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Case study: the crude MCHM chemical spill investigation and recovery in West Virginia USA

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Several recent chemical spills have caused large-scale drinking water contamination incidents in Canada and the USA. The study goal was to identify key decisions and actions critical to incident investigations using the 2014 crude MCHM chemical spill in West Virginia USA as a case study. Environmental testing records, scientific reports, government documents, and communication records were reviewed. Results showed that thorough characterization of the spilled liquid and impacted source water is critical to assessing potential public health risks, estimating chemical fate, and designing infrastructure decontamination procedures that can restore infrastructure use. Premise plumbing water testing was not carried-out by responders but testing conducted by other organizations identified the decontamination procedures issued by responders and drinking water screening levels were not adequate to protect public health. Rapid bench-scale tests should be considered to (1) examine water treatment breakdown products, (2) evaluate chemical sorption and leaching by infrastructure materials (*i.e.*, activated carbon, plastics), (3) predict water heater decontamination, and (4) estimate chemical volatilization during fixture use. Key actions to support an effective response and research needs were identified.

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Water impact

Large-scale drinking water contamination incidents can render water utility and premise plumbing infrastructure unusable or marginally effective. Contaminated water exposure can also cause adverse health impacts prompting the need for immediate medical attention. Loss of safe water access can result in economic losses and decrease public confidence for a community. Rapid investigations and responses are needed to protect the population from harm and quickly recover affected infrastructure. The 2014 Elk River chemical spill in West Virginia USA was reviewed as a case study and key actions and decisions essential to better protecting drinking water, the population, and infrastructure were identified.

Introduction

Between 2014 and mid-2015 a series of large-scale drinking water contamination incidents prompted the issuance of do not drink and do not use orders to the entire service population for several U.S. and Canadian water suppliers.¹ Source water contaminants included algal toxins, diesel fuel, crude oil, and coal processing liquids (Table 1). In most cases, the specific chemical makeup and toxicity of chemicals in the contaminated source water were either poorly understood or unknown, and contaminated water was distributed to the communities.

Three incidents in early 2015 resulted in source water contamination and led to large-scale drinking water contamination

in Nibley City, Utah (diesel fuel), Glendive, Montana (crude oil), and Longueuil, Quebec (diesel fuel). These reference cases revealed a wide array of investigative approaches applied by government agencies and utilities. In all cases, the contaminated source water was chlorinated prior to distribution, and contamination was first detected by customer complaints of petroleum odours at the tap. Upon the discovery that customers were receiving contaminated water, a water ban was established followed by flushing of water utility infrastructure. Customers were then directed to flush their premise plumbing.

Limited information regarding water testing activities during the Glendive and Longueuil incidents was available while no water testing information for the Nibley incident² was found. In Glendive, a variety of semi-volatile (SVOC) and volatile organic chemicals (VOC) were found in the source water and water distribution system (Table 2).⁴ Before premise plumbing flushing was authorized, airborne VOC testing was conducted indoors while faucets were running.^{9,10} Unfortunately, this premise water was not chemically analysed. At

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Table 1 Recent water contamination incidents that caused drinking water outages in the United States and Canada

City, state	Incident characteristics			Population affected (people)	First detection	Water use order	Outage duration (days)
	Date	Contaminants	Source water type				
Nibley City, UT ^a	Apr. 2015	Diesel fuel	Spring	5000	Odour complaint	Do not use	1
Glendive, MT ^b	Jan. 2015	Crude oil	Yellowstone River	5500	Odour complaint	Do not use	5
Longueuil, CN ^c	Jan. 2015	Diesel fuel	St. Lawrence River	230 000	Odour complaint	Do not drink	2
Toledo, OH ^d	Aug. 2014	Microcystins	Lake Erie	500 000	Chemical monitoring	Do not drink	2
Charleston, WV ^e	Jan. 2014	Coal processing liquid	Elk River	300 000	Odour complaint	Do not use	9

^a City of Nibley^{2,3} and contaminated spring water was disinfected with free chlorine. ^b EPA.⁴ City of Glendive⁵ water treatment plant processes included sedimentation, filtration, softening, and free chlorine disinfection. ^c Atkin (2015).⁶ City of Longueuil⁷ utilized a conventional treatment process with coagulation, filtration, disinfection enhanced with ultraviolet, and free chlorination. ^d City of Toledo⁸ utilized free chlorination, filtration, and softening. ^e Ref. 13.

Table 2 Glendive's Yellowstone River and water distribution system sampling results, ppb

Contaminant reported by responders	Source water (January 19, 2014)	Water distribution system (January 21, 2014)
Benzene	14	4.09 (max)
<i>n</i> -Butylbenzene	0.83	nr
<i>sec</i> -Butylbenzene	0.58	nr
Ethylbenzene	4.9	0.37 (max)
Isopropylbenzene	1.1	nr
<i>p</i> -Isopropyltoluene	0.71	nr
Naphthalene	1.0	nr
<i>n</i> -Propylbenzene	1.8	nr
Toluene	21	6.64 (max)
1,2,4-Trimethylbenzene	15	nr
1,3,5-Trimethylbenzene	3.9	nr
<i>o</i> -Xylene	8.6	nr
<i>m</i> + <i>p</i> -Xylenes	32	7.39 (max)

Water was analysed in accordance with EPA Method 524; nr = records not found. Water distribution system samples contained 1.37 ppm free chlorine residual at pH 7.6.

least one resident reported becoming ill while following the flushing guidance issued by government agencies and the water utility.¹¹ In Longueuil Canada, water quality and chemical analysis data for the water treatment plant and distribution system were available (Table 3), but it is unclear if premise plumbing water testing was conducted.^{7,12} In all incidents, no post-flushing premise water analysis seems to have been carried-out.

The observed inconsistency in reference case response actions indicates a deficiency in current investigation approaches. For example, it is unclear whether a thorough chemical analysis of the spilled liquid was completed, as data were not readily available. No data describing how water quality information was used to design subsequent water and indoor air sampling actions or actions to examine water treatment process generated by-products were found.

Furthermore, it is unclear if the sorption and desorption capabilities of water treatment media, plastic water distribution and premise plumbing components were considered in the response. No justifications for premise plumbing flushing protocol design, and estimates of indoor chemical volatilization during flushing were found. After an exhaustive literature review, no study that reviewed other drinking water contamination incidents to this detail was found. This lack of available data inhibits the identification of post-incident lessons learned for reference during acute, time-sensitive contamination events.

The study goal was to identify key decisions during a large-scale chemical drinking water contamination incident. Results were intended to assist the water, public health, and government sectors improve their decision-making judgments during incident response and recovery. This case study was also conducted to identify research needs.

Table 3 Maximum contaminant concentration in the St. Lawrence River and treated drinking water exiting the City of Longueuil water treatment plant, ppb drinking water outages in the United States and Canada

Contaminant category reported by responders	Source water	Exiting water treatment plant
Benzene	0.3	0.2
Toluene	3.8	2.6
Ethyl benzene	nd	nd
Xylenes	3.0	2.7
1,2,4-Trimethylbenzene	10.0	5.0
Dichloro-2,2-propane	nd	nd
Other VOCs	nd	nd
Total PAHs	nd	nd
Other organic compounds	nd	nd
C10–C50	nd	nd

Water samples were collected between January 15 and January 18, 2015 and were analysed in accordance with EPA Methods 524 and 624. PAH = Polynuclear aromatic hydrocarbons the mobile laboratory reported total xylenes (*o*-, *m*-, *p*-) and laboratory testing reported *o*-xylene only; nd = not detected above the method detection limit. Data was reported by City of Longueuil.⁷



The 2014 Elk River chemical spill in Charleston, West Virginia was used as a case study because a large number of organizations conducted independent water sampling and limited information was available to the responders:

1. The liquid that contaminated the source water was a chemical mixture,
2. More than 2 million people downstream relied on the affected source water as a water supply,
3. The population that received contaminated drinking water exceeded 300 000 people (Charleston area 300 000 and City of Huntington, 86 000), and
4. A water ban remained in effect for up to 10 days in some parts of the Charleston area.

Specific objectives of this study were to (1) review all available records pertaining to incident response and recovery actions created by private, public, and university organizations that participated, (2) use these results to outline key decisions, and (3) identify research needs for improving water contamination incident response and recovery.

Elk River incident overview and case study approach

Incident overview

On January 9, 2014 more than 10 000 gallons of a coal cleaning liquid spilled from two above-ground storage tanks into the Elk River. This river was the sole water supply for the Charleston, West Virginia area.¹³ The spilled liquid was used in coal preparation plants.^{14,15} An investigation by the State of West Virginia revealed that carbon steel tanks 396 and 397 had corroded and were leaking.¹⁶ As of March 2016, the exact spill volume was still under investigation by the U.S. Chemical Safety and Hazard Investigation Board,¹⁷ but the spilled liquid is known to have contained a mixture of “crude 4-methylcyclohexanemethanol (MCHM)” and “stripped poly glycol phenyl ethers (PPH).”

Like the aforementioned reference cases, contaminated Elk River water passed through the Kanawha Valley Water Treatment Plant (KWWTP) in Charleston. This facility and the distribution system was owned and operated by West Virginia American Water (WVAW).¹⁸ Potable water with a distinct black-liquorice smell was distributed to 300 000 people on January 9 through 2200 miles of water distribution pipe, 107 storage tanks, and 120 booster stations across 124 pressure zones to upwards of 90 000 buildings.^{18,21,22} Contaminated river water also travelled downstream, entered and passed through the City of Huntington's water treatment plant. Contaminated river water continued 390 miles further downstream which prompted water municipalities in Ohio, Kentucky, and Indiana to shut down their river water intakes. The do not use order in Charleston was in effect for up to 10 days in parts of the KWWTP distribution system. The do not use order warned the population “do not use tap water for drinking, cooking, cleaning, washing, or bathing”.^{23,24} The do not use order also warned customers not to use water except for toilet flushing and firefighting activities.^{25–27}

Federal health officials established short-term screening levels (*i.e.*, concentrations considered safe for 14 days of ingestion) for three drinking water contaminants: 4-methylcyclohexanemethanol (MCHM), polypropylene glycol phenyl ether (PPH), and dipropylene glycol phenyl ether (DiPPH). After the KWWTP and distribution system had undergone flushing, the order was lifted and the population was directed to flush the contaminated water out of their premise plumbing. Two and a half months after the spill, GAC filter media in the KWWTP that had been desorbing 4-MCHM from treated water was replaced. Several public, private, and non-profit organizations conducted bench- and field-scale testing. A detailed timeline of events for one year following the incident can be found in a supplemental data file published elsewhere.¹⁹

Case study approach

Several organizations that collected information and issued guidance in the wake of this spill are described in Table 4. Information collected included material safety data sheets (SDS) provided to emergency responders, along with records for tank liquid analysis, spill site and waterway environmental sampling, water treatment plant and water distribution system sampling, and premise plumbing sampling. Public health data and premise plumbing flushing protocols issued by the state, WVAW, Kanawha-Charleston Health Department (KCHD), and American Federation of Teachers (AFT) were also reviewed. Communications by organizations that contributed to incident response and recovery decisions were also reviewed. Additionally, available fact sheets and reports prepared by government agencies, private companies, and academic researchers were evaluated.

Results

Constituents in tank 396 liquid and their chemical properties

Hours after the State of West Virginia and WVAW (referred to collectively as RESP) discovered the spill, they reviewed the crude MCHM product SDS, which indicated 4-MCHM was the main constituent. Using this information, RESP developed analytical methods to detect 4-MCHM in the tank 396 liquid and in water.¹³ Numerous other chemicals were present in the tank liquid (Table 5), as indicated by the crude MCHM SDS.²⁸

RESP had difficulty identifying the numerous chemicals present in the water supply. After initial drinking water testing for 4-MCHM had occurred January 9 and the CDC established a health based screening level,³⁶ Freedom Industries, Inc. disclosed that an additional product called stripped PPH had also been present in the tank,²⁹ and thus had not yet been considered in health risk assessments. This disclosure did not come until 12 days after the spill. In response, RESP³⁷ investigated and found PPH and DiPPH in contaminated drinking water, and the CDC established screening levels for these compounds.³⁸ Eleven months after the spill, the U.S. Geological Survey (USGS) reported that methyl



