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Residential Tap Water Contamination Following the Freedom Industries Chemical Spill: Perceptions, Water Quality, and Health Impacts

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S *Supporting Information*

ABSTRACT: During January 2014, an industrial solvent contaminated West Virginia's Elk River and 15% of the state population's tap water. A rapid in-home survey and water testing was conducted 2 weeks following the spill to understand resident perceptions, tap water chemical levels, and premise plumbing flushing effectiveness. Water odors were detected in all 10 homes sampled before and after premise plumbing flushing. Survey and medical data indicated flushing caused adverse health impacts. Bench-scale experiments and physiochemical property predictions showed flushing promoted chemical volatilization, and contaminants did not appreciably sorb into cross-linked polyethylene (PEX) pipe. Flushing reduced tap water 4-methylcyclohexane-methanol (4-MCHM) concentrations within some but not all homes. 4-MCHM was detected at unflushed (<10 to 420 μg/L) and flushed plumbing systems (<10 to 96 μg/L) and sometimes concentrations differed among faucets within each home. All waters contained less 4-MCHM than the 1000 μg/L Centers for Disease Control drinking water limit, but one home exceeded the 120 μg/L drinking water limit established by independent toxicologists. Nearly all households refused to resume water use activities after flushing because of water safety concerns. Science based flushing protocols should be developed to expedite recovery, minimize health impacts, and reduce concentrations in homes when future events occur.

■ INTRODUCTION

Early on January 9, 2014 a Freedom Industries, Inc. chemical storage tank was found leaking. An investigation revealed more than 10 000 gallons of an industrial coal processing liquid had been released into West Virginia's Elk River. Freedom Industries, Inc. initially reported that "Crude MCHM" was spilled, but 12 days later, the company also disclosed that an additional product called "Stripped PPH" was also present in the spilled liquid (Table 1; Supporting Information (SI) Figure SI-1).[1] The Elk River was the regional water company's sole drinking water source used to supply the state capitol, including 300 000 people, 15% of the State's population.

Contaminated river water traveled downstream and entered West Virginia American Water's (WVAW) Kanawha Valley 50 million gallon per day (MGD) drinking water treatment plant.[2] In the days leading up to the spill, water demand was approximately 43 MGD, cold weather (−5 °C) was attributed to water main breaks, and residents were allowing faucets to drip to prevent their plumbing pipes from freezing. WVAW estimated that it had less than 3 h of tap water in reserve. WVAW predicted that if the raw water intake was shutdown, then water for fire-fighting as well as basic hygiene and sanitation purposes would not be available and at least 45 days would be needed to restore service to large sections of the distribution system. At 4:00 pm, WVAW detected contaminated drinking water entering the distribution system and observed a licorice odor.[3] A Do Not Use order was issued at 5:50 pm for the entire service area. Little to no toxicological data and physiochemical properties were available for many of the solvent's ingredients.[4] The Governor declared a State of Emergency for the nine counties affected, and at 12:46 am January 10 President Obama declared the incident a Federal disaster.[5]

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Table 1. Chemicals Suspected to be in the Spilled Tank Liquid According to Declarations by Eastman Chemical Company and Freedom Industries, Inc.

product	reported ingredient	estimated composition of the spilled liquid
crude MCHM	4-methylcyclohexanemethanol (MCHM)	68% to 89%
	4-(methoxymethyl)cyclohexanemethanol	4% to 22%
	water	4% to 10%
	methyl 4-methylcyclohexanecarboxylate	5%
	dimethyl 1,4-cyclohexanedicarboxylate	1%
	methanol	1%
	1,4-cyclohexanedimethanol	1% to 2%
stripped PPH[a]	propylene glycol phenyl ether (PPH)	amount unclear
	dipropylene glycol phenyl ether (DiPPH)	amount unclear

[a]Thirteen days after the spill, the Centers for Disease Control and Prevention (CDC) reported that the spilled product contained "88.5% Crude MCHM, 7.3% Stripped PPH, and 4.2% water", although the CDC's calculation methodology was not disclosed. Stripped PPH was blended into Eastman Chemical Company's Crude MCHM by Poca Blending Company in Nitro, WV. The Stripped PPH product contained both PPH and DiPPH compounds.

During the next 10 days, the Do Not Use order remained in effect for much of the area. Tap water remained relatively stagnant in premise plumbing systems as only toilet flushing and fire-fighting were permitted. The greatest measured concentration of 4-MCHM, the main ingredient of the spilled liquid, entering or leaving the water treatment facility was 3350 μg/L (Figure 1). The greatest concentration detected during rapid water distribution system sampling by WVAW and the State was 3773 μg/L. It remains unclear if 3773 μg/L was the greatest concentration that exited the water plant because testing did not begin until January 10, when contaminated water had already entered the distribution system.[3] Tap water samples were also analyzed for propylene glycol phenyl ether (PPH) and dipropylene glycol phenyl ether (DiPPH), but these compounds were found in only two water samples collected and at concentrations of 11 μg/L and 10 μg/L, respectively. An analytical method for detecting and quantifying the spilled liquid's ingredients in water did not exist when the incident occurred. This method was developed after WVAW was notified of the spill.

Flushing was conducted by WVAW to remove contaminated water from its 2200 miles of water mains, 107 storage tanks, and 120 booster stations within 124 pressure zones. Water samples were collected at various locations to monitor flushing effectiveness (Figure 1). WVAW's initial flushing objective was to reduce 4-MCHM concentrations below the U.S. Centers for Disease Control and Prevention (CDC) health based screening level of 1000 μg/L.[6] Subsequent response objectives included reducing 4-MCHM concentrations below 50 μg/L and then below a 10 μg/L, a screening level established by a State of West Virginia. The 10 μg/L concentration was the lowest MDL at the time. During the following months, WVAW would flush its distribution system to achieve 4-MCHM concentrations less than 2 μg/L once a lower MDL was developed. In March 2014, another research team hired by the State called WVTAP, or West Virginia Testing Assessment Project, issued a health based 4-MCHM screening level of 120 μg/L using the same toxicological data CDC reviewed, but with different assumptions (Table 2).[7]

Four days after the spill, WVAW had flushed parts of its distribution system and began advising residents in those areas to flush their premise plumbing systems using a stepwise protocol.[8] The procedure had been reviewed by government public health officials before release. Residents were told that after flushing, tap water would be "appropriate to use" by health officials but may still have an odor. No in-home tap water or air quality testing was

