WV TAP FINAL REPORT

Jeffrey S. Rosen

Andrew J. Whelton

Michael J. McGuire

Jennifer L. Clancy

Timothy Bartrand

Andrew Eaton

Jacqueline Patterson

Michael Dourson

Patricia Nance

Craig Adams

CORONA ENVIRONMENTAL CONSULTING, LLC, 6 Old Country Way, Scituate, MA 02066

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- Mr. Jeffrey S. Rosen, President, Corona Environmental Consulting, LLC, WV TAP program manager and project leader for WV TAP sampling plan design
- Dr. Andrew Whelton, Assistant Professor of Environmental Engineering, University of South Alabama, project leader of the WV TAP 10 home sampling and survey program
- Dr. Michael J. McGuire, Michael J. McGuire Inc., project leader of the WV TAP odor threshold and oxidation studies
- Dr. Mel Suffet, Distinguished Professor, Dept. of Environmental Health Sciences, UCLA School of Public Health
- Dr. Andrew Eaton, Eurofins Eaton Analytical Inc., project leader for the WV TAP analytical chemistry analyses and method development at Eurofins laboratories
- Mr. Duane Luckenbill, Vice President, Eurofins, Lancaster Laboratories Environmental, LLC
- Mr. Charles Neslund, Technical Director, Eurofins, Lancaster Laboratories Environmental, LLC
- Dr. Jennifer Clancy, Chief Scientist, Corona Environmental Consulting, LLC, leader of WV TAP field sampling logistics
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- Mr. Paul Painter, ALS Laboratories, Laboratory Director
- Ms. Rebecca Kiser, ALS Laboratories, Laboratory Supervisor
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- Michael Dourson, Ph.D., DABT, ATS, Toxicology Excellence for Risk Assessment (TERA)

Shai Ezra, Ph.D., Mekorot, Israel National Water Company
James Jacobus, Ph.D., Minnesota Department of Health
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The press was instrumental in focusing the work of the WV TAP program and in communicating results and issues to all stakeholders.

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List of Acronyms

Acronym	Meaning
ATSDR	Agency for Toxic Substances and Disease Registry
BDL	Below Detection Limit
CDC	Centers for Disease Control and Prevention
DiPPH	Dipropylene glycol phenyl ether
GAC	Granular Activated Carbon
GC/MS	Gas Chromatography/Mass Spectrometry
KVWTP	Kanahwa Valley Water Treatment Plant
MCHM	4-methylcyclohexanemethanol
MDL	Method Detection Limit
MRL	Method Reporting Limit
MSDS	Material Safety Data Sheets
NIST	National Institute of Standards and Technology
OTC	Odor Threshold Concentration
ORC	Odor Recognition Concentration
OOC	Odor Objection Concentration
ppb	Parts per billion, also equal to micrograms per L (µg/L)
PPH	Propylene glycol phenyl ether
ppm	Parts per million, also equal to milligrams per L (mg/L)
TIC	Tentatively Identified Compound
US EPA	United States Environmental Protection Agency
WVAW	West Virginia American Water
WVBPH	West Virginia Bureau for Public Health
WV DEP	West Virginia Department of Environmental Protection
WVDHHR	West Virginia Department of Health and Human Resources
WV TAP	West Virginia Testing Assessment Project

Executive Summary

Background

This document is the final report of the independent scientific review team organized by the West Virginia Bureau for Public Health (WVBPH) in response to the January 9, 2014, chemical spill of "crude[1]" 4-methylcyclohexanemethanol (MCHM) into the Elk River. Crude MCHM has a strong licorice odor. When the crude MCHM entered the West Virginia American Water (WVAW) Kanawha Valley Water Treatment Plant (KVWTP), the treatment processes in place could not completely remove it, resulting in contaminated drinking water being supplied to approximately 300,000 citizens in nine counties. By 5:23 pm a decision was made to issue a "Do not use" order for all residents of the nine county area that received their water from WVAW. West Virginia Governor Earl Ray Tomblin declared a state of emergency for the nine county area and requested a federal emergency declaration and guidance from the Agency for Toxic Substance and Disease Registry (ATSDR), an arm of the US Centers for Disease Control and Prevention (CDC) regarding the concentration of MCHM in drinking water that was safe for humans. Their response was that a concentration of 1 part per million (ppm) of MCHM was an appropriate screening level. Early on Friday morning, January 10, 2014 President Obama declared the nine counties affected by the spill as a federal disaster area.

WVAW started lifting their "Do not use" order on January 13. By January 18 the "Do not use" order was lifted for all residents. Samples collected in the affected area continued to have some MCHM detections but by January 25 samples from the distribution system and from public buildings (including schools) collected by the West Virginia Army National Guard and analyzed by two separate laboratories had concentrations that were consistently below the method limit of detection at the time of sample collection. The response to the spill was a rapidly changing process, with laboratories striving with every set of samples to lower detection limits. Before WV TAP was formed, the lowest MCHM detection limit used by the State was 10 parts per billion (ppb). However, the residents of the affected areas were still detecting odors that were associated with crude MCHM. The seemingly inconsistent results of the analytical chemistry versus the perception of the citizens were confusing. Although the "Do not use" order had been lifted and the concentrations were well below the levels that CDC concluded were safe for short term exposure (1 ppm), residents remained skeptical because they could still smell odors associated with the spill.

The WV TAP Program

On February 9, 2014, Mr. Jeffrey Rosen and Dr. Andrew Whelton proposed a plan to the WVBPH to evaluate the contradictory consistent odor of licorice with the consistently below detection level (BDL) analytical results to evaluate the safety of the treated water being delivered to the citizens of the affected area. This was the initiation of the West Virginia Testing Assessment Project (WV TAP). The WV TAP team was expanded to include science and engineering experts from across the US.

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[1] Crude MCHM is a mixture of pure 4-methylcyclohexanemethanol (referred to as MCHM in this report) and other organic compounds (Eastman Chemical Company, 2011). According to the Safety Data Sheet for crude MCHM (Eastman Chemical Company, 2011), pure 4-MCHM makes up 68 - 89% of crude MCHM by weight. In this report crude MCHM denotes the mixture spilled into the Elk River and MCHM denotes pure 4-methylcyclohexanemethanol.

The basis for the WV TAP research was that in order to understand if the water was safe to use in all intended ways (drinking, cooking, washing, flushing) there were four questions that needed to be answered: (i) what were the concentrations of crude MCHM that people could smell; (ii) was there any evidence that components of crude MCHM had been converted into other compounds that might be associated with health effects or odors in the water; (iii) what concentrations of the contaminants spilled into the river were safe for all intended uses by all members of the population; and (iv) what concentrations of the spilled chemicals were present in people's homes?

These four questions became the framework for the WV TAP research program. This report summarizes results of this independent scientific assessment of the spill of crude MCHM into the Elk River and its distribution throughout the nine counties served by WVAW. To answer these questions WV TAP designed and conducted four scientific studies: (1) an in-depth analysis to determine the odor threshold for crude MCHM; (2) an assessment of the breakdown products that may have been created as a result of the oxidation of crude MCHM by chlorine and potassium permanganate; (3) establishment of an independent panel of experts to evaluate the screening level for MCHM; and (4) an initial assessment of the concentration and variability of MCHM at taps in homes and the perceptions of the owners of the homes that were sampled. The results of the fourth task were used to design a sampling plan to suggest the number of houses that would be necessary to sample to establish the percentage of homes with water containing MCHM concentrations above a level of concern should a follow up study be deemed necessary.

This report summarizes each of the tasks completed by the WV TAP team and provides detailed reports on each of the inquiries in Appendices. Full reports can also be found on the WV TAP website (http://www.dhsem.wv.gov/wvtap/test-results/Pages/default.aspx).

WV TAP Results

Odor Threshold

Because drinking water contamination with a licorice odor was one of the defining problems with the chemical spill, odor thresholds needed to be determined for crude MCHM. Both expert and consumer panels were used to evaluate the detection, recognition and objection concentrations of crude MCHM in water.

