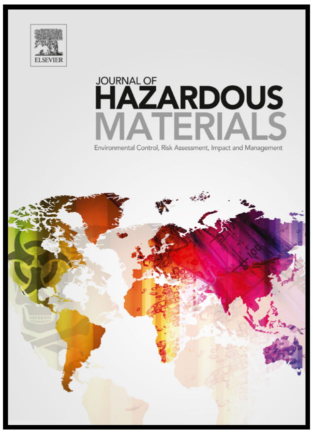

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Formation and Aqueous Phase Leaching of Organic Compounds following Thermal Degradation of Commercial Drinking Water Plastic Pipes

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Abstract

After a wildfire, drinking water quality may be impacted by the thermal degradation of polyethylene pipes in drinking water distribution systems. Volatile organic compounds (VOC) and semi-VOCs (SVOC) have been detected in at least fifteen water distribution systems following wildfires between 2017 and 2024. This study investigated if plastics could potentially contaminate water directly by submerging four commercially available plastic drinking water pipes (crosslinked polyethylene (PEX)-a, PEX-b, PEX-c, and high density polyethylene (HDPE)) and one HDPE resin in water and heating them to various temperatures (100-285°C) in a continuously stirred tank reactor (CSTR). After cooling, clean water was pumped through the CSTR to assess flushing's efficacy as a decontamination strategy. Each plastic leached up to 10 VOCs out of 36 VOC/SVOCs examined at the highest exposure temperature of 285°C, including various monoaromatic and phenolic compounds. Benzene, a carcinogen, leached from all plastics at temperatures of 150°C and above. PEX-a leached the greatest concentrations of most detected VOCs, where the number and magnitude of compounds leached increased with increasing exposure temperature. Flushing removed the compounds over time, but flushing was slower than expected for the more hydrophobic compounds and not so for the more hydrophilic ones, due to their continuous leaching from the plastics. Similar compounds (7 of the 12 total found) were extracted from exhumed materials from wildfire impacted water systems, including several polyaromatic hydrocarbons which were not detected in the laboratory experiments. Benzene was found to leach from all exhumed plastic pipes above maximum contaminant levels. Results confirm that plastics may be a source of contamination, flushing removes contaminants over time, and procedures must be optimized to ensure their complete removal from water distribution systems post-wildfire.

Keywords: Drinking Water, Plastics, Thermal Degradation, Contamination, Wildfires

Synopsis: Wildfires have caused contamination of drinking water systems. This study found that the thermal degradation of plastic drinking water pipes may be one source of detected contaminants and evaluated the efficacy of flushing as a decontamination strategy.

1. Introduction

The deadliest, most destructive wildfires occur at the wildland interface (WUI), which is currently the fastest growing land use in the United States (Radeloff et al. 2018). The WUI exists between wildland fuels and structures, and its growth coincides with increased wildfire frequency and severity due to the shifting climate (Schoennagel et al. 2017). After wildfires, communities face many long-term challenges, one being the contamination of drinking water distribution systems and property plumbing. Volatile organic compounds (VOCs) and semi-VOCs (SVOCs) have been detected in several water systems following wildfires, and uncertainty about the magnitude and source of these contaminants has hindered community recovery. Various VOCs, such as benzene, naphthalene, styrene, and vinyl chloride, have been detected in drinking water systems exceeding their health-based state and federal maximum contaminant levels (MCL) (USEPA 2018; Proctor et al., 2020; Whelton et al. 2024). SVOCs, such as phthalates, furans, and polyaromatic hydrocarbons (PAHs) have also been detected in both water distribution systems and private wells on fire-damaged properties (Jankowski et al. 2023). Despite such testing data, water testing guidance frequently directs water utilities or well owners to limit testing to only benzene, toluene, ethylbenzene, and xylene (BTEX) or, in some cases, just benzene. However, with other VOCs/SVOCs being detected in water systems at levels that exceed health-based drinking water limits, in the absence of benzene or BTEX, characterizing the source of the contaminants is necessary.

One contamination source potentially originates from thermally damaged plastic materials present in distribution systems and property plumbing. Plastic materials commonly used include high density polyethylene (HDPE), polyvinylchloride (PVC), and crosslinked polyethylene (PEX) (Folkman, 2018). These plastics are increasingly used in water conveyance because of their flexibility, ease of installation, low cost, and lack of heavy metals. Plastics are also well known to release many of the same VOCs/SVOCs detected following wildfires into the air during thermal degradation (Mastral et al., 2003; Font et al., 2004; Aracil et al., 2005; Ueno et al., 2010; Părpăriţă et al., 2014, Chong et al. 2019; Jiang et al. 2023). Further, aqueous leaching of organic compounds from combusted drinking water pipes has been observed; however, direct transfer of organic contaminants into water during thermal degradation is less explored (Isaacson et al. 2021; Draper et al. 2022; Metz et al. 2023).

Evaluating the direct transfer of contaminants generated in the plastics into water is critical since it may significantly affect and alter the types of contaminants produced. One likely contributing factor is oxygen. Under air, plastics undergo incomplete combustion in the presence of oxygen to produce oxygenated compounds such as aldehydes, dioxins, and furans; whereas, in the absence of oxygen (i.e. under pyrolysis), non-oxygenated aliphatic and aromatic compounds are produced at a higher magnitude (Font et al., 2003; Font et al., 2004; Aracil et al., 2005). However, the trends can be inconsistent between materials, as studies demonstrate that the presence of oxygen can decrease PAH generation but increase monoaromatic hydrocarbon (MAH) generation in polyethylene, whereas a decrease or no change on PAHs and MAHs was observed with PVC (Panagiotou et al., 1996; Aracil et al., 2005; Conesa et al. 2009). It remains unclear how such differences translate to plastics degradation when the system is absent of air but contains water instead. Additionally, the direct contact of water may influence how quickly the contaminants physically partition from the thermally damaged plastic into water over time as water may penetrate the plastics, especially at higher temperature, thereby extracting contaminants more readily (Papiernik and Yates, 2002; Keller and Kouzes, 2017).

Such impacts could directly implicate how effective flushing is at decontaminating thermally degraded plastic pipes. This is especially important since one modeling study indicated that a considerable length of time (286 days) of continuous flushing would be required to remove benzene to lower than required minimum limits from new plastics (e.g., a HDPE service line) that had reached equilibrium with contaminated water (Whelton et al., 2019). The slow diffusion rate of benzene within HDPE likely slowed decontamination, as benzene diffusion through polyethylene obeys Fick's Law (Mao et al., 2015; Haupert et al., 2023). Subsequently, examining if a similar length of time is required to decontaminate thermally damaged materials is necessary since thermal damage may alter the plastic characteristics, which could alter contaminant diffusion. Further, the impacts on other contaminants besides benzene, which have similarly been observed in post-wildfire water systems, need to be examined since they have different physical and chemical characteristics influencing the leaching rate.