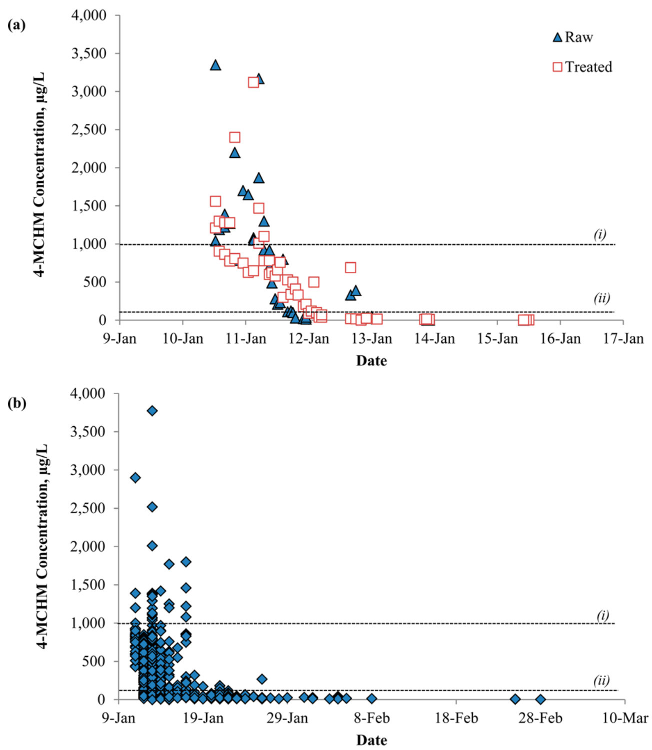

Figure 1. 4-MCHM Monitoring Results for the (a) Kanawha Valley Water Treatment Facility from January 10 to January 15, 2014 and (b) Water Distribution System from January 10 to March 6, 2014. 4-MCHM has both trans- and cis-isomers[9] and 4-MCHM concentrations reported by WVAW, the State, and in the present study were reported as the combined trans- and cis- isomer concentration. Distribution system samples were collected at various locations to include hydrants, storage tanks, booster stations, public buildings including schools, hospitals, and private businesses. The dotted horizontal lines represent the (i) CDC's 4-MCHM screening level (1000 μg/L), (ii) WVTAP's 4-MCHM screening level (120 μg/L). Only results where the value was greater than the MDL are shown (i.e., more than 1100 "non-detect" results are not shown). Also not shown are March 2014 testing results where water leaving the water treatment plant contained 0.42 to 0.60 μg/L 4-MCHM. Testing was also conducted in June 2014 after the water treatment plant's activated carbon filters were replaced. 4-MCHM was not found above a MDL of 0.38 μg/L exiting the water treatment plant or in the distribution system.

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Table 2. Comparison of Drinking Water Screening Levels Established by the U.S. Centers for Disease Control and Prevention (CDC) and West Virginia Testing Assessment Project (WVTAP)[a]

contaminant name and assumption by health officials	CDC (January 2014)	WVTAP (March 2014)
4-MCHM, μg/L	1000	120
PPH, μg/L	1200	850
DiPPH, μg/L	1200	250
exposure duration	14 days	28 days
most sensitive population	1 year old child	formula fed infant
exposure routes	ingestion only	ingestion, inhalation, dermal

[a]WVTAP included toxicologists from academic and public health organizations located in Israel, the United Kingdom, and United States. In January 2014, the State of West Virginia applied a 100-fold safety factor to the CDC's 4-MCHM screening level because of concern that limited toxicology data existed. The State of West Virginia's screening level for 4-MCHM was 10 μg/L.

conducted by WVAW or responding local, county, state, or federal organizations before, during, or immediately after plumbing system flushing activities.

The goal of this rapid response study was to understand resident responses and tap water quality within unflushed and flushed residential plumbing systems. Specific objectives were to rapidly: (1) determine resident behaviors and perceptions following the spill, (2) characterize plumbing system characteristics and chemical levels in homes, and (3) determine the ability of the flushing procedure to reduce chemical levels within homes. To complete this work, the research team visited the affected area from January 18 to 22, 2014. The visit was conducted when residents were being authorized by WVAW to flush contaminated water from their premise plumbing systems. To interpret results of this field effort, syndromic surveillance records as well as public health survey results obtained by government agencies were also reviewed. A detailed timeline of events can be found in the SI.

MATERIALS AND METHODS

Survey Instrument and Participating Households. More than 80 households were identified by the West Virginia Clean Water Hub and People Concerned About Chemical Safety and wanted to participate in the research project. These nonprofit organizations were helping distribute water to affected households and assisted the authors to make contact with these households. Due to time, financial, and logistical limitations, the authors could only include a fraction of those households expressing interest in this study. Sixteen households participated in the research.

All participating households were provided tap water by the affected water distribution system and were located in Kanawha, Putnam, and Boone Counties; specifically, in Cross Lanes, Elk View, Nellis, South Charleston, and Charleston. A map showing the locations of homes where tap water was sampled can be found in Figure SI-2. One representative of each household was interviewed by the authors and completed a 10 question survey. The survey was designed to evaluate resident behaviors and perceptions in households directly affected by the contamination incident (Table SI-1).

Sampling Activity and Analysis. Two faucets were sampled at each home. Kitchen faucets were chosen in every home based on their high use frequency, while the second location (usually a bathroom faucet or outside spigot) was chosen to represent low frequency use. Amber glass bottles with polytetrafluoroethylene (PTFE)-lined caps precleaned with HNO_3 and/or shipped direct from the manufacturer were used. Glass bottles were used for water sample collection where 4-MCHM, total organic carbon (TOC), UV_{254} absorbance, alkalinity, chloride, fluoride, hardness, nitrate, orthophosphate, and phosphorus analyses were desired. Glass bottles did not contain preservatives. Plastic bottles were used for metal sample collection and contained 16N HNO_3 preservative. Water samples were stored on ice at 4 °C and refrigerated until analysis and waters were analyzed within 96 h of collection.

Any point-of-use water filtration devices were removed from the faucets before water collection. Next, about 100 mL of first draw tap water was analyzed for pH and temperature (Thermo Scientific Orion 5 Star portable pH meter), free and total chlorine (HACH Pocket Colorimeter II with *N*,*N*-diethyl-*p*-phenyldiamine reagents), and turbidity (HACH turbidimeters). After these initial measurements, tap water odor was evaluated. Field blanks were obtained by filling containers with laboratory-purchased deionized water. Next, a total of four water containers were filled per tap for (a) 4-MCHM, chloride, fluoride, hardness, nitrate, orthophosphate, phosphorus [1 L], (b) TOC [0.125 L], (c) metals [0.250 L], and (d) alkalinity, color, ultraviolet absorbance at 254 nm (UV_{254}) [0.250 L]. All containers were headspace free. After premise plumbing flushing, a second series of water samples were collected from flushed taps. Water samples were shipped to three different laboratories. A more detailed water analysis methods description can be found in the SI. Particulate material released from a Home 8 bathroom faucet was collected and analyzed by X-ray photoelectron spectroscopy (XPS) at the University of New Mexico.

