PEX and PP Water Pipes: Assimilable Carbon, Chemicals, and Odors

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Eleven brands of plastic drinking water pipe were evaluated for assimilable organic carbon (AOC) release at 23°C for 28 days: polyvinyl chloride, high-density polyethylene, polypropylene (PP), and cross-linked polyethylene (PEX) pipes. Three of eight PEX pipe brands exceeded a 100 µg/L AOC microbial regrowth threshold for the first exposure period, and no brands exceeded this value on day 28. No AOC increase was found for PP or PEX-a1 pipes; the remaining pipe brands contributed marginal AOC levels. Pipe water quality impacts were more fully evaluated for two PEX-b brands and one PP brand. PEX pipes caused greater odor than the PP pipe and released more organic carbon as well as volatile and semi-volatile organic compounds. Water quality impacts were less after 30 days. Regulated and unregulated contaminants were found in three PEX plumbing systems. Drinking water odors were attributed to toluene, ethyl-tert-butyl ether, and unidentified contaminants.

Keywords: assimilable organic carbon, leaching, odor, PEX, plastic pipe plumbing, regrowth

Plastic drinking water plumbing pipes are increasingly being used in the United States because they are inexpensive, easy to install, and have reported service lives of >50 years. High-density polyethylene (HDPE), cross-linked polyethylene (PEX), and polyvinyl chloride (PVC) pipes are used for cold water domestic plumbing systems, but PEX is also used for hot water applications. Polypropylene (PP) drinking water pipes are used for hot and cold water conveyance, especially in large buildings such as hospitals, schools, and commercial structures. Increased plastic pipe use can be partly attributed to the US Green Building Council’s Leadership in Energy and Environmental Design (LEED) rating system, which has offered design credit for PEX and PP pipe use (USGBC 2008).

As plastics have entered premise plumbing inventories, a growing number of chemical, odor, and microbiological water quality problems have emerged (Kelley et al. 2015, 2014; Zhang & Liu 2014; Lutzhoft et al. 2013; Pruden et al. 2013; Bucheli-Witschel et al. 2012; Kowalska et al. 2011; Lund et al. 2011; Durand & Dietrich 2007; NRC 2006; Koch 2004; Skjevrak et al. 2003; Brocca et al. 2002, Hametner 1999, Anselme et al. 1985a). Drinking water odor can also be impacted (Durand & Dietrich 2007, Heim & Dietrich 2007). Recent work by Kelley et al. (2014) revealed differences in the performance of six brands of PEX pipes during a 30-day exposure period; TOC release, odor, and specific ultraviolet absorbance (SUVA) levels differed with and without chlorine disinfectant present. Both regulated and unregulated contaminants have been found. In Europe, regulated contaminants were released by HDPE (Skjevrak et al. 2005, Anselme et al. 1986, Anselme et al. 1985b) and PEX piping systems (Nielsen et al. 2007, 2005; Brocca et al. 2002). In the United States, in the few PEX plumbing systems investigated (Kelley et al. 2014, Chemaxx 2007), antioxidant, additive degradation product, and odor-causing contaminants were found. Contaminant migration studies from PP pipes available in Europe revealed the presence of antioxidants and their degradation products in drinking water, but PP pipes caused little to no impact on drinking water odor (Zhang & Liu 2014, Van der Kooij 2007, Hametner 1999). However, PP potable water pipes have not received any scrutiny in the United States and, as
of September 2015, only one brand of PP pipe was commercially available in the United States. Publicly available leaching data for US PEX and PP materials is essential for building and plumbing professionals to make decisions that limit building inhabitant chemical exposure and aesthetic impacts.

Another concern with plastic pipes is their potential to promote microbial regrowth within plumbing systems, specifically because of the release of assimilable organic carbon (AOC) (Bucheli-Witschel et al. 2012, Yu et al. 2010, Silhan et al. 2006, Lehtola et al. 2004, Niquette et al. 2000, Szewzyk et al. 2000, Rogers et al. 1994). Coliforms, a broad class of ubiquitous gram-negative organisms, can indicate drinking water system contamination (Edberg et al. 2000, Szewzyk et al. 2000). LeChevallier (2003) showed that bacterial regrowth was based on a complex interaction of factors, with the frequency of total coliform detection increasing when AOC levels were greater than 100 µg/L, water temperatures were >15°C, and the distribution system had low disinfectant residuals (<0.2 mg/L free chlorine or <0.5 mg/L chloramines). TOC concentration alone is a poor predictor of a tap water's microbial regrowth support potential (Bucheli-Witschel et al. 2012, Escobar & Randall 2001). Only two studies were found that reported AOC release from plastic drinking water pipes (Bucheli-Witschel et al. 2012, Corfitzen et al. 2002). Because each employed drastically different analytical methods, exposure durations, and temperatures, and materials were obtained in Europe, the results of these studies are not directly comparable (Bucheli-Witschel et al. 2012, Corfitzen et al. 2002). AOC levels ranged from 30 to 100 µg/L for the six drinking water pipes tested, two PVC brands, two PEX brands, one medium-density polyethylene brand, and one poly(1-butene) brand.

As a result of the limited literature available, US construction professionals currently have no infallible system for selecting plumbing pipes with minimal chemical, odor, and microbial regrowth impacts. This research builds on the existing literature and examines the variability of water quality impacts between different pipe brands of the same material as well as between different materials and incorporates both laboratory and installed plumbing system studies. Specific objectives of this study were to (1) quantify the AOC release from multiple brands of plastic pipe over 28 days (i.e., eight PEX brands and one brand each of PP, PVC, and HDPE); (2) describe chemical release and odor contribution of two brands of PEX-b pipe and one brand of PP pipe under laboratory conditions; and (3) describe chemical release and odor contribution of three PEX plumbing systems of varying ages in three residential homes.

