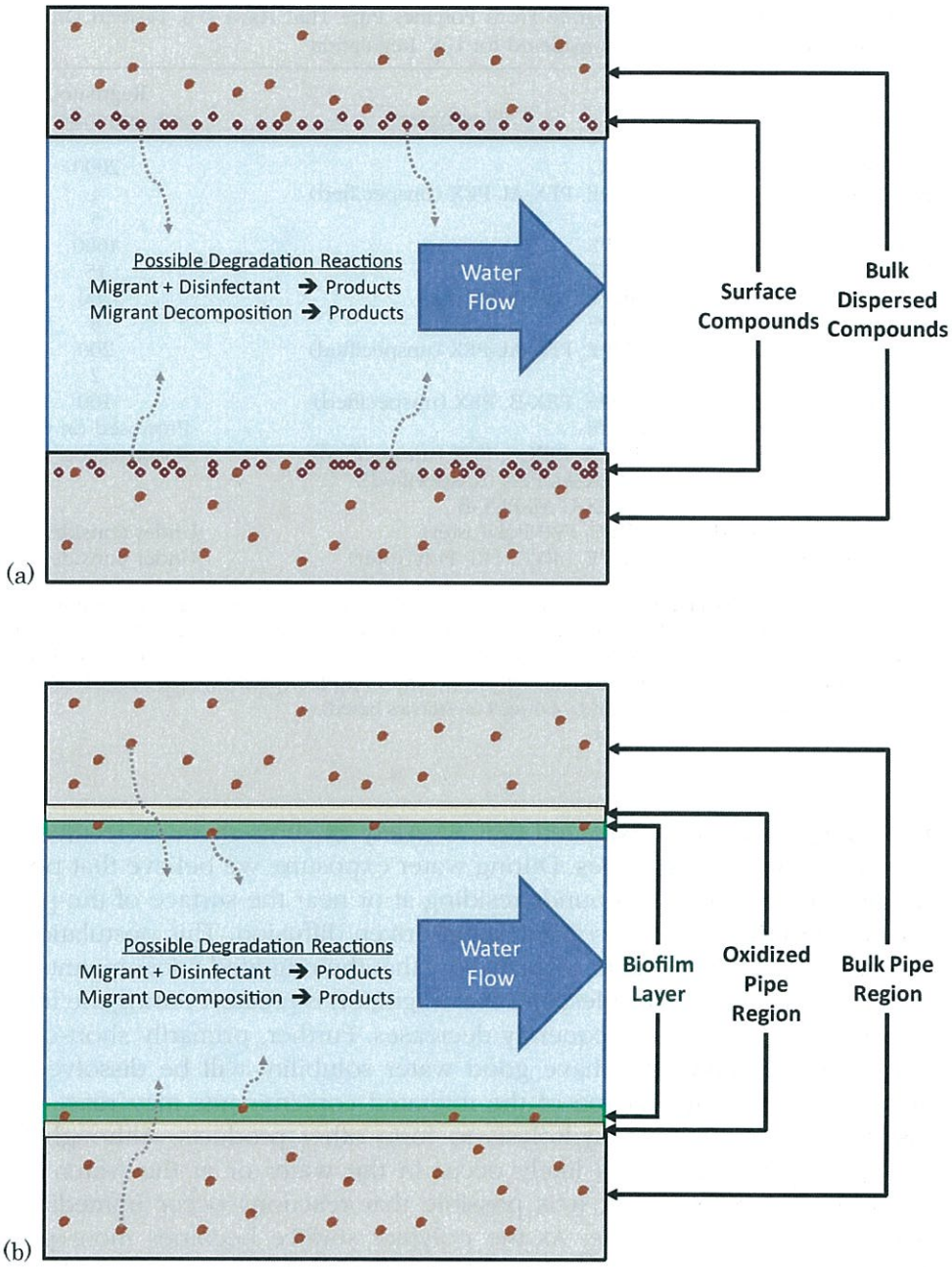

FIGURE 6. Conceptual diagram showing the fate of contaminants from (a) new and (b) aged polymer potable water pipe. Part (a) contains the model historically applied for contaminant migration investigations. Based on the present literature review, we propose (b) the more complicated model that includes an oxidized pipe surface and biofilm. The influence of these phenomena on migration has not yet been elucidated (Color figure available online).

TABLE 9. Contaminants That Migrate From Polymer Pipe That Have U.S. Federal Drinking Water Limits and Those Being Considered for U.S. Regulation

Contaminant	Pipe types	Regulated concentration, μg/l
Barium	uPVC	2000
Benzene	HDPE, PEX-AL-PEX (unspecified)	4
Cadmium	uPVC	5
Ethylbenzene	HDPE	1000
Lead	uPVC	15
Styrene	HDPE, FRP-Poly(ester)	700
Trichloroethylene	HDPE	5
Toluene	HDPE, PEX-AL-PEX (unspecified)	200
VCM	uPVC	2
Xylenes	HDPE, PEX-B, PEX (unspecified)	100
n-Propylbenzene	HDPE	Proposed on CCL3
MTBE*	PEX-A, PEX-C, PEX (unspecified), PEX-AL-PEX (unspecified), PEX-C-AL-PEX-B	Proposed on CCL3
Bisphenol compounds	uPVC, FRP-Poly(ester)	Under consideration
Phthalate compounds	HDPE, uPVC, FRP-Poly(ester)	Under consideration

Note. Suspect that all HDPE pipes are unimodal PE materials because no studies reported resin modality and pipes used before the 1990s were generally all unimodal, not bimodal PE. Some PEX studies did not describe the type of PEX examined. *The states of New Hampshire and New York have adopted health based MTBE regulatory drinking water limits of 13 μg/l and 10 μg/l, respectively. The state of California also has an enforceable secondary MCL of 5 μg/l (aesthetics based).

