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## Organic Chemical Contaminants in Water System Infrastructure Following Wildfire

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### Abstract

Wildfires have destroyed multiple residential communities in California in recent years. After fires in 2017 and 2018, high concentrations of benzene and other volatile organic compounds (VOCs) were found in public drinking water systems in fire-affected areas. The sources of the contamination and appropriate remediation have been urgent matters for investigation. This study characterizes target and non-target VOCs and semi volatile organic compounds (SVOCs) in water from a highly contaminated service line after the 2018 Camp Fire (Paradise, CA). Ninety-five organic compounds were identified or tentatively identified in the service line. Laboratory combustion experiments with drinking water pipes made of polyvinyl chloride (PVC), cross-linked polyethylene (PEX) and high-density polyethylene (HDPE) and a review of the literature were used to evaluate potential sources of the detected chemicals. Among the service line contaminants were thirty-two compounds associated with PVC pyrolysis and twenty-eight organic compounds also associated with the pyrolysis of polyethylene. The service line sample also contained fifty-five compounds associated with uncontrolled burning of biomass and waste materials. The findings support hypotheses that wildfires can contaminate drinking water systems both by thermal damage to plastic pipes and intrusion of smoke. Residual chlorine disinfectant in the water system modifies the contaminant distribution observed.

### Graphical Abstract

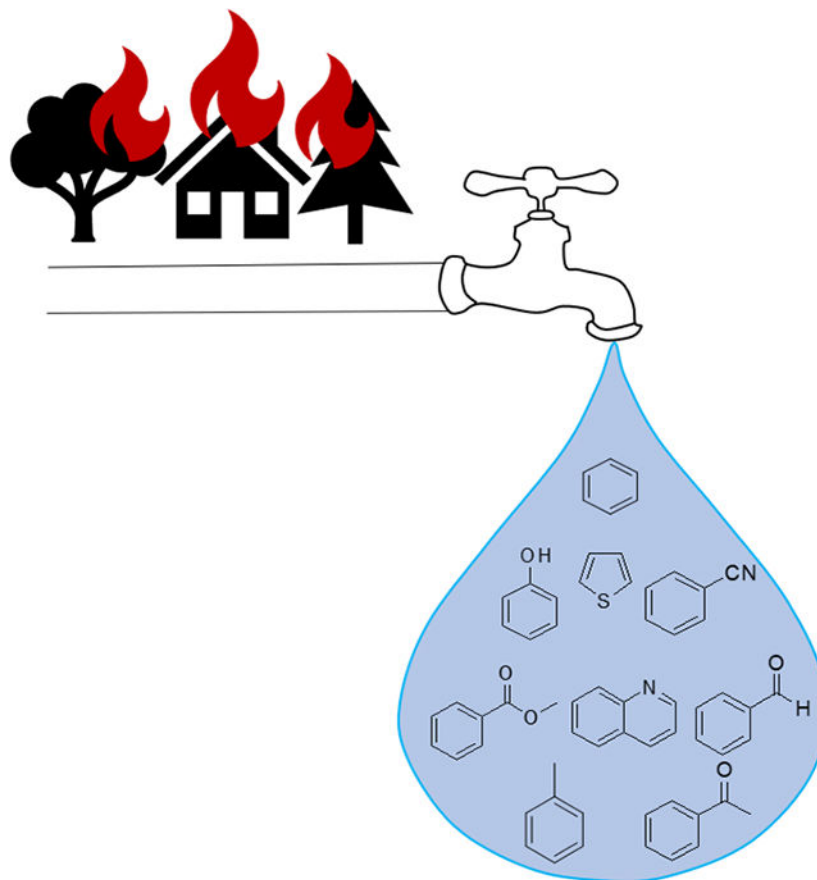
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Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/...>

Additional data and experimental details, combustion simulations and combustion product databases.



### Keywords

drinking water infrastructure; wildfire damage; organic chemical contaminants; sources; mechanisms

## INTRODUCTION

There has been considerable recent interest in the impacts of wildfire on water quality.<sup>1,2</sup> In 2017, drinking water in a neighborhood in Santa Rosa, California destroyed by wildfire was discovered to be contaminated by relatively high concentrations of volatile organic chemicals (VOCs) including benzene.<sup>3</sup> The origin of these contaminants was not well understood but two sources were theorized: 1) thermal damage to plastic plumbing materials and appurtenances<sup>4,3,5</sup> and 2) intrusion of combustion products into service lines.<sup>4,3</sup> Distribution system dewatering relating to both fire suppression activities and system leaks may lead to entry of gaseous combustion products, soot, and ash.

There is considerable literature on the incineration of plastics. PVC combustion products include aliphatic, aromatic, halogenated, oxygenated and nitrogenated compounds.<sup>6,7</sup> Benzene is the major constituent of PVC pyrolysis oil<sup>6</sup> and numerous thermal degradation products of PVC and polyethylene polymers have been identified.<sup>7,8,9</sup> Recent laboratory studies confirm that thermally-damaged plastic pipes release benzene, toluene, ethylbenzene

and xylenes (BTEX) to water.<sup>4,5</sup> Yet there is a paucity of information on water contamination related to burning structures and cellulosic biomass.<sup>5</sup> If damaged plastic pipes are indeed the principal contaminant source, it is not established which materials are optimal in fire-prone communities.<sup>4</sup> PVC, for example, is inherently fire resistant when compared to other plastics due to elevated ignition temperature.

On November 8, 2018, the Camp Fire destroyed over 18,000 homes and other buildings in the town of Paradise, California and nearby communities; approximately 1,700 homes were left standing in the area. Due to prior discovery of VOCs in drinking water after the 2017 Tubbs Fire in Santa Rosa, the local water utilities and California Division of Drinking Water collected water samples after the Camp Fire to screen for contaminants. VOCs were widely detected in Paradise and surrounding areas in service lines and smaller water mains, but not in water treatment plants or large water mains. Spatial distribution analysis demonstrated that leaking underground fuel tanks did not contribute significantly to the contamination.<sup>10,11</sup>

Removal of VOC contamination required numerous rounds of continuous flushing depending on contaminant levels.<sup>12,3</sup> This may be because some plastic pipes have a substantial capacity to sorb contaminants<sup>13</sup> potentially serving as a long-term contamination reservoir. Alternative remediation strategies involved limited or complete replacement of contaminated pipes at huge cost<sup>4</sup> and long delays to reestablish safe drinking water supplies. Previous investigators emphasize that the exact causes of water system contamination after wildfire are unknown due to insufficient data.<sup>3</sup> A lack of scientific information confounds attempts to develop recommendations and policies regarding design of resilient infrastructure in fire-prone communities and appropriate testing and remediation strategies after a fire.