This study's aim was to determine how the direct contact of water during plastic thermal degradation impacts the formation and aqueous leaching of various compounds routinely detected in water distribution systems following wildfires. The compounds included BTEX, phenol, *o*-cresol, *p*-cresol, 2,4-dimethylphenol, *p*-chlorocresol, and isophorone, among others (see Table S1 in the Supporting Information (SI) for the full list of compounds). Bulk parameters were also measured including total organic carbon (TOC) and the specific UV absorbance (SUVA; = UV absorbance at 254 nm (UV_{254})/TOC) to examine how they compared to typical treated waters and to assess if such parameters correlated with compound leaching. Experiments used a continuously stirred tank reactor (CSTR) to expose various commercial drinking water plastic pipes (PEX-a, PEX-b, PEX-c, and HDPE) and one resin (HDPE resin), to a range of elevated temperatures (100 to 285 °C) in the presence of water. Next, the efficacy of flushing was evaluated by pumping clean water through the reactor over 180 min. Mass balance equations were applied to the CSTR experiments to evaluate if plastic pipes continuously leached contaminants as the system was flushed. The CSTR system configuration was chosen as it allowed for plastics to be exposed to elevated temperatures and pressures under controlled gas-tight conditions. This was an important consideration since the generation and leaching of volatile organic compounds could be accurately measured by avoiding exposure to the air. We recognize that using a CSTR has certain limitations, as diffusion coefficients of compounds formed during thermal degradation cannot be measured and mass transfer effects within a typical pipe configuration (i.e. plug flow reactor) cannot be assessed. However, no other known systems could be properly configured to keep the system closed under high temperature and pressure conditions beyond using a CSTR. Bench-scale CSTR results were then compared to leaching responses from plastic materials exhumed from wildfire impacted distribution systems. Overall, this study (1) evaluated contaminant formation and leaching from thermally damaged drinking water pipes, (2) evaluated what mass transfer effects control flushing and decontamination, and (3) identified possible bulk parameter proxies for contamination, all to help inform disaster response and recovery decision-making following a wildfire event.

2. Materials and Methods

2.1 Standards and Reagents

All compounds and analytical standards were purchased from commercial vendors at reagent grade or higher and used without further purification. Additional details are provided in the Supplementary Information (SI) (Text S1).

2.2 Types of Plastic Pipes and Resins

Four different plastic drinking water pipes were purchased from local plumbing supply stores including various types of crosslinked polyethylene (PEX-a, PEX-b, PEX-c) and HDPE. The different types of PEX (-a, -b, and -c) denote different crosslinking methods used during production. All plastic pipes tested had a 1.9 cm (0.75-inch) diameter and were reported to be certified with ANSI/NSF Standard 61. Additionally, a sheet of HDPE resin was purchased from McMaster Carr. Exhumed materials (five copper pipes, one PVC pipe, and six water meters) were also gathered from various drinking water systems by water utility partners from California and Colorado and shipped to Indiana for testing (Figure S1). Three polyethylene pipes were exhumed by this study's authors from two separate private water systems in Colorado. Five of the six water meters received were not visibly damaged but were in a wildfire impacted and chemically contaminated drinking water distribution system. The remaining materials were all visibly damaged.

2.3 Plastic Pipe Characterization

The new and exhumed plastics were characterized using thermogravimetric analysis (TGA) (TA Instrument Q50), differential scanning calorimetry (DSC) (TA Instrument Q2000) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) (Perkin Elmer Spectrum 100) to better understand how materials composition affects their performance in thermal degradation experiments. Additional details about the material analyses are provided in the SI (Text S2).

2.4. Thermal Degradation and Leaching Experiments

Thermal degradation and leaching experiments were performed using a stainless steel 300 mL CSTR (Parr Instruments, Inc.). Additional details and pictures of the reactor are provided in the SI (Figures S2 and S3, Text S3) At the start of the experiment, a sample of plastic pipe material (5 g) was added to 180 mL of reagent water in the reactor vessel. No salts were added to the water for pH or ionic strength control in order to avoid precipitation and/or corrosion issues. Headspace was left in the vessel to account for the large amount of water expansion that occurs during high temperature experiments. The samples of plastic pipe were die cut into 1x1 cm squares to ensure consistency in the surface area between samples. The surface area to water volume ratio (SA/V) was 5.2 to 8.4 times less than the ratio in a 1.9 cm pipe, a common diameter of pipe used for service lines. Therefore, the lower ratio is expected to also lower the concentration of aqueous contaminants leached when compared to thermally damaged in-service drinking water pipes.

The reactor vessel was then heated to temperatures ranging between 100 to 285 °C. The temperature that a plastic pipe will be exposed to during a wildfire will vary widely depending on an array of variables including, surface temperatures (range from 200 to 800 °C), burial depth, location within the walls of a structure, and proximity to fire (Neary et al., 1999; Busse et al., 2005). Although water distribution infrastructure is generally buried at least 0.305 m underground, there have been several wildfire impacted communities with shallow (under 0.152 m) or above ground water mains, service lines, and meter boxes that sustained thermal damage (Castillo, 2020; Magladry and Boak, 2021; Metz et al., 2023; Whelton et al., 2024). As a result, this range was chosen to thermally damage the plastics to a varying degree, but the upper temperature was limited by the heating time required to exceed 285 °C. Once the reactor reached the desired temperature, that temperature was held for 60 min. The reactor was then cooled to 50 °C by blowing air across the outside surface of the vessel. Once the reactor reached 50 °C, the reactor inlet and outlet were opened, and reagent water was pumped through at 15 mL/min resulting in a 12 min residence time. The temperature ramp and cooling times varied across different exposure temperatures (Figure S4). Effluent samples were collected through stainless steel tubing attached to a luer lock syringe tip which was directly inserted through the septa of a 40 mL volatile analysis vial to minimize compound volatilization. Samples from the reactor were collected every 15 min for the first 60 min and every 30 min for the next 120 min and stored at 4 °C under headspace free conditions prior to VOCs/SVOCs analysis. Additional effluent samples were collected every 30 min over the duration of the experiment for TOC and UV_{254} analyses.

Following thermal degradation and flushing, the plastic pieces were dried at room temperature over the course of 12 hr, placed in a 40 mL vial, and immersed in water for 7 d at room temperature with no headspace. After 7 d, the water was removed and analyzed for VOCs/SVOCs.

2.5 Modeling Contaminant Flushing

Three model equations were developed to further interpret the results and differed in complexity by incorporating different mass contributions from different phases (water, air, and the solid plastic). The first model equation represented the mass balance of a select contaminant only around the liquid phase of the reactor (eq. 1 is the ODE and eq. 2 is its analytical solution):

$$\frac{\mathrm{dC_w}}{\mathrm{d}t} = \frac{\mathrm{Q*C_{in} - C_w*Q}}{\mathrm{V_w}} \qquad (1)$$

$$\mathrm{C_w} = \mathrm{C_{w,inital}} * \mathrm{e}^{-(\frac{\mathrm{Q}*t}{\mathrm{V_w}})} \qquad (2)$$

where *t* represents time (min), Q represents the volumetric flow rate (L/min), C_w represents the contaminant concentration in the reactor outlet (µg/L), C_{in} represents the contaminant concentration in the reactor inlet (= 0 in all cases; µg/L), $C_{w,initial}$ represents the concentration at the start of flushing (t = 0 min) (µg/L), and V_w represents the volume of water in the reactor (L). Although there is an analytical solution (eq. 2), the ODE equation was instead solved numerically in Matlab using ode45 (code provided in Text S4).