METHODS AND MATERIALS
Pipes and pipe cleaning. Eight brands of PEX pipe, and one brand each of PP, HDPE, and PVC pipes, all ¾-in. diameter, were examined. PEX type a (PEX-a), PEX type b (PEX-b), and PEX type c (PEX-c) pipes, which are created by different manufacturing processes (Whelton & Nguyen 2013), were examined. Pipes were certified according to National Sanitation Foundation International (NSFI) 61 health effects standards for potable water (NSFI 2013). Sections from each brand were cut to a

![Typical examples of residential cross-linked polyethylene (PEX) manifolds: (A) blue and red tubing connects to individual plumbing fixtures, (B) red tubing is insulated while blue tubing is not, and (C) a copper pipe manifold was created and a separate piece of PEX tubing connects the manifold to individual plumbing fixtures.](image-url)
length of 6 ft (for AOC testing) and 10 ft (for 30-day leaching testing). Pipes were disinfected according to the California plumbing code for PEX pipe installation guidelines (CPC 2010): 10-min tap water rise followed by stagnation of laboratory-prepared tap water\(^1\) spiked with 2 mg/L free chlorine for seven days. Following disinfection, pipes were rinsed with laboratory-prepared water, then filled with a laboratory-generated synthetic drinking water. The synthetic water contained the following as milligrams per liter: K\(^+\) (4.9), Na\(^+\) (41.7), Ca\(^{2+}\) (19.6), Mg\(^{2+}\) (19.8), Al\(^{3+}\) (0.3), HCO\(_3^-\) (28.5), HPO\(_4^{2-}\) (0.02), Cl\(^-\) (13.8), NO\(_3^-\) (4.9), SO\(_4^{2-}\) (33.0), and SiO\(_2^{2-}\) (13.2) (Zhang & Edwards 2009). The alkalinity was 30 to 35 mg/L as CaCO\(_3\), hardness was 130 mg/L as CaCO\(_3\), and water pH was 7.2 to 7.5. No disinfectant or corrosion inhibitor was added. Pipes were capped with rubber stoppers tightly wrapped in polytetrafluoroethylene\(^2\) tape, and had surface area-to-volume ratios (SA/V) between 1.9 and 2.4 cm\(^2\)/mL, similar to other studies (Kelley et al. 2015, 2014). Experiments were conducted at 23°C.

**AOC release from multiple plastic pipe brands.** Glass jars (1-L cylindrical wide mouth with polytetrafluoroethylene caps) were cleaned with a laboratory detergent,\(^3\) soaked in 10% nitric acid for 4 h, rinsed with deionized water, and baked in a muffle furnace at 450°C for 1 h. Four consecutive exposure periods of seven days were applied. For each brand, four water samples were collected into pre-cleaned, amber glass vials with no headspace. To eliminate interference by native microorganisms, samples were pasteurized by bringing them to 70°C in a hot water bath and maintaining temperature for 30 min. Samples were cooled and refrigerated overnight, then cold-shipped the following morning to the American Water Laboratory in Delran, N.J., for AOC assays. The luminescence method described in Weinrich et al. (2009) was chosen for its sensitivity and commercial availability. AOC content was calculated by converting mean peak luminescence of the bacterial strains Pseudomonas fluorescens (P-17) and Spirillum (NOX) to \(\mu\)g/L as acetate carbon using a standard curve. These two AOC values were summed to obtain total AOC for each sample and were compared with controls consisting of glass jars kept in the dark at 23°C. Concentrations were reported relative to the control sample for migration periods one and four, corresponding to seven and 28 days of exposure. AOC in the control was 137 ± 22 \(\mu\)g/L and 106 ± 6 \(\mu\)g/L for periods one and four, respectively.

**Water quality impact experimental design.** A subset of new pipes tested for AOC contributions underwent a more expansive 30-day water quality impact investigation. Two brands of PEX-b pipe available in the United States, PEX-b4 and PEX-b5, not previously examined by Kelley et al. (2014), were examined in the present study. PEX-b pipes were selected because “type b” materials were the most commonly available on the US market. One PP pipe brand was examined.

The 30-day leaching test applied was modeled after the “water utility quick test” (Schweitzer et al. 2004). Ten consecutive 72-h exposure periods were carried out. Water was collected after three, nine, 15, and 30 days of exposure. Three replicate pipes, cut from the same initial roll, were used for each material. Water was sampled from each pipe section. Mean and standard deviation values were calculated. Controls consisted of pre-cleaned glass jars, kept in the dark, holding test water for the same 72-h exposure periods and tested along with pipe samples.

**Water characterization.** **Volatile compounds.** Volatile organic compound (VOC) concentrations were characterized through headspace-solid phase microextraction (HS-SPME) with gas chromatography mass spectrometry (GC-MS) (Lutzhoft et al. 2013, Koch 2004). This method was adopted from Cassada et al. (2000), Oh and Stringfellow (2003), and Durand and Dietrich (2007). A GC system\(^4\) with a 5975C inert mass selective detector (MSD) multi-purpose sampler and GC column\(^5\) (length 30 m, diameter 0.250 mm, film 0.25 µm) were used. The extraction process used an SPME fiber assembly (75 µm carboxen/polydimethylsiloxane [CAR/PDMS), 23-ga).\(^6\) The GC-MS oven program used helium as a carrier gas at a rate of 1.0 mL/min. The GC oven was held at 40°C for 4 min then ramped up at a rate of 20°C/min to 300°C and was held there for 2 min. The injector was run in splitless mode and held at 300°C. GC vials (20 mL) were filled with 10 mL of sample water and agitated for 30 min at 50°C. Following agitation, the SPME fiber was held in the headspace for an adsorption time of 5 min. The fiber was placed into the GC injector where it was thermally desorbed of analytes for 3 min. Calibration curves were created using standards of ethyl-\(-\)-butyl ether (ETBE) (1.0, 4.0, 7.0, and 10.0 \(\mu\)g/L), toluene (0.25, 0.5, 1.0, 2.0, and 4.0 \(\mu\)g/L), and xylene (0.25, 0.5, 1.0, 2.0, and 4.0 \(\mu\)g/L). A single cyclohexane (0.4 \(\mu\)g/L) standard was used to examine the presence of this compound in pipe contact water. Analytical standards were supplied by Fisher Scientific (toluene, mixed xylenes), Alfa Aesar (ETBE), Sigma-Aldrich (cyclohexane), and Matrix Scientific (methyl-3-(3,5-di-tert-butyl)-4-hydroxyphenyl)-propanoate).