ASTM E679-04 (ASTM, 2011) was used to estimate the odor threshold concentration (OTC) for crude MCHM by both panels. The expert panel estimated that the OTC for crude MCHM is likely less than 0.15 parts per billion (ppb). The ability of the expert human nose to detect this compound is far greater than any analytical method available today. The experts reported Odor Recognition Concentrations (ORC) and Odor Objection Concentrations (OOC) of 1.6 ppb and 4.0 ppb, respectively. The consumer panel study showed that untrained consumers were able to detect this compound at a concentration in water (0.55 ppb) at least as low as the most sensitive analytical method available during this study (0.5 ppb). Consumer panel results estimated ORC and OOC of 7.4 and 9.5 ppb, respectively.

The most important finding of this work can be stated succinctly. The estimated thresholds determined in the consumer panel study support consumer observations in Charleston, WV that people recognized and objected to the licorice odor caused by crude MCHM in their drinking water even in the presence of high concentrations of chlorine and even though the analytical reports were showing non-detects at a minimum reporting level of 10 ppb.

Breakdown Compounds

The second question addressed by the WV TAP team was whether any breakdown compounds of crude MCHM were present in finished drinking water at significant concentrations. Such breakdown compounds could result in odors or represent human health hazards. Two efforts were undertaken to identify the constituents and potential breakdown/reaction products of crude MCHM: an analysis of the compounds present in tap water of affected homes and batch experiments for determining the degree to which crude MCHM reacts with oxidants used in drinking water treatment at the KVWTP.

Eurofins' laboratory in Lancaster, PA conducted analyses of tap water samples from homes sampled in a 10 home pilot sampling and survey to determine whether breakdown products were present in household tap water at measurable concentrations. Eurofins developed a method for the evaluation of semivolatile organic compounds that followed EPA SW-846 method 8270. The resulting method was able to achieve low levels (sub µg/L) for both a method detection limit (MDL) and a method reporting level (MRL). This method was applied to samples collected in the 10 home sampling program. The analytes that can be detected with this method include MCHM, propylene glycol phenyl ether (PPH) and dipropylene glycol phenyl ether (DiPPH) and a variety of possible breakdown compounds. This study reached the conclusion that there were no breakdown products of any contaminants that were part of the crude MCHM spill that could be measured in the 10 homes sampled.

WV TAP conducted experiments to evaluate whether oxidants used to treat water at the WVAW KVWTP (free chlorine and potassium permanganate) had the potential to produce breakdown products of crude MCHM at measurable concentrations and potentially change the odor characteristics and/or the health concerns of the spilled material. The conclusion of the laboratory team was that chlorine at concentrations typical of those used at the KVWTP does not oxidize MCHM or PPH. Potassium permanganate at concentrations typical of treatment in the KVWTP produced a small reduction in MCHM concentration in oxidation studies, but would have produced a minimal reduction in MCHM during the early period after the spill when MCHM concentration in the plant was at its highest.

Health Effects Expert Panel

WV TAP was tasked to evaluate the safe levels of MCHM and PPH for all members of the population for all intended uses. This was done through convening an independent expert panel to review and discuss available toxicity data on chemicals released to the Elk River from the Freedom Industries, Inc., storage tank. The expert panel addressed the following charge questions:

- Given data now available, what would be appropriate screening levels for MCHM and PPH in drinking water?
- What additional data, analyses, or studies might reduce uncertainty and provide greater confidence?
- How should the presence of multiple chemicals in the release to the Elk River be considered?
- Are the screening values protective for all potential routes of exposures (i.e., ingestion, dermal and inhalation)?

For MCHM, the panel recommended a short-term health advisory level of 120 ppb. The panel reviewed the available information on PPH and DiPPH and recommended a short-term health advisory of 880 ppb for PPH, and a short-term health advisory of 260 ppb for DiPPH. These values were recommended for short term exposures of one day to three months (and perhaps longer) for public health protection use with the 2014 Elk River spill and the subsequent contamination of the local water supply. For MCHM, the WV TAP safe level was an order of magnitude lower than the CDC screening level and the State of West Virginia advised a level that was still an order of magnitude lower than the WV TAP safe level.

The panel identified two research or data needs specifically for MCHM and suggested three other areas where further analysis and research would aid in better understanding the hazard and risk from this spill. The panel could not determine the long term safe exposure levels with the data and time available for this study.

Ten Home Pilot Sampling and Survey

As part of the WV TAP project Task 4, 10 homes affected by the crude MCHM chemical spill were studied. The objective was to conduct a focused residential drinking water sampling field study to be used to support the design of a larger more comprehensive program for the nine counties affected. Households were visited from February 8 to 11, 2014 in eight of the nine counties affected by the drinking water contamination incident. During each household visit, residents were interviewed by the WV TAP project team, the team performed chemical analyses of tap water at kitchen and bathroom fixtures, and they collected water samples for additional commercial laboratory analysis. Samples were sent to two analytical laboratories.

The survey size was very small and results from the survey must be considered anecdotal and not necessarily representative of the entire effected area. The survey indicated that residents in the affected area were all aware of the spill and "Do not use" order the evening of January 9; none of the homes previously treated their water as it entered the house; nine of 10 homes reported the licorice smell as unbearable soon after the spill; all residents flushed their plumbing, on average 14 days after the 'Do not use' order was issued. Four homes were still not using water for showering and nine were not using tap water for teeth brushing in mid-February. None were using tap water for drinking, cooking, or making baby formula.

Chemical analyses of hot and cold water samples collected at the four taps in each home were analyzed for total organic carbon (TOC), MCHM, and PPH. TOC concentration was in the expected range for uncontaminated water from the WVAW treatment plant and did not vary widely across or within the 10 homes studied. No PPH was detected in any home by either laboratory. The contaminant MCHM was detected in all 10 homes by the Eurofins laboratory, but not detected in any of the same sample sites by ALS Environmental Laboratory in replicate samples. This finding is significant and underscores the importance of selecting laboratories that can reliably detect and quantify low levels of contaminants during a chemical contamination incident. Eurofins laboratory's MDL and MRL for 4-MHCM were less than 0.5 ppb and 1.0 ppb while ALS Environmental Laboratory's MRL and MDL values were 2.7 ppb and 5.0 ppb. Ninety percent of the MCHM concentrations reported by Eurofins 1aboratory were less than 2.4 ppb. Where Eurofins did detect MCHM above ALS's MDL and MRL, they were still reported as non-detect by ALS. No MCHM concentrations detected in any home exceeded the 10 ppb State of West Virginia screening level.

Sampling Plan Design

Following the spill there had been persistent calls from the area residents for in-home sampling to establish the concentrations of the constituent chemicals in all people's residences. An evaluation of sampling strategies based on the pilot 10 home sampling program was undertaken. Key questions addressed in the sampling plan design are:

1. What is the concentration of MCHM in people's residences?
2. Is the average concentration observed in homes below a level of concern?
3. What proportion of the homes has MCHM concentrations below a level of concern?

If the main concern is that the water is safe for residents to use for all intended uses by all members of the community then all that is required is to evaluate samples relative to the WV TAP short term health effects safe level of 120 ppb, which only requires a single sample given that the expected concentrations will be in the single digit ppb or lower. To increase confidence, the state may consider testing 30 homes in each of the 24 regions established for flushing. In order to verify that the variability is properly characterized by the 10 home sampling program it would be best to take two samples per home so there is a measure of the within home variability. Since the only chemical detected in the sampled homes was MCHM, it is the only chemical that needs to be analyzed.

This recommended sampling program would result in a total of 720 residences being sampled. This number of sampled homes would allow a good estimate of the percent of homes in the affected area that are below any critical value of interest.

Summary

WV TAP was contracted by the WVBPH to conduct an independent scientific assessment of the spill of crude MCHM and other chemicals into the Elk River and its distribution throughout the nine counties served by WVAW. WV TAP designed and conducted four scientific studies to answer a variety of questions related to the spill. The key finding of these studies were that (i) affected residents were accurate in their perception that MCHM remained in the system at very low concentrations after initial analytical results showed all concentrations to be below detection levels, (ii) no breakdown compounds were found that would affect the odors or the toxicity of the materials spilled into the Elk River, (iii) concentrations below 120 ppb for MCHM, 880 ppb for PPH and 260 ppb for DiPPH are safe for all uses and for all members of the population for short term exposures, and that (iv) concentrations below 10 ppb of MCHM were consistently detected in residences a full month after the spill. Determination of long-term safe exposure levels was not possible with the data available and within the timeframe of this study. Based on the 10 home sampling study, options for a large scale sampling program were developed.

