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Fire and Water: Assessing Drinking Water Contamination After a Major Wildfire

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Abstract

We investigated patterns of volatile organic compound (VOC) contamination in drinking water systems affected by the California 2018 Camp Fire. We performed spatial analysis of over 5,000 water samples collected over a 17 month period by a local water utility; sampled tap water for VOCs in approximately 10% (N=136) of standing homes, and conducted additional non-targeted chemical analysis of 10 samples. Benzene contamination was present in 29% of service connections to destroyed structures, and 2% of service connections to standing homes. A spatial pattern was apparent. Tap water in standing homes eleven months after the fire contained low concentrations of benzene in 1% of samples, but methylene chloride was present in 19% of samples, including several above regulatory limits. Elevated methylene chloride was associated with greater distance from the water meter to the tap, longer stagnation time, and presence of a destroyed structure on the service connection; it was inversely associated with certain trihalomethanes. Non-targeted analysis identified multiple combustion byproducts in the water at 2/10 homes. Our findings support the hypothesis that pyrolysis and smoke intrusion from depressurization contributed to the benzene contamination. Further research is needed to test the hypothesis that methylene chloride may be generated from dehalogenation of disinfection byproducts stagnating in galvanized iron pipes.

Keywords: Wildfire, benzene, methylene chloride, volatile organic compounds (VOCs), drinking water, non-targeted analysis, California

Synopsis: Drinking water systems in wildfire-damaged areas may be contaminated with benzene and other volatile organic compounds, requiring prevention and rapid response to protect the health of returning residents.

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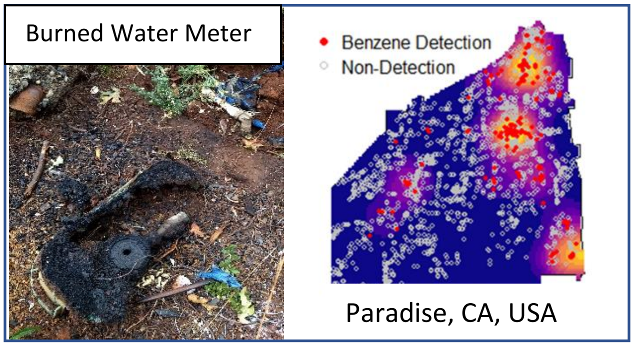


Burned Water Meter
Benzene Detection
Non-Detection
Paradise, CA, USA

Introduction

Massive wildfires tore through towns in California in recent years. The magnitude and destruction from these fires is unprecedented, with loss of life and property, air quality impacts lasting weeks, large-scale generation of hazardous and municipal waste, and disruption of the social fabric. A new and unanticipated problem arose after recent California fires: Contamination of drinking water systems by volatile organic compounds (VOCs). Benzene and other VOC contamination in tap water was first reported after the Tubbs Fire in Santa Rosa, California in 2017.[1] The water contamination in Santa Rosa affected mostly vacant lots, and only 13 standing homes. In contrast, after the Camp Fire in November 2018 approximately 1,700 homes were still standing in the burn zone.

The Camp Fire destroyed about 14,000 homes; at least 86 people lost their lives when the towns of Paradise, Concow, and Magalia burned over a period of a few hours. Although the water treatment facilities and pumps continued to operate during the fire, there was a loss of system pressure in most areas due to large outflows of water from firefighting activities and broken pipes. In the weeks after the fire, the California Division of Drinking Water and local water utilities tested for VOCs, based on the experience in Santa Rosa. The agencies found no VOCs in the source water or at the treatment plant, but detected benzene and other VOCs in numerous samples from water mains, hydrants and service connections. Many of the benzene detections exceeded regulatory levels. The Paradise Irrigation District (PID) issued a “Do Not Drink/Do Not Boil” water advisory that was not lifted for standing homes until May, 2020.[2,3]

Two water utilities were affected by the Camp Fire: PID and the Del Oro Water Company (DOWC) (Figure 1). Drinking water in the Town of Paradise is supplied by PID from a reservoir and treatment plant just north of the town. Smaller surrounding areas are supplied by non-contiguous districts of DOWC, with Paradise Pines and Magalia on groundwater systems to the north, Lime Saddle on surface water to the south, and Buzztail on a groundwater well to the west. A small number of homes that survived the Camp Fire had private wells.

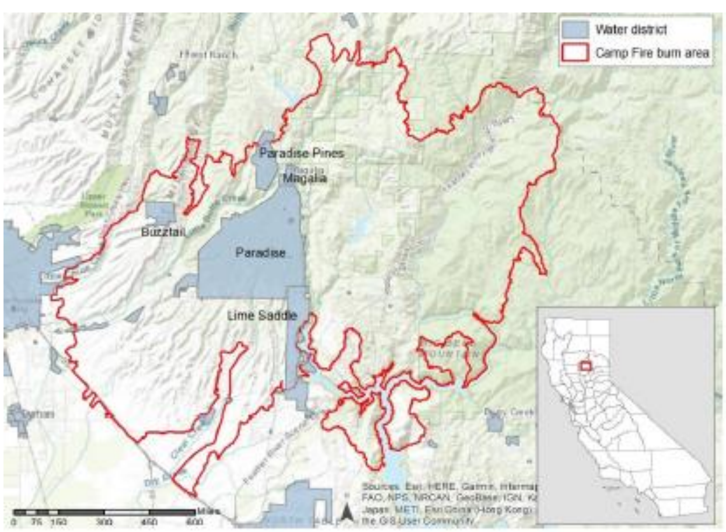


Figure 1. Camp Fire burn area and drinking water systems around Paradise, California. The fire burn area is outlined in red and the water system service areas are shown in blue. (Created by C.C. from the following data: [4,5,6])

Prior research has reported water contamination after fires from heavy metals, per- and poly- fluoro-alkyl substances (PFASs) and microbes.[7,8,9] VOC contamination after fires is a newly identified issue.[10] The absence of VOCs at the sources and treatment plants of all affected water systems made it clear that the contaminants were being introduced within the distribution system. A recent analysis suggests that burn severity, as measured by density of damaged structures, is correlated with the probability of VOC contamination exceeding maximum contaminant levels (MCLs).[11] Our project was designed to test for VOCs and conduct non-targeted testing at the tap in standing homes after the Camp Fire in order to characterize potential risk to inhabitants and sources of contaminants. We also analyzed patterns of contamination within the PID system to aid in the interpretation of our tap water findings.