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processing. Thus, it is expected that a variety of short-chain molecules are present in the polymer pipes. During water exposure, we believe that polar, low molecular mass compounds residing at or near the surface of the pipes migrate into the water by concentration-driven diffusion. This postulation is supported by available data, which show that the migrated contaminants are mostly small, polar molecules, and that migration is greatest during the initial exposure period and subsequently decreases. Further, primarily short-chain and polar molecules that have good water solubility will be dissolved or associated with water. Some of the migrated contaminants may react with disinfectants or undergo hydrolysis to form other products. Although the majority of these reactions likely occur in the water or at the water/pipe interface during exposure, it is possible that reactions occur immediately below the polymer surface. As the polymer surface becomes more polar due to disinfectant exposure, water likely migrates deeper into the polymer. Subsequent contaminants in the pipe and reaction products could then more easily migrate to water media. Research is needed to address where these reactions occur, under what conditions, and migration of reaction products. This information is important because pipe manufacturers and users could then develop a strategy to reduce both drinking water contaminant concentration and off-flavors. Water pH plays an important role in the hydrolysis

process and may have an effect on the reactions between contaminants and disinfectants. Its significance, however, has primarily gone unstudied.

We also propose that contaminants that migrate from the polymer into water are homogeneously distributed in the pipe, clustered near the pipe surface, and/or there may be a concentration gradient within the pipe wall. This postulation is supported by the literature where contaminant migration is greatest during the initial water exposure period, and decreases after this initial period. Work conducted by B.F. Goodrich in the 1970s proposed this distribution phenomenon to describe VCM migration from uPVC pipe, but similar work has not been conducted for other polymer pipe systems or contaminants. The exact definition of initial period, however, is difficult to define as past migration studies applied different exposure times (1 hr to greater than two years), and drinking water regulations can be based on long-term exposure (70 years). Unfortunately, much of the work summarized in this review only represents migration testing results for new polymer pipes.

Finally, a recent study has demonstrated that contaminant fate in new polymer pipe may not represent migration phenomenon that occurs in actual drinking water distribution systems. Polar contaminants diffused 50% slower out of HDPE pipes that had been exposed to chlorinated water/oxidized in comparison to diffusion from new HDPE pipes (Whelton et al., 2011b). These aged pipes had polar carbonyl functional groups (>C=O) on their surface. The role of aging on PE pipe and other materials must be better understood in order for water utilities, environmental engineers, and public health officials to have accurate contaminant migration models and health risk assessments.

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The Role of the Biofilm

Some studies have indicated that biofilm lining the interior pipe wall can affect contaminant migration (Richardson and Edwards, 2009; Skjevrak et al., 2005), though the scale of this effect has not been well documented. Other research has also shown that biofilms play an important role in drinking water quality and can proliferate on polymer pipe surfaces in buried water distribution systems (Camper and Jones, 2000; Lehtola et al., 2004; Momba and Makala, 2004; Ndiongue et al., 2005; Tsvetanova, 2006; Yu et al., 2010). Further research should be conducted to examine the role of polymer pipe contaminants on biofilm formation and how biofilm formation affects contaminant migration from the pipe into water. Because organic molecules are a good source of food for organism growth, we suspect biofilms could directly influence contaminant fate through metabolisis, transformation, or physically accelerate/decrease their migration rate.

Estimating the Migration Period and Aqueous Concentration

While contaminant migration from polymer pipe is greatest during the initial water exposure period, several investigators have found certain organic and inorganic contaminants continue to migrate out of in-service uPVC pipes installed for 30+ years. This same statement cannot be stated for PE-based materials because few studies have been conducted to examine long-term contaminant migration from in-service PE based piping. Most recently, Denberg (2009) calculated chemical diffusion coefficients for additives and their degradation products in HDPE pipe and predicted that these compounds could migrate from HDPE pipe for 170–900 years. While a large amount of contaminant may migrate into drinking water during the initial water exposure period, continued migration of lesser amounts of contaminant can be expected over the material's service life.

Contaminant drinking water concentration will vary based on pipe service conditions and even between pipe brands as shown by the limited published data. Aqueous concentration is affected by water demand, lengths of sequential pipe, dead-ends, and the pipe/water SA/V ratio. Contaminant flux (mass/surface area-time) from lab- and field-tested pipes can vary substantially, and while one contaminant may be found migrating from one type of pipe, it may not be detected being released from a different pipe (Table 8). Table 8 results clearly show testing the same name of pipe (e.g., PEX or a thermoplastic PE) does not guarantee a good representation of expected aqueous contaminant concentration. At present, the water industry does not understand contaminant migration variability between different brands of the same pipe type.

Because water chemistry can influence contaminant release from some polymer pipes (e.g., lead from uPVC), changes to drinking water quality initiated by a need to achieve utility regulatory compliance could also increase/decrease contaminant migration. For example, in the 1990s many U.S. water utilities switched from using free chlorine as a residual disinfectant to combined chlorine in an effort to comply with the disinfectant/disinfection byproduct rule. Consequences of this switch, however, changed drinking water chemistry and this new water chemistry caused extensive lead leaching from installed lead water pipes (Edwards et al., 2009). It is possible that future changes to water chemistry in response to utility compliance efforts could also affect contaminant migration from polymer pipe.

Optimize Material Manufacturing to Reducing Migration

Resin and pipe manufacturers could make decisions to reduce chemical migration from their materials. First, manufacturers could consider treating the pipe after extrusion. Treatment could simply involve rinsing the interior pipe surface with local tap water at high turbulence for 4 hr (Reynolds Number >

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6000) as recommended by Wu et al. (1989) for reducing tin migration. This approach would likely remove trace compounds that would have ultimately been released after installation, but would not necessarily remove all surface contaminant and/or would not remove contaminants that are located deeper in the pipe wall, which would migrate out during the long-term. No studies were found that evaluated the value of rinsing on a pipe's long-term contaminant release or included quantification of contaminant loading in the pipe before and after rinsing. Ideally, exposing the entire pipe wall to a solvent for contaminant extraction would be optimum, but solvent exposure may alter pipe mechanical performance, possibly leave residual solvent in the product, and/or be cost prohibitive from an operations/safety standpoint.