Table 4 Organizations involved in the incident response and recovery

Name	Role
Eastman Chemical Company	Manufacturer of crude MCHM present in the Freedom Industries, Inc. storage tank.
DOW Chemical Company	Manufacturer of product that was ultimately processed into stripped PPH present in the Freedom Industries, Inc. storage tank.
Freedom Industries, Inc.	Owner of the corroded storage tank and tank farm site on the Elk River. Provided responders a copy of the material safety data sheet of crude MCHM and stripped PPH. Hired various consulting firms to conduct spill site characterization. Originator of stripped PPH.
West Virginia American Water (WVAW)	Regional water supplier that withdrew, treated, and distributed contaminated water to the 300 000 service population from their Charleston water treatment plant and to 86 000 people from their Huntington plant. Conducted water quality monitoring at their treatment plant and distribution system. Issued premise plumbing flushing guidance.
State of West Virginia	Various agencies such as the Departments of Environmental Protection, Homeland Security, Health and Human Resources conducted water quality monitoring at the water treatment plant and distribution system, collected and analysed public health data. Issued premise plumbing flushing guidance.
Kanawha Charleston Health Department (KCHD)	Regional health department that served 250 000 of 300 000 people affected by the water outage in the Charleston area. Compiled and analysed syndromic surveillance records. Issued premise plumbing flushing guidance.
Centers for Disease Control and Prevention (CDC)	Established health based 14 day drinking water screening levels for 4-MCHM, PPH, and DiPPH for the ingestion exposure pathway.
Environmental Protection Agency (EPA)	Deployed a regional on scene coordinator (OSC) to the spill site shortly after the incident. Conducted chemical analysis of water and soil samples collected from the Freedom Industries, Inc. spill site. Issued a 14 day drinking water screening level for 4-MCHM for the inhalation exposure pathway.
The Authors (AUTH)	With collaborators, conducted in-home drinking water sampling before and after residents were advised to flush their premise plumbing, created a water heater decontamination model, conducted plastic pipe sorption experiments for two crude MCHM ingredients, conducted acute toxicity testing of the spilled liquid on aquatic organisms, developed an indoor air exposure model, estimated physical chemical properties of the liquid's ingredients, and analysed public health data.
West Virginia University (WVU)	Conducted in home drinking water sampling before and after residents were advised to flush their premise plumbing. Conducted activated carbon and river sediment sorption, and river water sampling.
Downstream Strategies, Inc. (ENVC)	Conducted in-home drinking water sampling before and after residents were advised to flush their premise plumbing.
West Virginia Testing Assessment Project (WVTAP)	Independent researchers funded by West Virginia that conducted in-home drinking water sampling, odour analysis of the contaminated water, evaluated the health based screening levels established by CDC and the State of West Virginia, examined breakdown products formed by water treatment processes.
Virginia Tech (VT)	Experimentally measured physical and chemical properties of <i>trans</i> - and <i>cis</i> -4-MCHM isomers, conducted odour analysis of pure 4-MCHM and crude MCHM, examined 4-MCHM sorption to activated carbon, and potential for aerobic degradation in activated sludge wastewater treatment processes.
Group of Attorneys (ATTY)	Filed a class-action lawsuit against multiple parties involved in the spill. Conducted Elk River water testing, premise plumbing, and carried-out acute toxicity testing of an aquatic organism with crude MCHM available in 2014.
United States Geological Survey (USGS)	Conducted water quality monitoring of the Elk River, Ohio River, and drinking water sampling at their Charleston, West Virginia office.
Louisville Water Company (LWC)	Conducted drinking water odour analysis, bench-scale powdered activated carbon (PAC) study for 4-MCHM removal from the water column, and water sampling of the Ohio River.

4-methylcyclohexanecarboxylate (MMCHC), another ingredient in the tank liquid, was present in the water distribution system.³³ Although MMCHC was listed on the crude MCHM SDS, USGS was the only organization that tested for it. Customers were directed to flush their premise plumbing and it is unknown the degree airborne exposure occurred due to PPH, DiPPH, and MMCHC volatility.

Another complexity was that as the catalyst used to create crude MCHM aged, proportions of crude MCHM ingredients changed,³⁹ however, no compositional analysis data was available for how the levels of major and minor ingredients were affected. Furthermore, Freedom Industries indicated that once the crude MCHM product was obtained from Eastman Chemical Company this product was sometimes blended with stripped PPH, exposed to HCl to reduce pH, and water was removed.⁴⁰ These discoveries emphasize the

risk government agencies and water suppliers face when relying on information generated and provided by parties connected to the spill. For example, SDSs did not contain any of this information.^{28,30} Also evident is the risk encountered when toxicity information is not updated and/or not provided to users/regulators in their entirety and under context.

While some data regarding the tank liquid are available, its exact composition remains poorly understood. All testing laboratories reported the total 4-MCHM concentration (*i.e.*, total concentration of *trans*- and *cis*-isomers), which was the most abundant contaminant (Table 5). 4-MCHM isomers were present at a *trans* : *cis*-isomer ratio of 2 : 1.^{33,41} Two major ingredients and nine additional compounds not reported on product SDSs were detected in the tank liquid and were quantified. Their concentrations sometimes differed between reporting organizations. USGS was



Table 5 Chemical composition of the spilled liquid, presence of chemicals in the drinking water and environmental media from the spill site, tentatively identified vs. confirmed compounds

Product	Contaminant	Product SDS		Est. by CDC/ F. IND 1/14	Spilled liquid				Env. Media	
		EAST 1/14	F. IND 1/14		REIC 3/14	WVTAP 3/14	USGS 12/14	ATTY 4/15	PW	Tank site
Crude MCHM	4-Methylcyclohexanemethanol (MCHM)	68–89%		88.5% ^a	79.63% ^b	Y ^b	77–89% ^b	940 ^b g kg ⁻¹	Y	Y ^c
	4-(Methoxymethyl)cyclohexanemethanol (MMCHM)	4–22%								
	Water	4–10%								
	Methyl 4-methylcyclohexanecarboxylate (MMCHC)	5%					Y ^b		Y	
	Dimethyl 1, 4-cyclohexanedicarboxylate (DMCD)	1%								
	Methanol	1%								
Stripped PPH* Not on SDS	1,4-Cyclohexanedimethanol (CHDM)	1–2%			5.60% ^d	Y ^c				
	Polyglycolethers		100%	7.3% ^a						
	Propylene glycol phenyl ether (PPH)								Y	Y ^c
	Dipropylene glycol phenyl ether (DiPPH)				11.33% ^d				Y	
	Formaldehyde							86 ^b ppm	Y	
	Methylene chloride							15 ^b g kg ⁻¹		
	2-Methoxyethoxybenzene (MEB)					Y ^c				
	Cyclohexanemethanol (CHM)				1.84% ^d	Y ^c				
	Dimethylester 1,4-cyclohexanedicarboxylic acid					Y ^c				
	4-Methyl, methyl ester cyclohexanecarboxylic acid (MMCHCA)					Y ^c				Y ^c
	4-Methyl cyclohexanecarboxylic acid (MCHCA)									Y ^c
	1-Hydroxymethyl-2-methyl-1-cyclohexane (HMC)				1.60%					Y ^c
	<i>n</i> -Hexadecanoic acid									Y ^c
	Octadecanoic acid									Y ^c
	Other unidentified compounds				<5%					

Significant figures and units differed because all data was reported “as-is” from sources. EAST is an abbreviation for Eastman Chemical Company; F. IND is an abbreviation for Freedom Industries; PW = potable water; values shown with listed decimal places exactly what were reported by the testing organization; EAST = Eastman Chemical Company;²⁸ CDC/Freedom Industries;^{29,30} REIC = Cortruvo;³¹ WVTAP;³² USGS;³³ ATTY = Attorneys.³⁴ ^a Values were estimated by the CDC and the calculation methodology was not found. ^b Compound confirmed with an analytical standard. ^c Compound identification was tentative (TIC). ^d Information provided by reporting organization insufficient to describe analytical confirmation. ^e Compound detected in spill site groundwater or storm water one month after the spill by the EPA.³⁵ A variety of aromatic chemicals were detected in groundwater, but are likely not due to the Freedom Industries chemical spill and are not listed above. The spill site was formerly the home of a petroleum handling company that was not completely remediated. Units for % detection (w/w, w/v) were not reported.

the only organization to detect MMCHC in the liquid and confirm its presence with an analytical standard. CHDM was found at a much greater concentration (5.6%) when compared to the 1–2% reported on the crude MCHM SDS.

During the spill response, RESP attempted to understand the fate of the tank liquid's constituents in the Elk River, KVVWTP, and distribution system. Physiochemical properties such as water solubility, vapour pressure, and log K_{ow} values for tank liquid ingredients were sought, but most were not found by RESP because SDSs contained little to no data for these properties.^{28,30} Follow-up work by others weeks after the spill revealed that publicly accessible EPA databases such as SPARC and EPIWEB either contained or could be used to estimate these properties.^{19,42} Based on these databases many of the tank liquid ingredients were moderately to highly soluble in water (up to 28 000 ppm for some ingredients at 21 °C), volatile (up to 118 mmHg at 21 °C), and their fate was temperature dependent. Others confirmed through experiments months after the spill that 4-MCHM volatilized from wa-

ter,^{14,15} and the water solubility and log K_{ow} for each 4-MCHM isomer was found to be similar (1010 ppm and 2.46 and 1300 ppm and 2.35 at 21 °C for *trans*- and *cis*-isomers, respectively). The *trans*-isomer however was three times more volatile than the *cis*-isomer.^{42,43} EPA databases could only estimate the properties of total 4-MCHM, not properties for each isomer.

Short-term drinking water screening levels. In the hours following the spill's discovery the State of West Virginia asked the CDC to determine a safe drinking water concentration for 4-MCHM. After reviewing Eastman Chemical Company's limited^{36,44,45} toxicological data for crude MCHM, pure 4-MCHM, and the crude MCHM SDS, the CDC established a 14 day health based screening level of 1 ppm for 4-MCHM.^{36,45} This screening level was based on the ingestion exposure pathway. Hours later, the State of West Virginia added a 100-fold safety factor, establishing a lower screening level of 0.010 ppm. During the early days of the response, 0.010 ppm was the minimum detection limit (MDL) of 4-MCHM in water.¹³ The State of West Virginia used their screening level to determine when



the water in the KVVTP and distribution system was safe to use.⁴⁶ WVAW, relied on the CDC recommended 1 ppm screening level to determine when the water was safe to use.¹⁸ The water ban was not lifted until 4-MCHM concentrations exiting the KVVTP were near 0.010 ppm.

Because health officials did not understand which chemicals were present in the tank liquid and contaminated water when the spill occurred, they were unable to fully evaluate drinking water safety before issuing initial drinking water safety guidance. On January 9, the CDC issued a 28 day 4-MCHM screening level of 1 ppm.³⁶ But, 12 days after this CDC announcement, Freedom Industries' disclosed stripped PPH, another chemical mixture, was also in the tank liquid. This disclosure prompted the CDC to reactively establish 14 day health based screening levels for PPH (1.2 ppm) and DiPPH (1.2 ppm).³⁷ On January 13 WVAW eliminated the do not use order for some parts of their distribution system. The USGS initiated their own tap water study of their Charleston, West Virginia office building nine days after the spill and detected MMCHC in the drinking water distribution system.³³ While the CDC and State of West Virginia health risk assessments considered pure MCHM and crude MCHM, for which MMCHC is a constituent, pure MMCHC was not the subject of independent risk assessments. The presence and toxicity of breakdown products created as contaminated water travelled through the KVVTP and the water distribution system were not considered in these assessments. Limited tank liquid and water sampling data have resulted in an incomplete understanding about the presence of other chemicals in the water supply.

Two months after the spill, toxicologists working with the West Virginia Testing Assessment Project (WVTAP) reviewed available toxicology data for the ingredients listed on SDSs.⁴⁷ WVTAP toxicologists established lower screening levels than the CDC for 4-MCHM (0.120 ppm vs. 1 ppm), PPH (0.850 ppm vs. 1.2 ppm), and DiPPH (0.250 ppm vs. 1.2 ppm).⁴⁸ These lower screening levels were due to differences in risk assessment methodologies and assumptions: exposure pathways (WVTAP considered ingestion, inhalation, and dermal exposure not just ingestion), a longer exposure period (28 days not 14 days), and a more inclusive sensitive population (formula-fed infant not 10 kg child).²⁰ It is the first-hand experience of author Dr. Whelton that WVTAP did not consider a screening level for MMCHC because WVTAP was unaware that this chemical was present in the drinking water when their investigation took place. The 0.010 ppm 4-MCHM screening level established by the State of West Virginia was lower than both the CDC 1 ppm and WVTAP 0.120 ppm screening level. The State of West Virginia accepted the CDC screening levels for PPH and DiPPH.

Exposure to the contaminated water however occurred for 2.5 months, past the 14 day CDC screening levels and 30 day WVTAP screening levels. GAC filters in the KVVTP were found to be contaminated with 4-MCHM and were not replaced until 2.5 months after the incident.⁴⁹ While the CDC issued screening levels as a short-term urgent evaluation based on limited information, these levels were not revised to account for the longer exposure duration that occurred.

A variety of academic and government organizations are conducting toxicological research studies and two studies have been completed as of March 2016. One study found pure 4-MCHM exhibited toxicity to yeast and human lung cells including DNA damage.⁵⁰ To date, the authors do not know of any studies that have been conducted to identify short- and long-term health impacts of inhalation exposures experienced due to this incident. Since the spill, several conference presentations have also been made regarding chemical toxicity. One study reported that a compound similar to PPH caused "impacted developmental physiology in embryonic zebrafish and negatively affected developing motor, behavioural, and social systems."⁵¹ Another study indicated additive toxicity was detected *in vitro* when several different cell lines were exposed to 4-MCHM and PPH.⁵² Also reported was that crude MCHM exposure induced toxicity for *Danio rerio*.⁵³ The authors are aware that additional studies are underway and will be made available by academic institutions in the coming years. Results from follow-up human health impact studies on the tank liquid were not found.