**Semi-volatile compounds.** Liquid–liquid extraction (LLE) followed by GC-MS was used to detect semi-volatile organic compounds (SVOCs). Three separate 20-mL portions of dichloromethane (DCM) were used to extract from 200 mL of test water, and combined. The resulting 60 mL of extract was dried over anhydrous sodium sulfate. Rotary evaporation at 300 mbar pressure and room temperature reduced the extracted sample size from approximately 60 mL to 0.5 mL. Each 0.5-mL sample was then directly injected into the GC-MS port. The GC-MS oven program used helium as a carrier gas at a rate of 2 mL/min. The GC oven temperature was held at 40°C for 4 min and ramped up to 300°C at a rate of 12°C/min. Temperature was held at 300°C for 10 min. The injector was in split mode at a 20:1 ratio and held at 280°C. Percent recoveries for the extraction were tested on three synthetic standards (toluene, naphthalene, and phenanthrene) as in Koch (2004). Toluene has previously been detected in water that contacted PEX pipes (Koch 2004); naphthalene and phenanthrene are structurally related and were chosen to represent the extractability of a range of aromatic compounds. Percent recoveries for three replicates of each compound were as follows: 92.8 ± 19.5% (toluene), 68.5 ± 20.4% (naphthalene), and 74.0 ± 29.3% (phenanthrene).

Contact waters were also examined using electrospray ionization mass spectrometry (ESI-MS). PEX-a1, PEX-b4, and PEX-b5 pipes were rinsed with deionized (DI) 18 MΩ water\(^1\) for 15 min,
immediately filled to no dead space with DI water, and capped with polytetrafluoroethylene (MIL SPEC T-27730A)-wrapped corks. A polytetrafluoroethylene control was created by filling a glass Erlenmeyer flask with DI water and capping it with a polytetrafluoroethylene-wrapped cork. After seven days of stagnation, 7 mL of each sample and the control were dried in an acid-resistant concentrator \(^2\) in glass test tubes. Dried samples were dissolved in 100 µL 30% methanol, 70% DI water, sonicated for 3 min, and centrifuged for 2 min at 1,000 rpm. For direct-injection ESI-MS, samples were injected into a custom-built 9.4 T electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer (ESI-FTICR-MS) at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, Fla., at 0.5 µL/min in positive-ion mode. The needle voltage was set to ~2,400 V. The capillary heater was set at 32.1 V and 0.15 A. A positive ion calibration solution \(^8\) was used as internal standards for half the samples. Samples that were analyzed without internal standards were calibrated through accurate masses obtained for common analytes in samples with internal standards. For liquid chromatography ESI-MS (ESI-LC-MS), samples were injected into an ion-trap mass spectrometer \(^9\) at 200 µL/min in positive-ion mode. The liquid chromatography column used was a reverse-phase column \(^10\) (250 mm × 2.1 mm 120 Å 5 μL). The mobile phase was held isocratic at 30% methanol, 70% DI water for 20 min, then ramped to 100% over 1.5 min and held at 100% methanol for 4.5 min. The column was then re-equilibrated. Mass scan range was m/z 250–800, and the instrument was tuned to fluorescein (332.31 Da).

**Organic carbon.** TOC represents an overall quantity of organic carbon present in water and was measured using a TOC analyzer \(^11\) in accordance with US Environmental Protection Agency (USEPA) method 415.1 (USEPA 1999). Ultraviolet light absorbance at 254 nm (UV \(_{254}\) ) was measured using a spectrophotometer \(^12\) in accordance with USEPA (2005). UV \(_{254}\) absorbance describes the aromatic portion of the dissolved organic content. SUVA was calculated according to USEPA (2005).

**Odor.** Odor analysis was carried out in accordance with Standard Method 2150-B \(^13\) (Standard Methods 1995). A minimum of five panelists was used for each test. Individuals prohibited from participating included tobacco smokers, pregnant women, those who recently ate or drank, people wearing cologne or perfume, and those suffering any type of illness within the past week. Panelists were both men and women, ages 20 to 57 years. Threshold odor number (TON) tests have their limitations because the odor is diluted until it is no longer detected. But TON tests are frequently employed by water utilities for drinking water odor evaluations (Mallevalle & Suffet 1987), and a drinking water secondary maximum contaminant level (SMCL) of 3 TON exists in the United States.

**Plumbing system field investigations.** To determine the impact of PEX plumbing systems, tap water quality was characterized at one house each in Colorado, Oklahoma, and Maryland. Each house contained PEX plumbing pipe that had been installed for 0.8, one, and two years, respectively. Kelley et al. (2014) previously examined water quality in the Maryland PEX plumbing system 0.5 years after installation. Here, water sampling was conducted in the early morning, and control samples were collected near the copper service connection before water entered each PEX piping system, which enabled characterization of the local water utility distribution systems’ water. Samples were also collected from two taps at each home. First-draw water samples were collected and analyzed. Upon collection in 1-L, pre-cleaned amber bottles with no headspace, homeowners overnight-shipped samples packed in coolers at 4°C to the corresponding author’s laboratory in Mobile, Ala. Samples were refrigerated at 4°C until analysis. No preservatives were added. Waters were analyzed within 24 h using TON, TOC, UV \(_{254}\), HS-SPME/GC-MS, and LLE-GC-MS methods.

**Statistical analysis.** Mean and standard deviation values were calculated for all AOC, TOC, UV \(_{254}\), and SUVA results. Geometric mean and standard deviation were calculated for TON results. Statistical software \(^13\) was used to perform all statistical analysis. To evaluate variation of AOC migration between different brands of PEX pipe, one- and two-way analysis of variance (ANOVA) was applied to compare AOC estimates from days seven and 28. Fisher’s pairwise comparison grouped materials on the basis of amount of AOC released. For the 30-day migration tests, ANOVA and Kruskal–Wallis tests were used to compare TOC and TON values between the three pipe brands. A Type I error of 0.05 was applied for null hypothesis rejection.