The purpose of this study was to fully characterize organic chemical contaminants in a highly contaminated service line from the 2018 Camp Fire in an attempt to better understand potential source(s) of the contamination. This was accomplished by chemical analysis of a highly contaminated water sample obtained from the burn zone 11 weeks after the fire. At the study location the home had burned to the ground and both the service line and water main had remained dewatered for 6–8 weeks after the fire. A surveillance sample tested for VOCs nine weeks after the fire, after rewatering and then stagnation of water in the line for several days prior to sampling, contained 923 µg/L of benzene, nearly 1000-times the regulatory Maximum Contaminant Level (MCL) for this contaminant. This was the highest concentration of benzene reported in a drinking water system sample after the fire. This service line was constructed of HDPE on both the water system side (before the water meter) and leading to the residence. The destroyed residential structure itself had copper water lines. The water main serving the service line was PVC C900 and water mains and service lines at this location had all been installed in 2008. Target and non-target analysis of the sample was conducted to identify a broader list of contaminants in the water. Interpretation of the origins of the contaminants was then aided by both laboratory simulations of contaminant transfer to water from fire-damaged plastic pipes as well as combustion literature related to plastics, biomass, building materials and other fuels likely consumed in wildland-urban fires.

## MATERIALS AND METHODS

### Burn Zone Water Samples.

Drinking water was obtained from a contaminated service line on Jan 31, 2019 in the community burn zone of the November 8, 2018 Camp Fire, the most destructive and deadly wildfire in California history. Unimpacted drinking water samples were obtained from the Paradise, CA water treatment plant for use as controls – water samples obtained at the drinking water treatment plant 11 weeks after the fire did not exceed federal or state primary drinking water standards. VOC sampling technique was used including collection in zero-headspace glass containers, i.e., 40 mL volatile organic analysis (VOA) vials or one-liter glass bottles filled without headspace. Samples were chilled at collection and transported to the laboratory at 4°C on water ice and analyzed within 14 days of collection. Additional burn zone samples were analyzed including the adjacent water main as well as the service line which was resampled a month later.

### Materials.

Polyvinyl chloride (PVC) tubing (Product ID: ½ IPS Schedule 40; 600 psi @ 73°C; ASTM D1784-96b), PVC joint (Product ID: 049081137502), PVC primer (P-70™ Primer, purple) and PVC glue (Weld-On® 705™ PVC), Cross-linked polyethylene (PEX) tubing (Product ID: 6 97285 36005; SDR9 PEX 5106) were obtained at a local supplier. High-density polyethylene (HDPE) (SKU: # BLK IPS 0300 DR17 040; 3” IPS SDR17PE4710 Black) tubing was obtained commercially (HDPE Supply, Duluth, MN). Laboratory reagent water was prepared with a Millipore Milli-Q Gradient A10 water purification system equipped with ion exchange resins, charcoal filter and UV lamp (Billerica, MA, USA).

### Chemical analysis of water for VOCs and SVOCs.

The majority of the analytical testing focused on VOCs determined by purge and trap (P & T) electron ionization (EI) GC-MS using a Hewlett Packard 5973 instrument equipped with a 30 m × 0.25 mm id × 1.4 µm DB-5 column. A Vocarb 3000 trap was used and the purge cell volume was 25 mL. The mass spectrometer was autotuned and multipoint calibrated with 60 regulated VOC compounds for target compound analysis – samples were fortified with 10 µg/L of fluorobenzene internal standard (IS) and 10 µg/L each of 4-bromofluorobenzene and 1,2-dichlorobenzene-d<sub>4</sub> surrogates to monitor analyte recovery. Non-target compounds were identified using computerized search of the NIST 17 and Wiley 11 NBS libraries. Peak deconvolution software (AMDIS Ver. 2.73, 2017) was used to improve the accuracy and fidelity of spectra and assignments were verified by manual inspection of spectra. For target compounds identification was based on both mass spectra and retention times. Non-target compound concentrations were estimated by comparison to averaged internal standard response factors.

The Camp Fire water sample was also analyzed for SVOCs which were determined by solid phase extraction (SPE) using hydrophilic-lipophilic balance (HLB) cartridges (Waters, Part # WAT106202)(200 mg; 30 µm; 500 mL load volume). HLB cartridges were conditioned with methylene chloride (5 mL), methanol (5 mL) and reagent water (10 mL) before extracting 250 mL water samples. Compounds were eluted with methylene chloride and the extract was

concentrated to 0.25 mL under nitrogen. SPE extracts were introduced to a Hewlett Packard 5973 EI GC-MS instrument fitted with split-splitless inlet and a 30 m × 0.25 mm id × 25 μm DB-5 column. Compounds were identified by computerized search using NIST 17 and Wiley 11 mass spectral libraries and AMDIS (Ver. 2.73, 2017) software was used as needed.

### Pyrolysis and Combustion Simulations.

Simulations were conducted in the laboratory to characterize VOC combustion products from plastic plumbing materials – SVOC compounds were not analyzed in these experiments. PVC tubing (3.5 inch) with glued joints (2 inch) was heated with a heat gun or under a methylacetylene-propadiene propane (MAPP) torch flame under various conditions in open air prior to immersion of test samples in 250 mL of reagent water. The heat gun attains a maximum temperature of ~175°C whereas the air supplied MAPP torch reaches 2050°C at the flame tip.

PVC pipe sections were glued according to manufacturer instructions (e.g., prime, allow to dry 2 min, apply glue to surfaces, join pieces and cure at room temperature (RT)). Five conditions were examined: 1) control – cured pipe joint immersed in reagent water with no headspace; 2) cured pipe joint heated with a heat gun until melting and reaching 100°C; 3) cured pipe joint heated with a heat gun until charring and reaching 102°C; 4) cured pipe joint exposed to MAPP flame until melting and reaching 150°C; and 5) cured pipe joint exposed to MAPP flame until charring and reaching 150°C.

Plastic temperatures were determined with a non-contact IR thermometer (Omega Model OS-DT8855W, Omega Engineering, Stamford, CT) and treated plastic samples were then transferred immediately to zero headspace glassware and immersed in water for 24 or 72 hours to extract contaminants. An emissivity setting of 0.93, typical of plastic emission coefficients, was used for the IR thermometer measurements. Forty mL water samples withdrawn at 24 hours were replaced with reagent water to avoid headspace in the 250 mL bottles. At 72 hours the water samples withdrawn (also 40 mL) were replaced with reagent water containing 228 μL of sodium hypochlorite (3,280 mg/L free chlorine) to obtain a free chlorine concentration of ~2.5 mg/L (ppm). Thus, PVC samples were analyzed at 24 hours, 72 hours and 168 hours – only the final sample having been treated with chlorine for a total of 96 hours.

Similar experiments were conducted with HDPE and PEX plastics although use of the heat gun was discontinued and no glue or primer was used. PEX experiments were conducted using 4-inch tubing. HDPE experiments were conducted using a strip (5-inch length, 1-inch width) cut from the HDPE pipe. Both PEX and HDPE samples were exposed to the MAPP flame inside and out until charred and unheated controls were also maintained as in the PVC experiments. On exposure to flame both PEX and HDPE surface temperatures were considerably higher (e.g., reaching 250 – 400°C) due to ignition of accumulated pyrolysis oils whereas PVC did not ignite under conditions studied.