Premise Plumbing Flushing Procedure. Six homes that had unflushed pipes were visited. These homes underwent premise plumbing flushing in accordance with the protocol issued by WVAW[8] with slight modification. The protocol entailed flushing all hot water taps for 15 min, all cold water taps for 5 min, and finally flushing all other appliances for 5 min. The document stated that any lingering licorice odor detected would not be harmful. The details for the flushing protocol design (i.e., estimated flow rate, water volume removed) were not found. Flushing protocol modifications were made after members of the research team experienced chemical exposure symptoms, such as eye-burning and dizziness. Modifications included turning off hot water heaters and allowing them to cool before flushing, flushing one room in the house at a time, opening doors and windows, using fans to ventilate rooms while flushing, and following the flushing protocol more than once to improve the chance of contaminant removal. At the time of this rapid response, there were no data pertaining to the interaction of the spilled liquid's ingredients or its breakdown products with premise plumbing materials (i.e., metal and plastic pipes, gaskets, and hot water heaters). The authors requested that children and immunocompromised persons leave the house during flushing activities. Tap

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water sampling was only conducted before and after the first flushing procedure.

Contaminant Interaction with PEX Pipe. Bench-scale sorption experiments were conducted to understand the interaction of 4-MCHM [TCI America, 99.0%] and cyclohexanemethanol (CHM) [Acros Organics, 99.0%] with cross-linked polyethylene (PEX) type A and type B pipes. These two compounds were present in the spilled liquid. The presence of both 4-MCHM and CHM was confirmed by WVTAP investigators who characterized the liquid remaining in the Freedom Industries, Inc. tank. CHM however was not listed on any safety data sheets provided to WVAW, State, or Federal response agencies (Table 1).

PEX type A and type B pipes were examined because they were both present in some of the homes visited. PEX-A pipe is also more susceptible than PEX-B pipe to contaminant permeation because of its low bulk density.[10] PEX pipes purchased from a local building supply store were cut into 1.1 to 1.3 g dog-bone shaped specimens (2.5 to 2.6 mm thick), then were immersed in pure solvent at room temperature. During several weeks, specimens were periodically weighed.[10] PEX interaction with toluene and cyclohexane [Fisher Scientific, 99.8% and 99.0% purity, respectively) was also examined; neither compound was found in the spilled liquid but were used as controls.

Syndromic Surveillance. Data on illness frequency from 10 sentinel multiprovider and multilocation medical practices were compiled and analyzed in the present study. Information pertained to 224 patients from the impacted area that sought medical attention with self-reported symptom onset from January 9 to February 10. The list of symptoms included multisystem symptoms (respiratory, digestive, integumentary [skin], and neurological); respiratory: cough, sore throat; digestive: nausea, vomiting, diarrhea; skin: rash, skin irritation; neurological: headache; and "other symptoms" for symptoms that had not been defined. Providers did not report names, addresses, or other identifying information on the patients beyond gender and age. Patients were asked whether or not they were in a flushed or unflushed building when tap water exposure occurred, and only those with clear associated exposure were included.

Physiochemical Properties and Statistical Analysis. Contaminant physiochemical characteristics were estimated using SPARC[11] chemical modeling software (Danielsville, GA U.S.A.), and water solubility was also estimated using COSMOS-RS[12] (Amsterdam, The Netherlands). These programs allowed for the authors to estimate the fate and transport of contaminants at different temperatures. Water temperatures chosen were representative of the Elk River (5 °C) and within plumbing systems (21 °C, 60 °C).

Minitab 14 Student (Minitab, Inc. State College, PA)[13] was used to perform two-tailed student *t*-tests and linear regression statistical analysis was also carried-out. Any water quality result less than the method MDL was assigned a value of zero. An alpha value of 0.05 was selected as the significance level for all data interpretation.

Logistic regression modeling was applied to syndromic surveillance data. Response variables were binary (i.e., patients answered whether they had a symptom of nausea or not) and were coded as 1 and 0, respectively. In a logistic setting, the odds of an event happening were modeled where Y was a binary random variable. Then, the odds of Y being 1 was given by the ratio of probabilities of Y being 1 and Y being 0. The equation was: Odds $(Y=1) = P(Y=1)/P(Y=0)$. Note that the odds could be any number more than 0; an odd of 1 implied a fair chance. The following model was applied: $\text{Log}_e\text{Odds}[Y=1] = \beta_0 + \sum_{i=1}^{K}\beta_i X_i + \varepsilon$. In the above model, ε implied the unexplained model error; X_1, X_2, ..., X_K were covariates (factors) and $\beta_0, \beta_1,...,\beta_K$ were unknown coefficients estimated using Minitab. The above model provides an effective interpretation for coefficients involved with each factor in terms of the odds. If the factor was also binary, then e^{β} was interpreted as the ratio of the odds for X=1 and X=0.

RESULTS AND DISCUSSION

In-Home Survey Results and Comparison to Public Health Studies. *Household Demographics and Premise Plumbing Characteristics.* Single story, multistory, and manufactured homes were visited. Households had similar demographics to the 2012 West Virginia census (Table SI-2).[14] Sixteen persons, 32 to 68 years old, representing 16 households were interviewed. A range of 1 to 5 persons lived in each household. Children under 18 years of age and/or adults with medical concerns lived in 12 of the households. Children lived in half of the households. Five residences had pets with at least one cat or dog.

Ten of the 16 home plumbing systems entirely or partly contained copper pipe. Pipe materials found that were not copper were: Chlorinated polyvinyl chloride (cPVC) [five homes] > cross-linked polyethylene (PEX) [three homes], galvanized iron [two homes], and poly(1-butene) (PB) [single home]. Renovated homes typically contained some cPVC, PEX, or PB plastic drinking water pipe.

The visit was conducted when WVAW was advising residents to flush contaminated water from their premise plumbing systems. Between January 18 and 22, seven households reported they had not flushed their plumbing systems. Another seven households reported having already flushed their plumbing systems. A single household was considered partially flushed because the second story was not flushed, while remaining faucets had been flushed.