From a material production perspective, contaminant migration could be reduced by initially selecting an optimized loading of additives and processing conditions. These selections could not only promote desired properties (e.g., crosslinking, service life) but also minimize residual compounds that could migrate from the polymer to drinking water. This could be considered a green strategy if chemical usage was reduced and the major economic benefits of this material design strategy would be additive and energy cost savings.

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Regulatory Implications

Of the more than 150 contaminants that have been found migrating from polymer pipes (see Appendix), several unregulated compounds are known or potential endocrine disruptors, and only fourteen contaminants have existing or proposed U.S. drinking water regulatory limits, or have limits under consideration (Table 9). The Danish Environmental Protection Agency instituted a provisional 20 μg/l drinking water concentration for 2,4-DTBP, a known polymer pipe antioxidant degradation product (Nielsen et al., 2005). Although no U.S. drinking water standard exists for this compound nor is this compound listed on the CCL3 or is being monitored as an unregulated contaminant. To date, more polymer pipe field and laboratory studies have been conducted in Denmark than any other country. Directly translating Danish results to the United States is difficult because different pipe brands (and manufacturers/formulations) are used in each country, reports sometimes did not describe pipe types, and experimental conditions were not well described.

Existing state drinking water regulations of California and New Hampshire as well as proposed U.S. federal drinking water regulations for CCL3 contaminants underscore a fundamental deficiency of ANSI/NSFI Standard 61 (Table 9). ANSI/NSFI Standard 61 test results for certified materials represent short-term exposure and are not publicly available. Moreover, ANSI/NSFI testing is based on drinking water standards in place at the time of testing:

Normative drinking water criteria (USEPA, Health Canada, NSFI etc. derived short- and long-term exposure limits). As a result, utilities are not provided information that enables them to retrospectively evaluate how ANSI/NSFI certified material will affect regulatory compliance with pending or future USEPA regulations. Without public contaminant migration data, utilities will need to conduct extensive pipe network field testing to determine their ability to comply with any new USEPA regulations that may be specific to their installed ANSI/NSFI Standard 61 certified pipes. Because of the lack of public migration data, utilities may also need to remove and replace previously installed ANSI/NSFI certified pipes as a strategy to comply with new regulations if operational adjustments are not effective (e.g., increase hydrant flushing frequency, turnover). Utilities have carried out these actions in the past when responding to VCM leaching issues from PVC pipe. ANSI/NSF Standard 61 was partly intended to prevent such expensive remedial measures, but as designed and applied it does not. As designed, ANSI/NSFI Standard 61 does not fit the demands of dynamic regulatory drinking water environment in the United States and requires revision. We propose that this testing approach be revised in the existing framework to, at a minimum, require the publication of contaminant migration and concentration data for each certified product over the entire period of testing. Product formulations, manufacturing data, other proprietary information should continue to be protected (not released).

In the absence of contaminant migration results, data synthesized in this literature review are the only publicly available information available for estimating how polymer pipe may affect utility compliance with U.S. drinking water regulations. As can be deduced from the existing literature, there is insufficient information available to predict how polymer pipes will affect long-term water quality or impact long-term water utility regulatory compliance. Failure to publicly disclose water quality test results for ANSI/NFSI Standard 61 certified materials will continue to inhibit utilities from understanding how these approved pipes affect compliance with proposed or new regulations.

If more stringent drinking water regulations are passed in the future, contaminants and their concentrations reviewed in the present work may become significant in later years. This finding is important because little work has been conducted to document contaminant migration. Existing data may be conservative or greatly skewed and utilities that base pipe purchasing, rehabilitation decisions on the existing data (and ANSI/NSFI Standard 61) are doing so with little to no knowledge of how these materials will impact drinking water quality. In addition to public release of ANSI/NSFI Standard 61 water quality test results and types of pipes tested, more work is needed to document contaminant concentration variability in buried water distribution systems and aged pipe.

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CONCLUSIONS

Considering future water pipeline investment costs, the continued installation of polymer pipes into drinking water distribution systems, and importance of water quality to the public, the contamination migration in polymer pipe is highly relevant and important. With regulatory stringency and drinking water–polymer pipe contact area increasing, the overall impact of contaminant migration on drinking water quality will only become more significant. For future regulatory compliance planning purposes, water utilities should continue to select polymer pipes for repair, replacement, and new construction applications based on the best available publicly available migration data. Unfortunately, the NSFI does not publicly disclose contaminant migration test results for ANSI/NSFI Standard 61 certified materials.

The public literature clearly demonstrated contaminant migration has been poorly documented and is not well understood. Many times data reported were incomplete and were not comparable to other pipes or studies. Numerous reports simply raised awareness about contaminant migration from some new and in-service pipe systems, but lacked consistent reporting methods and experimental conditions that inhibit data interpretation across the literature within and between countries. Little public effort has been put forth to identify diffusion coefficients of polymer pipe contaminants or understand contaminant migration from aged materials, FRPs, PEXs, and multilayer aluminum polymer pipes. No public effort has been dedicated to evaluating contaminant migration issues of mPVC, oPVC, fPVC, bimodal PE, or FRP-epoxy materials. Many knowledge gaps can be attributed to investigators not fully understanding the properties or manufacturing methods for polymers or how experimental conditions influence contaminants they detected in water. Because polymer pipes are estimated to last 50–100 years, understanding how contaminant migration from these materials affects drinking water quality is necessary.

During preparation of this review, discussions with resin and pipe manufacturers as well as water utility staffs revealed that this emerging research area does not receive adequate funding. Major reasons interviewees provided were that new contaminants could be discovered and these compounds may or may not have regulated MCLs. With the existing ANSI/NSFI Standard 61 approach incapable of providing utilities or regulators critical information they need understand long-term water quality impacts of polymer pipe, pipe users and owners are ill-equipped to plan for regulatory compliance. No comprehensive U.S. effort is underway to identify key polymer pipe migration aspects. In order to protect drinking water consumers and continue provision of high-quality drinking water, a rational strategy with sufficient financial resources is needed to build knowledge.