Because some contaminants were volatile, eq. 1 was anticipated to not fully describe contaminant partitioning from the water to the air phase during thermal degradation. Therefore, the mass balance was expanded to include the air phase. Instantaneous equilibrium was assumed to occur during the full flushing period, and Henry's Law constants (H) were used to estimate the partitioning between phases (eq. 3). Again, a mass balance equation was derived, where eq. 3 is the ODE with its derivation provided in Text S5 and eq. 4 is its analytical solution:

$$\frac{dC_w}{dt} = \frac{Q*C_{in} - C_w*Q}{V_w + V_g*H(t)} \qquad (3)$$

$$C_w = C_{w,inital} * e^{-\left(\frac{Q*t}{V_w + V_g*H(t)}\right)} \qquad (4)$$

where V_g represents the volume of the gas phase (L) and H(*t*) represents H which changes with temperature and thus time. H(*t*) was estimated using previously reported H values at various temperatures (Table S2) and using the Van't Hoff equation to interpolate values. Eq. 3 was similarly solved in Matlab using a numerical approach (Text S6).

The mass balance was further expanded to include the compound diffusion from the plastic, where again eq. 5 is the ODE with its derivation provided in Text S7 and eq. 6 is its analytical solution:

$$\frac{dC_w}{dt} = \frac{Q*C_{in} - C_w*Q}{V_w + V_g*H(t) + K_{pw}(t)*V_p} \qquad (5)$$

$$C_w = C_{w,inital} * e^{-\left(\frac{Q*t}{V_w + V_g*H(t) + K_{pw}(t)*V_p}\right)} \qquad (6)$$

where additionally, $K_{pw}(t)$ represents the partitioning coefficient between the plastic and the water for each contaminant with respect to time and V_p represents the volume of the plastic in the reactor (L). Similar to $H(t)$, $K_{pw}(t)$ was estimated by using previously reported values at different temperatures, and using the Van't Hoff equation to interpolate values. BTEX were the only compounds for which K_{pw} values were found at various temperatures (Table S2). For the remaining compounds, values at 25 °C were used. Eq. 5 was similarly solved in Matlab using a numerical approach (Text S8).

2.6 Exhumed Material Leaching Experiments

Exhumed copper pipes and water meters were filled with reagent water and capped with polytetrafluorethylene lined stoppers for 7 d at room temperature to measure VOC/SVOC leaching. The plastic pipes were severely damaged and could not hold water and were drilled into spirals using a 3/16-inch drill bit. Spirals (5 g) were added to a 40 mL vial and filled with reagent 1 water with no headspace, following methods described previously (Isaacson et al., 2021; Metz et al., 2023). Aliquots of all aqueous samples were then analyzed for VOCs/SVOCs.

2.7. Analytical Methods

Aqueous samples were analyzed for select VOCs and SVOCs using gas-chromatography coupled with mass spectrometry (GC-MS) using either headspace injection (Agilent GC-7890B coupled to 7000C MS) or liquid injection (Shimadzu GC-2010 Plus coupled to Shimadzu TQ8040 MS). Method detection limits (MDL) and percent recovery ranged from 0.26 to 20.1 μg/L and 50.2 to 106.4% respectively (Table S1). Further details are provided in the SI (Text S9).

The TOC concentration of select samples was measured as non-purgeable organic carbon with a high sensitivity catalyst (Shimadzu TOC-L CPH/CPN). UV_{254} was measured to assess the level of aromaticity in each sample by measuring each sample's absorbance at 254 nm with a 1.0 cm path length quartz cuvette using a Shimadzu UV/vis spectrophotometer. Additional details on both analytical methods are provided in the SI (Text S10).

3. Results and Discussion

3.1 Impact of Plastic Type

3.1.1. Individual Compound Leaching

Thermal degradation of all five materials at the highest temperature examined, 285 °C, resulted in leaching of up to 10 compounds. The compounds detected in the leachate included four monoaromatic compounds (BTEX), several phenolic compounds (phenol, *o*-cresol, *p*-cresol, 2,4-dimethylphenol, and *p*-chlorocresol), and a cyclic ketone (isophorone). All of these compounds have been detected in water distribution systems following wildfires (Solomon et al., 2021; Whelton et al., 2023). Data for two compounds, benzene and phenol, are presented in Figure 1, given the relevance to post-wildfire water quality monitoring and the high levels formed, respectively. Data for all other compounds are presented in Figure S5. BTEX leaching was not surprising given that it is well known to form during combustion or pyrolysis of polyethylene and leach into water (Isaacson et al., 2021; Draper aet al., 2022; Metz et al., 2023). However, prior thermal degradation studies have not identified the remaining six compounds as thermal degradation products of polyethylene. Phenolic compounds, such as phenol and *p*-cresol, have been found to leach in low concentrations from new plastic pipes that are not thermally damaged, indicating they may be impurities in the material (Reingruber et al. 2010; Kelley et al., 2014; Connell et al., 2016). While phenol was detected in the leachate of control experiments (no thermal degradation) for the PEX-a pipe at relatively low concentrations (0.012 mg/kg) (see later discussions), the elevated concentrations observed here suggest thermal degradation processes are the primary generators.

To compare leaching results between different compounds and plastic materials, the mass of each compound leached was normalized by the initial mass of the material placed in the reactor (mg/kg) since the latter variable varied slightly across experiments. Across all materials, benzene, phenol, and *p*- chlorocresol were generally detected in the leachate at concentrations of an order of magnitude higher than other compounds (Figure 1a and S5). Maximum levels of up to 12 (Figure 1a), 15 (Figure 1d), and 28 (Figure S6) mg/kg, for benzene, phenol, and *p*-chlorocresol, respectively, were observed at the initial stage of the flushing period, which decreased steadily over time (see modeling discussions for details on flushing trends). Notably, the phenomenon remained somewhat consistent even after the full flushing period ended and after 7d stagnation of the thermally damaged materials, since benzene was the only compound detected (Figure 1a).

The relatively high amounts of benzene leaching were unsurprising as it is a well-established product of PE combustion and pyrolysis, and previous works have found benzene to leach significantly higher concentrations than the other BTEX compounds (Isaacson et al., 2021; Draper et al., 2022; Metz et al., 2023). However, the phenolic compounds (e.g. phenol and chlorocresol) may instead dominate leaching due to plastic formulation and chemical properties. For example, hindered phenolic antioxidants are commonly used in plastic manufacturing and can degrade into a variety of water-soluble phenolic compounds, including phenol (Reingruber et al., 2010; Frey, 2022). However, the additives used in commercial plastic pipes are proprietary information, making drawing conclusions about the source of each contaminant difficult. Chemical characteristics such as solubility and partitioning coefficients would also factor into observed leaching as many of the phenolic compounds have K_{pw} values two to three orders of magnitude smaller than the BTEX compounds (Table S2), indicating they would more readily partition into the water.