ESI results were statistically analyzed using the log-rank test proposed by Mantel (1966) and modified later by Peto and Peto (1972). The log-rank test uses a chi-square test statistic to compare cumulative density weighted by abundance. Only peaks with relative abundance greater than 1% were considered. Additionally, pairwise comparison was used to determine whether spectra of contact waters from PEX-a1, PEX-b4, and PEX-b5 pipes were significantly different. Finally, the Benjamini-Hochberg (Benjamini et al. 2006) procedure was considered to control against false positives.

**RESULTS AND DISCUSSION**

**AOC release from multiple plastic pipe brands.** AOC contributions varied across pipe types, in particular PEX brands \((p < 0.001)\); levels were also influenced by exposure time \((p < 0.001)\). As Figure 1 shows, a detectable increase in AOC level was not found for PP pipe, PVC pipe contributed some AOC as of day 7 \((22\% \text{ increase relative to the control})\), and a 58% AOC increase was observed for HDPE on day 28. However, neither PVC \((\text{maximum } 30 \mu g \text{ AOC/L})\) nor HDPE \((\text{maximum } 61 \mu g \text{ AOC/L})\) caused AOC levels to exceed the microbial regrowth threshold value of 100 µg AOC/L. Corfitzen et al. (2002) reported similar AOC release from PVC pipe following a single exposure period, but they applied different AOC quantification methods and migration conditions. No literature data were found for HDPE.

PEX pipes caused a wide range of AOC concentrations in the water and some pipes caused water to exceed the microbial regrowth criterion. Fisher’s pairwise comparisons revealed that PEX pipe brands were grouped into five distinct bins on day 7 and three distinct bins on day 28. While some AOC levels for PEX pipe brands were still significantly different on day 28, AOC levels caused by PEX pipes were becoming more similar after four
weeks of exposure. Six of eight PEX pipe brands caused AOC levels to be greater than zero on day 7 (Figure 1), of which three brands exceeded the microbial regrowth threshold criterion on day 7. This finding is significant because previous investigators had only found AOC concentrations below the threshold: 50 µg/L and 41 µg/L for two PEX pipe brands, albeit under different conditions (Butcheli-Witschel et al. 2012, Corfitzen et al. 2002). No PEX pipes in the present study caused AOC levels to exceed the microbial regrowth threshold on day 28. Interestingly, although PEX-a1 pipe released the greatest amount of TOC for all pipes tested during the AOC experiment (3.09 mg/L), it did not impart detectable levels of AOC.

**Drinking water quality impacts for PEX and PP brands of pipe—30-day exposure.** Organic carbon. Although all pipes studied over a 30-day period (PEX-b4, PEX-b5, PP) imparted carbonaceous compounds to the water (Figure 2), the magnitude of their releases differed. All observed TOC values were below 1.5 mg/L. In contrast, Kelley et al. (2014) reported TOC levels greater than 6 mg/L for six different ¾-in.-diameter PEX pipes in the absence of chlorine. PEX-b4 and PEX-b5 pipes did not leach more TOC than other brands sold in the United States examined by Kelley et al. (2014) during the first exposure period (p = 0.020, p = 0.030). TOC release from PEX-b4 and PEX-b5 pipes decreased with time (p < 0.001). Observed reductions in TOC concentration and flux for PEX pipes, after nine days of exposure, were also similar to PEX pipes examined in Europe (Butcheli-Witschel et al. 2012, Lund et al. 2011, Koch 2004, Hametner 1999). In contrast, PP pipe’s day 3 and day 9 TOC levels were not significantly different (p = 0.070). The difference between PEX-b and PP pipe performance is likely a result of pipe manufacturing ingredients and conditions. Further work is needed to explain reasons for these TOC differences.

**Nonvolatile components.** Because many ingredients in plastic pipe production are polar or ionic (Whelton & Nguyen 2013) and because water is a polar solvent, ESI-MS was applied to assess whether additional, nonvolatile components were imparted to drinking water. High-resolution ESI-MS data of PEX pipe contact water produced between 23 and 70 unique ions; statistical analysis using the log-rank test indicated that PEX pipes of the same type (PEX-b) were similar (p = 0.271), whereas there was little overlap (significantly different spectra) between contact water from PEX-a versus PEX-b pipes (p < 0.001). None of the accurate masses measured (e.g., those listed in Table 1) corresponded to any of the more than 60 PEX pipe ingredients or degradation products previously described (Whelton & Nguyen 2013). Thus, the data show that a notable number of unknown compounds leached from PEX pipes.

Because adducts and fragments can form in the ESI source and because isomers cannot be distinguished without prior separation, the number of peaks in direct-injection ESI-MS does not necessarily correspond to the number of different compounds in the mixture. Therefore, ESI-LC-MS experiments were conducted (Figure 3). PEX-a1 pipe produced the highest diversity of compounds (≥27 chromatographic peaks). As shown by the ESI-FTICR-MS data, the peaks formed by PEX-a1 shared virtually no overlap with PEX-b4 (≥16 chromatographic peaks) or PEX-b5 (≥18 chromatographic peaks). PEX-b4 and PEX-b5, however, shared a significant number of peaks (same retention time and mass). Compounds detected spanned essentially the entire m/z range examined (m/z 258–776 PEX-a1, m/z 253–776 PEX-b4, m/z 253–790 PEX-b5). Unfortunately, unlike electron-impact MS (as employed in GC-MS), ESI-MS cannot be used to identify compounds through library matching. Without significant constraints on the number and types of elements involved in each

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**FIGURE 1** AOC concentration in drinking water from PP, PEX, HDPE, and PVC pipes following migrations at 23°C relative to the glass control jars

![Graph showing AOC concentration in drinking water from different pipes](image-url)

AOC—assimilable organic carbon, HDPE—high-density polyethylene, PEX—cross-linked polyethylene, PP—polypropylene, PVC—polyvinyl chloride

Water utilities in the United States have concluded that AOC drinking water levels >100 µg/L at water temperatures >15°C greatly increase the probability of coliform occurrences. This experiment was conducted in the absence of disinfectant.
compound, it is not even possible to unequivocally assign molecular formulae based on the measured accurate masses. If the constraints were known (e.g., during production at the plant or testing at a regulating agency), ESI-MS data could provide direct information as to the types of compounds that leach and how they react with each other or degrade.