Resident Behaviors and Perceptions. Nearly all households surveyed (14 of 16) reported detecting an unusual tap water odor during the first 2 weeks of the incident, two reported an unusual taste, and six reported an unusual tap water color. The most commonly reported odor descriptors were licorice and sweet. These descriptors agreed with those found by other researchers who characterized odor threshold and recognition concentrations of the contaminated water with sensory panels.[9] Most households (10 of 16) reported detecting an unusual tap water odor on January 9, 2014. Two households indicated that they detected a licorice odor before January 9. This is an interesting finding because the U.S. Chemical Safety and Hazard Investigation Board investigation found that at least one other chemical storage tank was leaking before January 9.[15] Other tap water odor descriptors mentioned by the respondents included the terms acetone, chemical, metallic, organic chemistry lab, and rotten. Households reported noticing odors with different intensities between January 9 and the date this survey was conducted. The greatest odor intensity ratings occurred during January 9 to 13, and odor intensity levels generally decreased with time. These observations agree with findings by the WVTAP investigators who also found residents noticed that tap water odor intensity decreased with time.[16]

Resident Health Impacts. Contaminated water exposure impacted resident health. Almost half of the households in the present study (7 of 16) reported that the water caused at least one person in their home to become ill. In contrast, only a third

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Table 3. Comparison of the Present Work to Public Health Impact Studies Conducted by Local, State, and Federal, and Research Organizations[a]

	organization conducting study and date information was publicly released						
	household interview survey	syndromic surveillance record review	WVTAP household interview survey[16]	CDC/BPH emergency department record review[19]	BPH physician record review[20]	KCHD household telephone survey[17]	CDC household interview survey[18]
symptom	(this study) Jan. 2014	(this study) Jan. 2014	Feb. 2014	Mar. 2014	Mar. 2014	Apr. 2014	Jul. 2014
				dermatologic			
skin irritation		40.3				**63.2**§	**53.9**
rash	12.5	**47.6**	**40**	28.5	21.6	§	43.6
itching			10	19.8	**60.0**		
eye irritation	12.5	25.3	10	14.6 (pain)	13.3	26.4	5.1
				gastrointestinal			
nausea	**31.3**	21.0	30	**37.9**		26.42$^{\Delta}$	12.8
vomiting	0.0	13.7	10	28.2	8.3	$^{\Delta}$	5.1
abdominal pain	6.3			24.4	8.3	27.0$^{\Phi}$	5.1
diarrhea	6.3	16.3	0	24.4	5.0	$^{\Phi}$	12.8
				respiratory			
unspecified						17.0	
sore throat		9.4		14.9	8.3		10.3
cough		6.9		12.7	15.0		15.4
				orientation			
dizziness	18.8		40			25.2$^{\varepsilon}$	7.7
headache	12.5	13.7	30	21.9	11.7	$^{\varepsilon}$	10.3
other	12.5		80			14.1	23.1

[a]Numbers in columns total to greater than 100% because multiple symptoms were reported by each surveyed person/household. Blank entries indicate that the data set did not classify symptoms in that specific category; Kanawha-Charleston Health Department (KCHD) syndromic surveillance data represent 224 patients from 10 physicians; The household survey as part of WVTAP[15] represents 10 households in eight of the nine counties affected; The Centers for Disease Control and Prevention (CDC) and West Virginia Department of Health and Human Resources (DHHR) Bureau of Public Health (BPH) emergency department data represent 356 patients from 10 emergency departments; The West Virginia BPH physician record review represents 60 persons; The KCHD randomized telephone survey represents 499 persons and the title of the effort was Community Assessment Population Survey; The KCHD telephone survey included categories where multiple symptoms were listed. Symptoms that were used in combined categories are denoted with symbols; The CDC's Community Assessment for Public Health Emergency Response (CASPER) household survey data represent 171 households; The present study household survey data represents 16 households. For some of the reports there are significant differences between when the report was dated complete and when it was released to the public. Studies are presented chronologically as the data became publicly available.

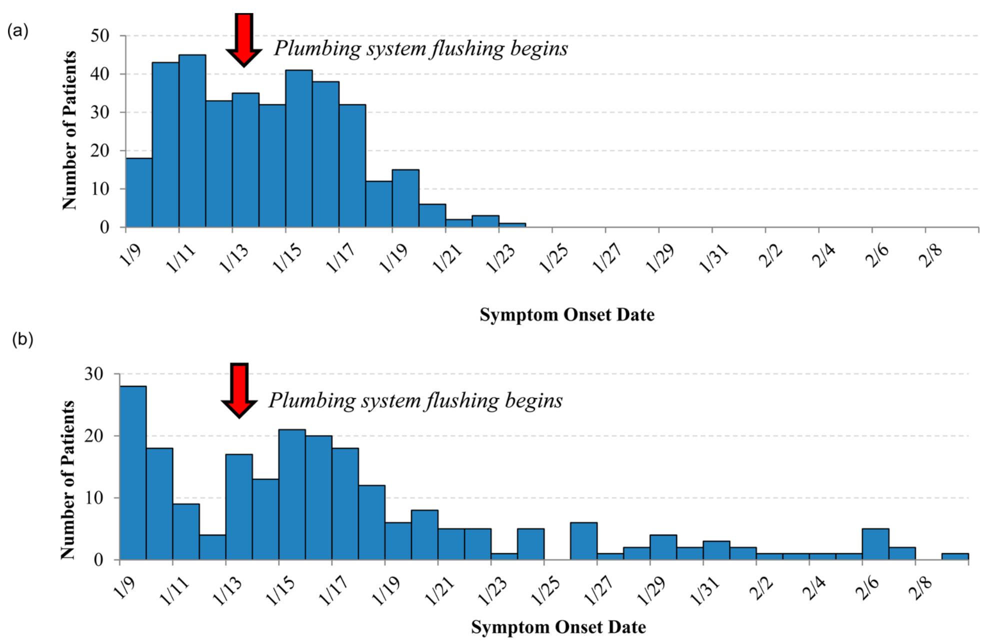

Figure 2. (a) Visits to emergency departments reported by the CDC and BPH (b) syndromic surveillance cases of clinically defined chemical exposure from January 9 through February 9, 2014. Records represent 10 emergency medical departments with 356 patients and 10 physician offices with 224 patients, respectively.

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of households surveyed by the Kanawha Charleston Health Department (KCHD)[17] and one-fifth of households surveyed by the CDC[18] experienced health issues they thought were attributed to the spill.