Between plastic materials, all compounds excluding *p*-cresol and *p*-chlorocresol leached to the greatest degree from PEX-a (Figure 1 and S5). The trend remained consistent over the full flushing period and the 7d stagnation. In contrast, *p*-cresol and *p*-chlorocresol leached to the greatest degree by the HDPE resin and HDPE pipe, respectively (Figure S5). PEX-a leached the highest mass of eight of the 10 compounds, likely partially because of differences in material characteristics such as crystallinity and density. PEX-a had the lowest density (0.939 g/cm^3) and crystallinity (46.2%) (Table S3), whereas thermal properties such as the onset degradation temperature were similar amongst the materials tested. Organic compounds have been found to permeate more readily into plastic pipes with lower densities and crystalline content, suggesting that compounds formed in the materials during degradation may more readily diffuse through plastic into the water in less dense and crystalline materials (Whelton et al., 2010).

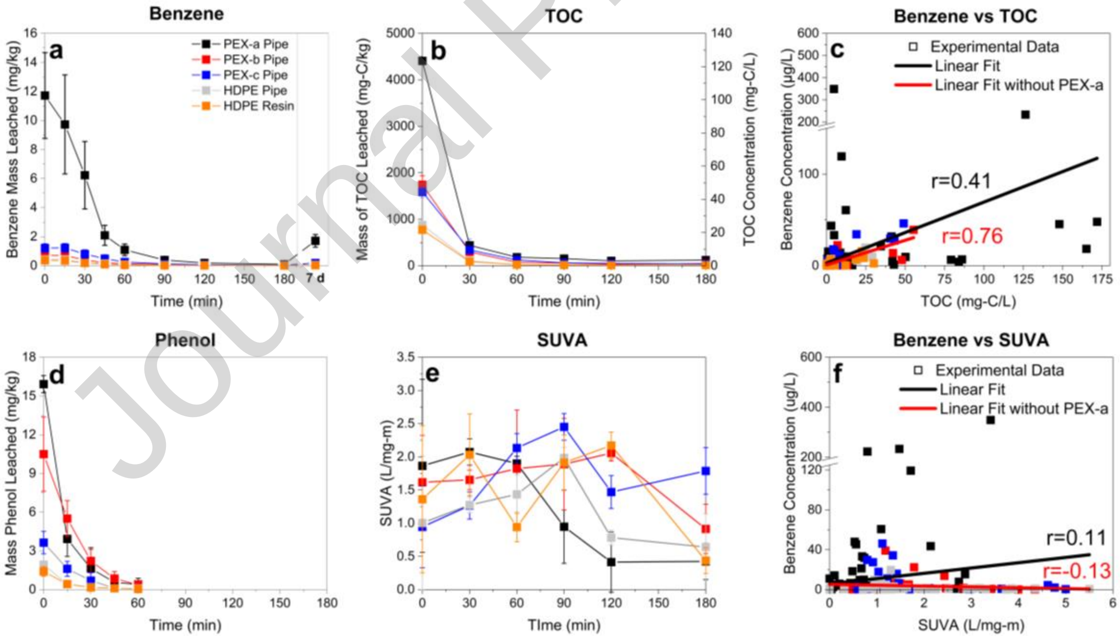

Figure 1: Mean mass leached of (a) benzene, (b) TOC, (d) phenol, and (e) specific UV absorbance (SUVA) in the CSTR effluent following flushing over 180 min (flow rate = 15 mL/min) from the PEX-a, PEX-b, PEX-c, HDPE pipe, and HDPE resin that were thermally degraded at 285°C. Error bars represent one standard deviation (n=3). Pearson correlation coefficients (r) were calculated for (c) benzene versus TOC and (f) SUVA both with and without the PEX-a pipe data.

3.1.2. Comparison to Bulk Parameters.

In addition to individual compounds, bulk parameters such as TOC and SUVA in the leachate were assessed. Like the majority of individual compounds measured, TOC levels decreased over the flushing period and varied between different materials, reaching the highest level (up to 4,400 mg/kg; 123 mg-C/L) for the PEX-a pipe (Figure 1b). These TOC values exceeded those typically found in surface water (1 to 20 mg-C/L) and treated waters (0.2 to 1 mg-C/L) (Crittenden, et al., 2012). The total mass of organic carbon content also exceeded the mass accounted for by the individual compounds alone (96.8 to 99.2% was unaccounted). The results parallel previous studies investigating carbon leaching from new undamaged plastic drinking water products, where up to 99.4 % of the leached organic compounds remained unidentified (Nielsen et al., 2007; Ryssel et al., 2015; Isaacson et al., 2024) .

SUVA values were calculated to assess the relative aromaticity in the leachate per unit carbon (L m^{-1}mg-C^{-1}). The calculated SUVA values were relatively low (ranging between 0.03 and 2.57), close to what may be detected in the effluent of drinking water treatment facilities and did not vary much over the course of flushing period or between plastic materials (Figure 1e) (Layonen et al., 2015; Pérez and Rodríguez, 2017). However, while the SUVA values were low, the total level of aromatic compounds present and their corresponding UV_{254} absorbances (Figure S6) remained relatively high given the high TOC levels present (up to 123 mg-C/L) (Figure 1b). These high levels could be due to additives in plastics such as plasticizers or antioxidants, which tend to be aromatic (Bertoldo and Ciardelli, 2004; Denberg et al., 2009). Phthalates, for example, are commonly used as plasticizers in plastics and have been found to leach from new PEX pipes into water (Faust et al., 2017; Mathews et al., 2023). Any ability to identify these aromatic degradation products was poorly characterized by the compounds measured in this study, as most of the measured compounds only absorbed a small proportion (0.18-0.38%) (see Table S2 for molar extinction coefficients) of total UV_{254} light. The composition of leached carbon clearly needs elaboration, especially as aromatic compounds can react with the free chlorine in drinking water, consume the chlorine residual, and produce disinfection by-products (Deborde and von Gunten, 2008).

Correlations between compound leaching and TOC or SUVA were also investigated to evaluate if these bulk parameters could serve as surrogates to assess water system contamination post-fire. The compound of interest, benzene, was chosen for its frequent detection in water distribution systems following wildfires, often above either federal (5 µg/L) or California (1 µg/L) MCLs. Thus, all samples where benzene was detected were plotted against their corresponding TOC (Figure 1c) or SUVA values (Figure 1f). A moderate linear correlation was estimated between benzene and TOC (Figure 1c), and a poor linear correlation was estimated between benzene and SUVA (0.41 and 0.11, respectively) (Figure 1f). The poor fit was partly because many samples contained high benzene concentrations that exceeded federal or CA MCLs, while imparting relatively low amounts of carbon. The lack of a strong correlation was unsurprising as organic compounds may not be proportionally created during thermal degradation especially when considering different plastic materials. Compound partitioning can vary widely because of chemical characteristics whereas differing plastic material properties can effect compound diffusion (Whelton et al., 2010). Additionally, such factors need to be weighed against the fact that organic compounds can also leach directly from new, undamaged plastic pipes, at levels that can vary with pipe age and brand (Cao et al., 2020; Isaacson et al., 2024).