WV TAP recommended additional research that could be initiated and funded by concerned federal agencies, states and other agencies. That research addresses the many data gaps that remain in our knowledge of the physical properties, reactivity, treatability and health effects of MCHM. Research was proposed to fill those gaps, to better assess the safety of water produced by the KVWTP and the homes it serves, and to be better prepared in the event of another spill. While these recommendations are specific to a crude MCHM spill, they frame the sorts of research that could be conducted for any credible chemical threat to a drinking water treatment plant as a part of a disaster preparedness effort. This event highlights the need for regular inspection of chemical storage facilities and associated pollution prevention infrastructure and planning. The ability for the State to respond is strongly contingent on relationships between the State and other critical agencies. These relationships should be carefully documented and

updated regularly to ensure that during an emergency little effort is wasted in developing a cohesive emergency response team. These relationships should be in place before an emergency and as part of an emergency preparedness plan. These plans should be regularly tested and updated to ensure that they will work effectively during an emergency. All agencies involved need to be sensitive to the need for clear, unambiguous communications of both what is and is not known.

The Elk River spill is a call to action for all water utilities with hazardous chemicals in close proximity to their water intakes. Regardless of the regulations and responsibilities of the State and Federal regulators, water utilities have responsibilities and liabilities that should prompt initiative in the identification of possible chemical threats, as well as biological and radiological threats. Utilities should consider deployment of water quality sensors in their source water, treatment plants and distribution systems to detect contamination events as quickly as possible and, ideally, before exposure of the public. During an event of this kind there is a need for collection and flow of a great deal of information via many different pathways requiring cooperation from dozens of agencies. When a spill occurs it is important that communications are well organized and coordinated to prevent the release of conflicting information. Decision makers and responders should have a well-considered and vetted communications plan in hand at the outset of a drinking water crisis. Such a plan minimizes the release of conflicting or incorrect information and reduces the amount of time responders must allocate to communication with the public.

1. Background

1.1 Spill and Response Chronology

At 7:30 am on the morning of January 9, 2014 a resident of Charleston, West Virginia who resided in a home near Freedom Industries, Inc., smelled what is now known to be MCHM. At 8:16 am the resident had reported the odor to the West Virginia Department of Environmental Protection (WV DEP), Division of Air Quality. By 10:30 am employees at the Freedom Industries, Inc., Barlow Drive chemical storage facility confirmed that there was a leak of "crude" 4-methylcyclohexanemethanol (crude MCHM) from tank 396 and by 11:15 am WV DEP inspectors had arrived at the Barlow Drive chemical storage facility. The Barlow Drive chemical storage facility runs parallel to the bank of the Elk River. It was initially estimated that the leaking tank could hold as much as 46,000 gallons of crude MCHM. The leak was officially reported to the WV DEP at 12:05 pm via the WV DEP spill hotline. Ultimately an estimate was made that as much as 10,000 gallons of crude MCHM might have spilled into the Elk River. The spill site is approximately 1.5 miles upstream of the raw water intake of the KVWTP operated by WVAW. By 4 pm the crude MCHM contaminated raw water had reached the water treatment plant intake. It is not clear when the contaminated water first reached the KVWTP intake. At some point a decision was made to not close the raw water intake because of concerns related to fire fighting and maintenance of pressure in the distribution system. WVAW augmented the treatment in their plant by increasing chemical doses and adding powdered activated carbon to the existing treatment process, which also included granular activated carbon (GAC). Augmentation of the treatment process did not remove all of the crude MCHM from the treated water and by 5:23 pm a decision had been made to issue a "Do not use" order for all residents of a nine county area that received their water from the KVWTP.

Just prior to 6:00 pm WVAW President Jeffrey McIntyre issued the "Do not use" order and a few minutes after this announcement, West Virginia Governor Earl Ray Tomblin declared a state of emergency for the nine county area and requested a federal emergency declaration. On January 9 the WVBPH requested guidance from the CDC's ASTDR on the level (concentration) of MCHM that is safe for human use. Early on Friday morning, January 10, 2014, President Barack Obama declared the nine counties affected by the crude MCHM spill as a federal disaster area. At some point between January 10 and January 13, the CDC informed the WVBPH that, based on the scant data available, 1 part per million (1 ppm or 1000 ppb) was the appropriate screening level for oral ingestion of water contaminated with MCHM. WVAW started lifting its "Do not use" order on January 13. By January 18 the "Do not use" order was lifted for all residents. Samples collected in the affected area (but not from any residences) continued to have some MCHM detections but by January 25, samples from the distribution system and from public buildings (including schools) collected by the West Virginia Army National Guard and analyzed by two separate laboratories were consistently below 50 ppb of MCHM. However, the residents of the affected areas were still detecting odors that were associated with crude MCHM. The seemingly inconsistent results of the analytical chemistry versus the perception of the citizens were confusing. Although the "Do not use" order had been lifted and the concentrations were well below the CDC levels that were believed safe for short term exposures, residents remained skeptical because they could still smell odors associated with the spill.

Data from samples collected by WV TAP for investigation of potential MCHM breakdown products and those collected by WVAW to clarify the source of persistent MCHM demonstrated that low concentrations of MCHM were being released from the KVWTP as late as the end of March 2014. WVAW traced the continued low, but detectable MCHM concentrations in the plant effluent to the release of MCHM from GAC filters. WVAW had announced plans, shortly after the spill, to replace all of the GAC in the KVWTP. Implementation of this plan was started the first week of April, 2014.

1.2 The WV TAP Program

On February 9, 2014, a group of independent scientists and engineers proposed a plan to the WVBPH to evaluate the seemingly inconsistent results and to evaluate the safety of the treated water being delivered to the citizens of the affected area. This was the initiation of the WV TAP.

The basis for the WV TAP research was that in order to understand if the water was safe to use in all intended ways (drinking, cooking, washing, flushing) there were four questions that needed to be answered: (i) what were the concentrations of crude MCHM that people could smell; (ii) was there any evidence that components of crude MCHM had been converted into other compounds that might be associated with health effects or odors in the water; (iii) what concentrations of the contaminants spilled into the river that were safe for all intended uses by all members of the population; and (iv) what were the concentrations of spilled chemicals present in people's homes?

These four questions became the framework for the WV TAP research program. This report summarizes the results of this independent scientific assessment of the spill of crude MCHM and other chemicals into the Elk River and its distribution throughout the nine counties served by WVAW. To answer these questions WV TAP designed and conducted four scientific studies: (1) an in-depth analysis to determine the odor threshold for crude MCHM; (2) an assessment of the breakdown products that may have been created as a result of the oxidation of crude MCHM by chlorine and potassium permanganate; (3) establishment of an independent panel of experts to evaluate the screening level for MCHM; and (4) an initial assessment of the concentration and variability of MCHM at the taps in homes and the perceptions of the owners of the homes that were sampled. The results of the fourth task were used to design a sampling plan that suggested the number of houses that would be necessary to be sampled to establish the percentage of homes with water with MCHM concentrations above a level of concern and the number of samples per house that should be collected and the location of those samples should a follow up survey be deemed necessary.

This report summarizes each of the inquiries undertaken by the WV TAP team and provides detailed reports on each of the inquiries in Appendices. Full reports can also be found on the WV TAP website (http://www.dhsem.wv.gov/wvtap/test-results/Pages/default.aspx).

2. Odor Threshold

Detailed reports for odor threshold studies are included in Appendix A and Appendix B.

Because drinking water contamination with a licorice odor was one of the defining problems with the chemical spill, the odor thresholds needed to be determined for crude MCHM. The WV TAP team decided to use both expert and consumer panels to evaluate the detection, recognition and objection concentrations of crude MCHM in water. Two technical memoranda provide the details of these evaluations (McGuire, 2014a; McGuire, 2014b). The first step was to decide which chemical to use in the odor testing.

Crude MCHM had a licorice odor that was penetrating, irritating and sharp. The pure MCHM had a definite licorice odor, but it was milder than the crude. Gas chromatography/mass spectrometry (GC/MS) analysis and the Material Safety Data Sheets (MSDS) forms for crude MCHM showed that crude MCHM is a mixture of compounds, of which, about 80 percent is pure MCHM. In order to determine the source of the odors, many of the minor compounds (20 percent) in the mixture were evaluated and it was determined that one of them (cyclohexanemethanol) was probably contributing the penetrating, sharp odor characteristic of the crude MCHM. Therefore, crude MCHM was used in all of the odor testing. Later analysis of the relative contribution of the *trans* and *cis* isomers of MCHM showed that it was critical that crude MCHM be used for quantifying the odor problems related to exposure of the public.