Methods

Analysis of Paradise Irrigation District Data

To provide background and context for tap water testing, we analyzed VOC testing data from the Paradise Irrigation District. We did not do a full analysis of data from the Del Oro Water Company because our tap water testing did not identify VOCs other than disinfection byproducts in homes in that system, and because there was far less data and fewer detections from that system.

PID tested most of its water system starting in December of 2018 and published water quality testing results over a period of nearly 18 months (https://pidwater.com/recovery). Contaminant concentration, compliance status, date, and sampling location were reported for each sample. For service line samples, PID reported whether the service line was connected to a vacant lot, standing structure, or destroyed structure. Water quality advisories for each service connection were lifted once the test results met California standards.

We obtained a downloadable data file from PID of all sampling results over a 17 month period from December 2018 through May 2020. We analyzed the results to explore the VOC concentrations and the extent of contamination over time and across the PID service area. Due to the relatively high detection frequency and concentrations of benzene and methylene chloride (MeCl; also known as dichloromethane), the analysis focused on these chemicals. For locations that were sampled multiple times, the maximum detected levels were used (almost always the first sample for that location). Geographic Information Systems (GIS) mapping and spatial analysis of the service line sample locations were conducted to identify any trends that could further explain possible contamination sources. Sample locations with benzene or MeCl detections were compared to locations without these detections to examine potential differences in spatial intensity using a kernel-based estimator approach[12] and differences in clustering using the K-function.[13] [14]

Tap Water Sampling

The tap water sampling strategy aimed to collect samples from 10% of the approximately 1,700 homes still standing within the burn zone of the Camp Fire. Because both PID and DOWC reported some benzene detections after the fire, all standing homes in the burn zone served by either water utility were eligible. Homes on private wells were excluded. Our study was reviewed and approved by the Institutional Review Board of the Public Health Institute (IRB# I19-020).

We invited people with standing homes in the fire zone to sign up for the study at a community meeting in September 2019 that was attended by over 100 local residents. We also posted flyers at local businesses, conducted outreach through social media, and email outreach by local organizations, with email and a phone number to sign up for the study. Stories in the local newspaper about the study also encouraged residents to participate. Additional recruitment was done by word-of-mouth and door-to-door in the community. All potential participants that met the inclusion criteria were screened to ensure they were served by water from one of the utilities. Homes that had private water tanks with trucked-in water were excluded, as were homes with point-of-entry multi-step filtration systems. Homes with point-of-use carbon filtration were eligible for inclusion because of the potential for saturation. Participants were instructed not to use their kitchen tap for a minimum of 12 hours prior to sample collection.

Sampling teams visited 136 homes in October or November of 2019 to obtain written participant informed consent, administer a questionnaire and collect tap water samples for analysis using EPA Method 524.2, the same VOC analytic method used by PID. Study personnel also collected information about the type of residential structure; the age of the home; whether the home was occupied; types of water pipes; distance from the service connection to the home; degree of fire damage of the home, yard, water meter, and outbuildings; and duration of water stagnation prior to sample collection. Details of the sample collection and analysis are provided in the Supplemental Information.

Due to the relatively high detection frequency and concentrations of MeCl, the analysis of the tap water sampling data focused on this chemical. Cross tabulations of observed household factors with detections and concentrations of MeCl were constructed, and p-values from the chi-square were calculated to assess statistical significance. The MeCl concentrations were highly skewed and log transformations failed to normalize the data distribution (Wilk-Shapiro p-value > 0.20). Therefore, non-parametric ANOVA was used to evaluate whether the median MeCl concentrations differed by potential predictive factors, using the Kruskall-Wallis statistic to assess statistical significance. For these analyses, samples that were below the practical quantitation limit (PQL) were assigned a value equal to the PQL/square root of two. Although we explored the use of multivariable regression models to simultaneously evaluate potential predictors of MeCl detections and concentrations, the high degree of correlation between factors and the relatively small number of MeCl observations precluded our ability to construct models with stable estimates.

Non-targeted Analysis

We sampled tap water at a subset of 10 homes for a larger number of potential contaminants. Five homes selected for non-targeted testing in October were vacant, and the owner reported minimal or no water use since the fire. Five additional homes were selected in November for follow-up non-targeted testing because benzene or MeCl was detected on initial sampling in October. Details of the non-targeted analysis methods are provided in the Supplemental Information.

Results

Water System Sampling

Within the PID service area, approximately 9,800 of 11,000 service connections were destroyed in the fire. Between December 27, 2018 and May 26, 2020, PID conducted 5,056 tests at over 2,000 locations. They collected 2,391 samples in main lines, 2,217 samples in service lines, and 448 appurtenance samples from hydrants, wharf heads, and blow-offs. The most frequently detected VOCs were trihalomethanes including chloroform and bromodichloromethane, benzene, MeCl, and xylenes. 326

samples were out of compliance, with one or more VOCs – generally benzene or MeCl – detected above the MCL.