In the case of PEX and using the protocol described previously, water samples were withdrawn for chemical analysis at 6 hours, replenished with reagent water and resampled at 100 hours. After replenishing with sodium hypochlorite solution samples were withdrawn

at 168 hours for chlorine exposure of 68 hrs. In the case of HDPE water samples were withdrawn for chemical analysis at 4 hours, replenished with reagent water and resampled at 72 hours. After then replenishing with sodium hypochlorite solution, samples were withdrawn at 168 hours resulting in chlorine exposure of 96 hours.

### Databases.

We reviewed literature on pyrolysis and combustion of plastics, building materials, biomass and uncontrolled burning of waste materials. Organic chemical compounds were compiled in two tables that appear in the Supporting Information (SI) section, one for combustion products produced by plastic materials (626 compounds) (Table S-6) and another for combustion products of biomass, building materials, etc. (369 compounds) (Table S-7). We compiled compound name, CAS number, formula, monoisotopic mass and source descriptors. The organic compounds in Table S-6 are combustion products of PVC, PEX, HDPE, PE, chlorinated polyvinyl chloride (CPVC), polypropylene (PP) and other plastics used in water distribution systems such as sealing materials, gaskets, O-rings, lubricants and thread compounds. We included chemicals identified as leachates from virgin plastic pipe materials as well.<sup>14,15,16,17,18</sup> Information on products related to PVC and PE were primarily obtained from Aracil et al.<sup>7,8,9</sup> Compounds identified in the present laboratory simulations of PVC, PEX and HDPE also are included. Information about plastic pipe leachates was obtained primarily from Pizzurro et al.<sup>14</sup>

Table S-7 compiles combustion products related to forest fires and structure fires. These include combustion products of a multitude of materials (e.g., biomass, building materials, furnishings, upholstery, paints, tires, liquid fuel, household wastes, etc). Table S-7 information was obtained largely from Lemieux et al.<sup>19</sup> Other references provided information on low-molecular-weight combustion products from burning of soft and hardwoods<sup>20,21,22</sup> and live or dead vegetation.<sup>23</sup>

These databases are useful for interpretation of mass spectral information as most of the compounds are compiled in EI mass spectral libraries. Additionally, information on monoisotopic masses and empirical formulas can be used for alternative mass spectrometry techniques such as electrospray LC-MS, chemical ionization GC-MS and high-resolution accurate mass MS.<sup>24</sup> Electronic versions of these databases can be obtained by contacting the corresponding author.

## RESULTS

### Contaminants in the Drinking Water Service Line.

The service line sample contained very high contaminant concentrations (Table 1): benzene (2,200 µg/L); naphthalene (690 µg/L); toluene (680 µg/L); styrene (380 µg/L); indene (230 µg/L); 2,3-benzofuran (200 µg/L); ethylbenzene (76 µg/L); xylenes (68 µg/L); 1-ethenyl-2-methylbenzene (59 µg/L); and 2-methyl-1-benzofuran (53 µg/L). The most abundant SVOCs (Table 2) were: benzonitrile (310 µg/L); acetophenone (130 µg/L); naphthalene (100 µg/L); benzaldehyde (71 µg/L); methyl benzoate (60 µg/L); 2-chloro-1-phenylethanol (52 µg/L); phenol (50 µg/L); 2-(3-chloro-2-propenyl)-phenol (two isomers 50 and 32 µg/L);

2-methylbenzotrile (46 µg/L); 4-methylphenol (29 µg/L); and 2-phenylpropane-1,2-diol (28 µg/L). Additional data for VOCs and SVOCs appear in Tables S-1 and S-2, respectively.

### **Additional Burn Zone Samples.**

Samples were collected 11 weeks after the fire from the water treatment plant, water main and the service line. In addition, service line sampling was conducted 15 weeks after fire. The highest concentration VOCs (benzene, naphthalene, toluene and styrene) detected in these locations were plotted (Figure 1). These VOCs were not detected in the water coming from the treatment plant. Additional drinking water samples analyzed exhibited a similar pattern of the major VOC contaminants but with a steep concentration gradient between the service line and adjacent water main.

### **Simulated Combustion of Plastic Pipes in the Laboratory: PVC.**

In the laboratory PVC was subjected to heat and open flame prior to immersion in water to identify combustion products. In controls (e.g., without heat or flame) PVC tubing released 6 compounds: oxolane (THF), butan-2-one (MEK), cyclohexanone, propan-2-one (acetone), chloromethane and 2,3-dihydrofuran (Figure 2). VOCs increased 3-fold between 24 and 72 hr. Each compound, with the exception of chloromethane, was an ingredient in the glue or primer used to join pipe sections. An identical glued pipe charred with a torch prior to soaking in water for 72 hours released higher concentrations of the primer/glue solvents, e.g., MEK and THF were increased by about 27 and 56%, respectively. Heating with the torch also visibly swelled the glued joints.

PVC polymer pyrolysis products found included chloromethane (860 µg/L), 2-ethylhexan-1-ol (88 µg/L), benzene (18 µg/L), 2-methylpropyl 2-methylprop-2-enoate (isobutyl methacrylate) (7.2 µg/L), 2-ethylhexanal (2.6 µg/L) and 2-ethylhexyl acetate (2.1 µg/L). Additional data from PVC combustion experiments appear in Table S-3.

### **PEX and HDPE.**

In lab simulations with PE pipes a somewhat different set of combustion products was found. The PEX control released no VOCs while HDPE controls contained traces of methylcyclopentane after 3 days immersion in water. PEX exposed to flame ignited and reached temperatures of 250 – 300°C -- its principal products after 100 hours were 2-methylprop-1-ene, propene, hex-1-ene, pent-1-ene, benzene, pentane and hept-1-ene (Table S-4). HDPE also ignited with surface temperatures reaching 375 to 400°C. HDPE combustion products were similar to those from PEX and included 2-methylprop-1-ene, propene, hex-1-ene, pent-1-ene, benzene, pentane, hept-1-ene, naphthalene, aldehydes (e.g., nonanal, octanal, pentanal, decanal, undecanal) and ketones (e.g., nonan-2-one, decan-5-one, decan-2-one, undecan-2-one (Table S-5).

### **Chlorine Reactivity.**

Many of the combustion products from the polyethylene plastics reacted with chlorine in lab simulations including: 2-methylprop-1-ene, propene, hex-1-ene, hept-1-ene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 1-methylcyclopentene, oct-1-ene and 1-pentene (Figure 3). Possible halogenated disinfection-by-products (DBPs) detected in laboratory experiments



included 3-chloro-2-methylprop-1-ene, 1-chloro-2-methylprop-1-ene and 1-bromobut-2-ene (Table S-5). Additional chlorine reactivity data appear in Tables S-3, S-4 and S-5.

## DISCUSSION

### Chemical Contaminants in the Drinking Water Service Line.

The wildfire contaminated drinking water sample contained a complex mixture of VOCs and SVOCs with high concentrations of some compounds. Of the 53 VOCs detected 45 (85%) were non-target compounds. We identified or tentatively identified a total of 95 compounds in the service line sample (Tables 1 and 2), nineteen of which were determined by both purge and trap GC-MS and solid phase extraction GC-MS. The most abundant VOCs and SVOCs are simple substituted benzenes (Figure 4).