The odor threshold work recognized that consumers react to odors in their drinking water by detection, recognition and objection. Table 1 organizes the concentrations of odorants in drinking water into aesthetic response levels.

Table 1. Odor Response Levels for Concentrations of Chemical in Water

Odor Response	Description	Aesthetic Response Levels
Detection (threshold)	Chemical concentration usually determined in a laboratory setting where approximately 50% of the panelists can just detect the odor of a chemical	Odor threshold concentration - OTC
Recognition	Concentration of a chemical at which a fraction of panelists (defined in the method) can correctly recognize and describe the odor characteristics of the chemical	Odor recognition concentration – ORC
Objection/Complaint	Chemical concentration, determined either in a laboratory or field setting, that causes consumers to object to their water supply and to call and complain	Odor objection concentration - OOC

Nine expert panelists were used in the first part of the investigation. All nine panelists were trained in the Flavor Profile Analysis method (Krasner, McGuire and Ferguson, 1985) and had been evaluating drinking water samples for either Hazen and Sawyer consultants or for the Environmental Health Science Department of the University of California at Los Angeles (UCLA).

For the consumer panel work, sixty untrained consumer panelists were selected to give a balance of gender and ages. Smokers were excluded and other selection requirements resulted in a consumer panel that could provide reasonable estimates of aesthetic responses.

ASTM E679-04 (ASTM, 2011) was used to estimate the OTC for crude MCHM by both the expert and consumer panels. Eight concentrations of crude MCHM were presented in groups of three (one cup with the compound and two cups with blank water) to panelists as part of the forced choice ascending concentration series method. Arrowhead spring water was used as the matrix water and for blanks. To determine detection, panelists were asked to pick the cup with the different odor in the grouping of three. For the cup with the different odor, panelists were then asked to describe the odor, rate the degree of liking and determine if they would object or complain about the odor in their water supply. Concentrations of crude MCHM spiked into the water samples were determined by GC/MS by Eurofins Lancaster Laboratory.

Table 2 compares the OTC, ORC and OOC values for the Expert and Consumer Panels. The expert panel estimated that the OTC for crude MCHM is likely less than 0.15 ppb. The ability of the expert human nose to detect this compound is far greater than any analytical method available today. The Consumer Panel study showed that untrained consumers were able to detect this compound at a concentration in water (0.55 ppb) at least as low as the most sensitive analytical method available during this study (0.5 ppb).

While the Expert Panel determined lower values for all four thresholds as compared to the results from the Consumer Panel, the actual thresholds that the consumers of WVAW tap water would have experienced during and after the spill were probably between the two sets of values. The consumers affected by the spill in WV learned and became more sensitive to the detection, recognition and objection of concentrations of crude MCHM because they had been subjected to it for weeks at concentration levels far above the concentrations presented on Table 2. It is clear from press reports that members of the public in Charleston and environs were able to recognize crude MCHM in their tap water even with the presence of high concentrations of free chlorine, approximately 3.5 ppb (and below).

Table 2. Comparison of OTC, ORC and OOC Values for Expert and Consumer Panels

Results	Expert Panel Geometric Mean, ppb	Consumer Panel Geometric Mean, ppb
Number of panelists	9	60
Odor Threshold Concentration (OTC)	Less than 0.15	0.55
Odor Recognition Concentration (ORC)	2.2	7.4
Odor Objection Concentration (OOC, based on degree of liking)	4.0	7.7
Odor Objection Concentration (OOC) based on objection/complaint	4.0	9.5

The most important finding of this work can be stated succinctly. The estimated thresholds determined in the Consumer Panel study support consumer observations in Charleston, WV that people recognized and objected to the licorice odor caused by crude MCHM in their drinking water even in the presence of high concentrations of chlorine and even though the analytical reports were showing non-detect at a minimum reporting level of 10 ppb.

3. Breakdown Compounds

The second question addressed by the WV TAP team was whether any breakdown compounds of crude MCHM were present in finished drinking water at significant concentrations. Such compounds could result in odors or represent human health hazards. Two efforts were undertaken to identify the constituents and potential breakdown/reaction products of crude MCHM:

- GC/MS assays of water samples collected from residence taps, and

- Oxidation of crude MCHM with oxidants employed in drinking water treatment at the KVWTP and GC/MS assay of the oxidized crude MCHM solutions.

Methods and results of these experiments are summarized below.

3.1 Analysis of Water Samples Collected from Residences

The detailed report for this study is included in Appendix C.

The Eurofins laboratory in Lancaster, PA conducted GC/MS analyses of tap water samples from homes sampled in the 10 home pilot sampling and survey study (described in section 5). This analysis allowed determination of whether breakdown products were present in household tap water at measurable concentrations and to allow evaluation of the analytical method and its limit of detection.

Eurofins developed a method for the evaluation of semivolatile organic compounds that followed EPA SW-846 method 8270. The resulting method was able to achieve very low levels for both a MDL and MRL. This method was applied to the samples collected in the 10 home sampling program. The analytes that can be detected with this method include MCHM, PPH, DiPPH and a variety of possible breakdown compounds.

Investigations conducted with waters not believed to contain MCHM and with different sample preparations indicated that tentatively identified compounds (TICs) observed in the samples collected in the WV TAP 10 home study were created as a result of the reaction of the chlorine in the treated water with:

a. Several surrogate standard compounds routinely used in 8270 analysis
b. One of the stabilizers used in the manufacture of methylene chloride, which is the solvent of choice for most 8270 type analyses.

Researchers found no evidence from preliminary analysis of tap water samples or in the course of the analysis of the 10 home study water samples indicating that during mid-February, more than 1 month after the spill, the crude MCHM contributed to the creation or presence of the observed TICs. The conclusion of the laboratory team was that there were no breakdown compounds related to the crude MCHM spill that could be measured when these samples were collected, at the detection levels attained in this study (which were very low).

Additionally the laboratory team found no evidence that the presence of chlorine in the samples interferes with the analysis of MCHM or PPH. However, it was advised that future sampling should include adequate amounts of dechlorinating agents to minimize the occurrence of TICs that are the result of reactions with chlorine. Initial results suggested that there might be breakdown compounds in the samples from the 10 home samples. Further investigations resolved that all but one of the compounds that appeared to be breakdown compounds were, in fact, byproducts of the analytical methods including breakdown products of the surrogates added to the samples as part of the analytical quality control. The surrogates were being broken down by their interaction with chlorine in the samples from the 10 homes. One peak was not attributable to this process, but was instead shown to be an artifact of the reaction of chlorine with the stabilizer used in the solvent (methylene chloride) used in method 8270.

Once the breakdown products which were artifacts of the analytical methodology were eliminated from consideration, no breakdown compounds remained that could be related to MCHM, PPH or di-PPH using the detection levels of the analytical methods applied.

3.2 Oxidation Products of Crude MCHM

The detailed report for this study is included in Appendix D.

In the final laboratory investigation of potential breakdown products, WV TAP scientist Dr. Michael McGuire conducted experiments to evaluate whether oxidants used to treat water at the WVAW KVWTP had the potential to produce breakdown products of crude MCHM at measurable concentrations. Free chlorine and potassium permanganate ($KMnO_4$) are used in the KVWTP and had the potential to oxidize crude MCHM. The objectives of this task were to evaluate the potential for free chlorine and $KMnO_4$ to oxidize crude MCHM and potentially change the odor characteristics and intensity of the compound.

In experiments, 10 ppb of crude MCHM were spiked into Arrowhead spring water. Based on the concentrations used in the water treatment plant, 3.5 mg/L of free chlorine and 1.3 mg/L of $KMnO_4$ were dosed into the spiked water samples and held for one and three days and three hours, respectively. An additional dosing with 4.0 mg/L $KMnO_4$ was conducted to see if there was any oxidative effect at a higher concentration.

Free chlorine did not appear to cause any reduction of the MCHM concentration. The 1.3 mg/L of $KMnO_4$ appeared to reduce the MCHM concentration by approximately 20 percent. However, the 4.0 mg/L dose did not reduce the MCHM concentration. Thus, it is not clear if $KMnO_4$ really oxidizes MCHM. A separate study at UCLA investigated the oxidation of crude MCHM with similar concentrations of chlorine and $KMnO_4$. Using a different analytical method, the UCLA study found no changes in the MCHM concentration after contact with the oxidants (Suffet and Nonezyan, 2014).