While several organizations have acknowledged the inhalation exposure pathway existed,^{13,45,54,55} no tests have been conducted to investigate the short- and long-term health effects due to that contaminated water exposure pathway. Shortly after January 9, the CDC chose not to consider inhalation toxicity in their screening levels "due to the lack of toxicological information on inhalation, lack of an effective model for inhalation, and lack of a method to analyse the actual amount of MCHM in the air".⁴⁵ Although months later the EPA⁵⁵ established a 4-MCHM inhalation screening level. The US National Toxicology Program⁵⁶ initiated testing to examine health effects caused by the ingestion and dermal exposure to contaminated water. However, both organizations have acknowledged these ongoing studies do not address the inhalation exposure pathway. There is a 20 year precedent that volatile contaminants can express different toxicity by the inhalation exposure pathway compared to the ingestion of contaminated water.⁵⁷ "Inhalation is recognized as being the easiest and fastest means of exposure because vapours are readily accessible to the respiratory tract."⁵⁸ To date, the authors are not aware of any studies conducted to identify the short- or long-term health impacts of inhalation exposures experienced due to this incident. This is surprising because building inhabitants were told to flush their premise plumbing with hot water and incidents of illness indicative of inhalation exposures were detected in the population by multiple local, county, state, and federal agencies.^{19,59}

Source water sampling

Upstream of the water intake. A lack of knowledge remains as to what tank liquid ingredients were present in the Elk River. Furthermore, the concentration of these chemicals at the spill site on the day of the spill remains unknown. During the incident response and recovery, RESP sampled water from the raw water intake and took no samples upstream towards or at the spill site. The day after the spill ATTY



collected one water sample from the Elk River near the spill site and found 0.47 ppm 4-MCHM. That same day, ATTY analysed the water for heavy metal concentrations and results were below state water quality standards. When additional chemical spills involving crude MCHM and contaminated storm water occurred at the spill site January 31, June 12–13, 2014 and July 12, 2015, Elk River testing was only conducted at the raw water intake for 4-MCHM.^{19,60}

Three weeks after the spill was detected contractors working for Freedom Industries, Inc. began chemically analysing spill site storm water, ground water, and soil samples. The contractors found significant surface and subsurface chemical contamination up to 20 feet below ground surface (Table 6).^{61,62} Subsurface characterizations revealed that contaminated groundwater flowing toward the Elk River. EPA³⁵ also tested spill site water samples and found 4-MCHM, PPH, and variety of TICs (Table 5). Neither contractors nor the EPA analysed environmental samples for DiPPH despite this compound having been detected in the contaminated drinking water and having a CDC established screening level. There was no central data repository for all environmental monitoring and sampling data so it was difficult to understand site conditions. Results show that different government and private organizations characterized environmental media for different chemicals and no justification for these dissimilar approaches was found.

At the water intake. The day after the spill was discovered, RESP began analysing 4-MCHM concentrations in Elk River water at the KVVWTP. 4-MCHM concentrations in river water decreased during the next several days (Fig. 1). On January 10, ATTY also conducted grab sampling near the KVVWTP intake and found 0.57 ppm 4-MCHM,³⁴ a concentration much lower than the 3.3 ppm detected at the KVVWTP that same day. This difference is likely due to the ATTY collecting grab samples at the surface of the Elk River whereas RESP water originated from lower in the water column where the intake structure was installed. This difference highlights the importance of consistent water sampling and how methodology can impact the data reported.

Downstream of the water intake. Several organizations analysed river water downstream of the KVVWTP water intake for 4-MCHM.^{33,63–65} The City of Huntington water treatment plant, owned and operated by WVAW, withdrew and distributed contaminated drinking water to its population with reported levels of 9 ppb 4-MCHM, while other downstream

communities shutdown their water intakes and allowed the contaminated river water to pass. Eight days after the spill, 4-MCHM was detected 390 miles downstream in the Ohio River near Louisville, Kentucky (Fig. 1). Hydraulic modelling studies have shown that 4-MCHM concentrations decreased as contaminated river water flowed downstream.^{66,67}

In the months following the spill, some environmental fate studies were completed. In downstream rivers the USGS detected the crude MCHM ingredient MMCHC.³³ Bench-scale studies indicated that 4-MCHM isomers were susceptible to aerobic and anaerobic degradation.^{68–70} However, knowledge-gaps remain. From January 13–18 grab samples were analysed by the Charleston Sanitary Board for 4-MCHM in their wastewater treatment plant influent and effluent. A total of 13 samples were collected and no 4-MCHM was detected above the 6 ppb 4-MCHM method detection limit. This was the only wastewater monitoring data found by the authors during this study. However, other wastewater facilities and collection systems (*i.e.*, Elk Valley) received 4-MCHM contaminated wastewater from communities that flushed their premise plumbing (and this WWTP discharged effluent upstream of the KVVWTP intake). The fate of 4-MCHM and other tank liquid ingredients in the wastewater infrastructure remains poorly understood. Another challenge is that biodegradation studies did not use the tank liquid (a mixture of stripped PPH and crude MCHM), but instead examined crude MCHM. It remains unknown if the liquid spilled into the river exhibited the same degree of biodegradation. No river water or wastewater testing was conducted for PPH, DiPPH, or any other tank liquid ingredient. Tank liquid dispersion and advection in the water column, chemical partitioning between the water and sediment, and the magnitude of volatilization that took place remain unreported, and thus unclear. While 4-MCHM river water monitoring was rapidly conducted by a variety of organizations, absence of thorough river water characterization has resulted in an incomplete understanding of what other chemicals were present and their fate. It is also unknown if MMCHC or other tank liquid ingredients were distributed to the City of Huntington population in treated drinking water due to lack of publicly available data.

Water treatment and distribution system monitoring

Water treatment plant. The day after the spill, RESP began monitoring finished drinking water exiting the Charleston KVVWTP for 4-MCHM (Fig. 2), and the highest 4-MCHM concentration detected in the finished water leaving the treatment plant was 3.35 ppm. After Freedom Industries, Inc. disclosed that stripped PPH was present in the tank liquid, archived water samples were re-analysed and 10 ppb PPH and 11 ppb DiPPH were detected. No additional testing for these compounds was conducted and the reasoning for this decision was not found.

Drinking water odour. In the days and weeks following the spill, laboratories reported “nondetect” 4-MCHM concentrations in drinking water samples but many residents still

Table 6 Maximum 4-MCHM and PPH concentrations detected at the spill site in water and soil, January 2014–October 2014

Environmental media	4-MCHM		PPH	
	<1 mo	1–8 mo	<1 mo	1–8 mo
Ground water, ppm	0.014	9.5	0.022	320
Storm water, ppm	190	0.610	95	18
Sump water, ppm	0.180	440	0.0095	3.2
Soils, mg kg ⁻¹ (20 ft bgs)	—	15 000	—	9000

Data from consulting firms hired by Freedom Industries;^{61,62} no organizations characterized environmental media for DiPPH.



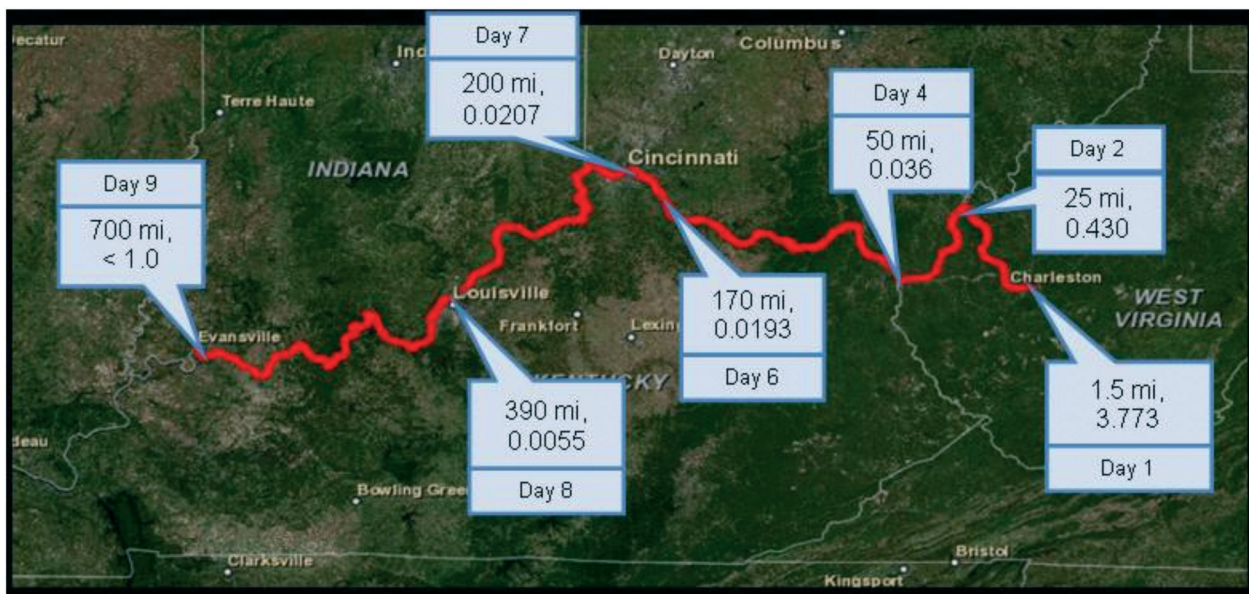


Fig. 1 Maximum known 4-MCHM concentration (ppm) in river water reported as distance downstream from the spill site starting January 9, 2015 as water flowed down the Elk River, into the Kanawha River, and Ohio River.

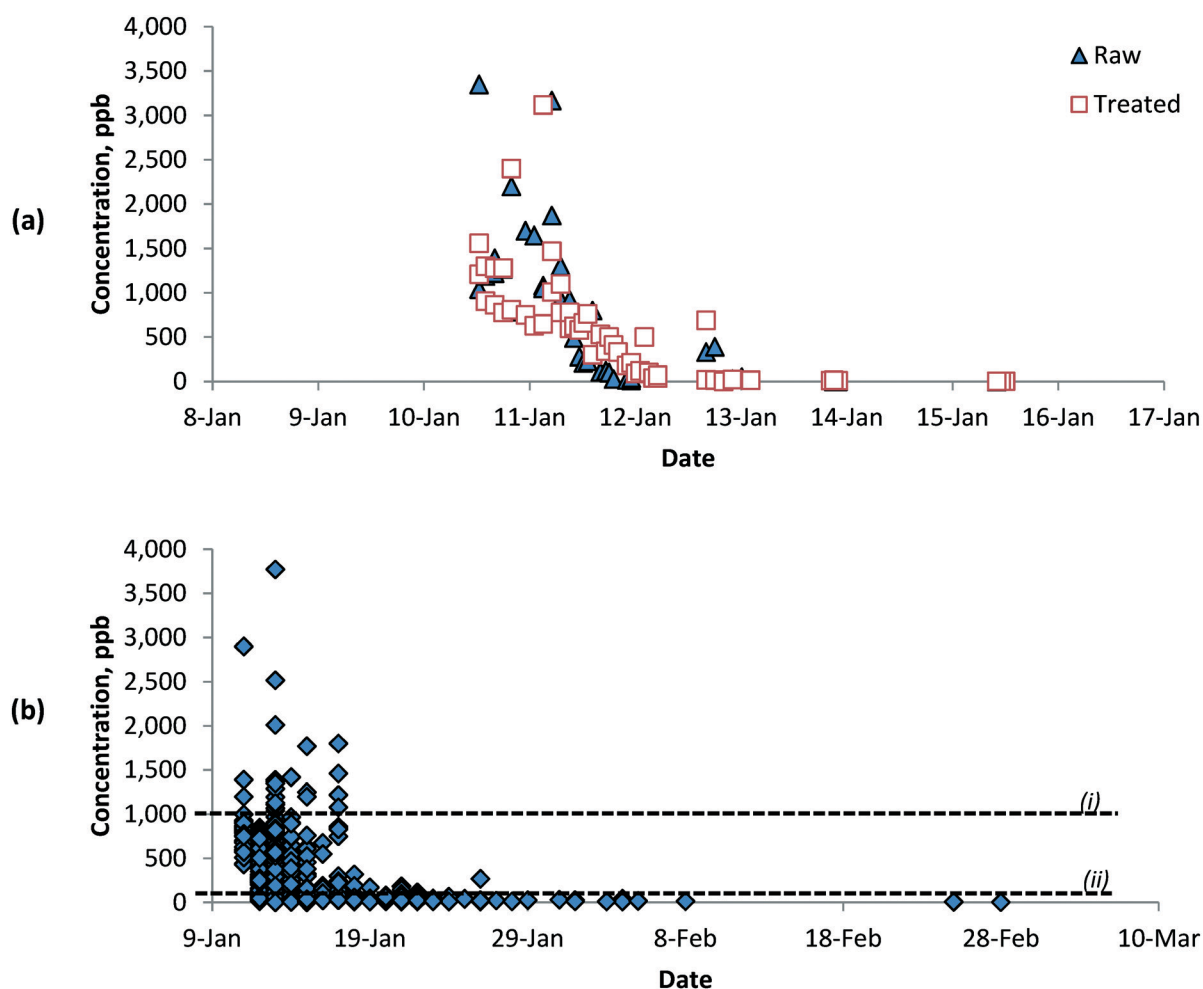


Fig. 2 4-MCHM concentration at the (a) Kanawha Valley water treatment plant and (b) water distribution system. The dotted lines represent the (i) CDC's 1 ppm health-based 4-MCHM screening level, and (ii) WVTAP's health-based 4-MCHM 0.120 ppm screening level. Reproduced from Whelton et al.¹⁹



reported a black liquorice odour in their drinking water.¹⁹ This information implied that the drinking water may still be contaminated but the odour threshold concentration of the contaminants present was below the 10 ppb MDL for 4-MCHM. Shortly after the spill, Louisville Water Company estimated the aqueous odour threshold concentration (OTC) of crude MCHM to be 1–3 ppb.⁶⁴ Approximately one month after the spill, WVTAP conducted a drinking water odour and chemical oxidation study.^{71,72} Using the tank liquid, researchers found that the aqueous OTC was less than 0.15 ppb, odour recognition concentration was 2.2 ppb, and odour objection concentration was 4.0 ppb. These researchers also suggested that other chemicals in addition to 4-MCHM contributed to odour, and odour characteristics of drinking water contaminated with tank liquid and pure 4-MCHM differed. Pure 4-MCHM had a different *trans*-/*cis*-isomer ratio than *trans*-/*cis*-isomers in crude MCHM. Two months after the spill, researchers at Virginia Tech reported that the aqueous OTC of pure 4-MCHM was 7 ppb.⁷³ Follow-up testing on pure 4-MCHM obtained from TCI America and crude MCHM obtained from Eastman Chemical Company revealed air OTCs for each isomer: 0.51 ppb-v (*cis*-) and 0.12 ppb-v (*trans*-).⁷⁴ Additionally, it was reported that the *trans*-4-MCHM isomer had a liquorice odour, while the *cis*-isomer's characteristic odour was not liquorice.⁷⁴