Many additional target and non-target substances were identified (Tables S-1 and S-2) including: substituted benzenes; polycyclic aromatic hydrocarbons; N-heterocycles; O-heterocycles; S-heterocycles; phenols/alcohols; ketones; aldehydes; chlorinated compounds; cyano compounds; alkenes and carboxylate esters. Many of these compounds have strong odors, e.g., sulfur compounds, ketones, aldehydes, esters, phenols and aromatics. Some returning community members reported strong odors in their drinking water<sup>3</sup> and odors were also noted by water system personnel. In fact, one of the initial goals at our laboratory was to identify the odorous contaminants.

Limited comparative analyses of additional fire zone samples demonstrated that the contamination pattern was representative of the drinking water distribution system, but that the concentrations varied dramatically with location. The highest concentrations of the principal VOC contaminants were found in the service line, low VOC concentrations were found in the adjacent water main and product water from the treatment plant sample had undetectable contamination (Figure 1). Contaminants were conceivably drawn into the water main from service line sources because of the high-water demand during the fire initially and slowly thereafter. Elevated contamination persisting many weeks or months after the fire confirm that sorbed VOCs continue to be dispersed over time<sup>3</sup>.

### Information Obtained from Burning Plastic Pipes in the Laboratory.

**Glue Solvents.**—Our initial attempts to identify sources of fire-related contaminants focused on laboratory studies of plastic plumbing materials. We investigated several variables during combustion of PVC pipes including contamination from glued pipe sections, influence of different heat sources and impacts of residual chlorine (Tables S-3). The principal VOCs determined after soaking an unheated, control pipe section in water were primer and glue solvents (Figure 2), especially THF and MEK. Heating or charring glued PVC pipes resulted in swelling of the glued joint and mobilization of these solvents. The high concentrations of these solvents found are probably not representative of those found in typical applications where fire damage is not a factor except possibly in new construction or after recent pipe repairs. However, THF was reported by other researchers investigating drinking water after the Camp Fire.<sup>11</sup> Glued PVC pipes are well flushed with water after installation substantially depleting them as a long-term source.<sup>11,25</sup>

**Pyrolysis Temperature.**—The relatively low concentrations of benzene released from the flame-treated PVC in our laboratory experiments suggested that the experimental temperatures -- only 150°C for PVC -- were inadequate to substantially degrade the PVC polymer. Polyethylene pipes, both PEX and HDPE, by comparison ignited in our laboratory simulations resulting in surface temperatures as high as 400°C. Polyethylene pipe combustion products were primarily low-molecular-weight olefins from PEX while HDPE transformation products also included aldehydes and ketones (Tables S-4 and S-5). Benzene and naphthalene also were among the combustion products. In total, more than 24 VOCs were leached from charred PEX pipes in 100 hr. More than 32 VOC transformation products of HDPE appeared after 72 hr.

The laboratory simulations were qualitative as heating of plastic samples took place in an open hood. A large fraction of volatile products may have escaped prior to immersion of heated pipes in water and thus product yields and mass balances cannot be estimated. In addition, experiments were not controlled as to oxygen levels, temperatures or duration of heating.

During pyrolysis, PVC and other halogenated plastics undergo a first-stage evolution of HCl followed by a second stage evolving additional HCl accompanied by aromatic and aliphatic hydrocarbons. Aracil et al.<sup>7</sup> have demonstrated that the pyrolysis and combustion of PVC and the distribution of products is controlled by temperature and oxygen. In their studies at 500°C, complex mixtures of VOCs and SVOCs are produced in oxygenated conditions – at higher temperatures most contaminants undergo complete oxidation. At the temperatures in the current PVC lab experiments, Phase I pyrolysis products begin to appear while the Phase II reactions, including aromatization and aromatic hydrocarbon production, are not yet prominent.

Wildfire temperatures are influenced by many variables including type and quantity of fuel, humidity, height above ground and velocity. Fire temperatures in shrublands and aspen forests are about 368 to 445°C.<sup>26</sup> Yet soil temperatures more than 5 – 10 cm below the surface, where water lines may be buried, may barely exceed ambient temperatures.<sup>27</sup> The quantity of fuel influences fire temperatures and bare mineral soil dissipates heat effectively.<sup>26</sup>

**Chlorine Reactions.**—Polyethylene combustion products reacted rapidly with chlorine at chlorine experimental concentrations of 2.5 mg/L with substantial reaction taking place after 96 hours (Figure 3). Consumption of olefin transformation products was accompanied by the appearance of probable disinfection by-products (DBP). DBP were more prominent in water extracts of charred PEX pipes. Supplemental treatment with chlorine yielded some chloroform as a DBP (e.g., 46 µg/L in the control) and chloroform found was increased when the PVC had been heated with the heat gun (e.g., 67–68 µg/L), but chloroform concentrations were lower for pipes exposed to flame (e.g., 27 and 3.7 µg/L) (Table S-3).

The laboratory data indicate that the typical chlorine residual in drinking water distribution systems (0.5 ppm) is adequate to modify the combustion product distribution observed after fires. The contact times in the lab were 4 days or less. The contact times in the

drinking water distribution system after the Camp Fire are difficult to estimate as there were periods of dewatering and two flush/stagnate/test cycles that preceded sample collection – the estimated contact time was 2 – 4 weeks total. In this time frame unsaturated or other easily-oxidized polyethylene combustion products would have been largely consumed.

### Understanding Sources based on Combustion Literature.

Our laboratory experiments did not provide a large number of combustion products for use as probes. In total we identified 29 compounds associated with PVC, HDPE and PEX combustion (Tables 1 and 2, last 3 columns). However, we utilized the substantial literature on the incineration of plastics as a further aid in interpretation. This information also provided a means to consider alternate sources such as burning biomass, building materials and other fuels which relate to the intrusion of smoke.<sup>4</sup>

Many of the combustion products including benzene and the common VOCs (e.g., BTEX) have multiple sources. Benzene, for example, is a combustion product of PVC, PEX, and HDPE as well as burning of biomass, tires/liquid fuel, household wastes, landfill, pesticide bags, automobile shredder waste, fiberglass and fabrics (Tables 1 and 2). As such, benzene is not a specific marker of the burning of any particular material.

Among the 95 organic contaminants found in the service line, thirty-two are PVC combustion products and twenty-eight are also combustion products of PE plastics including PEX and HDPE. PVC and PE have many combustion products in common, e.g., twenty-five service line contaminants. Only nine of the chemicals found in the Camp Fire service line sample appear to be specific to combustion of these two plastics: ethenylmethylbenzene (*o*, *m* and *p* isomers),  $\alpha$ -methylstyrene, propene, 1-ethyl-3-methylbenzene, 1,3-pentadiene, prop-1-ynylbenzene and fluorene-9-one.

Some plastic combustion products were not detected in the service line including “specific” pyrolysis products from PVC (e.g., 2-ethyl-1-hexanol, isobutyl methacrylate, 2-ethylhexyl acetate and 2-ethylhexanal). The same was true for some “specific” HDPE and PEX combustion products, (e.g., 2-methyl-1-propene, 1-hexene, ethyl cyclopropane, pentane, 1-heptene, octanal, pentanal, decanal and 2-decanone) – these products may have been absent due to chlorine reactivity. In contrast, certain non-specific probes, particularly benzene, were found in the service line at much higher relative concentrations than in laboratory simulations. Why benzene is so prominent deserves further investigation.