Here, the data illustrate that a significant number of unknown compounds spanning from low- to mid-molecular weight are present in PEX pipe contact water. It should be noted that ESI-MS in positive-ion mode is selective for polar compounds with high gas phase basicity and that it is unlikely that the chromatographic method resolved all components. Thus, even combined, the GC-MS data here and in the literature plus the LC-MS results presented here likely significantly underestimate the total complexity of PEX pipe contact water. Because the molecular composition of contact water is largely unknown, parameters such as disinfectant by-product formation potential (DBPFP), AOC, and toxicity cannot be looked up or predicted on the basis of individual components. Instead, these parameters must either be measured or estimated on the basis of best-available correlation parameters (e.g., SUVA for DBPFP) for the mixture as a whole.

**Disinfection by-product potential.** SUVA level, which has historically been used to describe dissolved organic carbon that could form DBPs, was calculated for each pipe using $\text{UV}_{254}$ absorbance and TOC values. SUVA results ranged from 0.36 to 3.0 L/mg-M and implied organic contaminants released by PEX and PP pipes may be susceptible to DBP formation. According to USEPA (2012), SUVA values <2 represent hydrophilic mixtures with low DBPFP; values between 2 and 4 represent hydrophobic/hydrophilic mixtures that may pose increased DBPFP; and values >4 represent aromatic hydrophobic mixtures with high DBPFP. For both PEX pipes, the greatest SUVA values were observed on day 30. Kelley et al. (2014) also found similar results for six other PEX pipe brands sold in the United States. More work is needed to identify the contaminants imparted to water by plastic pipes and their susceptibility to halogenation. Additional work should also be carried out to examine the reactivity of the leachates with chlorine and the extent to which regulated and unregulated DBPs are formed under the range of conditions expected to be encountered in drinking water distribution systems. Exposure duration did not affect $\text{UV}_{254}$ absorbance values.

**Volatile and semi-volatile organic compounds.** VOCs positively identified in pipe contact waters included ETBE, cyclohexane, toluene, and o- and p-xylene (Table 2). ETBE, toluene, p-xylene, and unspecified xylene isomers have been found previously in PEX pipe contact waters (Durand & Dietrich 2007, Koch 2004, Skjevrak et al. 2003). No previous PEX pipe investigations have identified cyclohexane. PEX-b4 pipe released all five of these compounds through day 15, as well as a few other analytes that could not be identified with strong library matching. Only ETBE and cyclohexane remained detectable on day 30 for PEX pipes. ETBE is known to cause drinking water odor but was detected well below its odor threshold concentration (OTC) of 2 µg/L (van Wezel et al. 2009). ETBE concentrations in water that contacted PEX-b4 pipe were 1.20 µg/L on day 3 and 0.54 µg/L on day 30. PEX-b5 pipe released ETBE; however, water concentrations were 0.47 µg/L on day 3 and were below the limit of quantification in subsequent migration periods. Toluene was found in PEX-b4 pipe water samples well below its USEPA primary maximum contaminant level (MCL) of 1 mg/L: 0.23 µg/L on day 3 and 0.17 µg/L on day 9. Toluene never exceeded its OTC of 24 µg/L (Alexander et al. 1982). For PP pipe, toluene was the only VOC found, but it was present below the lowest concentration standard (0.4 µg/L) and was not detected after day 15. All pipes examined were certified in accordance with NSFI Standard 61, and toluene, total xylenes, and ETBE were the only contaminants detected that were listed on the NSFI Standard 61 screening protocol. These contaminants were
present at orders-of-magnitude-lower concentrations than their allowable limits per NSF Standard 61 (NSFI 2013). ETBE also did not exceed the lowest-known state drinking water health-based standard of 40 µg/L (NHDES 2009).

Additionally, a number of antioxidant degradation products that did not have any NSF, state, or federal drinking water standards were isolated and included 7,9-dicarboxy-1-oxaspiro-(4,5)-deca-6,9-diene-2,8-dione and methyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propanoate, both of which have been previously identified as PEX and PP material migration products (Biedermann et al. 2014, Lilja et al. 2010, Koch 2004). Interestingly, some of the most commonly reported PEX and PP pipe migration products in European PEX studies (i.e., 2,4-di-tert-butylphenol, 2,6-di-tert-butylbenzoquinone, methyl tert-butyl ether [MTBE]) (Lutzhoft et al. 2013, Kowalska et al. 2011, Lund et al. 2011, Koch 2004, Skjevrak et al. 2003, Hametner 1999) were not found in any of the test waters. The same analytical methods in the present study were previously shown to be capable of detecting MTBE and 2,4-di-tert-butylphenol by others (Kelley et al. 2014, Durand & Dietrich 2007, Oh & Stringfellow 2003, Cassada et al. 2000).

Odor. All three pipe brands contributed noticeable drinking water odors that were frequently described as either sweet or plastic-like (Figure 2). Both PEX pipe brands greatly exceeded the USEPA SMCL of 3 TON during the entire 30-day experiment. These findings support the results of a recent US PEX investigation (Kelley et al. 2015, 2014) and European PEX pipe studies (Lund et al. 2011, Koch 2004, Skjevrak et al. 2003) in that PEX pipes impart contaminants to drinking water that cause odor.