Identified knowledge gaps pose a challenge to environmental engineers who strive to select polymer pipe based on drinking water quality, system

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operation, and regulatory compliance issues. More work is needed to identify the contaminants, their quantities, occurrence in actual water distribution networks, and the processes that control their migration from polymer pipes. To improve U.S. drinking water quality and continue to protect public health, water utility staffs, public health officials, and regulators must have access to well-designed and reported scientific studies that thoroughly characterize contaminant migration from polymer pipe. Polymers are progressively becoming the new interface between safe drinking water that leaves the water treatment facility and the customer's tap, and for public health and infrastructure economic reasons, science-based investigations are needed.

ACKNOWLEDGMENTS

This work was partly conducted while Dr. Whelton held a National Research Council Research Associateship from the National Academy of Sciences at the National Institute of Standards and Technology (NIST). Certain commercial equipment, instruments, or materials are identified in this article to foster understanding. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose. The authors are grateful to Drs. Joannie Chin, Douglas Fox, Jonathan Martin, Stephanie Watson, and Lee Yu, NIST, who graciously provided feedback on this manuscript. The authors also appreciate the constructive feedback provided by the three anonymous peer reviewers.

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NOTE

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APPENDIX

TABLE A-1. Compounds Detected in Water in Contact with PVC Pipe

Compound Name	Purpose	Country	References
Inorganics			
Antimony	Stabilizer	USA	Boettner et al. (1991)
Barium	Stabilizer	SAU	Al-Malack (2001)
Cadmium	Stabilizer	DNK, SAU	Florsund (1991), Al-Malack (2001)
Calcium	Stabilizer, Filler	SAU, USA	Dietz et al. (1995), Al-Malack (2001)
Lead	Stabilizer	AUS, DEU, DNK, GBR, ITA, EGY, NLD, ROM, SAU, SGP, USA	Boelens (1960), Nikals and Meyer (1961), Visintin and Monteriolo (1965), Cosoveanu (1971), Packham (1971b), Gross et al. (1974), Poels and Dibbets (1982), Wong et al. (1988), Wong et al. (1990), Koh et al. (1991), Forslund (1991), Burn and Sullivan (1993); Sadiq et al. (1997), Al-Malack (2001), Koh et al. (2004), Lasheen et al. (2008)
Magnesium	Filler	USA	Dietz et al. (1995)
Tin	Stabilizer	CAN, DNK, FRA, RUS, SAU, USA	Mazaev and Slepnina (1973); Rhodes et al. (1980), Boettner et al (1982), Jirackova-Audouin and Verdu (1985), Wu et al. (1989), Quevauviller et al (1991), Quevauviller et al (1991), Forsyth et al (1993), Dietz et al. (1995), Sadiki-A-D and Williams (1999, Al-Malack (2001), Neilsen et al. (2005), Koh et al. (2004), Johnson and Clark (2006), Impellitteri et al. (2007), Richardson and Edwards (2009)
Organics			
Benzothiazole	Unknown	GBR	Crathorne et al. (1996)
Chloroacetic acid	Free chlorine reaction byproduct	JPN, SGP	Ando and Sayato (1984), Wong et al. (1990)
Chloroacetaldehyde	Free chlorine reaction byproduct	JPN, SGP	Ando and Sayato (1984), Wong et al. (1990)
Cyclohexanone	Solvent for resin[c]	USA	Boettner et al. (1981), Heim and Dietrich (2007)
Decanal	Mfg byproduct[c]	FRA, NOR, USA	Anselme et al. (1985), Skjevrak et al. (2003), Durand (2005)

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TABLE A-1. Compounds Detected in Water in Contact with PVC Pipe *(Continued)*

Compound Name	Purpose	Country	References
Dibutyl phthalate	Plasticizer	USA	Rhodes et al. (1980), Trussell et al. (1980)
Diglycidyl ether Bisphenol A	Infrequent used as PVC stabilizer	GBR	Carthorne and Warren (1986), Crathorne et al. (1990)
Dodecaonic acid	Lubricant	GBR	Crathorne et al. (1990)
Hexadecanoic acid	Lubricant	GBR	Crathorne et al. (1990)
Hexadec-9-enoic acid	Lubricant[e]	GBR	Crathorne et al. (1990)
Hexanal	Mfg byproduct[e]	NOR	Skjevrak et al. (2003)
Methyl ethyl ketone	Solvent for resin[e]	USA	Boettner et al. (1981)
Nonanal	Mfg byproduct[e]	FRA, NOR, USA	Anselme et al. (1985), Skjevrak et al. (2003), Durand (2005)
Octadecanoic acid	Lubricant, accelerator	GBR	Crathorne et al. (1990)
Octanal	Mfg byproduct[e]	NOR	Skjevrak et al. (2003)
Palmitoleic Acid	Lubricant	GBR	Crathorne et al. (1990)
Phenylacetaldehyde	Unknown	GBR	Crathorne et al.(1990, 1996)
Phthalates (Unspecific)	Plasticizer[e]	FRA, GBR, USA	Anselme et al. (1985), Crathnorne et al. (1990), Durand (2005)
Tetradecanoic acid N-N-bis(2-hydroxyethyl)alkyl-amine	Lubricant	GBR	Crathorne et al. (1990)
Tetrahydrofuran	Solvent for resin[e]	USA	Skjevrak et al. (2003)
Tris(chloroethyl) phosphate	Flame retardant	GBR	Crathorne et al. (1990, 1996)
Vinyl chloride monomer (VCM)	Monomer	CAN, DEU, JPN, SAU, SGP, USA	Berens and Daniels (1976), Dressman and McFarren (1978), Banzer (1979), Fishbein (1979), Rhodes et al. (1980), Bauer (1981), Ando and Sayato (1984), Flournoy et al. (1999), Al-Malack et al. (2000), Al-Malack et al. (2000), Al-Malack and Sheikheldin (2001), Beardsley and Adams (2003), Al-Malack (2005), Richardson and Edwards (2009), Walter et al. (2011)

Suspect that all PVC results represent uPVC materials since many studies did not report the type of PVC examined and uPVC pipes have been historically used until recently; Superscript "e" indicates compound origin is estimated based on available data.