To better assess the impact of material properties on the correlations, data from the PEX-a pipe was subsequently excluded because this plastic type served somewhat as an outlier, given its lower density and crystallinity compared to the other materials (Table S3). The removal caused the

Pearson's coefficient between TOC and benzene to increase to 0.76 (Figure 1c), indicating a stronger but not excellent correlation, whereas there was a minimal change in the SUVA correlation (Figure 1f). Again, such limited correlations demonstrate the complexity inherent in predicting water contamination when using different plastic types of varied material properties, an issue further exacerbated by over 70 PEX brands being approved for potable water use (Cao et al., 2020). Using bulk parameters can be further complicated in practice as TOC levels in water distribution systems can vary with season, water temperature, and sampling locations (Salehi et al., 2020). Further, water main repairs and source water changes, common following wildfires, can lead to transient spikes in carbon content (Gauthier et al., 1999; Besner et al., 2008; Chen et al.. 2020). Ultimately, these results indicate that TOC and UV_{254} are poor surrogates for contaminant formation and do not indicate health risks present in a plastic damaged water distribution system after a wildfire.

3.2 Effect of Temperature

Exposure temperature impacted the mass leached of all compounds from all plastic types (Figures 2 and S7). At each exposure temperature, compound leaching data was initially obtained as a function of flushing time (examples provided for benzene (Figure 2a) and phenol for PEX-a (Figure 2c)) but also integrated using trapezoidal estimation to assess the total mass released throughout the full flushing period. The total mass released was compared against: (1) different compounds for an individual plastic type (Figures 2b and S7) or (2) in one case, different plastic types for one compound, phenol (Figure 2d). Total mass integration accounted for the different leaching trends observed during flushing, which will be discussed in more detail later. Overall, results show that the total mass leached increased as the exposure temperature increased for all compounds, a trend that has been observed previously (Isaacson et al., 2021; Metz et al., 2023).

At the starting point of 21 °C (the no heating controls), compound concentrations were typically below the MDL, with a few exceptions for PEX-a. This result was expected since prior studies show that organic compounds leach from untreated pipes and was confirmed by measuring the TOC leaching after flushing from our controls (Figure S8) (Whelton and Nguyen, 2013).

Over the full temperature range, comparisons in total mass leached between different compounds and plastic types remained consistent with the results observed at 285 °C (Figure 1). Benzene, phenol, and *p*-chlorocresol dominated in mass leached for PEX-a, while *p*-cresol and *p*-chlorocresol dominated in mass leached for HDPE and HDPE resin. PEX-a similarly leached higher mass totals for most of the compounds tested and consequently started leaching compounds at lower exposure temperatures than the other materials. For example, phenol leached from PEX-a at the 100 °C exposure temperature but was not detected to leach from other materials until 150 °C (Figure 2b and Figure S7).

One critical finding suggests that, while the effect of temperature was relatively small from 0 °C up to 200 °C, a greater impact was observed between 200 °C and 285 °C where the mass of compounds leached from some materials increased by up to two orders of magnitude. The increase also directly resulted in an increase in the total number of compounds detected in the leachate from all materials. To further evaluate the increase, PEX-a was thermally degraded at an additional temperature (250 °C). Predictably, the mass leached of all contaminants increased at the 250 °C exposure temperature; however, the increase was modest relative to the 285 °C exposure condition. One important consideration is that the heating time varied between exposure temperature, with the higher temperatures taking longer to reach (Figure S4). For example, heating the vessel to 250 °C took 64 min and to 285 °C took 124 min. This substantial non-linear increase in total exposure time when trying to achieve higher set temperatures likely impacted the non-linear increase in total mass generated of the measured compounds.

Despite the non-linearity, increasing compound leaching with higher temperatures was likely due to a combination of factors, including an increase in the degradation of both the polymer chain and various additives in the plastics. When exposed to elevated temperatures, polymer chains undergo chain scission producing alkene fragments of varying lengths, which can then undergo cyclization and aromatization reactions resulting in various MAHs and PAHs (Ueno et al., 2010; Zhang et al., 2020; Song et al., 2022). Increased exposure temperature produces additional alkene fragments that may undergo the aforementioned reactions. Similarly, the materials' various additives may degrade more rapidly at increased temperatures as well. For example, antioxidants are added to plastics to react with free radicals or hydroperoxides produced during polymer oxidation and are also vulnerable to thermal degradation at relatively low temperatures. Irgafos 168® and Irganox 1010®, two commonly used antioxidants in plastic pipe manufacturing, have onset degradation temperatures of 180 °C and 270 °C, respectively, indicating that their thermal degradation may also contribute to the detected contaminants (Nare and Hlangothi, 2019).

Along with degrading the plastics to a higher degree, the increased temperature may also increase the physical partitioning of the contaminants from the plastics into the liquid phase. The physical partitioning is affected because as the temperature increases, intermolecular forces holding the polymer chains together decrease, resulting in enhanced organic compound diffusion through polyethylene (Xiao et al., 1997). Further, increased temperatures alter the properties of water, resulting in density decreases, thereby increasing the permeability within polyethylene (Keller and Kouzes, 2017). At temperatures above 100 °C, the dielectric constant and relative polarity of water also decrease, potentially allowing for the non-polar contaminants, such as

BTEX, to be more readily extracted from the materials (Cheng et al., 2021). Increasing diffusion rate and water permeation and, conversely, decreasing water polarity, could potentially enable contaminants to partition from the plastics more readily at higher temperatures.