A trained panel conducted a flavor profile analysis of the oxidized, spiked samples. No difference in the odor characteristic or intensity was detected with chlorine oxidation. $KMnO_4$ at a dose of 1.3 mg/L appeared to cause slight reductions in odor intensity of the 10 ppb spiked sample. The 4.0 mg/L dose did not appear to affect the characteristic licorice odor or its intensity. No breakdown product of the MCHM was identified most likely due to the fact that, if it was present, the concentration was too low to detect using the current analytical methodology.

In summary, a screening level evaluation of MCHM oxidation indicated that there was a possible minimal effect of $KMnO_4$ oxidation on the compound and there was no effect with chlorine. More work is needed to confirm these findings, which were done at low MCHM concentrations, but are not representative of the oxidation that would be observed at higher concentrations of MCHM that would have been present in the treatment plant in the first day or two of the spill.

3.3 Conclusions from the Breakdown/Reaction Products Research

There is no evidence from the research performed by WV TAP that there are any breakdown compounds at measureable concentrations that resulted from the treatment of source water contaminated with crude MCHM by chlorine or $KMnO_4$ at concentrations used in drinking water treatment at the KVWTP. High percent recoveries of MCHM after exposure to the oxidants suggest that there are no significant breakdown compounds from the treatment of MCHM with either chlorine or $KMnO_4$. In GC/MS analysis of MCHM treated with chlorine and $KMnO_4$, no peaks were identified that could be related to the breakdown of any of the components in the crude MCHM. Further, there is no evidence that MCHM in the treatment process, distribution system or people's homes was chemically altered producing other breakdown compounds that changed the odor characteristics or the possible health effects of the chemicals in the crude MCHM.

4. Health Effects Expert Panel

The full Health Effects Expert Panel report is presented in Appendix E.

4.1 Rationale for Convening the Health Effects Expert Panel

There were no compounds identified other than the components of crude MCHM and a few low level detections of PPH in the distribution system early in the event. The WV TAP program undertook an evaluation of the safe levels of these compounds for all members of the population for all intended uses. This was done through convening an independent expert panel. The expert panel and meeting were organized by Toxicology Excellence for Risk Assessment (TERA) under contract to Corona Environmental Consulting for the WV TAP.

4.2 Health Effects Expert Panel Objectives

The independent expert panel met on March 31, 2014 in Charleston, West Virginia to review and discuss available toxicity data on chemicals released to the Elk River in January 2014 from the Freedom Industries, Inc., storage tank. The expert panel addressed the following charge questions:

- Given data now available, what would be appropriate screening levels for MCHM and PPH in drinking water?
- What additional data, analyses, or studies might reduce uncertainty and provide greater confidence?
- How should the presence of multiple chemicals in the release to the Elk River be considered?
- Are the screening values protective for all potential routes of exposures (i.e., ingestion, dermal and inhalation)?
- Please identify any additional scientific issues or questions that the panel should discuss.

The panel discussed the initial screening value of 1 ppm (or 1,000 ppb) for MCHM, which was developed by the CDC for the State of West Virginia for short term exposure to MCHM via oral ingestion of drinking water. The panel evaluated the currently available data and developed short-term health advisories for MCHM, PPH and DiPPH. They also identified data gaps and made recommendations for additional studies and analyses to reduce uncertainty.

4.3 Health Effects Expert Panel Methodology

The panel recognized that the CDC used the United States Environmental Protection Agency (US EPA) Health Advisory method (as described in Donohue and Lipscomb 2002) to develop its screening levels for MCHM and PPH. The WV TAP panel recognized that the method CDC employed was a traditional approach that used reasonable and common assumptions to develop health protective drinking water health advisory levels. The panel drew upon its collective experience to discuss and consider other organizations' methods and approaches that might be suitable for developing health advisories for the Elk River spill.

People in the affected area were exposed to MCHM through their community water supply. People were exposed to the contaminated water through direct ingestion, but also on the skin, and through inhalation. The panel considered these other routes of exposure in setting short-term health advisories.

The panel reviewed the available data on crude and pure MCHM and recognized that there were limited toxicology data for MCHM. The WV TAP expert panel agreed with the judgment of CDC that the 4-week oral study in rats with pure MCHM (Eastman, 1990), and the 100 mg/kg-day no observed effect level (NOEL), was the most appropriate available study and end point to establish a short-term health advisory for MCHM. However, the expert panel chose to adjust this 100 mg/kg-day experimental dose to account for the dosing regimen of five days per week. In addition, the expert panel determined that without information on what life stage is most sensitive to the effects of MCHM, the health advisory should be designed to protect the most exposed life stage that consumes the most water on a body weight basis, that is, a formula-fed infant of 1 to 3 months.

4.4 Health Effects Panel Findings and Basis for the Findings

For MCHM, the panel recommended a short-term health advisory of 120 ppb. This value was recommended for public health use with the 2014 Elk River spill and the subsequent contamination of the local water supply. The panel determined that the development of a lifetime Reference Dose (RfD) or similar chronic duration toxicity value for MCHM would be difficult at the present time, because the longest duration toxicology study is only 4 weeks.

CDC developed a short-term screening level of 1200 ppb for PPH and indicated that this level would also be protective for DiPPH. The panel reviewed the available information on PPH and DiPPH and recommended a short-term health advisory of 880 ppb for PPH. This value was recommended for public health protection use with the 2014 Elk River spill and the subsequent contamination of the local water supply.

The expert panel discussed the available information on DiPPH and agreed that there is some evidence that DiPPH is structurally similar to PPH and that it would be appropriate to use the PPH results to estimate a DiPPH value. The panel agreed that a DiPPH short-term health advisory could be estimated from the PPH data, but that the uncertainty factor for the database should be a full factor of 10, rather than 3, to reflect the greater uncertainty in the DiPPH database. The panel recommended a short-term health advisory of 260 ppb for DiPPH. This value is recommended for public health protection use with the 2014 Elk River spill and the subsequent contamination of the local water supply.

The panel was asked to discuss how the presence of multiple chemicals in the release to the Elk River (i.e., crude MCHM, PPH and DiPPH) should be considered in the derivation or application of the screening values. They noted that in a situation such as this, where toxicity data were not available for the mixture of concern (i.e., the tank contents), nor for a similar mixture, combining the toxicity of the individual components would be a reasonable approach to evaluate the mixture toxicity. The panel thought that for these chemicals, the toxicity of their mixture could be approached by simple additivity of each component. In the case of crude MCHM, the panel thought that it was reasonable to assume its toxicity would be similar to the toxicity of pure MCHM.

The panel recognized that people are exposed to the contaminated water in various ways, and attempted to account for these additional exposures by including an extra factor (i.e., relative source contribution or water allocation factor) in the calculation of the short-term health advisories discussed in this report.

The panel discussed what additional data, analysis, or research might help reduce uncertainty. The panel identified two research or data needs specifically for MCHM and suggested three other areas where further analysis and research would aid in better understanding the hazard and risk from this spill.

1. Undertake research to determine what level of MCHM in water would cause skin irritation in humans. The panel recognized that the experimental animal results might be consistent with the patient surveillance reports, but that the available data were not sufficient to estimate a threshold for dermal irritation. The panel recommended that further research be undertaken to determine the potential concentrations of MCHM in water that could cause skin irritation in humans.
2. Conduct toxicology studies for MCHM in pregnant animals. The panel was concerned about the lack of any animal data on developmental toxicity hazard and they recommended that a developmental study in rodents would be useful to evaluate the potential for MCHM to act as a specific developmental toxicant.
3. Organize all available data on exposures and health effects (from immediately following the spill) to facilitate the estimation of initial conditions. The panel understood that multiple parties measured concentrations of the chemicals in the river, at the water plant and in finished water. The panel recommended that data be collated and analyzed to better understand and estimate exposure. In addition, data related to symptom reports should also be analyzed together with the monitoring data to better understand exposure and effects.
4. Pending results of #2 and #3, consider the need for a long-term animal health effects studies. If the studies in recommendation #2 show developmental effects that are specific to MCHM and not due to maternal toxicity, and a reliable estimate of exposure can be developed (#3) then the panel would recommend consideration of conducting a longer-term health effects (epidemiology) study among exposed individuals in the Charleston area.[2]
5. Determine chemical fate and transport for all of the detailed processes that occur within the treatment plant and water distribution system. The panel recommended that additional research be conducted on chemical fate and transport of the chemicals, to better understand how the chemicals in the spill interact with other chemicals in the water and the water distribution system.