Because of the high number of plastic combustion products found, it is likely that fire damage to plastic service lines and other residential plastic materials contributed to contamination observed in the water system. Investigators found physical damage to plastic pipes and water meters at both the Camp Fire and earlier Tubbs Fire.<sup>3</sup> PVC irrigation systems also reportedly melted at many homes with potential backflow of combustion products into the system.

Fifty-five organic compounds found in the affected service line are associated with burning biomass, building materials and wastes. Twenty-three of these compounds were not associated with burning PVC or PE plastics: benzonitrile, 2-methyl-1-benzofuran, 2-

methylbenzotrile, 1-benzothiophene, 7-methylbenzofuran, 2-methyl-1H-indene, thiophene, naphthalene-2-carbonitrile, 3-ethylbenzotrile, 2-methylphenol, 4-methylbenzaldehyde, naphthalene-2-carbonitrile, 2-methylfuran, quinoline, 4-methylbenzotrile, chlorobenzene, (3-methylphenyl) acetate, 2-methylthiophene, 2,4-dimethylphenol, 1-(4-methylphenyl) ethanone, (4-methylphenyl) acetate, dibenzofuran, and 2,5-dimethylbenzaldehyde.

The known sources of these compounds are varied, e.g., 2-methylfuran, methylbenzofurans, 1-(4-methylphenyl) ethanone, (3-methylphenyl) acetate, (4-methylphenyl) acetate, naphthalenecarbonitriles are produced by burning biomass (e.g., forest fires, grasses, lumber, agricultural wastes). Sulfur compounds (e.g., thiophene, methylthiophene, benzo[b]thiophene) are reported combustion products from burning tires. Notably, some reported wood combustion products (e.g., methoxyphenols) were not detected among the service line contaminants. A more extensive set of biomass combustion products is needed to better understand the importance of intrusion of airborne combustion products.

## CONCLUSIONS

Drinking water systems damaged by wildfire are vulnerable to contamination by benzene and a complex mixture of organic contaminants that require substantial cost and time to remediate. The present study provides a detailed analysis of these contaminants in one highly-contaminated service line sample from the 2018 Camp Fire. Thirty-two compounds associated with burning of PVC and twenty-eight transformation products associated with burning of polyethylene plastics were found. This sample also contained twenty-three organic compounds associated with biomass burning or open, uncontrolled burning of waste materials, but not burning of plastic pipes *per se*. The findings support hypotheses that drinking water infrastructure is contaminated with low-molecular-weight organic compounds by multiple mechanisms including fire damage to plastics and intrusion of airborne combustion products. Laboratory simulations demonstrate that residual chlorine consumes some plastic transformation products and may modify the contaminant profile observed.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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**Synopsis:**

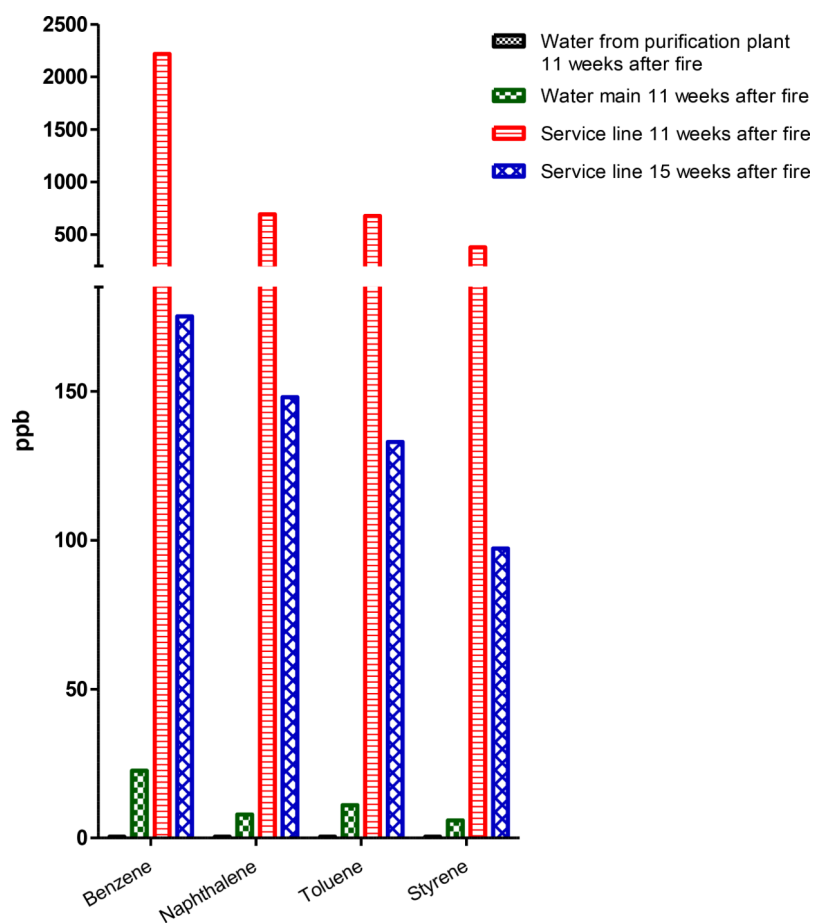
Comprehensive analysis of organic contaminants in fire-damaged drinking water service lines informs our understanding of contamination sources and mechanisms.