PEX-b4 pipe caused the greatest odor impact (p < 0.001) of any of the three pipe brands tested, as well as compared with six other PEX pipes available in the United States (Kelley et al. 2014). While MTBE and ETBE have been cited as major causes of PEX pipe–associated odors (Kelley et al. 2014, Chemaxx 2007, Durand & Dietrich 2007, Skjevrak et al. 2003), absence of MTBE and the low concentration of ETBE found indicate that other unidentified odorous compounds were present. Contaminants contributing to odor may include the unidentified compounds detected by ESI-MS. Significant TON decreases for PEX pipes were observed from day 3 to day 30 (p < 0.001). TON values for water that contacted PP pipe were equal to, or slightly above, the USEPA SMCL, ranging from 3 to 6 TON. Hametner (1999) also found that eight brands of PP pipe in Austria had similarly unremarkable odor impacts of 0 to 4 TON. While MTBE and ETBE have been cited as major causes of PEX pipe–associated odors (Kelley et al. 2014, Chemaxx 2007, Durand & Dietrich 2007, Skjevrak et al. 2003), absence of MTBE and the low concentration of ETBE found indicate that other unidentified odorous compounds were present. Contaminants contributing to odor may include the unidentified compounds detected by ESI-MS. Significant TON decreases for PEX pipes were observed from day 3 to day 30 (p < 0.001). TON values for water that contacted PP pipe were equal to, or slightly above, the USEPA SMCL, ranging from 3 to 6 TON. Hametner (1999) also found that eight brands of PP pipe in Austria had similarly unremarkable odor impacts of 0 to 4 TON. The difference between PEX and PP pipe-caused odors is likely because of the difference between material manufacture methods, but the exact causes of the observed odor remains unknown.

PEX-plumbed-house field investigations. Organic carbon. Source waters for each tap water analyzed (and treatment it underwent before reaching each building) differed greatly. Despite this difference, characteristic of water entering the building before the PEX plumbing system enabled a determination of drinking water quality at taps. Tap water organic carbon characteristics differed sometimes, but not always, between faucets within each

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Predominant electron spray ionization mass spectrometry (ESI-MS) peaks from PEX pipe contact water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accurate Mass&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Pipe Brand</td>
</tr>
<tr>
<td>---------</td>
<td>------------------</td>
</tr>
<tr>
<td>340.32087</td>
<td>a1</td>
</tr>
<tr>
<td>368.35213</td>
<td>a1</td>
</tr>
<tr>
<td>382.33153</td>
<td>a1</td>
</tr>
<tr>
<td>410.36275</td>
<td>a1</td>
</tr>
<tr>
<td>366.29841</td>
<td>b4</td>
</tr>
<tr>
<td>459.24853</td>
<td>b4</td>
</tr>
<tr>
<td>475.2211</td>
<td>b4</td>
</tr>
<tr>
<td>316.21176</td>
<td>b5</td>
</tr>
<tr>
<td>330.22745</td>
<td>b5</td>
</tr>
<tr>
<td>430.24345</td>
<td>b5</td>
</tr>
</tbody>
</table>

ESI-LC-MS—liquid chromatography ESI-MS, MS—mass spectrometry, PEX—cross-linked polyethylene

<sup>a</sup>Accurate mass—the measured mass of the ion from high-resolution ESI-MS

<sup>b</sup>t<sub>r</sub>—the low-resolution ESI-LC-MS retention times for ions with nominal mass corresponding to the accurate mass obtained in high resolution. Matching retention times and fragmentation patterns likely indicate identical compounds. Isomers and isobars have identical nominal mass but may have different retention times.

<sup>c</sup>MS/MS fragments—the low-resolution tandem MS fragments for ions of the same nominal mass as the measured high-resolution mass

Tabulated ions include only those that were major peaks (>10% abundance) in the direct-injection high-resolution ESI-MS spectra and also observed in chromatographic peaks in the low-resolution ESI-MS spectra.
residence and before drinking water entered the PEX plumbing system. For example, TOC levels did not differ between any tap water samples from the Colorado PEX system ($p < 0.001$). In Maryland, however, tap water collected from the upstairs master bathroom sink had a 1.86-mg/L-higher TOC concentration than water entering the house. This result was possibly influenced by faucet water usage frequency, chemical leaching from plumbing system materials, and microbial regrowth.

**Volatile and semi-volatile compounds.** Several VOCs and SVOCs were detected in all three PEX plumbing systems, and many, but not all, have been previously detected in European PEX plumbing systems (Table 3). In particular, previous tap water quality testing results from the Maryland PEX plumbing system (six months old) by Kelley et al. (2014) were compared with the present work (same building, two years old). Fourteen chemicals were initially detected in the Maryland plumbing system, but after two years in service only one contaminant was found, and it was not present during the six-month sampling study. No VOCs were found in tap water from the 0.8-year-old Colorado PEX system; two VOCs were detected in water collected from the one-year-old Oklahoma PEX-b3 brand system.

In summary, additive degradation products, antioxidants, plasticizers, and solvents were detected in water collected from two brands of PEX plumbing systems.

Water collected from the Oklahoma PEX-b3 pipe brand plumbing system bathroom sink contained ETBE and toluene.

---

**FIGURE 3** Base peak chromatograms of contact water from three different PEX pipes and the Teflon-wrapped stoppers and glass control

Not all chromatographic peaks are shown. Some peaks are only discernable in extracted-ion chromatograms; however, base peak chromatograms are the best visualization for the majority of chromatographic peaks here.

*Seven points, boxcar. In this technique every seven consecutive points (e.g., points 1–7, 2–8, 3–9, etc.) are averaged to reduce random noise and make a chromatogram appear smoother and easier to interpret.*
at 22 µg/L and 80 µg/L, respectively, well above their OTCs. This home was investigated because homeowners had complained about chemical odors in the shower and stopped drinking the water. Detection of ETBE as high as 22 µg/L is supported by Kelley et al. (2014), who previously found that the PEX-b3 pipe brand caused ETBE levels of 179 µg/L after three days of simulated use in the laboratory and nearly 65 µg/L after 30 days. For the same PEX-b3 pipe, Kelley et al. (2014) also detected toluene on day 30 but did not quantify its concentration. Other studies have reported ETBE levels for water in contact with PEX pipes (types and brands not specified) ranging from 0.14 µg/L to “>100 µg/L” (Lund et al. 2011, Durand & Dietrich 2007). Others have also detected toluene in water that contacted several PEX pipes, but toluene concentration was not quantified (Koch 2004). Results show that a wide range of contaminants and concentrations can be imparted to drinking water by PEX pipes.