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TABLE A-2. Antioxidants and their Degradation Products Detected in Water in Contact with PE Pipe

Compound Purpose and Name	Thermoplastic			Thermoset			Multilayer				Country	Ref.
	LDPE	MDPE	HDPE	PEX-A	PEX-B	PEX-C	PEX-B-PEX-C	PEX-AL-PEX	PEX-AL-PE	PE-AL-PE		
Antioxidants												
Alkyl thiophene			X								FRA	Anselme et al. (1985, 1986)
BHT			X	◊		X		X	◊	◊	DEU, FRA, NOR	Anselme et al. (1985, 1986), Skjevrak et al. (2003), Koch (2004)
4-Butoxyphenol				X	◊						NOR	Skjevrak et al. (2003)
1,5-Di-*tert*-butyl-3,7-dimethyl bicyclohexane-2-one			X								FRA	Anselme et al. (1985)
3,5-DTBHB	X	X	X	X	◊	X					DNK	Brocca et al. (2002), Neilsen et al. (2007), Brocca et al. (In Review)
3,5-DTBHS	X	X									DNK	Brocca et al. (2002), Neilsen et al. (2005), Brocca et al. (In Review)
2,6-DTBMP	◊	X		X	◊						NOR	Crathorne e et al., 1990; Skjevrak et al. (2003),
Irganox® 1010	X	X									DNK, GBR	Crathorne e et al. (1990), Neilsen et al. (2007)
Irganox® 1076	◊	X									GBR	Crathorne e et al. (1990)
PTBP	X	X		◊		◊					DNK	Brocca et al. (2002); Brocca et al. (In Review)
Sanatox			X								FRA	Anselme et al. (1985)
Antioxidant Degradation Products												
2,6-DBTP				◊		X			◊	◊	DEU	Koch (2004)
2,4-DTBP	X	X	X	X		X	X	X	◊	X	DNK, GBR, NOR	Anselme et al. (1985, 1986), Carthorne et al. (1990), Brocca et al. (2002), Skjevrak et al. (2003), Koch (2004), Durand (2005), Neilsen et al. (2005), Neilsen et al. (2007), Brocca et al. (In Review)

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TABLE A-2. Antioxidants and their Degradation Products Detected in Water in Contact with PE Pipe *(Continued)*

Compound Purpose and Name	Thermoplastic			Thermoset			Multilayer				Country	Ref.
	LDPE	MDPE	HDPE	PEX-A	PEX-B	PEX-C	PEX-B-PEX-C	PEX-AL-PEX	PEX-AL-PE	PE-AL-PE		
2,6-DTBQ	X	X	X	X		X	X	X	◊	X	DEU, DNK,GBR, NOR	Anselme et al. (1985, 1986), Crathorne e et al. (1990), Brocca et al. (2002), Skjevrak et al. (2003), Koch (2004), Neilsen et al. (2005), Neilsen et al. (2007), Brocca et al. (In Review)
3,5-DTBHA	X	X		X	◊	X	X	X	◊	◊	DEU, DNK	Brocca et al. (2002), Koch (2004), Neilsen et al. (2005); Neilsen et al. (2007); Brocca et al. (In Review)
3-(3,5-DTBHPMP)	X	X		X	◊	◊	X	X	◊	X	DEU, DNK	Brocca et al. (2002), Koch (2004), Neilsen et al. (2005), Neilsen et al. (2007), Brocca et al. (In Review)
3-(3,5-DTBHPPA)	X	X		◊		X		X	◊	◊	DEU, DNK	Brocca et al. (2002), Koch (2004)
2,6-Di-*tert*-butyl-4-ethylphenol	◊	X									GBR	Crathorne e et al. (1990)
7,9-DTBODDD	X	X		X	◊	X	X	X	◊	X	DEU, DNK	Koch (2004), Neilsen et al. (2005), Neilsen et al. (2007), Brocca et al. (In Review)
3,5-DTHB	X	X		X		X	X	X	◊	◊	DEU, DNK	Brocca et al. (2002), Koch (2004), Neilsen et al. (2005), Neilsen et al. (2007), Brocca et al. (In Review)
4-Ethylphenol	X	◊									DNK	Brocca et al. (2002), Brocca et al. (In Review)
2-*Tert*-butylphenol				◊		X		X	◊	◊	DEU	Koch (2004)
3-*Tert*-butylphenol				◊		◊		X	◊	◊	DEU	Koch (2004)

Suspect that all LDPE, MDPE, and HDPE results represent unimodal PE materials since no studies reported resin modality and pipes used before the 1990s were all unimodal; Letter "X" indicates contaminant was identified and diamond "◊" indicates polymer was tested but contaminant was not detected in water in contact with that polymer; CASRN's could not be located for several contaminants that were described in the literature; Abbreviations: PTBP = 4-*tert*-butylphenol; Irganox® 1010 = Tetrakis-(methylene-(3,5-di-(*tert*)-butyl-4-hydrocinnamate))methane, Irganox® 1076 = Octadecyl 3,5-Di-(*tert*)-butyl-4-hydroxyhydrocinnamate; Sanatox = 4-methyl-2,6-di-t-butyl phenol; BHT = 4-Methyl-2,6-di-*tert*-butylphenol; 2,6-DTBMP = di-*tert*-butyl-4-methylphenol; 3,5-DTBHB = di-*tert*-butyl-4-hydroxy benzaldehyde; 3,5-DTBHS = di-*tert*-butyl-4-hydroxystyren; 2,6-DTBQ = Di-*tert*-butyl-p-benzoquinone; 2,4-DTBP = Di-*tert*-butylphenol; 2,6-DTBP = Di-*tert*-butylphenol; 3,5-DTHB = di-*tert* -butyl-4-hydroxy benzaldehyd; 3,5-DTBHA = di- *tert* -butyl-4-hydroxyacetophenon; 3-(3,5-(DTBHPMP) methyl propanoat = (di- *tert* -butyl-4-hydroxyphenyl); 3-(3,5-DTBHPPA) propanoic acid = (di- *tert* -butyl-4-hydroxyphenyl); 7,9-DTBODDD = di-*tert*-butyl-1-oxaspiro(4,5)deca-6,9-dien-2,8-dion.