Impact of unit water treatment operations. KVVWTP's main treatment processes included oxidation with potassium permanganate and free chlorine, powdered activated carbon (PAC) dosing, sedimentation, and multimedia filtration with GAC filter caps. One month after the spill, 4-MCHM fate in the water treatment facility was investigated. Neither oxidant was found to have generated detectable breakdown products^{68,70,71} or altered the odour of the contaminated drinking water.⁷¹ Because 4-MCHM was detected in the water distribution system but not in the Elk River one month after the spill, GAC filter media was scrutinized by WVTAP and WVAW. Testing revealed GAC was releasing 4-MCHM into the treated drinking water. Weeks later powdered activated carbon (PAC) and GAC tests showed these materials were capable of removing 4-MCHM from water.^{64,70}

Water distribution system. Two days after the spill was detected in Charleston and contaminated water had been distribution to the population, RESP began quantifying 4-MCHM concentrations in the distribution system. RESP conducted water sampling at fire hydrants and from select buildings after premise plumbing had been flushed (Fig. 2). More than 2500 water samples were collected by RESP¹⁸ and the highest 4-MCHM concentration found in drinking water was in the water distribution system ("as reported" 3.773

Table 7 Contaminants specifically targeted during tap water characterization

Contaminant	Premise plumbing: first-draw sampling (days since spill detected)					Water main: 15 min flush before sampling (days since spill detected)	
	ATTY (1–39) ^{a,b}	WVU (6–20) ^{a,b}	AUTH (7–12) ^{a,b}	ENVC (9–55) ^{a,b}	WVTAP (35–40) ^{a,b}	RESP (2–153) ^c	USGS (13–47)
Organic contaminants							
Acetaldehyde					√		
Formaldehyde	√			√	√		
Formic Acid	√			√			
Methanol	√			√			
Methylcyclohexane	√			√			
4-MCHM	√	√	√	√	√	√	√
PPH					√	√	
DiPPH						√	
MMCHC							√
Metals							
Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mb, Ni, K, Se, Ag, Na, St, Tl, Sn, Ti, Zn	√		√				
Hg, Li, Si, V	√						
General parameters							
Odor	√		√		√		
Temperature	√		√		√		
pH			√		√		
Turbidity			√		√		
Chlorine			√		√		
Total organic carbon			√		√		
UV ₂₅₄ absorbance			√				
Particulates			√				

^a Organization tested both hot and cold water. ^b Organization tested unflushed plumbing systems; days after spill were calculated using 1/9/2014 as day 1. Non-residences include undisclosed sampling locations that are not in any of the aforementioned categories. ^c Locations of responder PPH data were not disclosed. PPH testing began 12 days after collection whereas 4-MCHM samples were tested within 24 hours of collection. No agents were added to neutralize any chlorine present in the sample.



Table 8 Number and types of buildings where drinking water was sampled

Building type	Premise plumbing: first-draw sampling (days since spill detected)					Water main: 15 min flush before sampling (days since spill detected)	
	ATTY (1–39) ^{a,b}	WVU (6–20) ^{a,b}	AUTH (7–12) ^{a,b}	ENVC (9–55) ^{a,b}	WVTAP (35–40) ^{a,b}	RESP (2–153) ^c	USGS (13–47)
Church	1						
Government office						3	1
Hotel	1						
Hospital						7	
Residence	21	3	10	16	11		3
Restaurant	1						
Retail business						4	
School	1					274	
Non-residence	6			4		86	

^a Organization tested both hot and cold water. ^b Organization tested unflushed plumbing systems; days after spill were calculated using 1/9/2014 as day 1. Non-residences include undisclosed sampling locations that are not in any of the aforementioned categories. ^c Locations of responder PPH data were not disclosed. PPH testing began 12 days after collection whereas 4-MCHM samples were tested within 24 hours of collection. No agents were added to neutralize any chlorine present in the sample.

ppm), not exiting the KVVWTP. This discovery implies that the tank liquid plume had already passed by the water intake before raw water sampling began and/or water distribution system sampling was not representative of the entire distribution system. No statistical method was applied during distribution system sampling. As of March 2016, no other water testing data was found.

USGS analysed drinking water collected from their own Charleston office building after their building was flushed.³³ The USGS found 4-MCHM concentrations similar to those observed by RESP. Unlike RESP however, the USGS screened for contaminants other than 4-MCHM and detected MMCHC,³³ but did not quantify its concentration.

Monitoring at premises

Chemicals in Drinking Water – before flushing. RESP did not conduct sampling to determine the drinking water quality within premise plumbing, only the water distribution system. Beginning the day after the spill organizations not associated with the RESP began conducting premise water sampling. According to publicly available records,^{75,76} these organizations analysed 121 first-draw water samples for a variety of contaminants (Table 7) from 75 buildings between January 2014 and February 2014. No organization applied a statistical approach for building selection (Table 8) and the majority of the premises sampled were residential. No

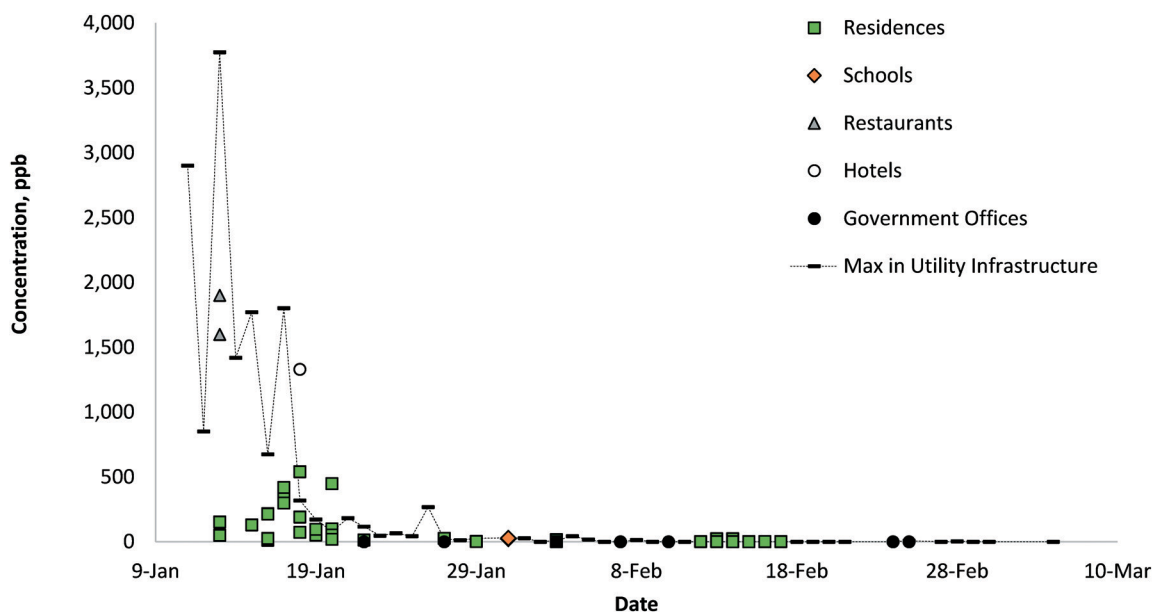


Fig. 3 4-MCHM concentrations in premise plumbing systems compared to the maximum concentration detected in the water utility infrastructure, January 9 through March 6, 2014. Non-detectable results not shown; building plumbing system flushing was authorized by WVAW on January 13 and the last zone was authorized for flushing on January 18; concentrations in USGS offices (January 22 through February 25) were reported as estimates due to matrix interference in analysed water samples; the 14 day and 28 day health based drinking water screening levels for 4-MCHM established by CDC and WVTAP were 1 ppm and 0.120 ppm, respectively.



hydraulic model for the distribution system was made available to the groups that conducted premise sampling. In some homes, 4-MCHM was detected above the CDC screening level but was non-detectable in others (MDL 10 ppb)^{19,33,70,77} (Fig. 3).

There remains an incomplete understanding of what chemicals and concentrations existed in premise plumbing because: (1) RESP chose to flush premises for 15 minutes before collecting a water sample, (2) water sampling did not begin until contaminated water had been distributed to the population, (3) water distribution system sampling data imply that the most contaminated water may have passed through the KVVWTP before water distribution system sampling was initiated, (4) while a do not use order was in effect, the population was permitted to use contaminated water for toilet flushing activities thereby allowing contaminated water to pass through premise plumbing without characterization, (5) chemical analyses of premise water was not exhaustive and thus the presence and concentration of other compounds (*i.e.*, PPH, DiPPH, MMCHC) was not determined. As a result, while the existing premise water testing data are informative, a poor understanding of the chemical composition and composition of contaminated premise water remains.

During the incident response, the public became concerned that chemicals present in their water might sorb into and out of plastic pipes found in premise plumbing thereby continually contaminating their drinking water over time.⁷⁸ The EPA publicly disputed this claim⁷⁸ and cited unpublished, restricted access documents.⁷⁸

Flushing of contaminated water. After 4-MCHM concentrations exiting the KVVWTP were near 10 ppb, portions of the service population were directed to flush their premise plumbing. To aide in this process WVAW, the State of West Virginia, KCHD, and the American Federation of Teachers each issued their own premise plumbing flushing procedures.^{79–83} None of the flushing protocols underwent field validation before use and their similarities and differences have been compared elsewhere.¹ A major difference was that some protocols warned residents to avoid exposure to contaminated water during flushing, while others did not.

Premise water testing conducted before and after flushing revealed that premise flushing procedures did not reduce 4-MCHM concentrations in some homes while 4-MCHM concentrations were greater after flushing in others.^{19,70} A water heater modelling study completed after the spill indicated some of the flushing procedures were not capable of reducing 4-MCHM below the CDC's 1 ppm screening level when homes contained large water heaters, low-flow fixtures, and when 4-MCHM was present in water used to flush water heaters.¹ An analysis of premise plumbing decontamination procedures issued in response to past water contamination incidents in the U.S. revealed similar deficiencies.¹

Review of syndromic surveillance and emergency room medical data indicated that some residents experienced adverse health effects due to contaminated drinking water contact for the weeks following the incident (Fig. 4). A review of public health studies and data¹⁹ revealed some of these ill-

nesses could be attributed to chemical volatilization from the contaminated water during flushing. Findings from a CDC⁸⁴ emergency response study conducted four months after the spill supported these findings. Although, some researchers have since reported no hospitalizations occurred⁸⁵ but conclusions by the CDC and the State of West Virginia indicate otherwise.⁸⁶ Also, not mentioned in the literature is that the West Virginia Poison Control Center previously admitted some persons receiving calls were untrained,⁸⁷ so their reported data may not be reliable. Also, only 36% of the total number of calls to the Poison Control Center could be answered due to call volume challenges.⁸⁵ The Poison Control Center data, while informative, may not be representative of the 300 000 population affected. Also confounding available data is that during the response to the water contamination incident the State of West Virginia Health Officer publicly stated that the chemical-related hospital admittances could be due to the flu.

During the incident persons who presented to emergency departments seeking medical care reported being exposed to drinking water by “breathing a mist of vapour.”⁸⁶ Nine months after the incident EPA established a 0.01 ppm-v inhalation 4-MCHM screening level based on the CDC's 1 ppm ingestion based screening level. EPA's methodology has been explained elsewhere.⁵⁵ Ambient air testing was conducted by EPA 10 months after the spill 2014 at the Freedom Industries spill site during site remediation activities. Air testing revealed 4-MCHM was present in air up to 0.142 ppb-v concentration.⁸⁸ More than a year after the spill, results from two indoor air modelling studies were released and predicted that (1) when residents flushed their premise plumbing to include showers, dishwashers, and faucets, the EPA 4-MCHM air screening level was exceeded⁸⁹ and (2) 4-MCHM could volatilize into the air during showering.⁴³ No studies were found that reproduced volatilization conditions in premises to confirm these predictions. In 2015 the spill site remediation contractor required respiratory protection for its workers citing that potential airborne 4-MCHM levels could exceed 0.01 ppm-v.⁹⁰ Despite inhalation exposure evidence and lacking inhalation toxicity data some state and federal organizations have not made clear that their toxicological evaluations conducted since the spill do not apply to the inhalation exposure pathway.^{91,92}

Chemicals in drinking water – after flushing. After premise plumbing flushing, 4-MCHM was sometimes detected in the premise water. Water distribution system sampling showed that 4-MCHM was as high as 0.269 ppm eight days after the “do not use” order was lifted (Fig. 3). On February 10, 2014 the West Virginia Poison Control Center⁸² declared 4-MCHM was present at or less than 10 ppb, but premise water sampling data showed concentrations as high as 24 ppb 4-MCHM after flushing (Fig. 3). While this concentration was less than both CDC (14 day) and WVTAP (28 day) screening levels, the exposure duration exceeded both screening levels. Unbeknownst to the Poison Control Center at the time, KVVWTP GAC filters were leaching 4-MCHM into the treated drinking water⁹³ and plastic pipes may have been desorbing 4-MCHM in premise plumbing.¹⁹ Because there was no