**Odor:** Of the three PEX plumbing systems examined, the one-year-old PEX-b3 system contained the most offensive tap water (Figure 4). Tap water from all homes exceeded the USEPA SMCL of 3 TON. However, TON values for the Maryland and Colorado building tap waters were not statistically different from TON values of tap water before it entered each PEX plumbing system. TON values for the Oklahoma building were much greater than water from the distribution system and can be at least partially attributed to the VOCs identified. The Oklahoma homeowners described the odor as “medical” and “like a box of Band-Aids.” Medical-like odors are typically associated with chlorophenols; however, individuals not trained in odor description frequently mislabel odors (Mallevialle & Suffet 1987). Because not all VOCs are separated and identified with a single instrumental method (Kowalska et al. 2011, Durand & Dietrich 2007, Skjevrak et al. 2003), other unidentified compounds may have contributed to the sample odor.

**CONCLUSION**

**AOC contributions from plastic pipes.** For the eight brands of PEX pipes examined, three pipes exceeded the 100 µg/L microbial regrowth threshold criterion. PVC, HDPE, and PP pipes (one brand tested for each) did not cause water to exceed the microbial regrowth threshold. For the final migration period (day 28) no pipes caused water to exceed 100 µg/L.

PEX pipe brands exhibited great AOC variability, implying that some PEX pipe brands may contribute more significantly to microbial regrowth than other brands. PP and PEX-a1 pipes contributed no detectable AOC. In practice, shorter durations than the seven days tested may be more common for premise plumbing pipes in inhabited homes. Longer duration periods could, however, be experienced in newly constructed, not-yet-inhabited buildings where contractors are still working or when building inhabitants are on vacation. Results do not show whether the bulk of organic compound leaching from the pipe into water primarily occurred during the first couple of days or was consistent through the seven-day period. Overall, different brands of PEX pipe caused widely different AOC levels in drinking water, a finding unique to this study. Future work is necessary to investigate different contact periods and elucidate the role of disinfectants in altering leached organic carbon.

**Chemical and odor impacts from PEX and PP pipes.** As examined with GC-MS, PP pipe released a smaller variety of organic compounds at lower concentrations than the evaluated PEX-b pipe brands. PP pipe also imparted significantly less odor than the PEX pipes. The literature focuses on MTBE and ETBE identification.

---

**TABLE 2**

Organic contaminants identified in plastic pipe contact waters during laboratory migration tests

<table>
<thead>
<tr>
<th>Compound</th>
<th>Time detected—days</th>
<th>Origin</th>
<th>CAS #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl tert-butyl-ether&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3, 9, 15, 30</td>
<td>Initiator degradation product</td>
<td>637-92-3</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>3, 9, 15</td>
<td>Solvent</td>
<td>110-82-7</td>
</tr>
<tr>
<td>Toluene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3, 9, 15</td>
<td>Solvent</td>
<td>106-42-3</td>
</tr>
<tr>
<td>p-xylene&lt;sup&gt;c&lt;/sup&gt; and o-xylene&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3, 9, 15, 30</td>
<td>Solvent</td>
<td>95-47-6</td>
</tr>
<tr>
<td>7,9-Di-tert-butyl-1-oxaspiro-(4,5)-deca-6,9-diene-2,8-dione&lt;sup&gt;e&lt;/sup&gt;</td>
<td>3</td>
<td>Antioxidant degradation product</td>
<td>82304-66-3</td>
</tr>
<tr>
<td>Methyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propanoate&lt;sup&gt;f&lt;/sup&gt;</td>
<td>3, 9, 15, 30</td>
<td>Antioxidant degradation product</td>
<td>6386-38-5</td>
</tr>
</tbody>
</table>

CAS #—Chemical Abstracts Service registry number, PEX—cross-linked polyethylene, PP—polypropylene

Dashes indicate that contaminants were not detected.

All contaminants reported in Table 2 were confirmed with an analytical standard except for 7,9-di-tert-butyl-1-oxaspiro-(4,5)-deca-6,9-diene-2,8-dione. Several of these contaminants have been detected previously for PEX pipe in Europe and the United States.

<sup>a</sup>Durand & Dietrich 2007 (USA)
<sup>b</sup>Koch 2004 (Europe)
<sup>c</sup>Kelley et al. 2014 (USA)
<sup>d</sup>Lund et al. 2011 (Europe)
<sup>e</sup>Nielsen et al. 2007 (Europe)
<sup>f</sup>Denberg et al. 2009 (Europe)
<sup>g</sup>Ryssel et al. 2015 (Europe)
to describe the odor impacts of new PEX plumbing installations. However, the ETBE concentration in waters analyzed here ranged from 0.47 to 1.20 µg/L, below the 2 µg/L OTC for ETBE. A higher ETBE concentration (22 µg/L) was found in a field sample. Since other volatile compounds (toluene, xylene, cyclohexane) were also detected below their OTCs during laboratory migration tests, it appears that unidentified contaminants contribute to PEX pipe odors. The ESI-MS technique, more suited for detecting polar organic contaminants in water, confirmed the presence of unidentified contaminants. The significant variation in TOC and TON values observed for different PEX pipe brands supports AOC migration test results. Drinking water chemical and odor quality impacts vary greatly depending on the brand of pipe selected in the United States, and existing GC-MS methods may not be capable of detecting the contaminants responsible for odor.