An examination of syndromic surveillance records revealed that several exposure routes were significant. Results of a KCHD telephone survey[17] and CDC[18] in-home survey conducted after this rapid response study support this finding. Syndromic surveillance records show that exposure routes such as drinking, washing or bathing were significant. Patients who drank contaminated water were more likely to report nausea ($p < 0.001$), vomiting ($p < 0.001$), diarrhea ($p < 0.001$), and sore throat ($p=0.002$) symptoms. Bathing or hand washing with contaminated water resulted in skin irritation ($p < 0.001$) and rash ($p=0.002$), symptoms, which was intuitively expected. Interestingly, female patients were more susceptible to vomiting ($p=0.023$) and sore throat ($p=0.025$) symptoms than male patients. The CDC[18] found that symptoms could be grouped into three exposure categories based on their household survey: (1) Bathing, showering, or skin contact [52.6%], (2) eating, drinking, or swallowing [43.9%], and (3) breathing mist or vapor [14.6%]. Table 3 compares the symptoms reported by emergency departments and physicians[19,20] in-home CDC survey,[18] a KCHD telephone survey,[17] and the WVTAP researchers.[16] Persons reported experiencing symptoms at home, work, and food facilities (SI).

Of the seven households that reported health impacts in the present study, only two reported their symptoms to a medical professional. Similarly, the KCHD telephone survey[17] found few households, one in five, that reported symptoms sought medical attention. The CDC[18] however found almost half of the households that reported symptoms sought medical care. All three data sets show that responders who only monitor physician and emergency department records in incidents such as this will significantly underestimate the population affected.

Interestingly, two distinct syndromic surveillance symptom peaks were found that corresponded with the January 9 Do Not Use order and plumbing system flushing activity initiated on January 13 (Figure 2). These two peaks were not statistically different. The West Virginia Poison Control Center[21] also noticed a surge in call volume as each pressure zone began flushing. Callers reported nausea, reddened skin, and rash symptoms[21] and call volume decreased during the next 2 weeks (Table SI-3). Syndromic surveillance data showed patients whose homes were flushed were likely to report experiencing a sore throat ($p=0.000$). Another notable finding is that eye irritation was 2.28 times as likely to be reported if the patient became ill during the first symptom peak (Table SI-4).

Estimated vapor pressure and Henry's Law Constants of the spilled contaminants show compound volatility increased as water temperature increased resulting in greater exposure (Tables SI-5 to SI-7). Laboratory testing also showed that a greater mass of 4-MCHM volatilized from water into air under hot water conditions than at room temperature (Figure SI-3). On the basis of the evidence examined, plumbing system flushing negatively impacted human health.

Water Use Activity. Before January 9, all households visited in the present study used tap water for hygiene activities and nearly all used it for drinking purposes. Approximately 2 weeks after the Do Not Use Order was lifted, few of the visited households chose to resume their prespill water use activities: Drinking (1 of 12), showering (4 of 15), clothes washing (3 of 15), brushing teeth (1 of 15), cooking (1 of 15), and water for animals (2 of 12). Households did not resume their prespill water use activities because they remained unconvinced that the water was safe to use based on (1) licorice odor observations after flushing, (2) self-reported symptoms, and (3) reports from friends and media organizations that tap water was causing illness. In fact, only a little more than a third of the households believed the tap water was safe after the Do Not Use order was lifted according to the CDC.[18] With time, more residents resumed their prespill water use activities. Seven weeks after the Do Not Use order was issued roughly 80% of the households were using the tap water to bathe but less than 12% for cooking or drinking.[17]

Households that participated in the present study were using alternate water sources for drinking, cooking, hygiene activities, and their pets. Survey results from both the KCHD[17] and CDC[18] support this finding. The majority of households visited in the present study relied solely on bottled water for all activities; including bathing during the first 2 weeks of the event. Two of the 16 households utilized rainwater catchment systems and the KCHD survey[17] similarly found few households (less than 10%) used rainwater as an alternate water source. One of 16 households purchased an outdoor camping shower for use in lieu of using the indoor shower, and others boiled rainwater for bathing. One household was bathing children in a plastic storage tub with bottled water. Representatives of one of the 16 households traveled 60 miles outside of the affected area to wash clothes and bathe. The KCHD survey[17] also found few households (20%) had persons who traveled out of the affected area to meet their water needs. A few households in the present study utilized PUR water filters in attempt to remove the contaminants, and rainwater and bottled water were the most commonly used water sources for feeding pets.

Surprisingly, a significant number of households surveyed by the KCHD[17] (23%) and the CDC[18] (37.4%) reported using the tap water *during* the Do Not Use order. Of those persons who used tap water during the Do Not Use order, the following activities were most popular [KCHD, CDC]: Bathing or showering [78%.0, 80.1%], hand washing [55.2%, 45.9%], clothes washing [44.0%, 37.7%], dish washing [42.2%, 32.2%], and feeding pets [28.6%, 19.2%]. KCHD[17] further reported residents used water during the Do Not Use order for teeth brushing (40.5%), drinking (37.1%), cooking (29.3%), and watering plants (23.3%), while CDC[18] also reported persons ate or drank food prepared with water (26.6%) and drank the water (26.6%). Results of the present study showed only one household of 16 did not learn about the Do Not Use order on January 9. According to both the KCHD[17] and CDC[18] however, approximately 20% of the households affected *did not* learn about the Do Not Use order until after January 9. Household water use during the Do Not Use order likely resulted in some of the illnesses reported (Table 3).

Organic Contaminant Levels in the Unflushed and Flushed Homes. *Odor and 4-MCHM Levels.* Of the 10 homes where tap water was analyzed, six homes were unflushed upon arrival and four homes had undergone the flushing procedure before the investigators arrived. Table SI-8 describes the plumbing system characteristics and tap water sampling locations. Tap water odors were detected by the authors in all homes at all taps. The authors described these odors as sweet chemical, strong, sweet licorice/chemical, candy-like, and earthy. Most of these descriptors are in agreement with odor analysis conducted by others[9] on the liquid removed from the Freedom Industries, Inc. tank.

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Despite a tap water odor being detected in all six unflushed homes, 4-MCHM was only detected above the 10 μg/L MDL in four of those residences. Detection of an odor when 4-MCHM was not present found at a concentration greater than the MDL was likely due to the extraordinarily low odor threshold concentration of contaminants in the contaminated water. WVTAP researchers reported that the odor threshold concentration of the liquid removed from the Freedom Industries, Inc. tank was less than 0.15 μg/L.[9] Results implied that the human olfactory system was capable of detecting contaminants when advanced analytical methods could not.