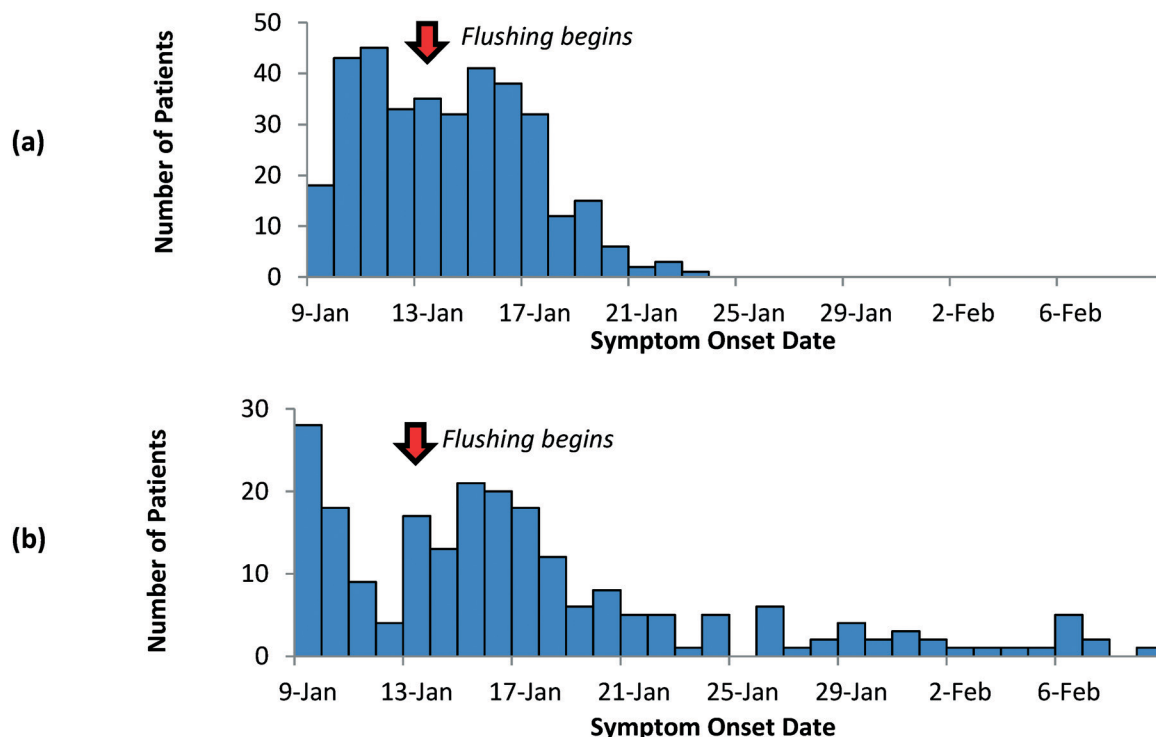


Fig. 4 (a) Visits to emergency departments reported by the U.S. Centers for Disease Control and West Virginia Bureau of Public Health (b) syndromic surveillance cases of clinically defined chemical exposure from January 9 through February 9, 2014. Records represent 10 emergency medical departments with 356 patients and 10 physician offices with 224 patients, respectively (source: open-access¹⁹).

coordinated premise water sampling effort, the highest 4-MCHM concentration that occurred in buildings remains unknown.

Premise 4-MCHM concentrations decreased in the weeks following the do not use order (Fig. 1). One month after the spill, WVTAP conducted the last known in-home water testing effort in 11 residences and detected a maximum concentration of 6.1 ppb 4-MCHM. PPH concentrations in 11 homes were also measured by WVTAP one month after the spill and were not detected (0.5 ppb MDL).²⁰ Based on records reviewed, no other organization characterized premise water for PPH during the response. No record was found for any organization that characterized premise water for DiPPH.

Two aldehydes were detected during premise water sampling and their source remains unclear. Formaldehyde was present in the spilled liquid and was detected in premise drinking water four days and one month after the spill.^{32,94,95} ATTY found formaldehyde in an affected restaurant's toilet during the water ban at 32 to 33 ppb. This result was presented by a scientist working for ATTY to a West Virginia legislative committee and received global press.^{94–96} The scientist speculated that formaldehyde was a breakdown product of the spilled liquid and residents were being exposed to this carcinogen.⁸⁴ The National Toxicology Program previously named formaldehyde as a carcinogen.⁹⁷ No studies were found that addressed the claim that 4-MCHM “broke down in showers or the water system.” WVTAP found formaldehyde and acetaldehyde in premise drinking water one month after the spill (5.6 to 11 ppb, 2.7 to 2.8 ppb, respectively).³² The literature indicates that both aldehydes could

have formed as a consequence of water treatment processes⁹⁸ present at the KWWTP and have been found in drinking water in other cities up to 20 ppb and 12 ppb, respectively.^{98–101} Formaldehyde and acetaldehyde were present well below World Health Organization health standards (50 ppb formaldehyde, 8 ppb acetaldehyde) and standards for drinking water odour (800 ppb formaldehyde; 4 ppb acetaldehyde).^{102,103}

Some TICs were detected in premise water by several organizations (Table 5). Work by WVTAP revealed that some TICs detected by chemical analysis of laboratory processed premise water samples were the result of interactions between chlorine disinfectant residual and stabilizers used in the laboratory's liquid–liquid extraction solvent.^{20,104} This result underscored the importance of understanding how TICs are formed and exposed a deficiency in that no standardized water sampling and processing method was applied during the incident response. 3-Chlorocyclohexene, was the only TIC found with an estimated concentration, 193 to 928 ppb. This contaminant was reported in drinking water obtained from flushed residences 18 days after the spill.⁷⁷

Very few researchers analysed drinking water for metal contaminants. Many metals were detected in premise drinking water and some exceeded health (Cu, Pb) and aesthetic based drinking water standards (Al, Fe, Mn) before premise flushing.¹⁹ After flushing, no metals were found to exceed drinking water standards in the very small number of residences sampled. Blue coloured solids were also collected in homes during flushing and were analysed by X-ray photoelectron spectroscopy.¹⁹ While the State of West Virginia reported



that the solids exiting the faucet during flushing were sediment,¹⁰⁵ chemical analysis revealed some material was not sediment. Blue coloured solids that were collected contained less than 1% silica, as well as oxygen (58%), aluminium (18%), carbon (17%), zinc (1.4%), phosphorus (1.4%), fluorine (1.0%), chromium (as Cr⁶⁺) (0.8%), calcium (0.2%), and copper (0.1%).

Odour analysis of premise water, combined with analytical results for 4-MCHM, enabled the discovery that (1) the tank liquid had a different characteristic odour than pure 4-MCHM, a standard some researchers studied for sensory analysis, and (2) black liquorice odour was present when 4-MCHM was not detected at or above 10 ppb, the MDL at the time of the early response. Premise drinking water was also analysed for other characteristics such as total organic carbon and ultraviolet absorbance, but these water quality characteristics were not found to indicate contaminated water.¹⁹ This is because drinking water contaminant concentrations were too low and did not have aromatic characteristics detectable by UV absorbance measurement or organic carbon concentrations greater than typical drinking water values.

Discussion

This case study underscores the difficulty in responding to a source water contamination incident when limited information regarding the chemicals present, water sampling approaches, techniques, analytical methods, and toxicity are lacking; and when all data, response, and recovery activities are not centralized. According to discussions with organizations involved in the response and the author's records requests, many of the key incident response and recovery decisions were made informally and no detailed water contamination response approach existed. Much of the decision rationale and supporting information was not found. For example, no customer complaint monitoring data has been disclosed by WVAW and the company declined providing it to the authors citing pending litigation. In the 1993 *Cryptosporidium* outbreak in Milwaukee customer drinking water complaints coincided with the detection of contaminated drinking water in the service area.¹⁰⁶ In numerous other water contamination incidents customer complaint data has been used to estimate when chemical exposures began and to identify when certain parts of the water distribution system received contaminated water.¹⁰⁷ Additional data that would help provide clarity includes any and all chemical characterization and physical and chemical property data from Eastman Chemical Company for the product provided to Freedom Industries, Inc. Also needed are internal communications by the companies and organizations about the chemicals, spill, decisions, and actions. This type of information could lend greater insight into the reasoning behind the incident response and recovery decisions and help other communities prepare for a response in the future. It is hopeful that additional information involved in the ongoing lawsuits is disclosed so that additional understanding of the in-

cident and its consequences can be obtained. Communities cannot prepare and respond effectively if they are denied access to critical information needed to protect public health. It is also evident water supplies and government officials cannot best protect public health if they do not understand what information is needed for key decisions during an incident response. This case study has identified several opportunities for government agencies and water suppliers to improve their ability to respond to and recover from time-critical, acute drinking water contamination incidents.

Chemical identification and properties

Rapid determination of the chemicals present in the raw water and distribution system was a focus once the spill was discovered. Unfortunately, little data was available about the constituents in the tank liquid and no detailed knowledge of which chemicals (and their properties) were in the water supply. Further, depositions have revealed the crude MCHM's composition varied and Freedom Industries sometimes altered its composition at their tank farm.

Many of the problems associated with this incident are a consequence of RESP not fully understanding what chemicals were present in the contaminated drinking water. RESP^{108,109} trusted Freedom Industries, Inc. to fully disclose the chemical products that were in the tank liquid which they did not. No SDS^{28,30} explained that the tank liquid that spilled into the Elk River had been previously treated with hydrochloric acid or dewatered after stripped PPH had been mixed into crude MCHM.⁴⁰ RESP did not know where to find physiochemical property data for many of the suspected tank liquid ingredients, and the RESP and CDC solely focused on the potential health impacts of 4-MCHM exposure despite a variety of other chemicals being present in the affected waters. As a result of these actions, health officials were unable to establish acceptable drinking water exposure limits for all of the chemicals present in the contaminated water. It is the author's conclusion that RESP and CDC underestimated the health risk posed to customers as well as the fate of the chemicals in the utility's water infrastructure and customer's premise plumbing. For example, the tank liquid chemicals that were present in the drinking water were not all identified³³ before their initial risk assessments were created³⁶ and flushing was recommended, nor was their fate in plumbing or indoor air understood.^{19,20,43,70,74,89}

Results of this case study show that once a spill occurs, the spilled liquid should be chemically characterized to ascertain its composition. The findings underscore the need for responders to also acknowledge toxicity information available on SDSs may not be accurate. For this reason, it is important responders obtain samples of the spilled product and rapidly investigate its composition and toxicity.

In future incidents, government agencies and water utilities should not only rely on the parties who either caused or were involved in the spill to fully disclose the liquid composition, but initiate their own rapid characterizations. Multiple



laboratories should analyse the liquid, as this increases the probability of detecting compounds some laboratories miss and ensures quality assurance and quality control methods. As WVTAP discovered in the response, at least one laboratory conducting 4-MCHM analysis for the State could not detect low levels of 4-MCHM in water that they claimed to be able detect.⁹¹ Failure to understand the chemicals present in the water amplified the consequences of RESP decisions. For example, premise plumbing flushing occurred without full knowledge of what chemicals customers would be exposed to in their homes or if flushing hot water would result in greater exposures. Disclosure that the USGS detected MMCHC in the water distribution system two to four weeks after the spill underscores the need to thoroughly characterize the contaminated drinking water. Officials cannot make scientifically sound judgments if they are unaware of which chemicals are in contaminated drinking water.

Once chemicals have been identified their physiochemical properties should be obtained so their fate in the affected infrastructure can be assessed. EPA's SPARC and EPISUITE databases can be used in this process. Water solubility, vapour pressure, $\log K_{ow}$, and Henry's Law Constants can be useful in making rapid decisions about chemical fate and transport in water infrastructure systems as well as potential exposure pathways. For incidents that are expected to take weeks to months to recover, experimentally measuring physiochemical parameters may be useful.

Tentative identified compound (TIC) reporting

The liquid that spilled into the Elk River contained a variety of organic chemicals without established analytical methods or drinking water standards. This undoubtedly contributed to the difficulty of the incident response. While responders rapidly established methods to detect 4-MCHM, the unconventional nature of the spilled liquid warranted a more extensive chemical characterization including TIC detection and reporting. TIC results from the spilled liquid, ground water, and storm water samples from the Freedom Industries site provided insight about the chemicals spilled into the water supply (Table 4). It is unknown if any of these TICs were present in the drinking water because testing was not conducted and sampling, handling, and analytical approaches differed across organizations. Also, the majority of laboratories involved in water testing did not report TICs, which is a limitation for an incident of this magnitude. Although, it is well-known that commercial laboratories sometimes charge more when TIC data is requested and can be more comfortable reporting analytical standard confirmed contaminants.

TIC identification is a standard practice when "there is reasonable probability of contamination with unconventional pollutants," and helps to gauge other compounds that might otherwise be missed in the water.^{110,111} The value of TIC reporting was evidenced by the USGS's TIC discovery that MMCHC was present in drinking and Elk River water samples. Because of MMCHC's tentative identification, USGS

followed-up and confirmed its presence with an analytical standard.³³ TIC reporting should be considered in future water contamination incident responses as a screening method. A challenge that occurred in West Virginia was that analytical standards did not readily exist for all TICs. In such scenarios, science grounded strategies must be developed to make certain the public is best protected from the contaminated water containing these possible contaminants.

Rapid bench-scale experiments

A variety of simple bench-scale experiments were conducted in the weeks to months following the spill and should be considered for rapid implementation at the onset of future spill events. These experiments examined the breakdown of chemicals present in the tank liquid that passed through the water treatment plant^{20,70,71} the ability of PAC and GAC to remove 4-MCHM from the water column,^{42,65,70} sorption and desorption of 4-MCHM and CHM ingredients into plastic plumbing pipe,¹⁹ and sorption of 4-MCHM into plastic coatings.⁴² The bench-scale experiments utilized resources at the disposal of many drinking water testing laboratories: beakers, oxidants, activated carbon, and plastic pipe samples. Water characterization was likely the most labour intensive aspect of these experiments. Many of these experiments could be conducted within hours to a few days after a spill and could offer much needed data to RESP. However, these experiments should be undertaken by learned personnel with laboratory experience to ensure that these bench-scale experiments are accurately performed to certify valid results.