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TABLE A-3. Compounds Detected in Water in Contact with PE Pipe Listed by Origin

	Thermoplastic			Thermoset			Multilayer						
Compound Name	LDPE	MDPE	HDPE	PEX-A	PEX-B	PEX-C	PEX-B-AL-PEX-C	PEX-AL-PEX	PEX-AL-PE	PE-AL-PE	Country	Known or Estimated Origin	Ref.
Benzene			X	◊		◊		X	◊	◊	CAN, DEU, FRA, ITA, NOR	Solvent for resin[c]	Anselme et al. (1985), Skjevrak et al. (2003), Koch (2004), Pinelli et al. (2010)
Bisphenol (unspecific)			X								USA	Stabilizer[c]	Heim and Dietrich (2007)
Butanoic acid-butyl ester				X	X						USA	Mfg. byproduct[c]	Durand (2005)
Cyclohexanone			X								USA	Solvent for resin[c]	Boettner et al. (1981); Heim and Dietrich (2007)
Cyasorb® UV 531	◊	X									GBR	Stabilizer	Crathorne e et al. (1990)
Decanal			X	X	X						FRA, NOR, USA	Mfg. byproduct[c]	Anselme et al. (1985), Skjevrak et al. (2003), Durand (2005)
n-Decane			X								FRA	Mfg. byproduct[c]	Anselme et al. (1985)
2-Decanone			X								NOR	Mfg. byproduct[c]	Skjevrak et al. (2003)
Decanoic acid				◊		◊		◊	X	◊	DEU	Lubricant[c]	Koch (2004)
2,2-Diethoxypropane				◊	X						USA	Mfg. byproduct[c]	Durand (2005)
2,5-Dimethyl-2,5-hexanediol				X	X	◊		X	◊	◊	DEN, USA	Mfg. byproduct[c]	Koch (2004), Durand (2005)
Dodecanal			X								FRA	Mfg. byproduct[c]	Anselme et al. (1985)
2-Dodecanone			X								NOR	Mfg. byproduct[c]	Skjevrak et al. (2003)
Dodecanoic acid				◊		◊		◊	X	◊	DEU	Lubricant[c]	Koch (2004)
1,3-Diol-di-isobutyrate			X								FRA	Stabilizer degradate[c]	Anselme et al. (1985)
Di-*tert*-butyl peroxide				X	◊	◊		X	◊	◊	DEU, USA	Crosslink initiator	Koch (2004), Durand (2005)
2-Ethyl-1-hexanol			X	X	X						FRA, USA	Mfg. aide[c]	Anselme et al. (1985), Durand (2005)
Ethyl-tert butyl ether (ETBE)				X	X	X		X	◊	◊	DEU, USA	Crosslink initiator degradate[c]	Koch (2004), Durand (2005)
Ethylbenzene			X								NOR	Solvent for resin[c]	Skjevrak et al. (2003)

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TABLE A-3. Compounds Detected in Water in Contact with PE Pipe Listed by Origin *(Continued)*

	Thermoplastic			Thermoset			Multilayer						
Compound Name	LDPE	MDPE	HDPE	PEX-A	PEX-B	PEX-C	PEX-B-AL-PEX-C	PEX-AL-PEX	PEX-AL-PE	PE-AL-PE	Country	Known or Estimated Origin	Ref.
1-Ethyl propyl Hydroperoxide				◊	X						USA	Crosslink initiator degradate[e]	Durand (2005)
Fluorene			X								ITA	Carbon black degradate[e]	Pinelli et al. (2010)
Heptanal			X								FRA	Mfg. byproduct[e]	Anselme et al. (1985)
2-Heptanone			X								FRA	Mfg. byproduct[e]	Anselme et al. (1985)
2-Hexanone			X	◊		◊		◊	X	◊	FRA	Mfg. byproduct[e]	Anselme et al. (1985); Koch (2004)
p-Isopropyl toluene			X								NOR	Solvent for resin[e]	Skjevrak et al. (2003)
2-Methyl-2-butanol								X	◊	◊	DEU	Crosslink initiator degradate[e]	Koch (2004)
5-Methyl-2-hexanone				X	◊	◊		◊	◊	◊	DEU, FRA, NOR	Solvent for resin[e]	Skjevrak et al. (2003), Koch (2004), Neilsen et al. (2007)
Methyl ketone (unspecified)			X								FRA	Mfg. byproduct[e]	Anselme et al. (1985)
Methyl-*tert*-butyl ether (MTBE)				X	◊	X	X	X		◊	DEU, DNK, NOR, USA	Crosslink initiator degradate[e]	Skjevrak et al. (2003), Koch (2004), Neilsen et al (2007), EDAW (2009)
Naphthalene						X					FRA, NOR	Lubricant[e]	Anselme et al. (1985), Skjevrak et al. (2003)
Nonanal			X	X	X						NOR, USA, FRA	Mfg. byproduct[e]	Anselme et al. (1985), Skjevrak et al. (2003), Durand (2005)
1-Octanol				◊		◊		◊	X	◊	DEU	Mfg. byproduct[e]	Koch (2004)
3-Octanone			X								FRA	Mfg. byproduct[e]	Anselme et al. (1985)
Octanoic acid				◊		◊		◊	X	◊	DEU	Lubricant[e]	Koch (2004)
Phthalimide	◊	X									GBR	Pigment	Crathorne e et al. (1990)