Chemical modeling software enabled physiochemical property predictions for many of the spilled liquid's ingredients. SPARC results indicated that the maximum 4-MCHM solubility from 5 and 60 °C ranged from 1340 mg/L to 14 900 mg/L (Tables SI-5 to SI-7). However, results from COSMOS-RS chemical modeling software implied that the range was nearly 2600 mg/L at 5 °C to 2,800 mg/L at 60 °C (Figure SI-4). While the exact reason for this prediction discrepancy is unclear, the 4-MCHM concentration found during in-home testing was much less than its maximum estimated water solubility.

The maximum 4-MCHM concentration found in the present study was 420 μg/L. This value was much less than the 3773 μg/L maximum concentration found by WVAW and the State during water distribution system testing, and 3120 μg/L concentration found at the water treatment plant (Figure 1). Because no in-home testing was carried-out by responders before flushing, a direct comparison between the maximum 4-MCHM concentrations found here to other affected homes cannot be carried-out. Concentrations found in the present study were within the range found in the distribution system, but are not representative of all homes affected.

No trend for 4-MCHM concentrations across or within homes was found (Figure 3). Some differences between faucets were

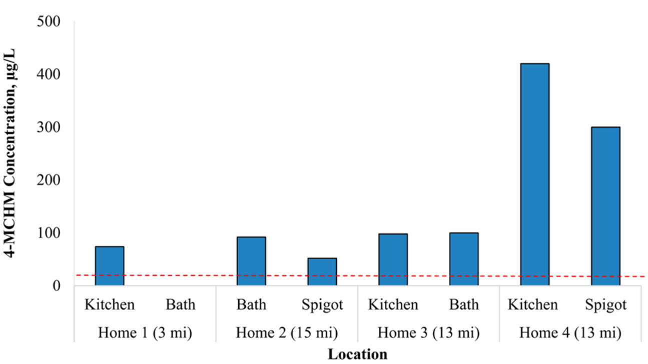

Figure 3. Tap water 4-MCHM concentration for unflushed homes at different in-home locations. The dashed line represents the method detection limit (MDL) of 10 μg/L; Homes 5 and 6 did not contain 4-MCHM in concentrations above the MDL; Home 1's bathroom faucet concentration was below the MDL; Distances shown in parentheses reflect the straight-line distance from each household to the WVAW treatment plant. Single water samples were analyzed from each tap.

very large (Δ = 120 μg/L in Home 4) while other differences were very small (Δ = 2 μg/L in Home 3). These observations could be due to a number of phenomena: (1) faucet water use frequency, (2) unstudied plumbing system material interactions, and (3) biodegradation. Bench-scale experiments conducted by the authors revealed that 4-MCHM had a low affinity for PEX plumbing pipe (Table SI-9). Chemical oxidation experiments conducted by WVTAP investigators using 4-MCHM and free chlorine showed free chlorine did not affect 4-MCHM concentration.[22]

Odors were detected before and after flushing. Prior to flushing, odors were described as "strong" and after flushing odors were described as "faint" or "very faint". While flushing Home 1's plumbing system, investigators experienced strong odors in poorly ventilated bathrooms and a kitchen that did not have functional windows or overhead vent fans. One person experienced eye irritation and another person experienced dizziness. Volatilized chemicals likely caused these symptoms. The strongest odors were most frequently associated with hot water and chemical volatilization likely occurred more rapidly from hot water. It should be noted that adverse health effects occurred well below the CDC's the 4-MCHM screening level of 1000 μg/L. WVAW, State, and Federal responders did not advise residents about potential chemical volatilization, inhalation, or dermal exposure concerns.

The ability of the plumbing system flushing method to reduce 4-MCHM tap water concentrations was evaluated at four unflushed households (Figure 4). Flushing reduced 4-MCHM

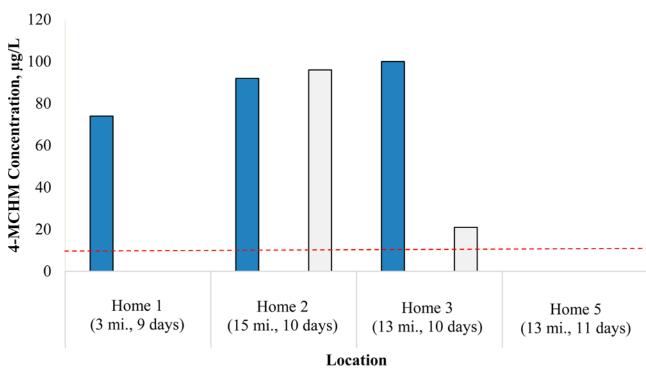

Figure 4. Tap water 4-MCHM concentration before and after the premise plumbing system flush. Results from a single kitchen or bathroom tap at each home is shown; Dark blue bars represent preflush concentration, light gray bars represent postflush; The text in parentheses describes the straight-line distance to the WVAW treatment plant and number of days after the Do Not Use Order was issued before the plumbing system was flushed; The dashed line represents the MDL of 10 μg/L. Postflush sample for Home 1 was below the MDL; No 4-MCHM was found above the MDL in Home 5 before or after flushing; Single water samples were analyzed from each tap; Water pre- and postflush was not analyzed from all 10 homes visited.

concentrations in Homes 1 and 3 by 86% and 79% respectively, while the 4-MCHM concentration in Home 2 was relatively unchanged. The observed 4-MCHM reduction in Homes 1 and 3 can likely be attributed to less contaminated tap water entering the home from the recently flushed WVAW water distribution system. Home 2 however was located on a cul-desac and its result implies equally contaminated water was present in the plumbing system after flushing. The 4-MCHM concentration in Home 5's tap water was not found above the 10 μg/L MDL either before or after flushing. Future work should be carried-out to understand chemical fate and design premise plumbing flushing protocols that reduce organic contaminant concentrations at building taps.

Homes that had been flushed before the research team arrived also contained tap water with characteristic odors, but 4-MCHM was only found greater than 10 μg/L in one home. The 4-MCHM concentration found at this home's bathroom tap was 12 μg/L, while the kitchen tap 4-MCHM concentration was 26 μg/

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Table 4. Tap Water Metal Concentrations Found in Unflushed and Flushed Homes[a]

parameter[1]	EPA limit	unflushed homes			flushed homes		
		min	max	above limit?	min	max	above limit?
health standards, maximum contaminant level (MCL)							
As	0.010	<0.000 58	0.000 66	no	<0.000 58	<0.000 58	no
Ba	<2	0.02	0.05	no	0.02	0.03	no
Be	0.004	<0.000 082	<0.000 082	no	<0.000 082	0.000 094	no
Cd	<0.005	0.000 08	0.000 20	no	0.000 073	0.000 703	no
Cr	<0.1	0.0003	0.0009	no	0.0003	0.0011	no
Cu	**< 1.3**	**0.006**	**1.700**	yes	0.006	0.030	no
Pb	**0–0.015**	**0.0001**	**0.0200**	yes	0.0002	0.0050	no
aesthetic standards, secondary maximum contaminant level (SMCL)							
Al	**0.05–0.2**	**0.01**	**1.00**	yes	0.001	0.15	no
Fe	**< 0.3**	**0.006**	**1.900**	yes	0.010	0.280	no
Mn	**< 0.05**	**0.0005**	**0.06**	yes	0.0002	0.0200	no
Zn	<5	0.19	0.86	no	0.20	0.32	no

[a]All values shown are reported in mg/L; MCL = Maximum contaminant level; Health standards are primary MCLs while aesthetic standards are secondary MCLs.