4.5 Health Effects Panel Conclusions

The panel reviewed available data for MCHM, PPH, and DiPPH and developed short-term health advisories for public health use with the 2014 Elk River spill and the subsequent contamination of the local water supply. Each of the screening values was intended to protect all

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[2] The WVBPH and the CDC conducted interviews with 396 affected households as part of a Community Assessment for Public Health Emergency Response (CASPER) study. Interviews were conducted 8 – 10 April, 2014 and results will be used along with those of an emergency department document review to strengthen future emergency responses.

portions of the population, including infants, children, and pregnant women. Each value is meant to protect for exposures to the water through direct ingestion, inhalation from showering and household water use, skin exposure, and incidental exposures such as brushing teeth. The MCHM advisory is based upon a 4 week rodent study and with the appropriate uncertainty factors is appropriate to use for human exposure situations from one day up to 3 months. The PPH and DiPPH advisories are based upon a 90-day rodent study and a formula-fed infant scenario, and therefore they are also appropriate to use in situations from one day up 3 months. Panel members thought that these values may also be useful for longer exposures, but this would entail determination of the most appropriate water intake to match the exposure duration of interest.

The panel reviewed the CDC screening values and this expert panel's conclusions were not incompatible with the CDC values; the panel used more refined methods to calculate the short-term advisories, including an adjustment to account for additional routes of exposure (dermal and inhalation). The panel developed these short-term health advisories for public health use with the 2014 Elk River spill and the subsequent contamination of the local water supply.

The final report reflects the panel's final opinion and conclusions. The final recommendations for toxicity values differ slightly from the preliminary report due to rounding to an appropriate level of precision during the calculations. The final report prepared by the health effects panel can be found at www.dhsem.wv.gov/WVTAP/test-results/Documents/POSTED_Health%20Effects%20Expert%20Panel%20Report_FINAL.pdf and is found in Appendix E of this report.

5. Ten Home Pilot Sampling and Survey

As part of the WV TAP project Task 4, 10 homes affected by the crude MCHM chemical spill were studied. The objective of Task 4 was to conduct a focused residential drinking water sampling field study to be used to support the design of a larger more comprehensive program for the nine counties affected. As part of this effort, households were visited in eight of the nine counties affected by the drinking water contamination incident from February 11, 2014 to February 18, 2014. The counties included Boone, Cabell, Clay, Kanawha, Lincoln, Logan, Putnam, and Roane counties.

During each household visit, residents were interviewed by the WV TAP project team in addition to the team chemically analyzing tap water at kitchen and bathroom fixtures, and collecting water samples for additional commercial laboratory analysis. Results of the resident interviews are contained in the report titled "The Crude MHCM Chemical Spill 10-Home Study: Resident Behaviors, Perceptions, and Residence Characteristics" found in Appendix F. Resident interviews were conducted using the questionnaire found in the report. Project team members completed the questionnaire on site while speaking with the household representative. Basic chemical and physical properties (temperature, pH, and chlorine residuals) were determined for tap water from hot and cold kitchen and bathroom faucets. **The survey results are from an extremely small convenience sample and no inferences should be made about the entire affected area on the basis of the survey findings.**

The survey findings are summarized as follows.

1. The majority of the residents learned about the "Do not use" order by word of mouth (4 of 10 homes) and television broadcasts (3 of 10 homes), followed by Facebook, radio, and phone alert. All of the residents interviewed had heard about the "Do not use" order on January 9.
2. Homes had a variety of plumbing materials including copper and a variety of plastics; nine of 10 homes had electric hot water heaters.
3. None of the homes had whole house water filters (point of entry water treatment), and only one had a treatment system after the tap. Two homes had refrigerator water filters.
4. Residents in one of the 10 homes never detected any odor in the water. The other nine homes reported moderate to unbearable odor at some point on or after January 9.
5. Three of the 10 homes noted a color change in their water. These color changes might have been a result of system flushing.
6. Nine of the 10 homes reported not tasting the water once the "Do not use" order was issued; in the home where one resident did drink the water he reported it as sweet tasting.
7. Residents flushed their plumbing, on average 14 days after the "Do not use" order was issued. One resident first flushed his system 37 days after the incident. Seven of the 10 respondents reported rashes or burning eyes associated with flushing.
8. All homes used water for toilet flushing before and throughout the event. At the time of the interviews four homes were not using water for showering and nine were not using tap water for teeth brushing. None were using tap water for drinking, cooking, or making baby formula; only one home used tap water for watering farm animals.
9. Prior to the contamination event, half of the households did not use tap water for drinking. Two of 10 did not use tap water for brushing teeth and three of 10 did not use tap water for cooking.
10. Five out of ten respondents felt that a West Virginia government agency was responsible for the contamination event for lack of oversight of industry. When more than one responsible party was named, WVAW was named in four instances.
11. Where households had an opinion of a particular agency prior to the spill, they generally reported a lack of confidence in that agency after the spill. Kanawha County Health Department was named specifically by half of the respondents as an agency in which they had confidence.

Results of the chemical analyses of hot and cold water samples collected at the four taps in each home are presented in the report titled "The Crude MHCM Chemical Spill 10-Home Study: Tap Water Chemical Analysis" found in Appendix G. Water samples were collected and shipped to two commercial laboratories for characterization. Commercial laboratories examined water for TOC, MCHM, and PPH concentrations.

Several important findings were made. TOC concentration was in the expected range for uncontaminated water and did not vary widely across or within the 10 homes studied. Thus, TOC concentration was not a good indicator of MCHM contamination. No PPH was detected in any home by either laboratory. MCHM was detected in all 10 homes by the Eurofins laboratory, but not detected by ALS Environmental Laboratory in replicate water samples. This finding is significant and underscores the importance of selecting laboratories that can reliably detect and quantify low levels of contaminants during a chemical contamination incident. Eurofins laboratory's MDL and MRL for MCHM were less than 0.5 ppb and 1.0 ppb while ALS Environmental Laboratory's MRL and MDL values were 2.7 ppb and 5.0 ppb. Ninety percent of the MCHM concentrations reported by Eurofins were less than 2.4 ppb. Thus, ALS Environmental Laboratory's method could not detect the low levels of MCHM present in tap water at a MCHM concentration equal to or less than 2.4 ppb. Home #8 had the greatest average MCHM concentration of 4.4 ppb and the maximum observed concentration of 6.1 ppb. ALS did not report any detections even in this home. No MCHM concentrations detected in any home exceeded the 10 ppb State of West Virginia screening level.

Among the water quality parameters assessed in tap water, only MCHM concentration, odor, temperature and chlorine concentration were useful in assessing the impact of the spill on premise plumbing. Any further sampling should be focused on those parameters. MCHM concentration and odor provide direct measures of the impact of the spill and temperature and chlorine concentration have indirect effects because they are related to odor.

MCHM analysis was valuable and should be included in additional studies. However, it is critically important that laboratories selected can reliably detect and quantify low concentrations of MCHM (e.g., at the Eurofins MDL of less than 0.5 ppb). As time since the spill elapses, MCHM concentrations are expected to continue declining in the absence of a source in the water treatment facility, distribution system, and/or premise plumbing systems.

6. Sampling Design

Details of the Sampling Design can be found in Appendix H.

6.1 Sampling Design Background and Objectives

Following the spill of crude MCHM into the Elk River on January 9, 2014, there have been persistent calls from the area residents for a large program of in-home sampling to establish the concentrations of the constituent chemicals in residences. WV TAP explored the properties of a sampling program that can answer the main questions being asked by residents and government officials. Statistical sampling design principals were applied to estimate the amount of certainty that can be established based on different sampling strategies. The evaluation of sampling strategies is based on MCHM concentration data collected during the pilot 10 home sampling program (see Section 5).