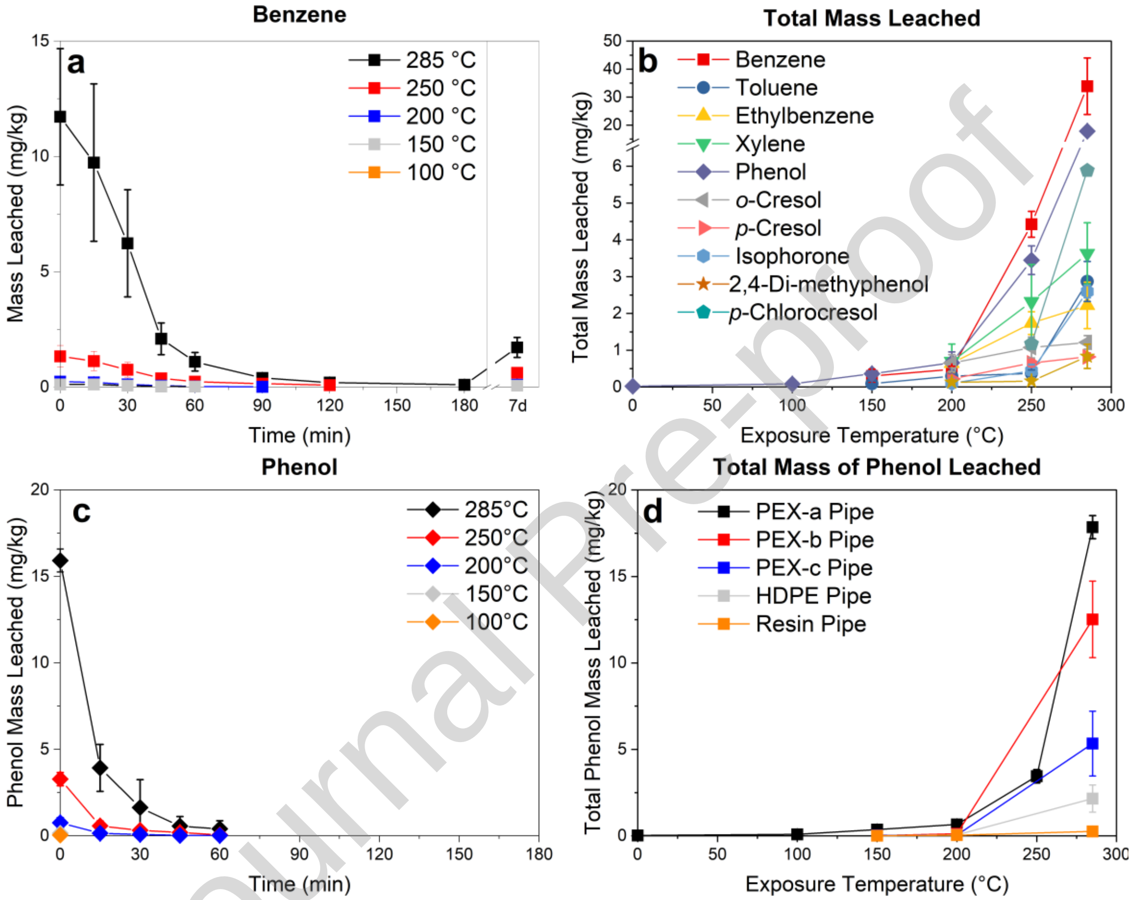

Figure 2. Mean mass of (a) benzene and (c) phenol in the effluent over 180 min of flushing following thermal degradation of the PEX-a pipe at 285 °C (black), 250 °C (red), 200 °C (blue), 150 °C (grey), and 100 °C (orange). The total mass leached throughout flushing for each exposure temperature was estimated (b) for all compounds leaching from the PEX-a pipe and (d) phenol leaching from all plastics. Error bars represent one standard deviation (n=3).

3.3 Factors Influencing Flushing Efficacy

The efficacy of flushing was evaluated by applying three different mass balance equations around compound flushing profiles obtained following thermal degradation of all materials at 285 °C (Figure 3 and Figures S9-S13). Three different mass balance equations were applied to account for compound mass transfer between different phases (air, water and plastic) to obtain better modeling fits when needed. At the outset, a mass balance was applied solely around the liquid phase of the CSTR, while ignoring mass transport from the air and plastic phases. Two distinct patterns emerged in how the model fit the data that were unique to specific compound types but that remained consistent among all plastic materials tested. Figure 3 provides an example of the two distinct patterns. First, the liquid mass balance clearly underpredicted the mass of compound leached throughout flushing. Underprediction is exemplified by the benzene flushing profile, but also for other compounds similar in structure and physical and chemical properties, including toluene, xylene, and ethylbenzene (i.e. BTEX). Conversely, for the second pattern, the liquid mass balance well predicted the mass of compound leached through flushing. The strong fit is exemplified by the phenol flushing profile but also for other phenolic compounds and the cyclic ketone, similar in structure and physical and chemical properties (Figure S9-13). These results indicate that the entire mass of phenol and other similar compounds were solely present in the liquid phase when flushing began, whereas the poor fit for BTEX indicates that there is likely an additional mass input from the air and/or plastic phases into the liquid during flushing.

To prove this latter hypothesis, the mass balance was expanded to include both the liquid and air phases. This expanded mass balance slightly improved the model fit with the experimental data for benzene and only marginally improved the model fit for toluene, xylene, and ethylbenzene. This was expected as BTEX are volatile compounds and likely partitioned to the air above the water in the reaction vessel during thermal degradation and partitioned back into the aqueous phase as the reactor cooled. However, the mass balance around the air and liquid still underestimated the aqueous BTEX concentrations by 56-83%, indicating that the plastic phase likely released a significant amount of mass as well. Impact on the phenolic compounds and cyclic ketone were less pronounced as they have lower Henry's Law coefficients (Table S2), meaning their likelihood of partitioning to the air phase is lower.

Lastly, the mass balance was expanded to include all three phases in the CSTR which either vastly improved or had little to no impact on how the model fit the experimental data. The model vastly improved for BTEX for all plastic types, even though differences in reported K_{pw} values at elevated temperatures (Table S2) resulted in a range of modeled concentrations (see blue shaded regions). This result implied that a portion of BTEX remained within the plastic at the beginning of the flushing period, as supported by their relatively high K_{pw} values (Table S2), but slowly leached from the plastic into the aqueous phase as the system was flushed. Interestingly, the BTEX concentrations observed between the first and second sampling point was often equal or in some cases larger at the second time point for all materials (Figure 3, Figures S9-S13). This could be attributed to a variety of factors, including a lag in diffusion from the air or plastic phases, and could be a phenomenon worth investigating further in future studies. However, the overall effect on the modeled BTEX results is relatively minor given the wide range of K_{pw} values reported in the literature. The addition of the plastic phase to the mass balance had little to no impact on the modeled leaching for the remaining compounds (excluding isophorone and *p*-chlorocresol, which could not be modeled since no K_{pw} values were found in existing literature) for all plastic types. This effect was likely due to the relatively low K_{pw} values of these other compounds, as compared to BTEX, enabling them to immediately partition into water rather than remain within the plastic at the start of flushing. Thus, these other compounds were sufficiently modeled by the aqueous phase alone.

The wide range of modeled BTEX concentrations (i.e. the blue shaded regions) emphasizes the importance that material properties such as crystallinity and density have on contaminant leaching (Jones and Rowe, 2016). These differences can have significant implications when considering post-fire response decisions. For example, the predicted concentration of benzene in the effluent at the end of flushing the PEX-a pipe ranged between 0.64 and 50.2 µg/L, the latter of which exceeds the federal MCL for benzene. This large difference emphasizes the complexity in disaster response and recovery situations, as some water distribution system assets may be readily decontaminated, while other, seemingly similar materials may take substantially longer.