L. Variation between 4-MCHM concentrations at different taps could be attributed to similar reasons discussed previously.

Surrogate Tap Water Contamination Indicators in Flushed and Unflushed Homes. To indirectly measure the removal of contaminated water from plumbing systems surrogate water quality indicators [TOC, UV_{254} absorbance, and specific UV absorbance (SUVA)] were evaluated. At the time this study was conducted, the exact composition including some major and minor ingredients of the spilled chemical mixture and breakdown products formed remained unknown. Previous researchers have recommended that TOC concentration should be applied to detect water distribution system contamination.[23] It was expected that if aromatic compounds with double bonds were present, differences between their concentrations would be indicated by differences in the amount of ultraviolet light at 254 nm wavelength the tap water absorbed.[24,25]

Tap water TOC values varied across flushed (0.72 to 2.62 mg/L) and unflushed households (0.74 to 2.02 mg/L). While some tap water TOC values exceeded WVAW's reported TOC concentration exiting their water treatment plant (1.0 and 1.2 mg/L),[26] the difference between the flushed and unflushed home TOC ranges was not significant ($p=0.658$). Theoretical TOC calculations showed that 4-MCHM would have contributed less than 0.5 mg/L of organic carbon to the water at concentrations found during this in-home study (Table SI-10), within the range of the observed variability within and across homes. Responders should conduct this calculation in response to future contamination incidents to determine if TOC is a valid tap water parameter to monitor.

No relationship was found between 4-MCHM concentration and UV_{254} or SUVA for flushed or unflushed systems. No UV_{254} absorbance was detected for laboratory prepared aqueous solutions of either 30 mg/L 4-MCHM or 30 mg/L Crude MCHM. It is logical that no correlation was found between 4-MCHM concentrations in flushed and unflushed homes with UV_{254} absorbance ($p=0.635$, 0.537) or with SUVA levels ($p=0.376$, 0.598). Results implied that minor ingredients of the spilled solvent were not present at in-home tap water or in sufficient quantity to influence surrogate water quality indicator results. The WVTAP researchers did not find any breakdown products or alterations in drinking water odor when the spilled mixture was diluted in drinking water and then exposed to free chlorine or potassium permanganate.[22]

Inorganic Contaminants in Unflushed and Flushed Homes. Water pH, chlorine concentrations, water temperature and turbidity results are shown in Table SI-11. Water pH and chlorine levels detected were within ranges reported on WVAW's 2013 drinking water consumer confidence report.[26] Plumbing system flushing had no overall impact on water pH across the homes; Tap water in flushed homes was generally above pH 7, while all unflushed homes had pH levels less than 7 ($p=0.010$). Free and total chlorine concentrations did not differ between flushed (1.0 ± 0.6 mg/L and 2.5 ± 0.7 mg/L) and unflushed homes (0.8 ± 0.6 mg/L and 1.7 ± 1.2 mg/L) ($p=0.884$, 0.859). During 2013, WVAW's finished water free chlorine concentration ranged from 0.8 to 2.7 mg/L.[26] Chlorine concentrations within homes at different faucets sometimes differed by orders of magnitude (2.65 mg/L vs 0.05 mg/L); Tap water stagnation in pipes likely contributed to chlorine decay.[27]

Alkalinity, hardness, chloride, fluoride, nitrate, and phosphorus concentrations were similar across the 10 homes studied (Table SI-12). However, in unflushed homes copper and lead concentrations were found above EPA health limits and aluminum, iron, and manganese were detected above EPA recommended aesthetic limits. Because tap water metal concentrations were lower after plumbing systems were flushed, elevated metal concentrations were likely due to water distribution and plumbing system corrosion potentially caused by prolonged water stagnation. Table SI-13 describes unregulated metals found in the tap waters.

Several homeowners complained of observing "colored" water or particles exiting their faucets during flushing. Testing revealed that copper and iron likely caused color (SI). Physical material captured exiting a faucet contained a variety of metals typical of water treatment coagulants as well as water distribution system and plumbing component corrosion (Figure SI-5).

LIMITATIONS AND IMPLICATIONS

This study has several limitations. Although, the results presented remain the only in-home tap water testing data available that describe odor and chemical quality before and after plumbing system flushing. Absence of WVAW as well as responding local, county, State, or Federal organizations to document chemical levels in-homes has resulted in this knowledge-gap. The results presented were obtained during a rapid response while contaminated water was being purged from

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area plumbing systems. Because of time and funding limitations, a large-scale sampling plan was not feasible. The results presented provide a unique contribution to the literature.

This study was designed to understand resident responses and tap water quality within a set of unflushed and flushed residential plumbing systems. There were more than 93 000 utility customers where approximately 83 000 were residential and 5000 were businesses spanning nine counties. While the households visited were not randomly selected, their comparison to government agency water distribution system testing, in-home surveys, and public health studies enables their interpretation. The data from the present work are unique.

By not conducting in-home testing immediately following the contamination incident, responding organizations failed to document chemical exposure differences within and across homes. This rapid response study found that different 4-MCHM concentrations were present at different taps within and across homes visited. In contrast, subsequent in-home testing conducted by WVTAP researchers revealed that 4-MCHM concentrations did not differ between faucets one month after the spill.[28] While the maximum 4-MCHM concentration found in the present study was 420 μg/L, water testing of the utility's distribution system revealed a significantly greater concentration, 3,773 ug/L. It remains unknown if the 3773 ug/L concentration reached resident taps or was the highest 4-MCHM concentration residents experienced.

The absence of 4-MCHM concentration data at the water treatment plant, within the distribution system on January 9, and inside homes during the response inhibits a more complete understanding of chemical exposures experienced by the community. Responding organizations should not only develop analytical test methods during the early hours of the response, but also, in parallel begin collecting water samples so that they can be analyzed once the analytical methods are developed. This approach could enable a retrospective examination of community exposures.