About 6% of samples collected by PID detected benzene with a median concentration of 2.3 µg/L and a maximum of 923 µg/L. The distributions of benzene and MeCl are summarized in Table 1 and Table 2 respectively. Benzene median concentrations were 2.4 µg/L in main lines and 2.2 µg/L in hydrants (i.e., appurtenance). The median concentration of benzene in service line samples from destroyed structures was 2.4 µg/L, compared to 1.2 µg/L in service line samples from standing structures. A majority of benzene detections (74%) were found in service lines, as well as about 70% of detections exceeding the MCL. Service line samples collected at destroyed structures had a much higher proportion of benzene detections above the MCL (21%) compared to samples collected at standing structures (1%) (Table 1). The distribution of service line samples also showed a higher proportion of benzene detections above the MCL during the first 6 months of sampling (Figure 2).

Table 1. Distribution of Benzene in Paradise Irrigation District Water Samples Collected December 2018-May 2020 (N=5056).

Samples		**Detections**			**Concentration (µg/L)**				
Type	**N**	**N**	**%**	**Over MCL (1 µg/L) %**	**Mean**	**Std Dev**	**Median**	**Min**	**Max**
Main line	2391	45	2%	1%	4.25	5.27	2.4	0.6	27
Appurtenance	448	32	7%	6%	5.61	7.41	2.2	0.5	29.7
Service line: standing structure	1569	35	2%	1%	8.58	19.23	1.2	0.5	93
Service line: destroyed structure	622	183	29%	21%	26.44	94.36	2.4	0.5	923
All	5056*	295	6%	4%	18.97	75.26	2.3	0.5	923

*Samples from service lines connected to vacant land or with unknown structure status did not have benzene detections and were excluded (N=26).

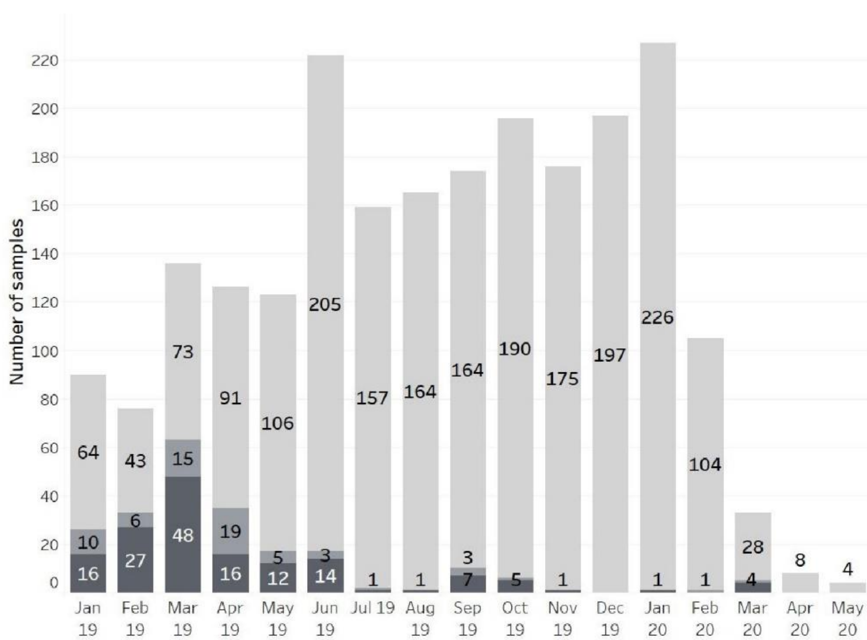
MeCl was reported in 328 samples (6%) at a median concentration of 3.2 µg/L (Maximum = 34 µg/L) (Table 2). About 81% of these detections (n=267) were in service lines to homes, with 117 above the MCL (5%). 198 of the total detections (176 from service lines) were flagged by PID as questionable because they were collected using a galvanized steel riser attached to the service connection. PID hypothesized that MeCl might be formed as the water passed through the sampling riser, due to the potential reaction of disinfection byproducts in the water with zinc or iron in the galvanized riser. Excluding the questionable detections, there were 29 MeCl detections in main lines with 2 over the MCL; and 91 MeCl detections in service lines with 24 over the MCL. MeCl was detected in 13 field blanks, 1 trip blank and 5 equipment blanks at generally low concentrations with no MCL exceedances.

Table 2. Distribution of MeCl in Paradise Irrigation District Water Samples Collected December 2018-May 2020 (N=5056).

Samples		Detections N (%)		Over MCL (5 µg/L) %		Flagged samples excluded*			
Type	N	All samples	Flagged samples excluded*	All samples	Flagged samples excluded*	Mean	Median	Max	SD
Main line	2391	47 (2%)	29 (1%)	6 (0.3%)	2 (0.08%)	2.97	1.2	28.1	5.55
Appurtenance	448	14 (3%)	10 (2%)	1 (0.2%)	0	1.38	1.11	2.4	0.81
Service line: standing structure	1569	167 (11%)	41 (3%)	68 (4%)	6 (0.4%)	3.53	1.8	26	5.1
Service line: destroyed structure	622	96 (15%)	48 (8%)	47 (8%)	18 (3%)	6.22	2.35	34	8.03
Service line: unknown structure status	25	4 (16%)	2 (8%)	2 (8%)	0	1.62	1.62	2.6	1.39
All	5056	328 (6%)	130 (3%)	124 (2%)	26 (0.5%)	3.80	1.5	34	6.08

*A total of 198 samples collected by PID in June 2019 were flagged for possible contamination because they were collected using a galvanized steel riser.

Figure 2: Benzene detections in service lines in the PID service area by sampling date (December 2018 – May 2020). Sample results displayed by status from lightest to darkest grey: no benzene detection (ND), benzene detected under the maximum contaminant level (MCL), and benzene detected above the MCL.