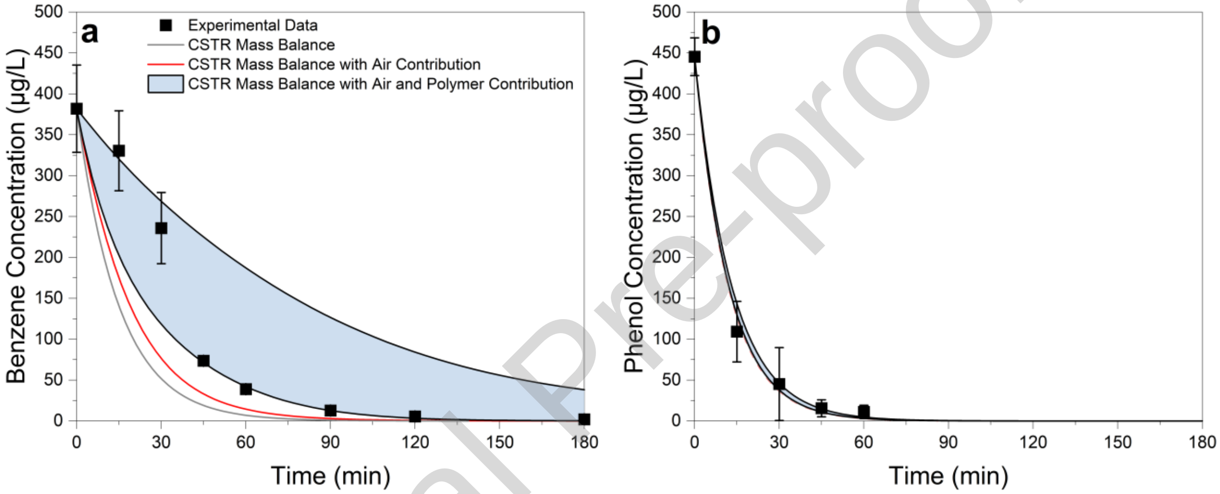

Figure 3. The results of three mass balance models applied to the average concentration of (a) benzene and (b) phenol leached from PEX-a pipe after thermal degradation at 285 °C. The blue shaded region is the mass balance around all three phases incorporating a range of K_{pw} values.

3.4 Exhumed Materials Testing

To directly assess how contaminant leaching in controlled experiments compared against real field samples, materials directly exhumed from wildfire impacted drinking water systems were evaluated for compound leaching using stagnation tests. A mixture of 12 VOCs and SVOCs were found to leach from the exhumed plastic pipes into water (Figure 4). The exhumed materials leached many of the same compounds as the plastics degraded under laboratory conditions including BTEX, phenol, *o*-cresol, and *p*-cresol. Three PAHs, naphthalene, fluorene, and anthracene were detected in the leachate of the exhumed polyethylene pipes at relatively low concentrations (1.2-23.2 µg/L), whereas no PAHs were detected in laboratory degraded plastics.

This difference could be due to exposure temperature or duration as wildfires may reach temperature in excess of 800 °C, and PAH formation is enhanced at increased temperatures (Font et al., 2004). All compounds detected in the leachate have EPA MCLs and/or health advisory limits except for *o*-cresol and *p*-cresol (USEPA 2018). It's important to note, that while cresols may not have published limits, both are considered acutely toxic and classified as "possible carcinogens" by the US Department of Health and Human Services (ATSDR, 2008). Benzene was the only contaminant detected in the leachate that exceeded published limits, which occurred in all four plastic materials.

Direct comparisons between exhumed plastic drinking water pipes are difficult to make, as they were collected from different water systems and may have undergone dissimilar thermal exposures. Further, contact with contaminated air or water during or after wildfires may also impact the results as it is well established that some plastics, such as polyethylene, are readily permeated by organic compounds in both the aqueous and air phases (Mao et al., 2015; Huang et al., 2017). However, material testing revealed that one of the plastic pipes was PVC, and unplasticized PVC has been found to be resistant to organic compound permeation, except at very high concentrations, indicating that the organic contaminants leached from the PVC pipe were likely from its thermal degradation (Mao et al., 2011). This is a noteworthy discovery, as it further implies that the thermal degradation of plastics is a contributing factor to water system contamination post-wildfire. As expected, the five copper pipes were not found to leach any contaminants as copper is resistant to organic permeation and any VOCs that may have sorbed to the surface would have likely volatilized prior to analysis.

Several PAHs were also detected in the leachate of a damaged water meter (Figure 4). One SVOCs detected, anthracene, has a USEPA health advisory limit, however the leached concentrations were below that limits. The water meter was primarily made of copper, so these PAHs may have originated from debris, such as ash or particles generated during combustion. Wildfire ash has been found to contain a range of PAHs and may have been sucked into the water meter if the distribution systems was depressurized (Harper et al., 2019). Alternatively, the turbine in the water meter was made of plastic, which may have been thermally degraded, and acted as a source of contaminants. Four additional water meters were tested from inside a burn zone, had no visible damage, and no organic compound leaching above MDLs was detected.

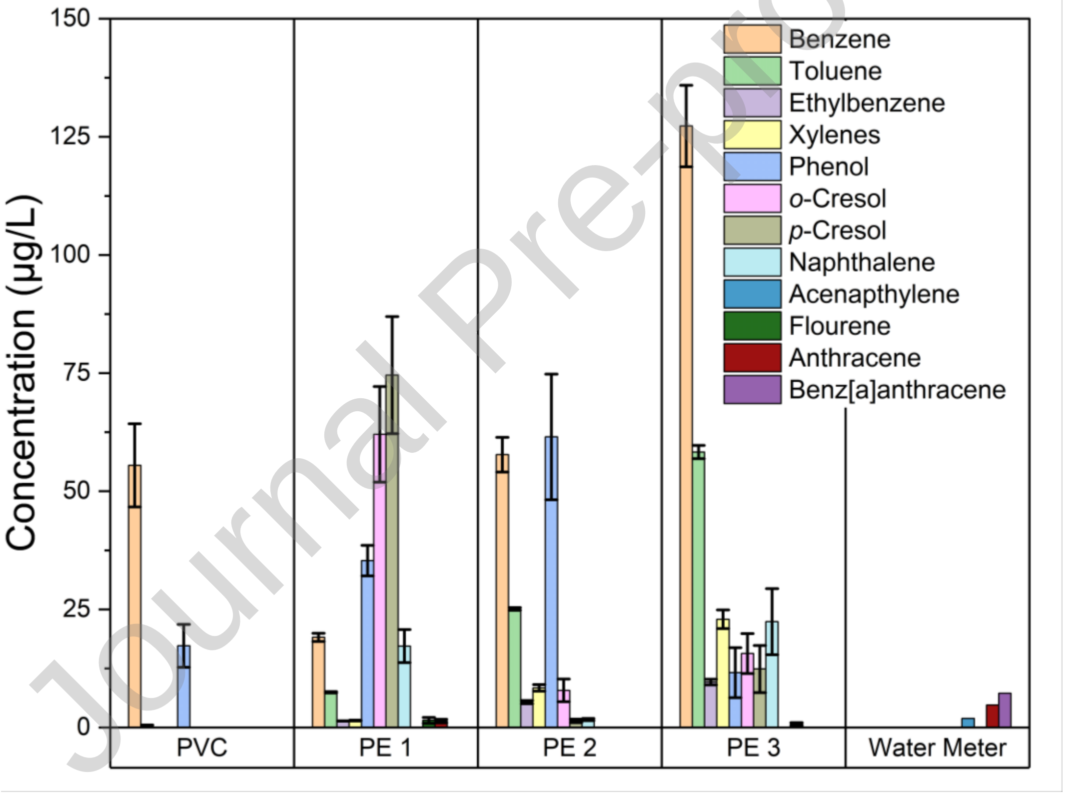

Figure 4. The mean aqueous concentration leached from four exhumed plastic pipes and one damaged water meter. Error bars represent one standard deviation (n=3).