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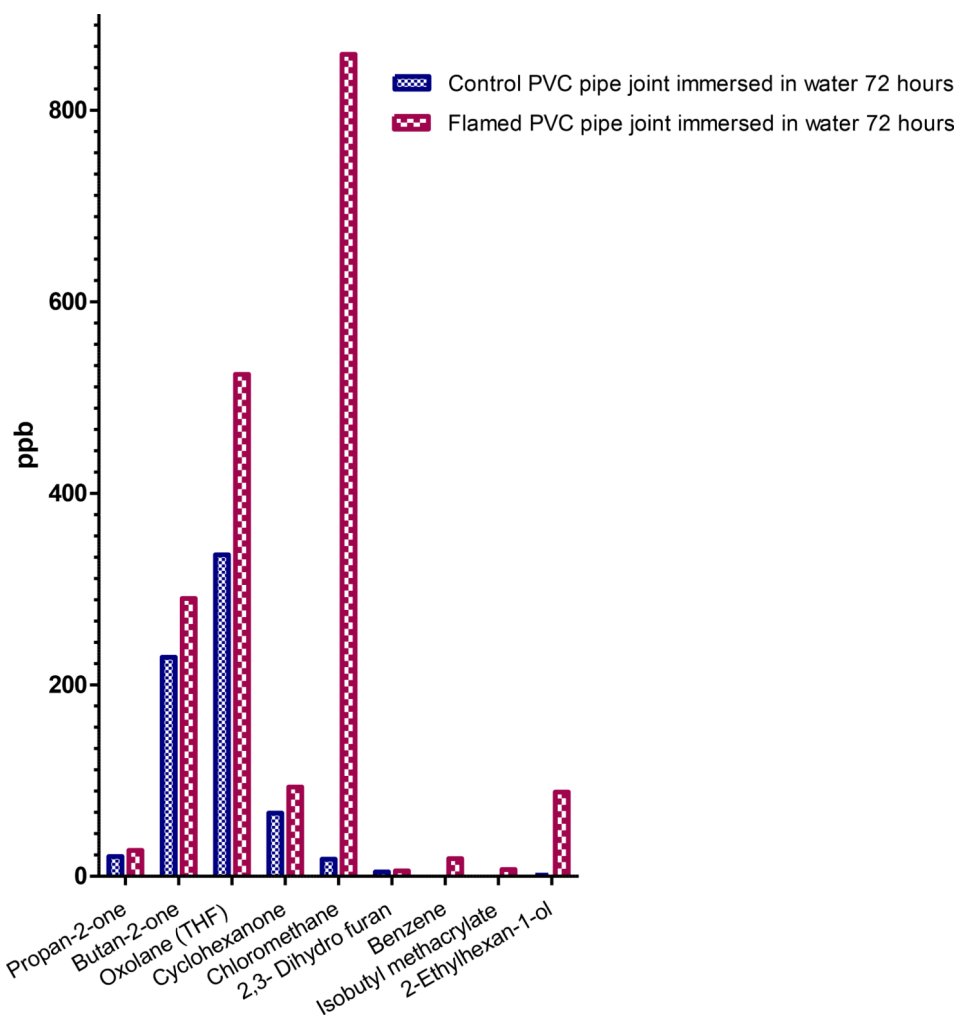
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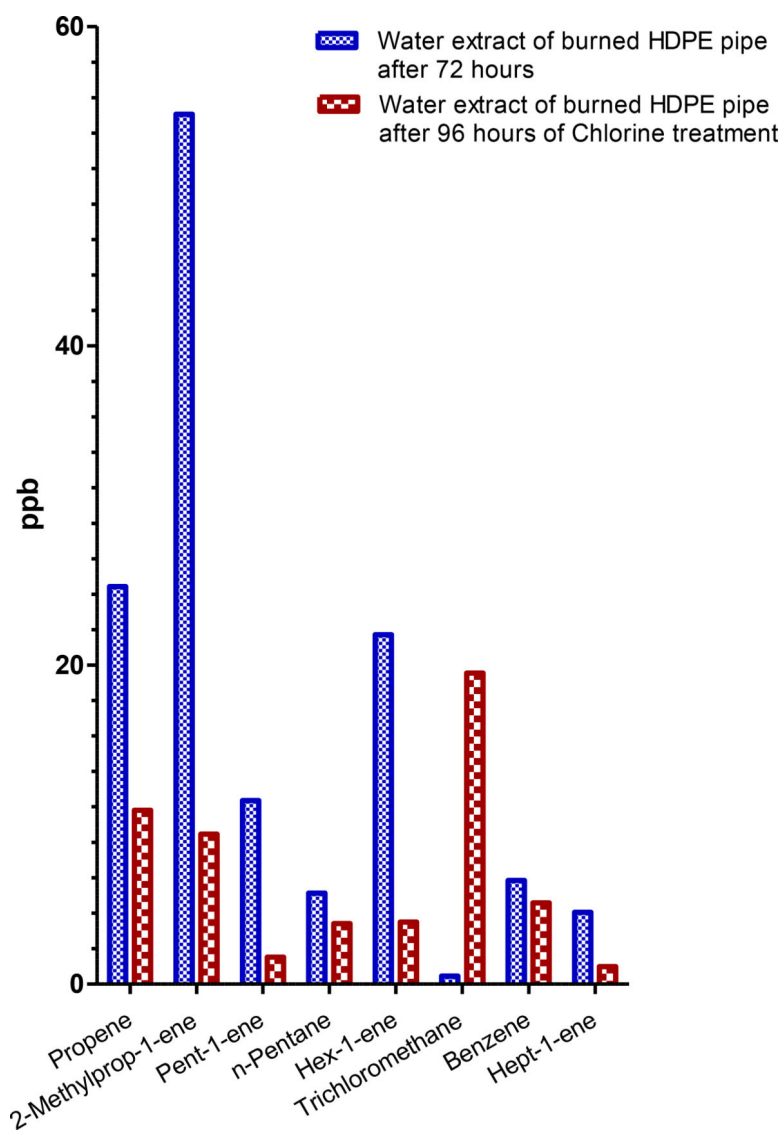