Overall, service line samples collected at destroyed structures had twice the rate of MeCl detections above the MCL (8%) compared to samples collected at standing structures (4%), and the median concentration of MeCl in samples from destroyed structures was 2.35 µg/L compared to 1.8 µg/L from standing structures. The pipe material for service lines was not a significant predictor for MeCl detection levels in this sample (p = 0.43, and p=0.11 with flagged samples excluded), although pipe material was not reported for many samples. Unlike with benzene, the MeCl detections and MCL exceedances did not decline over time (data not shown).

Over the sampling period, MeCl was detected at 260 service line locations (92 locations with exclusions), benzene was detected at 170 locations, and benzene and MeCl were both detected at 37 locations. Service line locations where benzene was detected above the MCL were more likely to also contain MeCl at detectable concentrations, compared to service lines where benzene was not detected above the MCL (25% vs. 12%, p <0.01). When samples collected through galvanized risers were excluded, the association between benzene and MeCl detections remained significant overall (15% vs 4%, p<0.01), and for service lines to standing structures (42% vs 11%, p<0.01), but not for service lines to destroyed structures (22% vs 17%, p=0.2).

Maps of the MeCl detections showed no clear spatial pattern in detections, MCL exceedances, or apparent association with destroyed structures compared to standing structures (data not shown). However, benzene contamination in service lines was significantly clustered in certain areas of PID's distribution system. A spatial comparison of locations where benzene was analyzed showed a higher intensity of benzene detections in the eastern sections of the town, especially the north-east and south-east corners of the service area (Figure S1). The areas where the number of benzene detections was higher than expected were compared to gas station locations, but no spatial association was observed (data not shown).

Tap Water Sampling

We collected tap water samples at 136 standing homes in October and November 2019. 108 participating homes were from the PID service area (representing about 9% of standing homes in Paradise), and 28 were from DOWC service areas (representing about 6% of standing homes in those areas). 22 samples had no detected VOCs, of which half were from DOWC groundwater-supplied systems and 10 were from PID homes with private water filtration systems. Water filtration was also present in 15% of the 114 homes with at least one VOC detected.

The most commonly detected VOCs were disinfection byproducts: Total trihalomethanes (TTHMs) were detected in 80% of homes at a median concentration of 33 µg/L (maximum = 71 µg/L). The MCL for TTHMs is 80 µg/L. The most frequently detected THMs were chloroform (78%) and bromodichloromethane (71%) (Table 3). These two THMs almost always co-occurred. Chlorodibromomethane (5%) and bromoform (4%) were detected much less frequently. MCLs have not been established for individual THMs.

Table 3. Distribution of chemicals detected in tap water samples collected October-November 2019 from the Fire and Water study homes (N=136).

Chemical	Detections			Concentration (µg/L)*				
	MDL (µg/L)	N	%	Mean	Std Dev	Median	Min	Max
Bromodichloromethane	0.20	96	71%	2.74	1.04	2.80	0.26	6.80
Benzene	0.11	2	1%	0.23	0.09	0.23	0.16	0.29
Bromoform	0.46	6	4%	1.72	0.15	1.65	1.60	1.90
Chlorodibromomethane	0.22	7	5%	1.56	1.34	0.83	0.52	3.60
Chloroform	0.14	106	78%	31.66	14.68	31.00	0.14	67.00
Methylene chloride	0.21	26	19%	1.79	2.53	0.62	0.48	9.20
Methyl ethyl ketone	3.3	2	1%	34.00	7.07	34.00	29.00	39.00
Methyl tert-butyl ether	0.14	1	1%	0.67	.	0.67	0.67	0.67
Tetrahydrofuran	5.2	3	2%	1201.67	1580.21	570.00	35.00	3000.00
Trichloroethene	0.19	1	1%	0.49	.	0.49	0.49	0.49
Trihalomethanes, total	0.97	109	80%	33.47	16.20	33.00	1.20	71.00
o-Xylene	0.13	3	2%	0.36	0.06	0.39	0.30	0.40
Xylenes, total	0.47	2	1%	0.60	0	0.60	0.60	0.60

* Distribution among samples with detects

Benzene was detected in only 2 samples (1%), both within the PID service area, at concentrations well below the MCL. Both homes were re-sampled one month later (November 2019) and no benzene was detected. MeCl was detected in 26 samples (19%), at concentrations ranging from just above the PQL to 9.2 µg/L. Four samples had MeCl concentrations above the MCL of 5 µg/L. Tetrahydrofuran was detected in 3 samples (2%), and concentrations ranged as high as 3,000 µg/L. No MCL exists for tetrahydrofuran, but 2 samples were above the Michigan guideline value of 350 µg/L.[15] Other VOCs were detected only at trace concentrations in small numbers of samples. All detections of benzene, MeCl, and tetrahydrofuran were from the PID system; none of these contaminants were detected in any of the districts of the Del Oro Water Company.

We conducted additional analysis to explore the MeCl detections because these were more frequent than anticipated, and some samples had concentrations above the MCL. Cross-tabulations of MeCl detections with a number of potential factors are presented in Table 4. Homes with detectable levels of MeCl were more likely to be vacant (42% vs. 16%, $p < 0.01$), and to have longer stagnation periods (50% vs. 23% $\geq$72 hours, $p=0.04$). Regardless of stagnation time, MeCl detections were twice as likely in homes where at least one other outdoor structure on the same water service line burned than in homes where no other structure on the service line burned (62% vs. 31%, $p<0.01$). The frequency of MeCl detections was also associated with the distance between the service connection and the home such that a higher percentage of detections were found among homes situated at distances greater than 120 feet compared to those within 50 feet (35% vs. 4% , $p<0.01$).