Infrastructure, water quality, and flushing

Two and a half months after the spill, WVAW had replaced GAC media in all 16 filters within the KVVWTP.⁴⁹ This was an important step in removing the continuing source of chemical spill contaminants from the entering water supply. This leaching duration exceeded the CDC and WVTAP's estimated safe exposure period of 14 and 28 days, respectively. It remains unknown what concentrations of 4-MCHM at premises can be attributed to GAC filter leaching. No reports were found that described the chemical sorption/desorption capacity of the GAC present in the KVVWTP. The purpose of the planned testing was to determine how much 4-MCHM and other spilled chemicals had sorbed onto the GAC and estimate the degree GAC filters contributed to 4-MCHM levels at customer taps during the 2.5 month exposure period. Thus, the amount of 4-MCHM and possibly other chemicals leached into the water supply before the filters were replaced remains poorly understood partly because the recommended testing was not conducted.

Considerations for premise water sampling and flushing

Premise water sampling applied by numerous non-profit, private, and academic organizations provided an understanding of building tap water chemical and odour quality that was not obtained from RESP distribution system sampling. No



statistical methods were used by any organization to determine a representative batch of buildings to sample. A wide variation in premise water sampling and characterization methods was observed.

On certain days, higher 4-MCHM concentrations were found in premises than in the water distribution system. This difference may have been caused by the lag in residents flushing water from their premise plumbing and/or because water distribution system sampling data were not representative of 4-MCHM concentrations the entire population encountered. The variety of water characterization techniques (organics, inorganics, and odour) had varying usefulness.

Premise plumbing decontamination and exposure

Premise plumbing flushing protocols released by WVAW, the State of West Virginia, KCHD, and the AFT differed from one another and were all found to be unclear and/or deficient in some capacity.¹ Specifically, the following was not adequately considered: large water heaters, low-flow fixtures, chemical sorption and desorption into plastic plumbing components, water being used to flush premise plumbing contained the contaminant that was targeted for removal, and the vulnerability of septic tanks to flooding with the recommended large volumes of flush water. As results show premise plumbing

was not decontaminated in some homes and the water distribution system also was not decontaminated before premise flushing was authorized.

Building inhabitant exposure to airborne contaminants that volatilized from the water during flushing and routine water use was not considered in the WVAW flushing guidance, the most widely circulated guidance.⁷⁹ The black-liquorice odour of the contaminated drinking water (at room temperature) indicated chemicals could volatilize and inhalation was a viable chemical exposure pathway. Spikes in patient admittances at physician offices and hospital emergency rooms seem to support this exposure pathway. The CDC dropped plans to consider inhalation as a viable exposure pathway during their initial 4-MCHM screening level development and cited: "lack of toxicological information and the lack of an effective model to estimate inhalation".⁴⁵ Nine months later, the EPA established an inhalation screening level for 4-MCHM. To accurately protect the population it is critical to understand all exposure pathways including dermal and inhalation rather than assuming ingestion alone and establish premise flushing procedures that minimize the risk to human health.

A review of past drinking water chemical contamination incidents revealed that premise flushing procedures issued in the U.S. have not been based on plumbing system design,

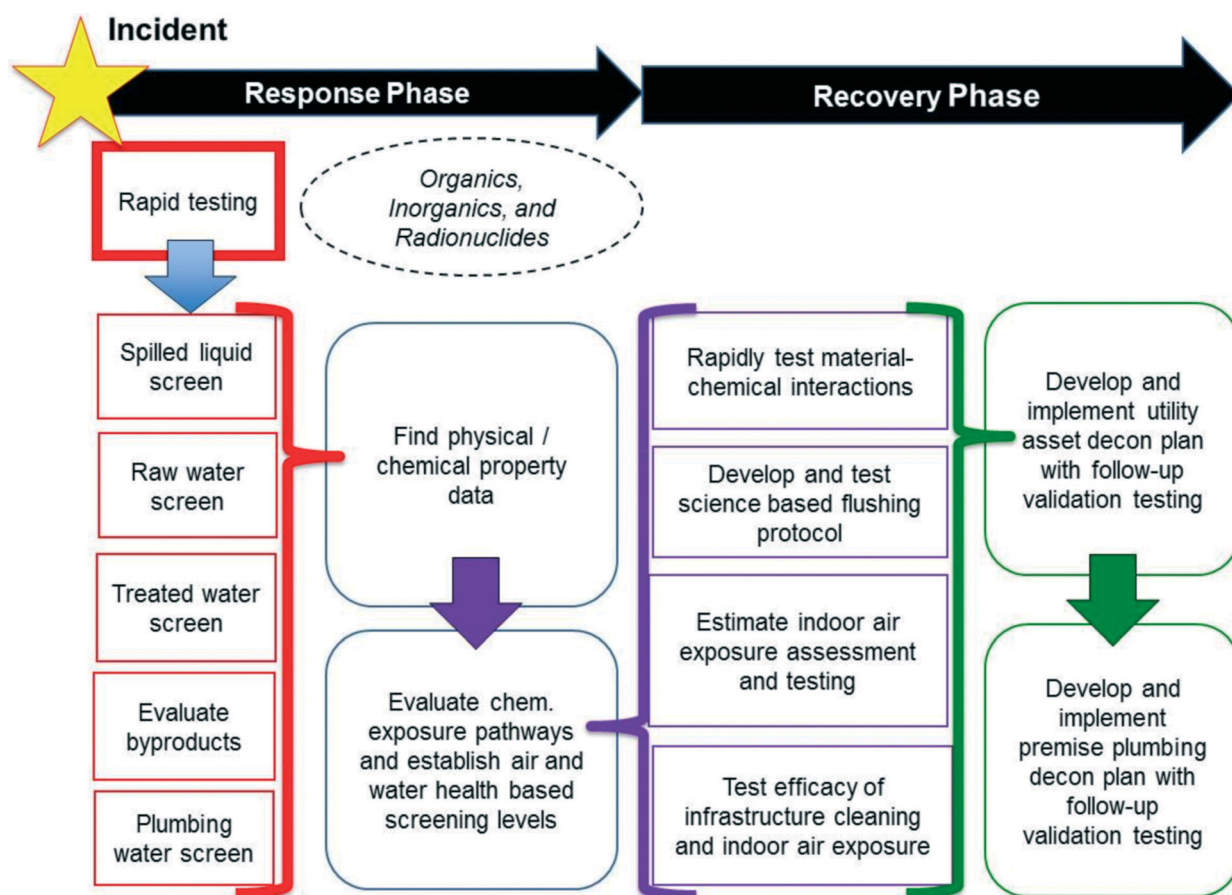


Fig. 5 Stepwise approach for investigating large-scale drinking water chemical contamination incidents.



operations, or materials. A recent study¹ and another underway define several premise plumbing decontamination considerations.¹¹² At present, water heater cleaning scenarios can be evaluated using a water heater flushing model¹ available as an MS Excel spreadsheet. A model for predicting chemical emission into indoor air during flushing from dishwashers, washing machines, faucets, showers has been developed⁸⁹ and will be refined. Government agencies and utilities should consider these easy to use models when determining how to flush premise plumbing. Additional work should be conducted to improve these models and better predict chemical levels in indoor air. Organizations should also consider recommendations for personal protective equipment and practices building occupants should implement to protect themselves from exposure.

Key incident response and recovery actions

Key incident response and recovery activities were identified through this case study (Fig. 5). The stepwise approach presented can be used to guide drinking water contamination incident response and recovery decisions. Some of the identified actions could be initiated in parallel (*i.e.*, environmental media characterization), while others should be conducted sequentially (*i.e.*, obtain physical chemical property data then estimate exposure risks during water heater flushing).

It is also important to recognize that results of the present study differ significantly from EPA efforts and their Response Protocol Toolbox (RPTB).¹¹³ The RPTB effort was initiated shortly after September 11, 2001 in an effort to better understand how to respond to drinking water contamination incidents. First, the RPTB contains a stepwise process for incident investigation, which primarily involves “assessing the threat, determining if it is credible, and confirming that an incident has occurred”. When chemical spills occur and the water supply is known to be contaminated, the EPA's RPTB approach does not seem applicable. Furthermore, cleaning out affected water infrastructure and premise plumbing and protecting the population during the process is critical for the community to recover from the incident. The RTPB guidance does not address these actions.

Eight years ago the U.S. water sector outlined several needed water contamination research activities, some in partnership with the EPA, but very few have been addressed.¹¹⁴ To obtain the necessary data and in light of the fact that large-scale drinking water contamination incidents continue to occur, the authors propose the U.S. water sector instead seek alternative research mechanisms and partners. In retrospect, many of the discoveries from the Elk River chemical spill could have been addressed many years ago.

A variety of activities should be considered to improve the water and public health sector's ability to investigate and respond to water contamination incidents.

- Develop an approach for rapid analytical characterization of complex liquids (*i.e.*, coal washing liquid, oils, *etc.*) and matrices (*i.e.*, river water, drinking water, wastewater).

- Develop methods to rapidly predict chemical fate in water treatment, water distribution systems, and premise plumbing.

- Further develop premise plumbing hydraulic and indoor air exposure assessment models, and develop a better understanding of chemical–material interactions.

- Establish mechanisms whereby persons/organizations not formally involved in the response can access samples available to responders and provide data to responders.

- Make data collected by responders centrally and publicly available during the incident response and recovery.

- Train and conduct disaster response water contamination exercises¹¹⁵ using realistic scenarios including conditions described in this case study.

Using this case study, the water and public health sectors can improve their ability to rapidly respond to and recover from incidents. The long-term health effects caused by drinking water contamination may continue until pertinent research is conducted. Despite this clear problem, if the water and public health sectors implement some of the recommendations identified in this study the chances that a population will be exposed to contaminated water could be diminished or avoided altogether. Results of this study can help expedite government agency and water utility decision making processes.

Conclusions

The goal of this study was to identify key decisions during the Elk River chemical spill. This incident was challenging to government agencies and WVAW for a number of reasons within and outside their control. Data from a variety of private, public, and university organizations was collected, analysed, and included in this case study.

As demonstrated by organizations that responded to the chemical spill, no widely accepted approach to rapidly identify and quantify chemicals present in contaminated drinking water was applied. As a result, health officials did not fully understand which chemicals residents were being exposed to in their drinking water for months following the January 9 spill's discovery. Future work is needed to determine adequate methods for rapidly collecting and characterizing spilled liquids, raw, and treated waters. This will not be trivial and could include a national expert workgroup.

The Elk River chemical spill response and recovery also underscored the need for rapid and standard tests that can identify breakdown and transformation products as contaminated water passes through water treatment plants. Also needed are methods to predict if contaminants are preferentially sequestered as water passes through water treatment processes (*i.e.*, oxidation, activated carbon) and infrastructure (*i.e.*, pipe/coatings).

The incident revealed that the actions needed to safely decontaminate premise plumbing are poorly understood. A stepwise decontamination process has been described elsewhere¹ but additional work is needed to address knowledge-gaps. It is recommended that flushing and other



infrastructure decontamination protocols be thoroughly tested and air monitoring should be conducted in conjunction with water sampling *before* the public is told to flush their premise plumbing. If responders do not fully understand the contaminants present in the contaminated water, health officials cannot issue guidance to best protect the population from harm. If chemical testing is not thoroughly conducted during the early stages of the incident, this lack of data will affect all downstream public health decisions possibly extending the recovery period, resulting in lost public confidence, spread of contamination, and causing the population to experience adverse health impacts.

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References

- 1 K. Casteloes, R. H. Brazeau and A. J. Whelton, *Environ. Sci.: Water Res. Technol.*, 2015, 1, 787–799.
- 2 City of Nibley, Water Emergency Updates, Accessed May 1, 2015. Nibley City, UT USA, <http://www.nibleycity.com/index.php/41-home-blog-2013/206-water-emergency-update>.
- 3 L. Anderson, Nibley City Water Master Plan, *Cache-Landmark Engineering prepared for Nibley City*, Logan, UT USA, 2012.
- 4 EPA (Environmental Protection Agency), *Bridger Pipeline Release Water Treatment Plant Analytical Data Summary*, Washington, DC, 2015, <http://www.epaos.org/sites/9708/files/WTP%20Analytical%20Summary%2002-24-15.pdf>.
- 5 City of Glendive, Department of Public Works (DPW), Glendive, MT, 2012, http://www.cityofglendive.us/departments/public_works/water/index.php.
- 6 E. Atkin, *230,000 People Told Not To Drink Their Water After Diesel Fuel Spill In Canada*, 2015, [accessed 2015 Aug 23] <http://thinkprogress.org/climate/2015/01/15/3612298/longueuil-do-not-drink-water-diesel-spill/>.
- 7 City of Longueuil, *Drinking water... from the river to your tap*, Ville de Longueuil, Canada, 2015, <https://www.longueuil.ca/en/drinking-water>.
- 8 City of Toledo, Department of Public Utilities, *Microcystin Event Preliminary Study*, Toledo, OH USA, 2014, vol. 73.
- 9 EPA, *Glendive Spill Ambient air and Headspace Monitoring*, Glendive, MT. <http://www.epaos.org/sites/9708/files/MonData%2001-19&20-2015.pdf>.
- 10 EPA, *Bridger Pipeline Analytical Summary Report*, Glendive, MT USA, 2015 <http://www.epa.gov/region8/bridger-pipeline-release>.
- 11 M. Brown, *Montana city gets OK to drink water after oil spill in river*, The Associated Press. Billings, MT USA, 2015, [accessed 2015 Oct 22] <http://www.greatfallsbtribune.com/story/news/local/2015/01/22/glendive-hear-water-safe-drink-oil-spill/22173407/>.
- 12 City of Longueuil, Points d'échantillonnage 2 et 3 - Usine régionale et puits d'eau brute. Concentration en benzène mesurée - Eau brute avant traitement - Puits et usine régionale. [In French] Ville de Longueuil, Canada, 2015 http://www.longueuil.ca/files/longueuil/images/PDF/compilation_resultats_echantillonnage.pdf.
- 13 P. Markham, J. Gianato and J. Hoyer, *After Action Review Emergency Response To January 9, 2014 Freedom Industries Chemical Leak*, Charleston, WV USA, 2014, <http://www.governor.wv.gov/Documents/After%20Action%20Review.PDF>.
- 14 Y. T. He, A. Noble and P. Ziemkiewicz, *Chemosphere*, 2015, 127, 158–163.
- 15 A. Noble, Y. T. He and P. Ziemkiewicz, *Int. J. Coal Prep. Util.*, 2016, 36, 69–81.
- 16 West Virginia, Attorney General (WVAG), *Elk River Chemical Spill Incident Report*, Charleston, WV USA, January 8, 2015.
- 17 J. Banks, Status of Freedom Industries, Inc. chemical spill investigation, Personal Communication, U.S. Chemical Safety and Hazard Investigation Board. Washington, D.C. USA, March 7, 2016.
- 18 J. L. McIntyre, Direct Testimony of Jeffrey L. McIntyre. Public Service Commission of West Virginia, Charleston; CASE NO. 14–0872-W-GI; General Investigation Pursuant to W.Va. CODE 24–2–7 into the Actions of WVAWC in Reacting to the January 9, 2014 Chemical Spill. Submitted by Jackson Kelly, PLLC, 46 pp. July 2, 2014. <https://www.pacer.gov/>.
- 19 A. J. Whelton, L. McMillan, M. Connell, K. M. Kelley, J. P. Gill, K. D. White, R. Gupta, R. Dey and C. Novy, *Environ.*