**Figure 1.** Profiles of VOC contaminants in additional water system locations and samples from the Camp Fire.

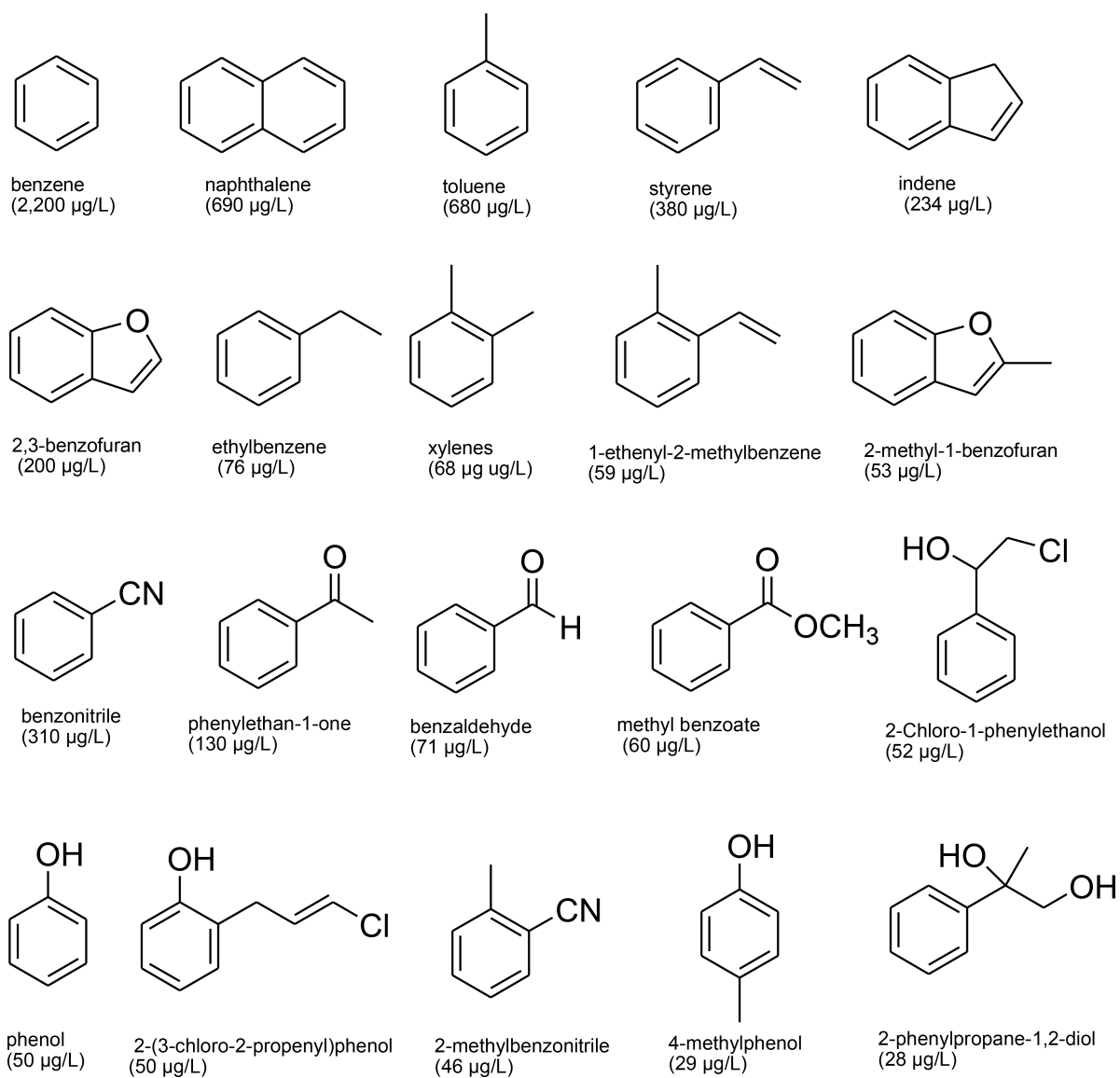




**Figure 2.** Mobilization of primer and glue solvents from and thermal decomposition products of PVC polymeric pipes.



**Figure 3.**  
Chlorine reactions with HDPE combustion products.



**Figure 4.** VOCs and SVOCs detected in the service line water sample from the 2018 Camp Fire.

**Table 1.**

VOCs Determined in Service Line Water Sample from Wildfire-Impacted Community and Potential Sources.

Con. ( $\mu$ L)	Identified Compound	CAS No.	Associated Based on Literature	Associated Based on Lab Simulations (Current Work)		
				PVC	PEX	HDPE
2200	Benzene **	71-43-2	HDPE,PE,PE*,PEX,PVC,PVC*; AB,BB,CB,DB,EB	PVC	PEX	HDPE
690	Naphthalene **	91-20-3	HDPE,PE*,PVC*; AB,BB,CB,DB,EB	PVC	PEX	HDPE
680	Toluene **	108-88-3	HDPE,PE*,PEX,PVC,PVC*,other; AB,BB,CB,DB,EB		PEX	HDPE
380	Styrene **	100-42-5	CPVC,HDPE,PE*,PVC,PVC*,other; AB,BB,CB,DB,EB	PVC	PEX	HDPE
230	Indene	95-13-6	PE*,PVC*; CB	PVC		
200	2,3-Benzofuran	271-89-6	PVC*; BB,CB			
76	Ethylbenzene **	100-41-4	HDPE,PE*,PVC,PVC*,other; AB,BB,CB,DB,EB	PVC	PEX	HDPE
59	1-Ethenyl-2-methylbenzene; or isomer	611-15-4	PE*,PVC*			
52	2-Methyl-1-benzofuran; or isomer	4265-25-2	DB			
48	Benzonitrile	100-47-0	BB,CB			
40	1,4-Xylene/1,3-Xylene **	106-42-3;108-38-3	PE*,PEX,PVC,PVC*; AB,BB,CB,DB,EB		PEX	HDPE
37	Ethynylbenzene	536-74-3	PE*,PVC*; CB		PEX	HDPE
32	2-Methylnaphthalene	91-57-6	PE*,PVC*; BB,CB,DB,EB			HDPE
31	Isopropenylbenzene ( $\alpha$ -Methylstyrene)	98-83-9	PE*,PVC*,other	PVC	PEX	
30	1,1'-Biphenyl	92-52-4	PE*,PVC*; AB,BB,CB,EB	PVC		
28	(2E)-3-Phenylprop-2-enal (Cinnamaldehyde); or isomer	104-55-2				
28	1,2-Xylene **	95-47-6	PEX,PVC,PVC*; AB,BB,CB,DB,EB			
28	1-Benzothiophene (3,3,5-Trimethylcyclohexyl) 2-	95-15-8	CB			
25	methylpro-2-enoate	7779-31-9				
24	Methyl benzoate	93-58-3				
24	Trichloromethane (Chloroform)**	67-66-3	CPVC,PVC; AB,EB	PVC	PEX	HDPE
24	1-Methylnaphthalene	90-12-0	PE*,PVC*; CB			HDPE
23	Benzaldehyde	100-52-7	PE,PE*,PVC,PVC*,other; BB,CB,DB,EB	PVC		
22	7-Methylbenzofuran; or isomer	17059-52-8	DB			
18	2-Methyl-1H-indene; or isomer	2177-47-1	CB			
16	Thiophene	110-02-1	CB			
16	1-Methyl-1H-indene; or isomer	767-59-9	PE*,PVC*; BB			
15	Propene	115-07-1	PE*,PVC*,other		PEX	HDPE
12	Acetophenone	98-86-2	HDPE,PE,PEX,PVC*,other; AB,DB,EB			
12	1-Methylcyclopropene	3100-04-7				

11	1-Ethyl-3-methylbenzene; or isomer	620-14-4	PE,PE*, PVC,PVC*			
10	1-Ethyl-2-methylbenzene; or isomer	611-14-3	PE*,PVC*; BB,CB,EB			
9.0	Chloromethane **	74-87-3	AB,BB,DB,EB	PVC		
9.0	Acenaphthylene	208-96-8	PE*,PVC*; BB,CB,DB,EB		PEX	HDPE
8.0	Azulene	275-51-4				
8.0	1-Ethenyl-3-methylbenzene; or isomer	100-80-1	HDPE,PE*,PVC,PVC*			
7.0	[(1E)-Buta-1,3-dienyl]benzene; or isomer	1515-78-2				
6.0	2-Methylfuran	534-22-5	BB			
6.0	1-Ethenyl-4-methylbenzene; or isomer	622-97-9	HDPE,PE*;			
<5	1,1'-Methylenedibenzene (Diphenylmethane)	101-81-5				
<5	Acetaldehyde	75-07-0	PE; AB,BB,CB,DB,EB			
<5	Furan	110-00-9	Other; BB			
<5	1,3-Pentadiene	504-60-9			PEX	HDPE
<5	2-Methylthiophene	554-14-3	CB			
<5	3-Methylthiophene	616-44-4				
<5	Chlorobenzene	108-90-7	AB,EB			
<5	(Propan-2-yl)benzene (Cumene); or isomer	98-82-8	PE; AB,CB,EB			
<5	Prop-2-enyl)benzene (Allylbenzene)	300-57-2	PE*,PVC*; CB			
<5	Propylbenzene	103-65-1	PE,PE*, PVC,PVC*; CB			
<5	1,3,5-Trimethylbenzene (Mesitylene); or isomer	108-67-8	PE*,PVC*; BB,CB,EB			
<5	2,3-Dihydro-1H-indane (Indane)	496-11-7	PE*; CB		PVC	
<5	Prop-1-ynylbenzene	673-32-5	PVC*			
<5	4-Methylbenzaldehyde; or isomer	104-87-0	CB,DB			
<5	2-2-Methylbenzoxonitrile; or isomer	529-19-1	EB			