**PEX performance in the field.** Field data show PEX plumbing pipes can be the source of drinking water odor as well as regulated and unregulated contaminants. Fewer VOC and SVOC contaminants were detected in a two-year-old PEX plumbing system compared with a 0.5-year-old system. However, this result does not take into consideration plumbing system use conditions, and laboratory data clearly revealed there is wide variability in PEX brand performance.

Drinking water odor analysis revealed that TON values of drinking water were not different before and after entering two PEX plumbing systems. However, a one-year-old PEX plumbing system inside a third residence caused a detectable drinking odor. ETBE (22 µg/L) and toluene (80 µg/L), VOCs known to be associated with PEX, were detected above their OTCs. Homeowners in this house refused to use drinking water for showering because of the water’s “gasoline-like” odor. More work is needed to further understand the degree plastic pipes sold in the United States affect drinking water quality as well as interactions between drinking water disinfectants, biofilms, and these increasingly popular plastics.

<table>
<thead>
<tr>
<th>Location (Type)</th>
<th>Age (years)</th>
<th>Chemicals Isolated From Water in Contact With PEX Pipes</th>
<th>CAS #</th>
<th>Estimated Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maryland (PEX-a1)</td>
<td>0.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Pyridine</td>
<td>110-86-1</td>
<td>Solvent</td>
</tr>
<tr>
<td>Toluene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>108-88-3</td>
<td>Solvent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1,2-Tetrachloroethane</td>
<td>630-20-6</td>
<td>Solvent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl trichloroacetate</td>
<td>598-99-2</td>
<td>Unknown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentadecane</td>
<td>629-62-9</td>
<td>Solvent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4-Di-tert-butylphenol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>96-76-4</td>
<td>Antioxidant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methyl pentadecane</td>
<td>1560-93-6</td>
<td>Unknown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methyl pentadecane</td>
<td>2882-96-4</td>
<td>Unknown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexadecane</td>
<td>544-76-3</td>
<td>Unknown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heptadecane</td>
<td>629-78-7</td>
<td>Unknown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7,9-Di-tert-butyl-1-oxaspiro-(4,5)-deca-6,9-diene-2,8-dione&lt;sup&gt;b&lt;/sup&gt;</td>
<td>82304-66-3</td>
<td>Antioxidant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl (3,5-di-tert-butyl-4-hydroxyphenyl)propanoate</td>
<td>6386-38-5</td>
<td>Antioxidant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bis(2-ethylhexyl) hexanediol</td>
<td>103-23-1</td>
<td>Plasticizer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Octyl-N-(4-octylylphenyl)-benzenamine</td>
<td>101-67-7</td>
<td>Plasticizer&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maryland (PEX-a1)</td>
<td>2</td>
<td>Triethyl citrate</td>
<td>77-93-0</td>
<td>Plasticizer</td>
</tr>
<tr>
<td>Colorado (PEX-a1)</td>
<td>0.8</td>
<td>Butyl-2-methoxyethyl-phthalate</td>
<td></td>
<td>Plasticizer</td>
</tr>
<tr>
<td>Androst-5,16-diene-3.beta-ol</td>
<td></td>
<td></td>
<td></td>
<td>Biolefinic steroid</td>
</tr>
<tr>
<td>Oklahoma (PEX-b3)</td>
<td>1</td>
<td>7,9-Di-tert-butyl-1-oxaspiro-(4,5)-deca-6,9-diene-2,8-dione&lt;sup&gt;b&lt;/sup&gt;</td>
<td>82304-66-3</td>
<td>Antioxidant</td>
</tr>
<tr>
<td>p-cresol</td>
<td>106-44-5</td>
<td>Manufacture by-product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-Di-tert-butylbenzene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1014-80-4</td>
<td>Unknown origin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl tert-butyl-ether (ETBE)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>637-92-3</td>
<td>Crosslink initiator degrade</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>108-88-3</td>
<td>Solvent for resin</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 3** Organic contaminants identified in drinking water collected from three houses where PEX-a1 and PEX-b3 brand plumbing pipe was installed

CAS #—Chemical Abstracts Service registry number, NIST—National Institute for Standards and Technology, PEX—cross-linked polyethylene

Only chemicals not found in blanks, or water collected before contact with the premise plumbing PEX, and returning a 75% or greater NIST library match are listed. CAS numbers are listed where available.

<sup>a</sup>Kelley et al. 2014

<sup>b</sup>Also found by European or American researchers in separate PEX leaching studies

<sup>c</sup>Park et al. 2004
FIGURE 4  Drinking water odor results from three houses in the United States where PEX-a1 and PEX-b3 brand plumbing pipe was installed

- Copper
- PEX line 1
- PEX line 2
- USEPA TON SMCL = 3

<table>
<thead>
<tr>
<th>Odor—TON</th>
<th>Maryland (a1, 2 years)</th>
<th>Colorado (a1, 0.8 year)</th>
<th>Oklahoma (b3, 1 year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>40</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>50</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PEX—cross-linked polyethylene, SMCL—secondary maximum contaminant level, TON—threshold odor number, USEPA—US Environmental Protection Agency

Only one PEX line (PEX line 1) was sampled in the Colorado house. The second tap sample was collected from the kitchen sink, which is supplied by copper lines.

ACKNOWLEDGMENT

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ENDNOTES

1 Ultrapure Milli-Q™ water, EMD Millipore Headquarters, Billerica, Mass.
2 Teflon™, DuPont, Wilmington, Del.
4 Agilent 7890A GC system, Agilent Technologies, Santa Clara, Calif.
5 Agilent J&W HP-5ms, Agilent Technologies, Santa Clara, Calif.
6 Supelco™ SPME fiber assembly, Sigma-Aldrich Co. Ltd., Dorset, England
7 CentriVap Concentrator, Labconco, Kansas City, Mo.

REFERENCES


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PEER REVIEW

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Date of acceptance: 09/23/2015


Shimadzu TOC-L CPH/CPN analyzer, Shimadzu Corp., Kyoto, Japan

HACH® DR 5000 UV-Vis Spectrophotometer, Hach, Loveland, Colo.