- Sci. Technol.*, 2015, **49**(2), 813–823, DOI: 10.1021/es5040969.
- 20 J. S. Rosen, A. J. Whelton, M. J. McGuire, J. L. Clancy, T. Bartrand, A. Eaton, J. Patterson, M. Dourson, P. Nance and C. Adams, *WVTAP final report*, West Virginia Testing and Assessment Project, Charleston, WV USA, 2014.
 - 21 J. Rosen, A. J. Whelton, M. McGuire, J. Clancy, T. Bartrand, A. Eaton and J. Patterson, *Chemical Spill of Crude MCHM into the Elk River*, Pres. at the New England American Water Works Association Conf. Rockport, ME USA, Sept. 21–24, 2014.
 - 22 US Census Bureau, Census Data for Putnam, Boone, Cabell, Clay, Kanawha, Logan, Lincoln, Putnam, and Roane counties, West Virginia, Washington, DC USA, 2015 <http://www.census.gov/>.
 - 23 West Virginia, Office of the Governor, Governor Tomblin Provides Update Regarding the State of Emergency, 01-10-14 @ 4 PM. [Accessed 2015 Sept 17] <http://www.governor.wv.gov/Pages/State-of-Emergency.aspx>.
 - 24 WVAW (West Virginia American Water), January 9, 2014, *FAQs for West Virginia American Water Kanawha Valley Customers*, Charleston, WV USA, Downloaded at.
 - 25 WVAW, January 9, 2014, *FAQs for West Virginia American Water Kanawha Valley Customers*, Charleston, WV USA, Downloaded at <http://amwater.com/files/WV%20-%20FAQs%20for%20WV%20Water%20Alert%20011113%20v2.pdf>.
 - 26 WVAW, *How to Flush Your Plumbing System*, Charleston, WV USA, January 2014, p. 3, <http://www.governor.wv.gov/Documents/HowtoFlushYourPlumbingSystem.pdf>.
 - 27 WV DHHR (West Virginia, Department of Health and Human Resources), Recommendations for flushing household plumbing at homes served by WV American Water which also use a septic system for sewage disposal, rather than public sewer, Charleston, WV USA, January 2014, p. 1, [http://www.wvdhhr.org/phs/flushing%20recommendations%20where%20septic%20systems%20are%20used%20\(3\).pdf](http://www.wvdhhr.org/phs/flushing%20recommendations%20where%20septic%20systems%20are%20used%20(3).pdf).
 - 28 Eastman Chemical Company, *Safety Data Sheet for Crude MCHM*, Kingsport, TN USA, 2015, <http://www.dhsem.wv.gov/West%20Virginia%20Public%20Water%20Supply%20Study%20Commission/Documents/Eastman-MCHM-MSDS.pdf>.
 - 29 Freedom Industries, Inc., Letter to West Virginia DEP describing the composition of the materials in Tank 396, Charleston, WV USA, January 22, 2014, <http://www.dep.wv.gov/pio/Documents/Freedom%20Response%20to%20WVDEP%20Order.pdf>.
 - 30 Freedom Industries, Inc., 2014, *Material Safety Data Sheet for PPH*, Charleston, WV USA, Preparation date: October 15, 2013, <http://www.dhsem.wv.gov/West%20Virginia%20Public%20Water%20Supply%20Study%20Commission/Documents/PPH%20Stripped%20MSDS.pdf>.
 - 31 J. A. Cortruvo, Direct testimony of Joseph A. Cortruvo, PhD, BCES, Testimony Manuscript. Charleston, WV USA, 2014.
 - 32 WVTAP, *WVTAP_database_20140328_release Charleston*, WV USA, 2014.
 - 33 W. T. Foreman, D. L. Rose, D. B. Chambers, A. S. Crain, L. K. Murtagh, H. Thakellapalli and K. K. Wang, *Chemosphere*, 2015, **131**, 217–224.
 - 34 Thompson and Barney, PLLC, Premise water sampling data collected on behalf of lawyers who filed a class action lawsuit: Interim Class Council, Goode v. Am Water, 2:14-CV-01374. (S.D., WV USDC), Charleston, WV USA, 2015, <https://www.pacer.gov/>.
 - 35 EPA, *Field Analytical Report, West Virginia Chemical Leak*, Sample collection dates 1/28/2014–2/8/2014. Project # DAS R34317, Fort Meade, MD USA, 2014.
 - 36 CDC (Centers for Disease Control and Prevention), *Summary Report of Short-term Screening Level Calculation and Analysis of Available Animal Studies for MCHM*, Atlanta, GA USA, January 20, 2014, <http://emergency.cdc.gov/chemical/MCHM/westvirginia2014/pdf/MCHM-Summary-Report.pdf>.
 - 37 CDC, *Summary Report of Short-term Screening Level Calculation and Analysis of Available Animal Studies for Dipropylene Glycol Phenyl Ether (DiPPH) and Propylene Glycol Phenyl Ether (PPH)*, Atlanta, GA USA, January 2014, <http://emergency.cdc.gov/chemical/MCHM/westvirginia2014/pdf/DiPPH-PPH-calculation.pdf>.
 - 38 WV DHSEM (West Virginia, Department of Homeland Security and Emergency Management), PPH/DiPPH Operational Sampling Results, Charleston, WV USA, April 24, 2014, <http://www.dhsem.wv.gov/West%20Virginia%20Public%20Water%20Supply%20Study%20Commission/Documents/PPH%20Results%201%20APR%2014%201500.pdf>.
 - 39 Eastman Chemical Company, Deposition testimony of Brent Tennant, March 12, 2015. Case No. 2:14-CV-01374. Crystal Goode, *et al.* vs. American Water Works Company, Inc. *et al.* District Court Southern District WV, USA.
 - 40 Eastman Chemical Company, Deposition testimony of Kevin Skiles. February 23, 2016. Case No. 2:14-CV-01374. Crystal Goode, *et al.* vs. American Water Works Company, Inc. *et al.* District Court Southern District WV, USA, <https://www.pacer.gov/>.
 - 41 M. J. McGuire, I. H. Suffet and J. Rosen, *J. - Am. Water Works Assoc.*, 2014, **106**(10), E445–E458.
 - 42 A. M. Dietrich, A. Thomas, Y. Zhao, E. Smiley, N. Shanaiah, M. Ahart, K. A. Charbonnet, N. J. DeYonker, W. A. Alexander and D. L. Gallagher, *Environ. Sci. Technol. Lett.*, 2015, **2**(4), 123–127.
 - 43 A. E. Sain, A. M. Dietrich, E. Smiley and D. L. Gallagher, *Sci. Total Environ.*, 2015, **538**, 298–305.
 - 44 E. R. Tomblin and K. L. Bowling, West Virginia Office of the Governor Letter to Dr. Tom Frieden, Director, Centers for Disease Control and Prevention, Atlanta, GA. February 8, 2014. Charleston, WV USA.
 - 45 T. R. Frieden, Centers for Disease Control and Prevention. Letter to The Honorable Shelley Moore Capito, U.S. House of Representatives, Washington, D.C., May 20, 2014.



- 46 E. R. Tomblin, State of West Virginia 4-MCHM Screening Level used to Determine Level at which Drinking Water Distribution System Would be Decontaminated. Personal Communication, *Governor of West Virginia*, Charleston, WV USA, February 2014.
- 47 C. Adams, A. J. Whelton and J. Rosen, *Literature Review: Health effects for chemicals in 2014 West Virginia Chemical Release: Crude MCHM compounds, PPH, and DiPPH; West Virginia Testing Assessment Project*, Charleston, WV USA, 2014, Accessed November 10, 2015 <http://www.wvtapprogram.com>.
- 48 Toxicological Excellence in Risk Assessment (TERA), *Report of Expert Panel Review of Screening Levels for Exposure to Chemicals from the January 2014 Elk River Spill*, Cincinnati, OH USA, May 12, 2014.
- 49 WVAW, *Press Release: West Virginia American Water Carbon Filter Change Out Project Complete*, Charleston, WV USA, June 12, 2014.
- 50 J. Lan, M. Hu, C. Gao, A. Alshawabkeh and A. Gu, *Environ. Sci. Technol.*, 2014, **49**(10), 6284–6293, DOI: 10.1021/acs.est.5b00371.
- 51 K. K. Abbas and R. D. Foushee, *Effects of Triphenylphosphine and Tripropylene Glycol Methyl Ether on Zebrafish (Danio Rerio) Embryo Physiology and Early Postnatal Development*, Pres. At Conference for the International Society for Developmental Physcobiology, Washington, D.C. USA, November 11–14, 2014, <http://www.isdp.org/assets/docs/2014isdpabstracts.pdf>.
- 52 E. Fabyanic, A. Han, M. Prediger and J. Boyd. *In Vitro Toxicological Assessment of 4-Methylcyclohexane Methanol and Propylene Glycol Phenyl Ether Mixtures*, Pres. at the Soc. Toxicol. Conf., New Orleans, LA USA, 2016 March 13–17.
- 53 K. A. Horzmann, A. J. Whelton and J. L. Freeman, *Acute development toxicity of crude MCHM in zebrafish (Danio rerio) and observed neurobehavioral alterations*, Pres. at the Soc. Toxicol. Conf. New Orleans, LA USA, 2016 March 13–17.
- 54 Associated Press. EPA to Gauge Safety of Inhaling MCHM, Charleston, WV USA, May 1 2014, <http://wvpublic.org/post/epa-gauge-safety-inhaling-mchm>.
- 55 EPA, *Derivation of an Extrapolated Short-term Inhalation Screening Level for 4-Methylcyclohexanemethanol (MCHM - CAS# 34885-03-5)*, Publicly released September 2014, Dated July 3, 2014. Washington, D. C. USA.
- 56 S. S. Auerbach, *NTP Research Project: West Virginia Chemical Spill*, Presentation at the NTP Board of Scientific Counselors Meeting, Raleigh, NC USA, December 10, 2014.
- 57 C. P. Weisel and W. K. Jo, *Environ. Health Perspect.*, 1996, **104**(1), 48–51.
- 58 *Hayes Principles and Methods for Toxicology*, ed. A. W. Hayes and C. L. Kruger, CRC Press, 6th edn, 2014, p. 2184.
- 59 C. P. Schade, N. Wright, R. Gupta, D. A. Latif, A. Jha and J. Robinson, *PLoS One*, 2015, **10**, e0126744.
- 60 J. Hickman, *Freedom Industries Spill Response Site Visit Report July 12, 2015*, Email to: Ryan Harbison, Brad Wright, West Virginia Department of Environmental Protection, November 18, 2015.
- 61 Civil and Environmental Consultants, Inc. *Remediation plan: tank 396 release freedom industries facility*, Export, PA USA, April 8, 2014, Prepared for: Freedom Industries, Inc, Charleston, WV USA, Accessed <http://www.dep.wv.gov/pio/Documents/Settlements%20and%20Orders/Remediation%20Plan.pdf>.
- 62 Arcadis, U.S. Inc., Freedom Industries: site investigation report. Freedom Industries - Etowah River Terminal, 1015 Barlow Drive, Charleston, Kanawha County, West Virginia VRP ID# 15017. April 30, 2015. Bluefield, VA, USA. Prepared for: Freedom Industries, Inc. Charleston, WV USA.
- 63 J. G. Schulte, *ORSANCO's Role in Source Water Protection, Emergency Response and the Protection of Drinking Water Utilities*, Pres. at the Nat. Resp. Training Regional Response IV Fall Meeting, Louisville, KY USA, October 2014, [http://www.nrt.org/production/nrt/RRTHomeResources.nsf/resources/RRT4Oct2014Meeting_2/\\$File/ORSANCO_2.pdf](http://www.nrt.org/production/nrt/RRTHomeResources.nsf/resources/RRT4Oct2014Meeting_2/$File/ORSANCO_2.pdf).
- 64 R. Song, E. Zhu and J. Schulte, *LWC's Response to Elk River/MCHM Spill*, Pres. at the Nat. Resp. Training Regional Response IV Fall Meeting, October 2014, Louisville, KY USA, October 16, 2014, [http://www.nrt.org/production/nrt/RRTHomeResources.nsf/resources/RRT4Oct2014Meeting_2/\\$File/LWCG%C3%87%C3%96s_Response_to_Elk_River_MCHM_Spill.pdf](http://www.nrt.org/production/nrt/RRTHomeResources.nsf/resources/RRT4Oct2014Meeting_2/$File/LWCG%C3%87%C3%96s_Response_to_Elk_River_MCHM_Spill.pdf).
- 65 R. Stuck and B. Whitteberry, *Responding to an Upstream River Spill: GCWW's Approach to the Elk River WV Spill*, Pres. at the One Water Conference, Ohio Water Environmental Association-American Water Works Association, Columbus, OH USA, August 27, 2014, http://www.onewaterohio.org/docs/0900.responding_to_an_upstream_river_spill.pdf.
- 66 R. Bahadur and W. Samuels, *J. Environ. Eng.*, 2015, **141**(7), 05014007.
- 67 L. Stolze and F. Volpin, *Environ. Sci. Pollut. Res.*, 2015, **22**(10), 7980–7985.
- 68 L. Yuan, W. Zhi, Y. Liu, E. Smiley, D. Gallagher, X. Chen, A. Dietrich and H. Zhang, *Sci. Total Environ.*, 2016, **547**, 78–86.
- 69 L. Yuan, W. Zhi, Y. Liu, E. Smiley, D. Gallagher, X. Chen, A. Dietrich and H. Zhang, *J. Hazard. Mater.*, 2016, **306**, 247–256.
- 70 J. Weidhaas, K. Buzby, A. Harris, P. Ziemkiewicz, K. Wang and L. Lin, *MCHM/PPH in the Elk and Kanawha Rivers after the January 2014 Spill: Lessons Learned*, Pres. at the West Virginia Mine Drainage Task Force Symposium. Morgantown, WV USA, 2015.
- 71 M. J. McGuire, *Oxidation Studies with Crude 4-methylcyclohexanemethanol in Water*, West Virginia Testing and Assessment Project, Santa Monica, CA USA, 2014.
- 72 M. J. McGuire, *Odor Study Technical Memorandum*, WVTAP, Santa Monica, CA USA, 2014.