\*\* Identified using authentic standard

**Chlorinated polyvinyl chloride (CPVC):** CPVC leachate, **HDPE:** HDPE leachate, **Polyethylene (PE):** PE leachate, **PE\*:** from pyrolysis of PE, **PEX:** PEX leachate, **Polypropylene (PP):** PP leachate, **PVC:** PVC leachate, **PVC\*:** from pyrolysis of PVC, **Other:** from other materials used in water distribution systems

**AB:** HAP (hazardous air pollutant) from open burning, **BB:** open burning of biomass, **CB:** open burning of scrap tires, liquid fuel, **DB:** open burning of household waste, landfill, pesticide bags, **EB:** Open burning of automobile shredder residue, fiberglass, fabric

**Table 2.**

**SVOCs Determined in Service Line Water Sample from Wildfire-Impacted Community and Potential Sources**

Con. (µg/L) <sup>1</sup>	Identified Compound <sup>2</sup>	CAS No.	Associated Based on Literature	Associated Based on Lab Simulations (Current Work)		
				PVC	PEX	HDPE
310	Benzonitrile	100-47-0	BB,CB			
130	Acetophenone	98-86-2	HDPE,PE,PEX,PVC*,other; AB,DB,EB			
100	Naphthalene	91-20-3	HDPE,PE*,PVC*; AB,BB,CB,DB,EB	PVC	PEX	HDPE
71	Benzaldehyde	100-52-7	PE,PE*,PVC,PVC*,other; BB,CB,DB,EB	PVC		
60	Methyl benzoate	93-58-3				
52	2-Chloro-1-phenylethanol	1674-30-2				
50	Phenol	108-95-2	PVC*,other; AB,BB,CB,DB,EB			
50	2-(3-Chloro-2-propenyl)-phenol; or isomer	86694-60-2				
46	2-Methylbenzonitrile; or isomer	529-19-1	EB			
32	2-(3-Chloro-2-propenyl)-phenol; or isomer	86694-60-2				
29	4-Methylphenol	106-44-5	PEX; AB,DB,EB			
28	2-Phenylpropane-1,2-diol	4217-66-7				
18	2,3-Benzofuran	271-89-6	PVC*; BB,CB			
18	1 <i>H</i> -Indene	95-13-6	PE*,PVC*; CB	PVC		
18	1,1'-Biphenyl	92-52-4	PE*,PVC*; AB,BB,CB,EB	PVC		
17	(E)-4-Phenylbut-3-ene-2-one	122-57-6				
15	Naphthalene-2-carbonitrile	613-46-7	BB CPVC,HDPE,PE*,			
14	Styrene	100-42-5	PVC,PVC*,Other; AB,BB,CB,DB,EB	PVC	PEX	HDPE
13	Phenyl acetate	122-79-2				
11	Diphenylmethanone (Benzophenone)	119-61-9				
10	Acenaphthylene	208-96-8	PE*,PVC*; BB,CB,DB,EB		PEX	HDPE
10	2-Methylphenol; or isomer	95-48-7	AB,BB,DB,EB			
10	beta-Hydroxy-4-Methylbenzenepropanenitrile	997097-18-2				
10	3-Ethylbenzonitrile; or isomer	34136-57-7	EB			
8.0	1-Phenylpropan-1-one	93-55-0				
8.0	4-Methylbenzaldehyde; or isomer	104-87-0	CB,DB			
8.0	1-Benzothiophene	95-15-8	CB			
8.0	Naphthalene-1-carbonitrile	86-53-3	BB			
8.0	Fluoren-9-one	486-25-9	PVC*			
6.0	2,4,6-Trichlorophenol	88-06-2	Other; AB,DB			
6.0	Naphthalene-2-carbaldehyde	66-99-9	PVC*; EB			

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				Associated Based on Lab Simulations (Current Work)		
6.0	Quinoline	91-22-5	AB			
6.0	4-Ethenylbenzotrile; or isomer	3435-51-6				
5.0	Dodecyl prop-2-enolate (Dodecyl acrylate)	2156-97-0				
5.0	4-Methylbenzotrile	104-85-8	EB			
5.0	(3-Methylphenyl) acetate	122-46-3	BB			
4.0	1-Methylnaphthalene	90-12-0	PE*,PVC*; CB			HDPE
4.0	2,4-Dimethylphenol; or isomer	105-67-9	BB, DB			
4.0	2-Methylnaphthalene	91-57-6	PE*,PVC*; BB,CB,DB,EB			HDPE
3.0	2-Methyl-1-benzofuran	4265-25-2	DB			
3.0	1-(4-Methylphenyl) ethanone	122-00-9	BB			
3.0	Ethylbenzene	100-41-4	HDPE,PE*,PVC,PVC*,other; AB,BB,CB,DB,EB	PVC	PEX	HDPE
3.0	Naphthalen-1-yl acetate	830-81-9				
3.0	3-Phenylpyridine	1008-88-4				
2.0	Benzo[c]cinnoline	230-17-1				
2.0	Ethynylbenzene	536-74-3	PE*,PVC*; CB		PEX	HDPE
2.0	(4-Methylphenyl) acetate	140-39-6	BB			
2.0	7-Methyl-1-benzofuran	17059-52 8	DB			
2.0	Methyl 3-methylbenzoate; or isomer	99-36-5				
2.0	Phenyl propanoate	637-27-4				
2.0	9H-Fluorene	86-73-7	PE*,PVC*; BB,CB,DB,EB			
1.0	Naphthalen-2-yl acetate	1523-11-1				
1.0	1,4-Xylene/1,3-Xylene	106-42-3;108-38-3	PE*,PEX,PVC, PVC*; AB,BB,CB,DB,EB		PEX	HDPE
1.0	2,5-Dimethylbenzaldehyde	5779-94-2	CB			
1.0	Benzo[f]isoquinoline; or isomer	229-67-4				
1.0	Phenanthrene	85-01-8	PE*,PVC*; BB,CB,DB,EB			
<1	1-Methyl-1H-indene; or isomer	767-59-9	PE*,PVC*; BB			
<1	(3,3,5-Trimethylcyclohexyl) 2-methylpro-2-enoate	7779-31-9				
<1	3,5-Di-tert-butyl-2-hydroxybenzaldehyde	37942-07-7				
<1	[1,1'-Biphenyl]-2-carbonitrile	24973-49 7				
<1	Dibenzofuran	132-64-9	AB,BB,DB,EB			

CPVC: CPVC leachate, HDPE: HDPE leachate, PE: PE leachate, PE\*: from pyrolysis of PE, PEX: PEX leachate, PP: PP leachate, PVC: PVC leachate, PVC\*: from pyrolysis of PVC, Other: from other materials used in water distribution systems

AB: HAP (hazardous air pollutant) from open burning, BB: open burning of biomass, CB: open burning of scrap tires, liquid fuel, DB: open burning of household waste, landfill, pesticide bags, EB: Open burning of automobile shredder residue, fiberglass, fabric