Table 4: Methylene Chloride Detections, Stagnation Time and Pipe Composition

Characteristic	All		Methylene chloride detection: Not Detected		Methylene chloride detection: Detected		p-value[±]
	N	%	N	%	N	%	
All Homes	136	100	110	100	26	100	
Vacant Home							<0.01
Yes	29	21	18	16	11	42	
No	107	79	92	84	15	58	
Stagnation Time (hours)							0.04[§]
3-12 hours	27	20	24	22	3	12	
13-24 hours	64	47	54	49	10	38	
25-48 hours	7	5	7	6	0	0	
72+ hours	38	28	25	23	13	50	
Type of Pipes in the Home *							
Galvanized Iron	86	63	68	62	18	69	0.48
Copper	97	71	80	73	17	65	0.46
Polyvinyl chloride (PVC)	62	46	51	46	11	42	0.71
High density polyethylene (HDPE)	17	13	12	11	5	19	0.32[§]
Cross-linked polyethylene (PEX)	4	3	3	3	1	4	0.58[§]
Water Meter Distance (ft)[†]							<0.01[§]
<50 ft	32	24	31	28	1	4	
50-74 ft	34	25	24	22	10	38	
75-120 ft	30	22	28	25	2	8	
>120 ft.	33	24	24	22	9	35	
Missing/unknown	7	5	3	3	4	15	
Water Meter Distance & Type of Pipes							<0.01[§]
< 75 ft and Galvanized Iron	46	34	38	35	8	31	
< 75 ft and No Galvanized Iron	20	15	17	15	3	12	
≥ 75 ft and Galvanized Iron	36	26	29	26	7	27	
≥ 75 ft and No Galvanized Iron	27	20	23	21	4	15	
Missing/unknown	7	5	3	3	4	15	
Damage to Home							0.23
No Fire Damage	112	82	92	84	20	77	
Fire Damage	20	15	16	15	4	15	
Missing/unknown	4	3	2	2	2	8	
Number of Outdoor Structures on Service Line Burned or Damaged							<0.01[§]
None	66	49	58	53	8	31	
One or more	57	42	41	37	16	62	
Missing/unknown	13	10	11	10	2	8	

[±] Based on Pearson Chi-Square, except where noted; [§] Based on Fisher exact; * Not mutually exclusive; †Distance from house to water meter.

Although the median level of MeCl did not statistically differ between homes with and without galvanized iron pipes (median=0.75 µg/L and 0.56 µg/L, respectively; p=0.30), the homes with iron pipes had many more outliers in the high range (Figure 3). Among the homes with iron pipes, 14% had concentrations of MeCl above the measured median concentration of 0.62 µg/L, whereas no homes without iron pipes had MeCl above that level. To investigate the hypothesis that bromodichloromethane (BDCM) and chloroform may be debrominated in the presence of zinc or iron to generate MeCl, we examined the sum of BDCM and chloroform concentrations compared to MeCl concentrations in the water (Figure 4). Overall, the sum of BDCM and chloroform was inversely correlated with MeCl (r=-0.43, p=0.03). The inverse correlation was stronger when only homes with iron pipes were examined (r=-0.56, p=0.02), and was non-significant in homes without iron pipes (r=-0.32, p=0.54).

Figure 3. MeCl concentrations in tap water by (A) type of pipes and (B) stagnation time. The diamonds represent the means; open circles are outliers; upper and lower box limits are the first and third quartiles. Note: samples below the practical quantitation limit (PQL) minimum level of detection (MDL) were assigned a value equal to the PQL/square root of two; no respondents reported stagnation times between 49 and 71 hours.

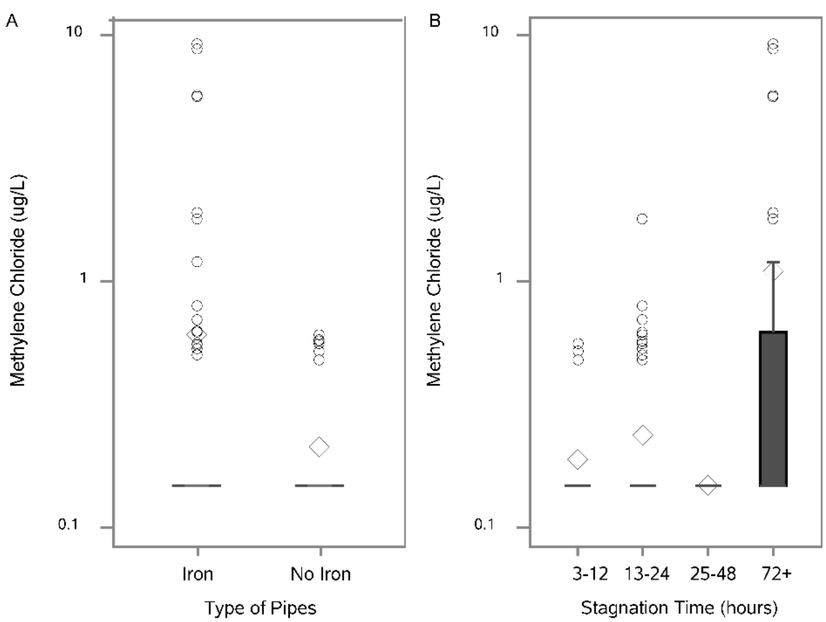
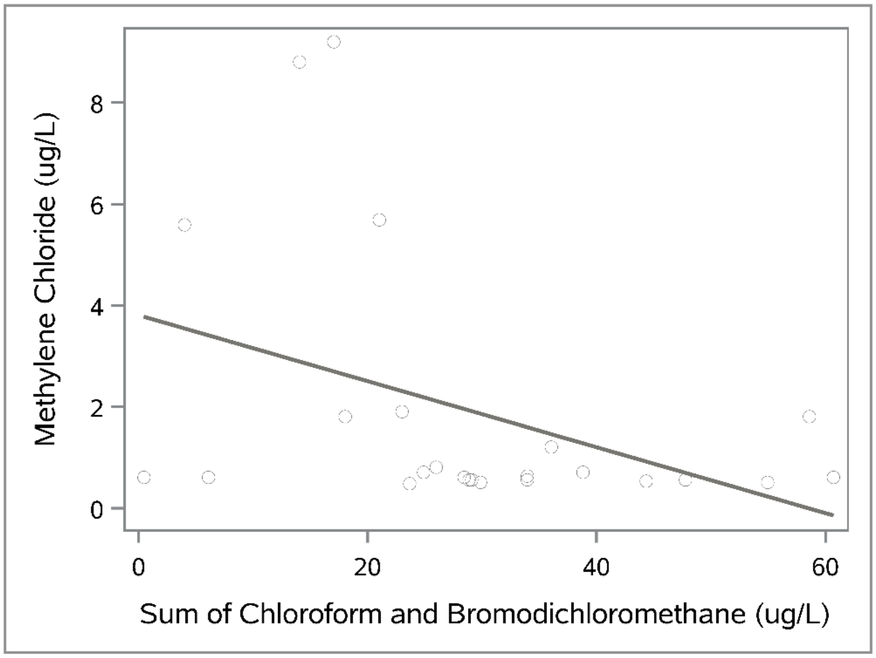