Designing a sampling program requires a clear understanding of the questions that the sponsors want to answer. In this case many questions are being posed. Since no single design is optimized for all questions a subset of the questions that have been posed to WV TAP were selected and sampling designs to answer these questions were explored. The key questions addressed were:

1. What is the concentration of MCHM in people's residences?
2. Is the average concentration observed in homes below a level of concern?
3. What proportion of the homes has MCHM concentrations below a level of concern?

Sampling plans were evaluated that would determine whether measured concentrations were statistically different from critical values established by the CDC, the State of West Virginia and WV TAP levels of concern. Standard statistical methods were used to estimate the likely confidence that would be observed for estimates of percentages of the residences in the affected area for which concentrations are above and below these critical values. Results from the 10 home sampling program demonstrated that, more than one month after the spill, there were still detectable concentrations of MCHM in water in people's homes. The concentrations ranged from below detection levels of 0.5 ppb up to 6.1 ppb. The standard deviations of the measurements ranged from a low of about 0.1 ppb to a high value of 1.5 ppb. These statistical properties were used to determine the number of residences that should be sampled and the number of samples that should be taken within each home. It is unknown whether plumbing systems in large buildings with more complex plumbing systems had similar mean MCHM concentration and ranges because no large buildings were sampled in the 10 home pilot study. This lack of data precludes development of a sampling plan for assessing the MCHM concentration in larger buildings.

6.2 Sampling Plan Design and Rationale

A list was made of the values that have been considered as critical health effect levels or levels of concern throughout the crude MCHM spill event. These values include the CDC screening level (1 ppm), the WV TAP short term health effects safe level (120 ppb), the odor recognition concentration (7.4 ppb), the odor objection concentration (9.5 ppb), and the odor threshold concentration (0.55 ppb) (see Fig ES-1 in report). These levels, along with estimates of the mean concentration, the standard deviation of concentration, the required level of certainty and the required statistical power determine the number of samples that must be analyzed to detect a specified difference from the screening level.

If the main concern is that the water is safe for residents to use for all intended uses by all members of the community then all that is required is to evaluate samples relative to the WV TAP short term health effects safe level of 120 ppb, which only requires a single sample per home given that the expected concentrations will be in the single digit ppb or lower. To increase confidence, the state may consider testing 30 homes in each of the 24 regions established for flushing. In order to verify that the variability is properly characterized by the 10 home sampling program it would be best to take two samples per home so there is a measure of the within home variability. Since the only chemical detected in the sampled homes was MCHM, it is the only chemical that needs to be analyzed.

This recommended sampling program would result in a total of 720 residences being sampled. This number of sampled homes would allow a good estimate of the percent homes in the affected area that are below any critical value of interest. For example, these data could be used to estimate the percentage of homes for which the MCHM concentration is below any of the critical values mentioned above. The confidence interval about any estimate of percent homes for the entire affected area would be in the range of ± 3% or better.

This approach is an effective means for demonstrating that either the concentrations are well below the levels of concern or that there are persistent concentrations that need to be further addressed. This approach would address the questions posed above and allow for robust answers to those questions. Based on the measurements made in the 10 home study including concentrations and variability the following conclusions can be reached regarding future sampling.

1. With a sample size of three samples per home, statistical power would be sufficient to determine if the concentrations observed in any one home could be safely considered to be below the upper value of the two estimates of the odor objection threshold concentration (9.5 ppb).

2. With a sample size of 13 samples per home, statistical power would be sufficient to determine if the concentrations observed in any one home could be safely considered to be below the odor recognition level (7.4 ppb).
3. If the goal of sampling is to determine if the concentrations measured in each home are below the OTC (0.55 ppb) then 5 samples per home would be required.
4. Sampling 30 homes per region will allow estimates of the average concentrations for each region with tight confidence intervals that would allow for meaningful comparisons of the mean concentrations between all regions.
5. If this hypothesis is rejected then at least one of the regions is different from the other regions. If this difference is positive and significant from a health or odor recognition perspective then more action may be required to continue the MCHM flushing of the region(s) with higher concentrations.
6. A total of 720 homes would be sampled under this plan or 0.82% of the total number of residences affected. This sample size is statistically defensible and would allow for percentages of homes above or below any screening level to be calculated with very tight confidence levels even at very low percentages. The widths of the confidence interval for different percentage positive results at a sample size of 720 can be derived using standard statistical techniques. These estimates would be satisfactory for the results over the entire area affected but would not be useful for samples within any one of the 24 regions.

7. Integrated Discussion and Conclusions

One month after the Elk River crude MCHM spill, MCHM concentrations in samples taken throughout the affected area were consistently below the then used level of detection, and contaminant concentrations were well below the CDC screening levels. Over the course of the study the method limits of detection reduced significantly as laboratories developed and improved methods for MCHM detection. At the same time analytical chemistry results indicated no detectable MCHM in the finished water supply, residents of the affected area continued to smell contaminants in water in their houses. WV TAP confirmed that the residents were correct and had smelled the crude MCHM at concentrations well below the then routine analytical detection limits in place at the time of the spill response. Eurofins Lancaster Laboratories Environmental LLC, WV TAP team members, was able to lower the detection limit to a level where the contaminants that were being smelled by residents could be detected analytically. This combination of facts confirmed that remnants of the material spilled from Freedom Industries, Inc., tank number 396 were still present in the affected area. MCHM was present at very low concentrations relative to 28-day short-term levels believed to be of human health concern.

Investigating the results of this unfortunate event required an understanding of what chemicals the team was trying to evaluate. There were concerns that the treatment of the contaminated water with chlorine and potassium permanganate might have resulted in breakdown chemicals which could be responsible for the odors that were being detected or pose health hazards to the exposed public. The WV TAP team evaluated the possible breakdown products and determined that there were no breakdown products likely either in the water plant or in the water that eventually reached the residents' homes. In the course of investigating possible breakdown products, the WV TAP team collected four samples to evaluate possible sources of unidentified chemicals observed in chromatograms from the 10 home sampling. Samples were collected in

March 2014 upstream of the Freedom Industries, Inc. Barlow Drive chemical storage facility (the site of the spill), at the KVWTP intake, in the finished water of the KVWTP and in a nearby home. Results demonstrated that the unidentified compounds were not in the Elk River. Analyses of MCHM in these samples showed no MCHM in the Elk River or at the intake, but low concentrations in the finished water and in the nearby home. These results indicated that there was a persistent low level source of MCHM in the treatment plant. Though the concentrations in finished water were very low (< 1.0 ppb), they were still at a level that would result in odors in the homes. These findings were communicated to WVAW with a recommendation that it initiate a sampling program to pinpoint the source of the MCHM. WVAW initiated this sampling shortly after it was informed and confirmed that low levels of MCHM were desorbing from the GAC in the filters. Results from the WVAW sampling effort were reported in a press release dated March 25, 2014 and are shown in Table 3. These findings supported the planned replacement of the GAC. Replacement of the GAC was started the first week of April, 2014.

Table 3. Results of WVAW Sampling through the KVWTP

Sample Date	Sample Time	MCHM Concentration (ppb)					
		Raw	East Settled	West Settled	East Filtered	West Filtered	Finished
3/21/2014	6:00 PM	ND[a]	ND	ND	0.6	0.44	0.52
3/21/2014	8:00 PM	ND	ND	ND	0.55	0.53	0.49
3/21/2014	10:00 PM	ND	ND	ND	0.6	0.43	0.53
3/22/2014	12:00 AM	ND	ND	ND	0.56	0.41	0.46
3/22/2014	2:00 AM	ND	ND	ND	0.57	ND	0.46
3/22/2014	4:00 AM	ND	ND	ND	0.42	ND	ND
3/22/2014	6:00 AM	ND	ND	ND	ND	ND	0.45

[a] ND denotes non-detect. Detection levels identified by Eurofins Lancaster Laboratories ranged from 0.38 ppb to 0.45 ppb and were dependent on the sample volume

With this conclusion reached, the team performed an independent evaluation of the levels of the chemicals that were present, which would be safe for all residents to use for all intended purposes including drinking, washing, cooking and the preparation of baby formula. The WV TAP team prepared an in-depth review of the literature (see Appendix I). An independent team of toxicology and water system experts evaluated the methodology applied by the CDC that led to the initial screening level of 1 ppm. The independent team validated that the CDC approach was sound given the method it used with the data it had available. The data available for these evaluations was not optimal and therefore all analyses included uncertainty factors. Use of uncertainty factors is a common practice in human health risk assessment (see, e.g., Dourson and Stara, 1983, and Pohl and Abadin, 1995). In performing its own evaluation, the independent team decided to protect for not only ingestion but also inhalation and dermal exposures. The WV TAP health effects panel also decided to utilize the water intake (i.e., the volume of water ingested) for the most exposed sub-population as the basis for risk estimation. Specifically, because there were no data to indicate what sub-population may be most sensitive to the toxicity of these chemicals, they used the water intake for formula-fed infants, since they consume more water on a per mass basis than any other age group. These assumptions resulted in levels which the panel agreed are without appreciable risk to public health and most of the members of the independent panel were willing to declare (or term) these levels as “safe” for all exposures. The resulting “safe” concentrations were lower than the levels determined by the CDC but well above the short-term screening level of 10 ppb adopted by the State of West Virginia in their recommendations to the affected citizens of the area.