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2-Propanone		X		◊		X	◊	◊	DEU	Mfg. byproduct[e]	Koch (2004)
n-Propylbenzene	X								NOR	Solvent for resin[e]	Skjevrak et al. (2003)
Styrene	X								NOR	Solvent for resin[e]	Skjevrak et al. (2003)
Tert-butanol (TBA)					X	◊	X		DEU, NOR, USA	Crosslink initiator degradate[e]	Skjevrak et al. (2003), Koch 2004), Durand (2005), EDAW (2009)
TBP*	X								FRA	Plasticizer	Anselme et al. (1985)
1,3,5-TMB*	X								NOR	Stabilizer	Skjevrak et al. (2003)
1,2,4-TMB*	X								NOR	Stabilizer	Skjevrak et al. (2003)
2,2,4-TPD*	X								FRA, NOR	Plasticizer	Anselme et al. (1985), Skjevrak et al. (2003)
Toluene	X	◊		◊		X	◊	◊	CAN, DEU, FRA, ITA, NOR	Solvent for resin[e]	Anselme et al. (1985), Skjevrak et al. (2003), Koch (2004), Pinelli et al. (2010)
Tetrahydrofuran		◊		◊		X	◊	◊	DEU	Mfg. aide[e]	Koch (2004)
2-Undecanone	X								NOR	Mfg. byproduct[e]	Skjevrak et al. (2003)
p-Xylene	X	◊	X						CAN, FRA, NOR, USA	Solvent for resin[e]	Anselme et al. (1985), Alben et al. (1989), Skjevrak et al. (2003), Durand (2005)

Suspect that all LDPE, MDPE, and HDPE results represent unimodal PE materials since no studies declared resin modality and older pipes were initially unimodal; Letter "X" indicates contaminant was identified and diamond "◊ " indicates polymer was tested but contaminant was not detected in water in contact with that polymer; Superscript "e" indicates compound origin is estimated based on available data. Abbreviations: Cyasorb UV 531 = 2-hydroxy-4-n-octoxy-p-benzophenone; 1,3,5- TMB = (Trimethylbenzene); 1,2,4-TMB = (Trimethylbenzene); TBP = Tributylphosphate; 2,2,4-TPD = (Trimethyl-1,3-Pentanediol Diisobutyrate).

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TABLE A-4. Compounds of Unknown Origin Detected in Water in Contact with PE Pipe

Compound Name	CASRN	Thermo-plastic	Thermoset			Multilayer				Country	Ref.
		HDPE	PEX-A	PEX-B	PEX-C	PEX-B-AL-PEX-C	PEX-AL-PEX	PEX-AL-PE	PE-AL-PE		
Acetic acid-1,1-dimethylethyl ester	540–88–5		◊		X		X	◊	◊	DEU	Koch (2004)
Acetophenone	98–86–2		◊		◊		X	◊	◊	DEU	Koch (2004)
Alpha, alpha-dihydroxy-p-diisopropylbenzene	2948–46–1		◊		◊		X	◊	◊	DEU	Koch (2004)
Alpha farnesene	502–61–4	X								NOR	Skjevrak et al. (2003)
Alpha pinene	80–56–8	X								NOR	Skjevrak et al. (2003)
Alpha terpinolene	586–62–9	X								NOR	Skjevrak et al. (2003)
Benzaldehyde-dimethylacetal	1125–88–8		◊		◊		X	◊	◊	DEU	Koch (2004)
Benzothiazole	95–16–9		X		X		◊	◊	◊	DEU	Koch (2004)
Butanoic acid-butyl ester	109–21–7		X	X						USA	Durand (2005)
Butyl acetate	123–86–4	X								NOR	Skjevrak et al. (2003)
Butyl hexanoate	626–82–4	X								NOR	Skjevrak et al. (2003)
Cyclohexadiene	U.I.	X								USA	Heim and Dietrich (2007)
Cyclohexene	110–83–8	X								FRA	Anselme et al. (1985)
Cyclopentanone	120–92–3	X								USA	Heim and Dietrich (2007)
Cyclotetradecane	295–17–0	X								USA	Heim and Dietrich (2007)
Delta-3-carene	13466–78–9	X								NOR	Skjevrak et al. (2003)
1,4-Diacetylbenzene	1009–61–6		◊		◊		X	◊	◊	DEU	Koch (2004)
1,3-Dichlor-2-methyl-2-propanol	U.I.		◊		◊		X	◊	◊	DEU	Koch (2004)
Dimethoxypropane	U.I.		◊		◊		X	◊	◊	DEU	Koch (2004)
2,3-Dimethyl-1-butene	563–78–0		X		◊		◊	◊	◊	DEU	Koch (2004)
Dimethylhexene	U.I.	X								FRA	Anselme et al. (1985)
3,3-Dimethyl-2-butanol	464–07–3		◊		◊		X	◊	◊	DEU	Koch (2004)
3-(1,1-Di-methylethyl)-2,5-furandione	U.I.		◊		◊		X	◊	◊	DEU	Koch (2004)
3,3'-Dimethyl-1-indanone	26465–81–6		◊		◊		X	◊	◊	DEU	Koch (2004)
4,4-Dimethyl-2-pentanone	590–50–1		X		◊		◊	◊	◊	DEU	Koch (2004)
Diphenylethylene	530–48–3		◊		◊		X	◊	◊	DEU	Koch (2004)
1,3-Di-*tert*-butylbenzene	1014–60–4		◊		◊		X	◊	◊	DEU	Koch (2004)
Di-*tert*-butoxymethane	U.I.		X		◊		◊	◊	◊	DEU	Koch (2004)
2,6-Di-*tert*-butyl-4-isopropylphenol	5427–03–2		X		◊		◊	◊	◊	DEU	Koch (2004)