- 73 K. Ward, Jr., *Virginia Tech experts pinpoint MCHM odors*, West Virginia Gazette, March 26, 2014, <http://www.wvgazette.com/News/201403260095>.
- 74 D. L. Gallagher, K. Phetxumphou, E. Smiley and A. M. Dietrich, *Environ. Sci. Technol.*, 2015, 49(3), 1319–1327.
- 75 West Virginia Department of Homeland Security and Emergency Management (DHSEM), *Water Crisis website: data file “WVAW Operation Log as of 18 Jan at 1800”*, Charleston, WV USA, 2014, Accessed at: <http://www.dhsem.wv.gov/Documents/Sampling%20Results/OPERATION%20LOG%2018JAN1800%20Water.pdf>.
- 76 WV DHSEM, *Water Crisis website: data file link title “Sample Data as of 1 April 2014”*, Charleston, WV USA, 2014, Accessed at <http://www.dhsem.wv.gov/Documents/1%20Copy%20of%20PUB%20MCHM%201APR14%201500.pdf>.
- 77 Downstream Strategies, Inc., *Building water testing results with type of sample and type of building and method*, January – March, 2014, Morgantown, WV, 2014.
- 78 K. Ward, Jr., *Study to test home plumbing for MCHM*, West Virginia Gazette, February 11, 2014, <http://www.wvgazette.com/News/201402110073>.
- 79 West Virginia American Water (WVAW), *How to Flush Your Plumbing System*, Charleston, WV USA, January 2014, p. 3, <http://www.governor.wv.gov/Documents/HowtoFlushYourPlumbingSystem.pdf>.
- 80 West Virginia, Department of Health and Human Resources, *Recommendations for flushing household plumbing at homes served by WV American Water which also use a septic system for sewage disposal, rather than public sewer*, Charleston, WV USA, January 2014, p. 1, [http://www.wvdhhr.org/phs/flushing%20recommendations%20where%20septic%20systems%20are%20used%20\(3\).pdf](http://www.wvdhhr.org/phs/flushing%20recommendations%20where%20septic%20systems%20are%20used%20(3).pdf).
- 81 West Virginia, Bureau of Public Health, Notice From Bureau For Public Health, Letitia Tierney MD JD, Commissioner and State Health Officer, Charleston, WV USA, January 13, 2014.
- 82 American Federation of Teachers (AFT), *Safety Precautions for Flushing Water Lines*, Washington, D.C. USA, 2014, p. 1.
- 83 West Virginia, Office of Environmental Health Services (WVOEHS), *Recommendations for flushing household plumbing at homes served by WV American Water which also use a septic system for sewage disposal, rather than public sewer*, Charleston, WV USA, January 2014.
- 84 CDC, *Disaster Response and Recovery Needs of Communities Affected by the Elk River Chemical Spill*, West Virginia, Atlanta, GA USA, April 2014, <http://www.dhhr.wv.gov/News/2014/Documents/WVCASPERReport.pdf>.
- 85 E. J. Scharman, Poison center surge capacity. Proc. Annual Meeting of the North American Congress of Clinical Toxicology (NACCT), *Clin. Toxicol.*, 2014, 52, 682–818.
- 86 *Elk River Chemical Spill Health Effects Findings of Emergency Department Record Review*, US Centers for Disease Control and Prevention (CDC) Agency for Toxic Substances Disease Registry (ATSDR) and West Virginia Bureau of Public Health (BPH), Charleston, WV, April 2014, <http://www.wvdhhr.org/Elk%20River%20Chemical%20Spill%20Health%20Effects%20-%20Findings%20of%20Emergency%20Department%20Record%20Review.pdf>.
- 87 WV Poison Center Response Roles and Responsibilities, *Presentation to the National Association of City and County Health Officials Webinar, Response and Recovery During an Environmental Disaster: Learning from the Elk River Chemical Spill*, West Virginia Bureau of Public Health, Charleston, WV, April 22, 2014.
- 88 Lockheed Martin, Inc., *MCHM-Response West Virginia*, Submitted to EPA-ERT, Edison, NJ USA, October 2014.
- 89 P. Omur-Ozbek, D. Akalp and A. J. Whelton, Tap Water and Indoor Air Contamination due to an Unintentional Chemical Spill in Source Water, *Proc. of the International Structural Engineering and Construction Society EURO-MED-SEC-01*, May 24–29, Istanbul, TUR, 2016, https://www.isec-society.org/ISEC_PRESS/EURO_MED_SEC_01/html/AW-11.xml.
- 90 CORE, Inc., *Interim Remedial Action Work Plan - Freedom Industries - VRP 15017*, Prepared for: West Virginia Department of Environmental Protection, Charleston, WV USA, November 2015, <http://www.dep.wv.gov/dlr/oer/voluntarymain/Documents/Interim%20Remedial%20Action%20Work%20Plan%20-%20Freedom%20Industries%20-%20VRP%2015017%20-%202011-2015.pdf>.
- 91 US National Toxicology Program, *West Virginia Chemical Spill: NTP Research Response and Findings*, Research Triangle Park, NC USA, February 2016, <http://ntp.niehs.nih.gov/results/areas/wvspill/>.
- 92 West Virginia, Department of Health and Human Services. *Press Release: NTP Findings Consistent with Actions Taken During Chemical Spill*, Charleston, WV USA, <http://www.dhhr.wv.gov/News/2015/Pages/NTP-Findings-Consistent-with-Actions-Taken-During-Chemical-Spill.aspx>.
- 93 West Virginia, Poison Control Center (WVPC), *Memorandum provided to Physicians and List of Experts Bureau of Public Health Relied Upon during the Water Crisis*, Charleston, WV USA, February 10, 2014.
- 94 Simonton S. Pres. to the West Virginia Legislature Joint Commission on Water Resources, Charleston, WV USA, January 29, 2014.
- 95 Simonton S. Dr. Simonton Discusses Formaldehyde in Water. Testimony to the West Virginia Legislature Joint Commission on Water Resources. Charleston, WV USA. Video accessible at: https://www.youtube.com/watch?time_continue=1555&v=H1C0vdh_Alw.
- 96 J. Mattise, West Virginia Official Says He 'Can Guarantee' Some People Inhaling Formaldehyde After Chemical Spill. The Associated Press. Charleston, WV USA, January 29, 2014, http://www.huffingtonpost.com/2014/01/29/west-virginia-chemical-spill-formaldehyde_n_4688419.html.
- 97 NTP (National Toxicology Program), *Report on Carcinogens*, U.S. Department of Health and Human Services, Public Health Service, Research Triangle Park, NC, 14th edn, 2016, <http://ntp.niehs.nih.gov/go/roc14/>.
- 98 A. Dabrowska, B. Kasprzyk, B. Hordern and J. Nawrocki, *Global NEST J.*, 2005, 7(1), 61–71, <http://journal.gnest.org/>



- sites/default/files/Journal%20Papers/7_1_Dabrowska-332_61-71.pdf.
- 99 H. S. Weinberg, S. W. Krasner, S. D. Richardson and A. D. Thurston, *The Occurrence of Disinfection By-Products (DBP's) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study*, Prepared for the National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA USA, 2002.
 - 100 B. A. Owen, C. S. Dudley, E. L. Tan and C. E. Easterl, *Regul. Toxicol. Pharmacol.*, 1990, 11(3), 220–236.
 - 101 S. W. Krasner, *Philos. Trans. R. Soc., A*, 2009, 367(1904), 4077–4099.
 - 102 World Health Organization, *Formaldehyde in drinking-water*, WHO/SDE/WSH/05.08/48, Geneva, CHE, 2005.
 - 103 G. Gilli, E. Scursatone, L. Palin, R. Bono, E. Carraro and L. Meucci, *Ozone: Sci. Eng.*, 1990, 12(3), 231–241, <http://www.ioa-pag.org/ozone-science-engineering-journal/water-disinfection-a-relationship-between-ozone-and-aldehyde-production/>.
 - 104 C. Neslund, D. Luckenbill, R. Karam and A. Eaton, *Assessment of Tentatively Identified Compounds in Tap Water Following the January 9 Chemical Spill from Freedom Industries*, West Virginia Testing Assessment Project, Charleston, WV USA, 2014.
 - 105 West Virginia, Office of the Governor. Press Release: Gov. Tomblin Directs Dr. Tierney and General Hoyer to Host Conference Call Addressing Community Concerns, Charleston, WV USA. January 18, 2014. <http://www.governor.wv.gov/media/pressreleases/2014/Pages/GOV.-TOMBLIN-DIRECTS-DR.-TIERNEY-AND-GENERAL-HOYER-TO-HOST-CONFERENCE-CALL-ADDRESSING-COMMUNITY-CONCERNS.aspx>.
 - 106 W. R. Mac Kenzie, N. J. Hoxie, M. E. Proctor, M. S. Gradus, K. A. Blair, D. E. Peterson, J. J. Kazmierczak, D. G. Addiss, K. R. Fox, J. B. Rose and J. P. Davis, *N. Engl. J. Med.*, 1994, 331, 161–167.
 - 107 A. J. Whelton, A. M. Dietrich, D. L. Gallagher and J. A. Roberson, *J. - Am. Water Works Assoc.*, 2007, 99(11), 62–76.
 - 108 WV DEP (West Virginia Department of Environmental Protection), Freedom verifies two chemicals (Crude MCHM, PPH) in tank, Charleston, WV USA, January 22, 2014, Accessible at: [http://www.dep.wv.gov/news/Pages/Freedom-verifies-two-chemicals-\(Crude-MCHM,-PPH\)-in-tank.aspx](http://www.dep.wv.gov/news/Pages/Freedom-verifies-two-chemicals-(Crude-MCHM,-PPH)-in-tank.aspx).
 - 109 West Virginia DEP, Consent Order Issued Under the Water Pollution Control Act, West Virginia Code, Chapter 22, Article 11, and the Groundwater Protection Act, West Virginia Code, Chapter 22, Article 12, Issued to: Freedom Industries, Inc., West Virginia Charleston, WV USA, November 12, 2014, Accessible at: <http://www.wvgazette.com/assets/PDF/CH62281113.pdf>.
 - 110 Texas Commission on Environmental Quality, Remediation Division, *Selecting Target Chemicals of Concern*, Austin, TX USA, 2008.
 - 111 EPA, Region III Quality Assurance Team, *TIC Frequently Asked Questions Revision No. 2.5.*, February 17, Philadelphia, PA USA, 2006, <http://www2.epa.gov/sites/production/files/2015-06/documents/tics.pdf>.
 - 112 J. Clancy, T. Bartrand, S. Masters, A. J. Whelton and K. S. Casteloes, *Flushing Guidance for Consumer Premise Plumbing and Service Lines to Avoid or Address a Drinking Water Advisory, Project 4572*, Draft Report, Water Research Foundation, Denver, CO USA, 2016.
 - 113 EPA, *Response Protocol Toolbox Planning for and Responding to Drinking Water Contamination Threats and Incidents Interim Final: Response Guidelines*, Washington, D.C. USA, August 2004, http://www2.epa.gov/sites/production/files/2015-05/documents/drinking_water_response_protocol_toolbox.pdf.
 - 114 Critical Infrastructure Partnership Advisory Council, Water Sector Decontamination Working Group, *Recommendations And Proposed Strategic Plan - Water Sector Decontamination Priorities Final Report*, Washington, D.C. USA, August 2008.
 - 115 A. J. Whelton, P. K. Wisniewski, S. States, S. E. Birkmire and M. K. Brown, *J. - Am. Water Works Assoc.*, 2006, 98(8), 63–73.