Figure 4. The relationship between methylene chloride concentration and the sum of the concentrations of chloroform and bromodichloromethane in 24 homes with detections of all three chemicals. Note: correlation coefficient = -0.43, p=0.02.



Non-targeted Analysis Results

A list of 48 target semivolatile compounds were quantified in samples from the 10 households selected for NTA to provide a quality check on the results and to perform retention index calibration for identifying non-targeted compounds. These chemicals included polycyclic aromatic hydrocarbons (PAHs), substituted benzenes, and phthalates; most (33/48) of these compounds were not detected at levels above the method detection limit (MDL) (Table S1). Concentrations of the 15 compounds that exceeded the MDL in one or more samples are reported in Table S2. The most commonly detected compounds, which included two PAHs, three substituted benzenes, a ketone and a phthalate, are also shown in Figure S2. Two homes in the PID service area (P108 and P113) had particularly elevated levels of phenol (8,490-13,650 µg/L) and methyl phenols (m- and p-cresol) (1,059-1,648 µg/L). Although these compounds do not have MCLs, phenol concentrations at both homes exceed the U.S. EPA acute health advisory level of 6,000 for a 10-kg child. One sample (P108) had 12 compounds that exceeded the MDLs, including naphthalene, fluorene, and several substituted benzene derivatives (1,2-dichlorobenzene, o-cresol, and 2-nitrophenol). Another home (P090) had an elevated level (1738 µg/L) of the widely used plasticizer benzyl butyl phthalate.

An overview of the non-targeted alignment results is presented in Table S3. The total aligned features (1914) were filtered to remove compounds that were not detected in any water samples (e.g., those only in the analytical standard) and to remove peaks that were not significantly higher than found in the blank samples or for which the average signal to noise ratio was too low. A total of 509 features met this set of filtering criteria. Tentative identifications were returned for 265 of these. Although the non-targeted method employed here is designed for semivolatile compounds rather than VOCs, there was a strong linear correlation (r=0.75) between the concentrations reported by the target VOC analyses described above and the non-targeted peak heights for bromodichloromethane, which was detected in all 10 samples (Figure S3). Good agreement was observed between the peak areas for a number of our

SVOC target compounds and the peak height of the features identified as the relevant target compound (Figure S4) despite the fact that many of the target concentrations were below the formal MDL. A number of the tentatively identified compounds present in numerous samples are readily identified as disinfection byproducts, including trihalomethanes (chlorodibromomethane), haloacetonitriles (HANs, dichloro- and trichloro-) and dichloroacetic acid methyl ester.

The non-targeted data set was further explored in two ways. First, a principal components analysis was applied. For two samples (P108 and P113), this analysis showed that their overall pattern of contaminant concentrations differentiated them from the other household samples (Figure S5). The plot also shows that the chemical signatures of these two samples observed in the non-targeted analysis are reproducible, with a high degree of overlap between the October and November sampling dates and for repeated method blanks and analytical standards. A second way to visualize these multi-dimensional results is using hierarchical cluster analysis (Figure S6). This manner of viewing the data also emphasizes the significant differences between samples P108 and P113 and the remaining household samples. These two samples had among the highest estimated stagnation times before sampling, which might allow additional time for chemical leaching from adsorbed smoke, deposited ash, or damaged piping materials.

Discussion

Contamination of drinking water systems with VOCs following large wildfires has now been documented on several occasions since the phenomenon was first reported in 2017.[10 11] Our study includes a large dataset on VOC contamination after the most destructive wildfire in California history, the 2018 Camp Fire. Our analysis includes over 5,000 samples collected over a period of 17 months throughout an affected water system, and samples collected at the tap in 136 standing homes in the burn zone 10 months after the fire. Although our tap water testing was limited and may not have been statistically representative - especially in the DOWC service area where we had difficulty recruiting participants - and it was not collected immediately after the fire, the data provide some clues to the sources of the VOC contamination and the time course of the problem.