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3-Ethylacetophenone	22699–70–3		◊		◊	X	◊	◊	DEU	Koch (2004)
Ethyl decadienoate	3025–30–7	X							NOR	Skjevrak et al. (2003)
Ethyl hexanoate	123–66–0	X							NOR	Skjevrak et al. (2003)
Ethyl ketone	U.I.	X							FRA	Anselme et al. (1985)
Ethyl methyl benzene	U.I.	X							NOR	Skjevrak et al. (2003)
Ethyl octanoate	106–32–1	X							NOR	Skjevrak et al. (2003)
Ethyl-4-*tert*-butylphenylether	U.I.		◊		◊	X	◊	◊	DEU	Koch (2004)
Hexanonacidmethylester	U.I.		◊		◊	X	◊	◊	DEU	Koch (2004)
Hexamethyl butanoate	U.I.	X							NOR	Skjevrak et al. (2003)
Hexyl acetate	142–92–7	X							NOR	Skjevrak et al. (2003)
Hexyl hexanoate	6378–65–0	X							NOR	Skjevrak et al. (2003)
m-Hydroxyacetophenone	121–71–1		◊		◊	X	◊	◊	DEU	Koch (2004)
Isobornyl acetate	125–12–2	X							NOR	Skjevrak et al. (2003)
Isopropyl benzene (cumene)	98–82–8	X							NOR	Skjevrak et al. (2003)
Limonene	5989–27–5	X							NOR	Skjevrak et al. (2003)
Mesityl oxide	141–79–7		X	◊					NOR	Skjevrak et al. (2003)
1-Methoxy-2-methyl-2-propanol	3587–64–2		◊		◊	X	◊	◊	DEU	Koch (2004)
1-Methoxy-2-*tert*-butyl-6-methylbenzene	U.I.		◊		◊	X	◊	◊	DEU	Koch (2004)
2,2'-(Methylbis(oxy))bis-2-methylpropane	U.I.		X		◊	◊	◊	◊	DEU	Koch (2004)
3-Methyl-2-buten-1-ol	556–82–1		◊		◊	X	◊	◊	DEU	Koch (2004)
Methyl ketone	U.I.	X							FRA	Anselme et al. (1985)
2-Methyl-2-((2-methyl-2-propenyl)oxy)-1-propanol	U.I.		X		◊	◊	◊	◊	DEU	Koch (2004)
2-Methyl-2-(1-methylethoxy)-propane	17348–59–3		X		◊	X	◊	◊	DEU	Koch (2004)
4-Methyl-2-pentanone	108–10–1		◊		◊	X	◊	◊	DEU	Koch (2004)
1-(4-(1-Methylethyl)phenyl)-ethanone	645–13–6		◊		◊	X	◊	◊	DEU	Koch (2004)

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TABLE A-4. Compounds of Unknown Origin Detected in Water in Contact with PE Pipe *(Continued)*

Compound Name	CASRN	Thermo-plastic HDPE	Thermoset			Multilayer				Country	Ref.
			PEX-A	PEX-B	PEX-C	PEX-B-AL-PEX-C	PEX-AL-PEX	PEX-AL-PE	PE-AL-PE		
Phenol	108–95–2	X								USA	Heim and Dietrich (2007)
2-Phenyl-2-propanol	617–94–7		◊		◊		X	◊	X	DEU	Koch (2004)
Phenylaceticacidethylester	101–97–3		◊		◊		X	◊	◊	DEU	Koch (2004)
Phthalates (unspecified)	U.I.	X								FRA, GBR	Anselme et al. (1985), Crathorne et al. (1990), Durand (2005)
Propyl hexanoate	626–77–7	X								NOR	Skjevrak et al. (2003)
Short chain aldehydes	U.I.	X								FRA	Anselme et al. (1985, 1986)
Tertachloroethylene	127–18–4	X								FRA	Anselme et al. (1985)
Tertiobutylcyclohexanone	U.I.	X								FRA	Anselme et al. (1985)
Tetradecane	629–59–4	X								USA	Heim and Dietrich (2007)
Tert-butyl isobutyl ether	33021–02–2		X	◊						NOR	Skjevrak et al. (2003)
Tert-butylhypochlorite	507–40–4		X		X		X	◊	X	DEU	Koch (2004)
Tert-Butylisopropylester	33021–02–2		X		◊		◊	◊	◊	DEU	Koch (2004)
3,3-Thio-bis-propaneaciddimethylester	U.I.		◊		◊		X	◊	◊	DEU	Koch (2004)
Tridecan	629–50–5		◊		◊		X	◊	◊	DEU	Koch (2004)
2,4,6-Tri-*tert*-butylbenzoic acid	66415–27–8		◊		◊		X	◊	◊	DEU	Koch (2004)

CASRN could not be located for some contaminants that were described in the literature because these compound names were unspecific (e.g., phthalates) or CASRN could not be directly found. These compounds are denoted as U.I. = CASRN unidentified. Letter "X" indicates contaminant was identified and diamond "◊ "indicates polymer was tested but contaminant was not detected in water in contact with that polymer.

TABLE A-5. Compounds Detected in Laboratory Water in Contact with a Fiber Reinforced Composite Poly(ester) Pipe in Great Britain

Compound	CASRN	Known or Estimated Origin
Acetophenone	98–86–2	Solvent for resin[e]
Styrene	100–42–5	Solvent for resin[e]
Dimethyl phthalate	131–11–3	Plasticizer[e]
Dioctyl phthalate (DEHP or DOP)	117–81–7	Plasticizer[e]
Dialkyl phthalate ester (DPE)	U.I.	Plasticizer[e]
Phthalic acid ester	U.I.	Unknown
Benzaldehyde	100–52–7	Unknown
Tris-chloroethylphosphate (TCEP)	115–96–8	Unknown
Benzoic acid	65–85–0	Unknown
Nonanol	143–08–8	Unknown
2-Ethyl hexanoic acid	149–57–5	Unknown

Data obtained from Carthorne et al. (1990), CASRN could not be located for some contaminants described in the literature because these compound names were unspecific (e.g., phthalates) or CASRN could not be directly found. These compounds are denoted as U.I. = CASRN unidentified; Superscript "e" indicates compound origin is estimated based on available data.

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