4. Conclusions

This study focused on evaluating the leaching potential of commercial plastic drinking water pipes following thermal degradation in the presence of water. Thermally degraded plastics may be a source of observed post-fire contaminations, as up to ten compounds were leached from the materials including BTEX, five phenolic compounds, and one cyclic ketone. All compounds found were previously detected in drinking water systems following a wildfire. Importantly, the compounds detected do not describe the totality of mass leached from the plastics, as most leached carbon remains unidentified. Material type impacted leaching, with the PEX-a pipe leaching a larger mass of 8 of the 10 compounds, which could potentially be attributed to differences in plastic formulation and material properties. This is an important consideration as water distribution systems contain various plastic types, and in-service pipes undergo degradation and antioxidant loss and may be coated with scale, which could impact vulnerability to thermal degradation (Viebke and Gedde, 1997; Dear and Mason, 2001; Whelton and Dietrich, 2009). Further, commercial plastics contain various additives, which have been found to leach into water under normal use conditions (Denberg et al., 2009; Thörnblom et al., 2011). Future work should consider these additive's impact on thermal degradation of polyethylene and subsequent aqueous leaching.

Exposure temperature impacted the aqueous leaching, with increasing temperature corresponding to increasing in the number and mass of compounds leached. At 150 °C, all plastics generated and leached compounds, including benzene which is lower than its previously reported threshold of 190 °C (Isaacson et al., 2021; Draper et al., 2022; Metz et al., 2023). Seven of the contaminants leached from the laboratory-degraded plastics also leached from the plastic pipes exhumed from wildfire-impacted water systems. These results further support the hypothesis that plastics are a potential primary source of contaminants detected in water systems post-fire. Several PAHs leached into water from the exhumed materials, including a water meter composed primarily of copper. Copper itself wouldn't leach organic PAHs, however, they may originate from either degradation to plastic components in the water metered (i.e. turbine) or due to contaminated ash or debris that entered the water system due to depressurization. Regardless of the source, this discovery warrants a need for SVOC testing of drinking water following wildfires.

Following wildfires, the recovery actions of water utilities depend on whether their assets can be sufficiently decontaminated. In some instances, it has taken over one year to remove fire-related VOCs from water distribution systems (Proctor et al., 2020). In this study, exhumed assets within wildfire impacted systems were confirmed to pose a contamination risk, and flushing was confirmed to remove some contaminants from damaged plastics. Here, the validated model equation found that relatively hydrophilic compounds, such as phenol, are readily removed from the polyethylene plastic pipes during flushing whereas hydrophobic compounds, such as BTEX, continue to leach into the water over a longer period of time due to their slow desorption from the plastic material. Further, a rebound in benzene leaching was observed at all exposure temperatures following stagnant conditions after flushing. The leached benzene concentration in the stagnant water from all materials increased by at least one order of magnitude relative to the concentration at the end of flushing. The results emphasize the importance of implementing stagnation testing in post-wildfire drinking water testing.

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Author Contribution

Kristofer P. Isaacson: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Validation, Visualization, Writing-original draft, Writing-review and editing. **Akshat Verma:** Methodology, Data Curation, Writing-review and editing. **Andrew J. Whelton:** Conceptualization, Funding acquisition, Investigation, Project administration, Resources, Supervision, Writing-review and editing. **Jeffrey P. Youngblood**: Supervision, Writing-review and editing. **Amisha D. Shah**: Conceptualization, Data curation, Funding acquisition, Investigation, Writing-original draft, Writing-review and editing, Supervision, Resources.

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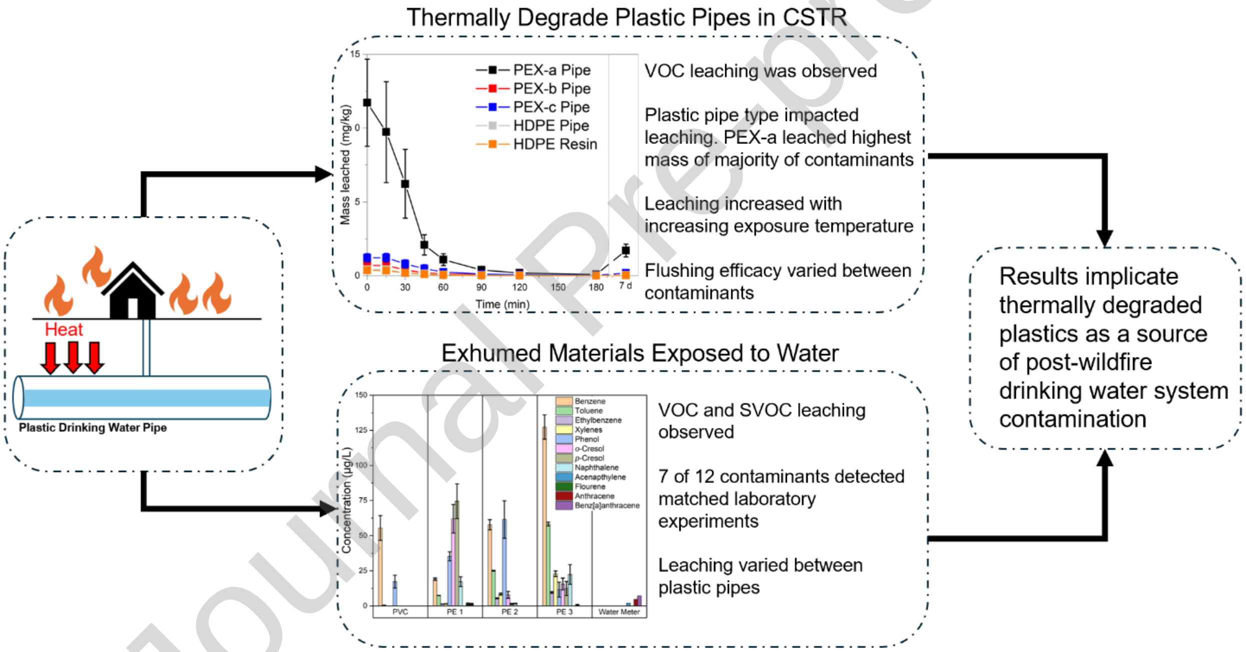
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Environmental Implication:

Following wildfires, drinking water systems in impacted communities are often chemically contaminated. Uncertainty about the magnitude and source of these contaminants has hindered community recovery. In this work, plastic drinking water pipes were thermally degraded in the presence of water to determine if plastic drinking water infrastructure may be a source of the observed contaminants. Further, the aqueous leaching from drinking water materials exhumed from wildfire impacted systems was also evaluated. Both volatile and semi-volatile organic compounds were found to leach from tested materials. The results of this work will inform post-wildfire recovery actions taken by water utilities.



For Table of Contents Only

Highlights:

- New commercial drinking water pipes were thermally degraded in presence of water.
- Thermally damaged plastics leached a variety of organic compounds, including benzene.
- Exhumed materials from wildfire impacted water systems leached VOCs and SVOCs.
- Chemical characteristics impacted the rate of leaching during flushing
- Post-flushing stagnation testing resulted in additional benzene leaching