VOC testing after the Camp Fire showed that, other than disinfection byproducts, benzene and MeCl were the two principal contaminants in the water samples. Our spatial analysis is consistent with that performed by the City of Santa Rosa after the Tubbs Fire in ruling out benzene contamination from leaking aboveground or underground petroleum storage tanks or other point sources of contamination. The fact that concentrations of benzene were highest in service lines to destroyed homes is consistent with the hypothesis that chemical pyrolysis products were pulled into the service lines due to loss of system pressure. The origin of the benzene may include combustion of residential materials, thermal degradation or pyrolysis of plastic pipes, water meters, and other components of the water system itself, as well as wood smoke.[10, 16, 17] A prior study on VOCs from crude oil indicates that adsorption and subsequent release of VOCs varies significantly by type of pipe material, with various types of plastic sequestering and gradually releasing contaminants over weeks or months.[18]

Our analysis of PID data showed that both the concentrations and the detection frequency of benzene declined over the months following the fire; during that time, the water system was being flushed, and highly contaminated sections of pipe were replaced. The overall detection frequency of benzene at concentrations above the MCL in service lines serving standing homes was 1%, compared to 21% in service lines serving destroyed homes, suggesting that tap water in standing homes may be relatively less affected. The fact that we did not identify concentrations of benzene near or above the MCL in 136 household tap water samples collected from standing homes 10-11 months after the fire is therefore not entirely surprising. Future investigations collecting samples at the tap in standing homes immediately after a fire could help distinguish between the effect of time and that of standing versus destroyed homes.

Our analysis generally supported prior findings that local burn severity may be associated with higher risk of contamination in service lines.[11] In particular, the cluster of elevated benzene detections in the southeastern portion of the PID service area is associated with a zone of particularly severe fire damage. However, our cluster analysis also identified higher prevalence of benzene detections in the northeast corner of the PID service area, an area of lower burn severity. This area was the highest of 7 pressure zones within the PID system and was the only area to which water was pumped uphill. This zone likely depressurized very quickly once power was lost in the system. An area toward the middle of town that also shows a cluster in our analysis underwent a service line upgrade in the late-2000's to high-density polyethylene (HDPE). These findings suggest that burn severity may be one of several factors determining contamination patterns.

The detection of elevated concentrations of MeCl in a significant number of tap water samples from standing homes was unexpected. Although MeCl is commonly used in laboratories, it is unlikely that it was a laboratory contaminant due to the low or negative results in blanks, and the relatively consistent results across study dates and laboratories, including in the PID samples. One prior study reported MeCl as a combustion byproduct of polyvinyl chloride (PVC), suggesting that the detections may be related to smoke from pyrolysis of pipes or other plastic.[16] However, our tap water testing found MeCl, sometimes at levels exceeding the MCL, in samples that did not contain benzene or other markers of combustion. The elevated concentrations of benzene and MeCl in the PID samples were also weakly correlated, raising questions about whether the only source of MeCl was combustion.

MeCl (dichloromethane) could potentially be produced from dechlorination of chloroform (trichloromethane), or debromination of bromodichloromethane (BDCM), especially in the presence of iron or zinc in pipes. One laboratory study found that chloroform can be transformed to MeCl within hours under experimental conditions, and that MeCl subsequently remains stable for days or longer.[19] The dehalogenation hypothesis is supported by the higher concentrations of MeCl we found in tap water samples with longer stagnation times and longer distances between the tap and the service connection, especially in homes with galvanized iron pipes. The inverse association we found between MeCl concentration and the concentration of chloroform and BDCM, especially in homes with galvanized iron pipes, also supports the hypothesis that these trihalomethanes may be converted to MeCl in the presence of iron and zinc. PID was concerned that a galvanized riser they were using for sample collection was responsible for some of the MeCl detections in their data even though the water may have only been in contact with the galvanized riser for seconds, and they flagged some MeCl detections as potentially unreliable for this reason; however they also found MeCl in samples when the riser was not used. If this hypothesis is correct, MeCl could be produced in the absence of a wildfire, from stagnant disinfected water in iron pipes.

We detected tetrahydrofuran (THF) in three tap water samples in the PID service area. THF was not included in the PID dataset. THF is used as a solvent in polymers and resins, and is commonly used in PVC adhesives for drinking water pipes. The Safety Data Sheet for the brand of PVC primer and cement used by PID contains 10-25% THF.[20] PID was removing residential water meters and installing “jumper” PVC pipe connections on service lines to standing homes during the time period of our tap water sampling. There is limited information on health effects of THF. Some *in vivo* bioassays showed evidence of hepatotoxicity, neurotoxicity, and developmental toxicity.[21] One study showed evidence of kidney and liver tumors in both rats and mice, based on which the U.S. EPA concluded that THF shows "suggestive evidence of carcinogenic potential".[21] The International Agency for Research on Cancer classified THF as “possibly carcinogenic to humans” (Group 2B), based on sufficient evidence of carcinogenicity in animals.[22]

Conclusions

Contamination of drinking water systems during wildfire events is a new environmental health challenge. Addressing the root causes of wildland-urban interface extreme fire events (e.g., climate change, forest management) are important components, but must be supplemented by resilience measures for water systems. The ability to quickly shut-off of sections of water systems that depressurize, coupled with backflow prevention, may reduce contamination from smoke being pulled into service lines and other pipes. Rapid post-fire testing throughout the system, with a focus on initially clearing water mains, followed by service lines to standing homes, is a critical element. Finally, the strategies of flushing pipes that have low levels of contaminants, and replacement of highly contaminated pipes, appears to have been effective in the area impacted by the Camp Fire. Further research to test water that has stagnated in galvanized pipe is needed, especially because the implications may extend beyond the relatively few fire-impacted water systems. MeCl is typically not tested in the distribution system or at the tap, and compliance testing at the water treatment plant would not ensure against chemical transformation within the system. More widespread monitoring for chemicals known to be used in water pipe repair, such as tetrahydrofuran, along with drinking water guidance values, would help ensure public health protection.