All water utilities and government agencies should determine which organization is responsible for rapid in-home testing during a crisis. In the U.S., water utilities generally argue their responsibility ends at the water meter and some public health officials counter that they do not understand plumbing system materials and engineering. This issue must be addressed. Any rapid response sampling plan should be representative of the affected area and include sampling sites and environmental conditions where residents were or are being exposed, in their homes.

Understanding chemical concentration differences within and between homes is important. Contaminants of concern could breakdown and contribute different chemical exposures to the residents during water use and flushing. Residual contaminant sources in plumbing systems could also pose continual exposure risks to residents. Because 4-MCHM was not found to react with free chlorine and had limited solubility in PEX plumbing pipe, concentration differences observed in the present study are likely due to water usage, other plumbing material interactions, abiotic, and biotic processes.

The premise plumbing flushing procedure reduced 4-MCHM concentrations within some, but not all homes visited and caused persons to experience adverse health impacts. The finding that the 4-MCHM concentration before and after flushing one of the plumbing systems was relatively unchanged can be attributed to equally contaminated water being drawn into the home during flushing. Because 4-MCHM concentrations found in the present study were below the CDC's screening level, exposure to this water should not have caused adverse health impacts. However, results of this study and those of others reviewed here show that illnesses were caused due to premise plumbing flushing. This consequence is likely due to the CDC's 4-MCHM screening level being inadequate for the water exposure conditions. Illnesses were caused because individuals were exposed to chemicals that had volatilized from the tap water into air and volatilization was promoted at higher water temperatures. Poor indoor air exchange conditions also contributed to the exposures.

It should be noted that the CDC did not establish an inhalation screening level and toxicological data is lacking for many of the spilled liquid's ingredients. Interestingly, nine months after the incident, the EPA announced a health based 30-day air screening level of 0.010 ppm_v[35] for 4-MCHM based on much of the same data the CDC used for its screening level calculation. It remains unknown if adverse health effects would occur at this concentration or if this concentration was exceeded inside affected homes during flushing. To date, no inhalation toxicological studies have been conducted regarding the spilled liquid; Oral and dermal toxicity studies are all that exist.

Numerous studies exist that describe plumbing system contamination and flushing approaches. Most of the incidents pertain to removing tap water contaminated with inorganic contaminants and there are too many to list. In these incidents, flow rate, volume of water flushed, and water chemistry were found important.[29,30] Less available are flushing case studies for organic contaminant incidents. There has been some discussion of these events, but little data are available.[31−34] None were found that estimated or monitored inhalation risks due to flushing. In some contamination incidents, affected plastic pipes and other plumbing system components including hot water heaters were replaced because of inadequate contaminant removal or decontamination was not deemed possible.[32] Also found was that some testing was carried-out on certain plastics not used for drinking water piping systems. Thus, some of the limited bench-scale flushing data may not apply to real-world events.

Methods are needed for predicting indoor air concentrations when flushing contaminated tap water into buildings. Any plumbing system flushing procedure should, at the minimum, consider: (1) contaminants present and their maximum quantities expected, (2) contaminant physiochemical properties (i.e., water solubility, Henry's Law Constant, vapor pressure, pK_a), (3) contaminant fate as influenced by water temperature, abiotic, and biotic processes, and (4) residual sources in the premise plumbing and water distribution systems (i.e., biofilm, corrosion scales, plastic materials, unflushed contaminated water). During future incident responses where indoor air contamination is possible, responders should test flushing protocols under worst-case conditions before premise plumbing flushing is recommended. Rapid testing could determine the procedure's contaminant removal effectiveness and help identify unanticipated indoor environmental quality and public health issues. Once premise plumbing flushing is recommended, responders should also monitor signs of illness in the community and conduct in-home surveys in parallel to detect any unanticipated issues. If illnesses occur, then the flushing guidance should be modified. Retrospectively, emergency department physician records and surveys of residents demonstrated that resident health was adversely affected by flushing.

To better prepare for an incident, water utilities and government agencies should document and describe the fixed

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(i.e., tanks, pipelines) and transient (i.e., roadway, barge, etc.) contaminant threats to their drinking water sources. A list of high use and high volume contaminants in or routinely passing through the watershed may help prepare for spill response. Additional information that should be considered includes the industrial product's ingredients, ingredient toxicity, analytical methods and sampling equipment needed for a response, as well as fate and reactivity data for the environment and water infrastructure. When a spill occurs, responders must quickly obtain and characterize a sample of the spilled product as some, but not all, product ingredients are listed on safety data sheets. This was important as WVTAP researchers detected several other contaminants in the spilled liquid not present on the safety data sheet and much of the initial information reported by Freedom Industries, Inc. including the spilled product's purpose, toxicity, volume spilled, and composition reported was inaccurate.

More than 11 months after the chemical spill, several investigations are ongoing and the community is still recovering. The U.S. Department of Justice and Chemical Safety and Hazard Investigation Board have ongoing investigations. The State of West Virginia has expended tens of millions dollars in its response. WVAW has spent more than $12 million, is facing approximately 54 lawsuits, and considering the installation of source water monitoring equipment. Most seriously though, many of the 300 000 people in the area suffered adverse health effects due to contact with contaminated tap water and in part due to being ordered to flush their plumbing systems. This incident demonstrated that a sound scientific approach for responding to and recovering from large-scale tap water contamination incidents is lacking and very much needed.

■ ASSOCIATED CONTENT

Supporting Information

Additional figure and tables related to the materials and methods, results and discussion, and event timeline. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Results and opinions presented in this manuscript only represent the opinions of the authors and not NSF or any other person. The authors declare no competing financial interest.

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■ ABBREVIATIONS

CDC	Centers for Disease Control and Prevention
cPVC	chlorinated polyvinyl chloride
DiPPH	dipropylene glycol phenyl ether
EPA	Environmental Protection Agency
KCHD	Kanawha-Charleston Health Department
4-MCHM	4-methylcyclohexanemethanol
GC/MS	gas chromatography–mass spectrometry
LLE	liquid liquid extraction
MCL	primary maximum contaminant level
MDL	method detection limit
PB	poly(1-butene)
PEX	cross-linked polyethylene
PPH	propylene glycol phenyl ether
SMCL	secondary maximum contaminant level
SPME	solid phase microextraction
SUVA	specific ultraviolet absorbance
TERA	toxicological excellence in risk assessment
TOC	total organic carbon
WVAW	West Virginia American Water
WV BPH	West Virginia Bureau of Public Health
WV DHHR	West Virginia Department of Health and Human Resources
WVTAP	West Virginia Testing Assessment Project

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