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Supporting Information: File containing a description of the methods for the VOC analysis and the non-targeted analysis; a figure showing the benzene cluster analysis of service line samples collected by the Paradise Irrigation District (PID) water system (December 2018 - May 2020); 5 figures and 3 tables presenting detailed results and a principal component analysis of the non-targeted testing of 10 tapwater samples collected from homes in the PID water system after the fire (October – November 2019). (PDF)

References:

[1] City of Santa Rosa Water. 2018. Technical Memorandum No. 1. Post-Fire Water Quality Investigation: Analysis of Cause of Water Contamination. March 22, 2018. https://srcity.org/DocumentCenter/View/19837/Post-Fire-Water-Quality-Investigation-Analysis-of-Cause-of-Water-Contamination. (Accessed December 29, 2020).

[2] Paradise Irrigation District Annual Consumer Confidence Report, 2019. https://pidwater.com/docs/about-your-water/water-quality/1750-2019-consumer-confidence-report. (Accessed March 19, 2021).

[3] Paradise Irrigation District Water Quality Advisory Update, May 20, 2020. https://www.pidwater.com/wqadvisory. (Accessed May 27, 2021).

[4] Esri. "Topographic" [basemap]. Scale Not Given. "World Topographic Map". June 13, 2013. https://www.arcgis.com/home/item.html?id=30e5fe3149c34df1ba922e6f5bbf808f. (Accessed January 29, 2021).

[5] Tracking California, Public Health Institute. Water Boundary Tool. www.trackingcalifornia.org/water. (Accessed June 30, 2020).

[6] The National Interagency Fire Center. National Incident Feature Service. 2018. https://data-nifc.opendata.arcgis.com/datasets/national-incident-feature-service-2018. (Accessed October 20, 2020).

[7] Abraham J, Dowling K, Florentine S. 2017. Risk of post-fire metal mobilization into surface water resources: A review. **Sci Total Environ** 599-600:1740-1755, DOI: 10.1016/j.scitotenv.2017.05.096.

[8] Dauchy X, Boiteux V, Bach C, Rosin C, Munoz JF. 2017. Per- and polyfluoroalkyl substances in firefighting foam concentrates and water samples collected near sites impacted by the use of these foams. **Chemosphere** 183:53-61, DOI: 10.1016/j.chemosphere.2017.05.056.

[9] Dauchy X, Boiteux V, Bach C, Rosin C, Munoz JF. 2017. Per- and polyfluoroalkyl substances in firefighting foam concentrates and water samples collected near sites impacted by the use of these foams. **Chemosphere** 183:53-61, DOI: 10.1016/j.chemosphere.2017.05.056.

[10] Proctor CR, Lee J, Yu D, Shah AD, Whelton AJ. 2020. Wildfire caused widespread drinking water distribution network contamination. **AWWA Wat Sci** 2(4):e1183, DOI: 10.1002/aws2.1183.

[11] Schulze SS. and Fischer EC. 2021. Prediction of Water Distribution System Contamination Based on Wildfire Burn Severity in Wildland Urban Interface Communities. **ACS ES&T Water** 1(2):291-299, DOI: 10.1021/acsestwater.0c00073.

[12] Diggle PJ. 1985. A kernel method for smoothing point process data. **Applied Statistics** (Journal of the Royal Statistical Society, Series C) 34(2):138–147, DOI: 10.2307/2347366.

[13] Ripley BD. 1976. The second-order analysis of stationary point processes. **J Appl Prob** 13(2):255-266, DOI: 10.2307/3212829.

[14] Rowlingson B. and Diggle P. 1993. Splancs: spatial point pattern analysis code in S-Plus. **Comp Geosci** 19(5): 627-655, DOI: 10.1016/0098-3004(93)90099-Q.

[15] Michigan DEQ. 2015. Tetrahydrofuran. Chemical Update Worksheet. Remediation and Redevelopment Division Toxicology Unit, Michigan Department of Environmental Quality. August 19, 2015. https://www.michigan.gov/documents/deq/deq-rrd-chem-TetrahydrofuranDatasheet_527532_7.pdf (Accessed December 28, 2020).

[16] Chong NS, Abdulramoni S, Patterson D, Brown H. 2019. Releases of fire-derived contaminants from polymer pipes made of polyvinyl chloride. **Toxics** 7(4): 57, DOI: 10.3390/toxics7040057.

[17] Isaacson KP, Proctor CR, Wang QE, Edwards EY, Noh Y, Shah AD, Whelton AJ. 2021. Drinking water contamination from the thermal degradation of plastics: implications for wildfire and structure fire response. **Environ Sci Water Res Technol** 7:274–284, DOI: 10.1039/D0EW00836B.

[18] Huang X, Andry S, Yaputri J, Kelly D, Ladner DA, Whelton AJ. 2017. Crude oil contamination of plastic and copper drinking water pipes. **J Hazard Mater** 339:385-394, DOI: 10.1016/j.jhazmat.2017.06.015.
[19] Matheson LJ and Tratnyek PG. 1994. Reductive dehalogenation of chlorinated methanes by iron metal. **Environ Sci & Tech** 28:2045–2053. DOI: 10.1021/es00061a012.
[20] Oatey. 2017. PVC Regular Clear Cement. Version 01, Revision date: 11-22-2017. Cleveland, OH. https://oateyassetcdn.azureedge.net/assets/Document/raw_01_PVC%20Regular%20Clear%20Cement_SDS_001.pdf. (Accessed March 19, 2021).
[21] U.S. EPA. 2012. Toxicological Review of Tetrahydrofuran. Integrated Risk Information System, EPA/635/R-11/006F, Washington, DC, February 2012. https://iris.epa.gov/static/pdfs/1023tr.pdf. (Accessed December 29, 2020).
[22] IARC. 2019. Some Chemicals That Cause Tumours of the Urinary Tract in Rodents. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Volume 119. IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, Lyon: World Health Organization, International Agency for Research on Cancer, ISBN-13: 978-9283201861.