The 10 home sampling and surveying program was initiated for multiple purposes. It was the first formal sampling of water in residents' homes that was sponsored by the State of West Virginia. While the sampling was not meant to provide a general characterization of the concentrations of the contaminants in residents' homes throughout the region, it supplied the following.

1. A snap shot of the concentrations throughout the impacted distribution system.
2. A preliminary comparison of concentrations from different household taps (hot and cold water, bathroom and kitchen taps.
3. An estimate of the variability in MCHM concentration both within and between homes.
4. Samples to evaluate the possible breakdown products of the contaminants both from oxidation by chlorine and potassium permanganate and from interactions with the distributions systems and premise plumbing.
5. Independent evaluation of the odors and the persistence of the odors in residents' homes.

The 10 home survey supplied insights into the experiences of the residents and their reactions to the contamination event. Most of the residents surveyed detected the licorice odor at some point following the spill. Some residents experienced health effects which were confirmed by a syndromic surveillance investigation done by Dr. R. Gupta (Gupta, 2014). The 10 home study indicated that many of the residents who were surveyed had not used tap water for drinking even before the spill occurred. The spill and response impacted people's perception of the government and the authorities who communicated with them during the event.

Though the small sample size of water samples collected and analyzed during the 10 home sampling project was insufficient to characterize the MCHM concentrations for the entire affected region, the results supplied insights and data required to design a larger sampling plan. There were no clear trends in the MCHM concentration with the water temperature or tap location. There were no clear trends in concentration by location in the homes, but the sample results confirmed reports from residents that they perceived different levels of odors in different location within their homes.

The results also confirmed that the method detection levels used are important. The non-detect results from sampling done prior to the WV TAP program were because the analytical methodology used could not detect levels less than 10 ppb. Non-detect observations were indicative that the concentrations measured were well below levels that should be considered safe (for short-term exposures) for all chemicals involved in the spill, but were not convincing to residents, some of whom based their perception of the safety of their drinking water more on odor than results of chemical assays.

At the time of the WV TAP 10 home sampling there were still detectable concentrations of MCHM in residents' homes. The data demonstrate that there may be homes with significantly higher concentrations than the average home. One home (#8) had concentrations three to five times greater than the average concentrations observed in all of the other homes. It is not clear from the work done by WV TAP what caused the differences in concentrations in different homes or in different locations within a home. The data collected as part of the 10 home sampling program provided estimates of the variability in MCHM concentrations that are likely to be observed in future sampling events. Standard deviations of MCHM concentrations in samples taken from individual homes varied from about 0.10 ppb to 1.5 ppb.

In future sampling efforts the number of samples collected per home and the number of homes sampled both need to be based on a specific objective of the sampling program. Since the average concentrations of MCHM that are expected in future sampling will be lower than the concentrations observed during the WV TAP sampling, very few samples are required per home in order to be confident that the concentration of MCHM in any home is less than the WV TAP short-term safe level (120 ppb). Two samples per home would allow sufficient power to detect differences if the concentrations are truly lower than the short-term safe (or screening) levels and would provide information on the variability in MCHM concentration among samples collected in an individual house. Characterizing the concentrations of MCHM in the entire affected area would require dividing the impacted area into regions with similar characteristics (e.g., regions selected by WVAW for flushing of the system) and sampling at least 30 homes within each region to establish a conservative estimate of the proportion of homes whose MCHM concentration is greater than a level of concern. Other sampling plans are possible depending on questions that are asked and the resources available for the sampling.

The most compelling reason for additional MCHM sampling is to determine if replacing the GAC at the KVWTP has resulted in all samples being below the detection limits as determined using the lowest detection limits available. Theoretically, once the GAC has been replaced, sampling will inform the community if there are any remaining sources or reservoirs of MCHM in the water system.

7.1 Recommendations to the State

In retrospect, the State of West Virginia discovered that there was no regulatory requirement for state inspection of the Freedom Industries, Inc., chemical storage site tanks before the leak occurred. If remediation of the damaged structure had been done, the event might have been averted. To rectify this situation the West Virginia legislature passed Senate Bill 373, which requires the state to inventory most above ground chemical storage tanks. Once the State of West Virginia was presented with this very complex emergency, its response was fast and decisive. As far as WV TAP can determine from our review, the State took reasonable steps in addressing this emergency once it happened. At all steps they sought input from experts. The state initiated sampling as quickly as possible and sought expert input from the CDC, the Department of Homeland Security and other agencies. The early characterization of the material of concern was well done with extremely qualified experts in chemical analysis and interpretation. WVAW was brought into the discussions as soon as the threat to the water system was apparent. WVAW's expertise was factored into many important decisions including the decision to issue the "Do not use" order, the determination of methods for sampling and flushing and the decision to remove the "Do not use" order. Involvement of the West Virginia National Guard was crucial through the entire event. The West Virginia National Guard supported collection and processing of samples, flushing, and routing information to the affected citizens and businesses. Its actions should be considered a blueprint for other communities in need of emergency assistance.

In similar instances the State should consider bringing in an independent team of experts as early in the response as possible. The resources that WV TAP brought to the response enabled rapid integration of sound scientific information to address complex problems. In order for an independent team to work effectively in a crisis, strong unequivocal support from state authorities is required. The WV TAP team would not have been able to complete its work without the support of the WVBPH, the WVDHHR and the Office of Governor Tomblin.

WV TAP was charged with doing a rapid assessment. While this report answers many of the questions that emerged in the aftermath of the crude MCHM spill, many complex questions remain. The next section explains some of the questions which are likely too large for the State of West Virginia to address independently. Further, this emergency situation should be a lesson for all states and all water utilities to prepare for other spills which could be larger and more dangerous than the crude MCHM spill in the Elk River. Section 7.3 presents recommendations from the WV TAP team for other entities to prepare for future contamination events.

7.2 Recommended Additional Research

After the research conducted within the WV TAP effort, many data gaps remain in our knowledge of the physical properties, reactivity, treatability and health effects of crude MCHM. Research to fill those gaps, to better assess the safety of water in the KVWTP and the homes it serves, and to be better prepared in the event of another spill is provided below. Many of these questions are critical not only for West Virginia and for MCHM but for the entire country for future spills including other chemicals. The following research should be considered and funded by a wider group that may include States, the Federal government, industry as well as organizations that fund research aimed at protecting public health. While these recommendations are specific to a crude MCHM spill, they frame the types of research that could be conducted for any credible chemical threat to a drinking water treatment plant as a part of a disaster preparedness effort. The following research should be considered.

- Development of methods for detection of MCHM at MRLs as low as the odor threshold concentration. Similar research should be considered for other common chemicals.
- Another round of statistically designed sampling to assess the residual level of MCHM in the KVWTP plant effluent, distribution system and connected premise plumbing once the GAC is completely replaced and the system is flushed. If positive samples are detected, intense sampling should be undertaken in the vicinity of the positive samples to determine the concentrations and sources of residual contamination.
- Statistically designed sampling in residences as well as buildings with more complex premise plumbing (e.g., office buildings and multi-family residences).
- Quantification of the efficacy of different flushing strategies in eliminating MCHM from premise plumbing and the impact of premise plumbing design (materials and configuration) on flushing efficacy.
- Development of a better understanding of the interactions of MCHM with premise plumbing, including water heaters.
- Identification of minor compounds in crude MCHM and in tap water samples from residences. This research may need to be simulated in the laboratory since the concentrations in the system are likely to be very low in future sampling.
- If minor components of crude MCHM are identified, then aesthetics responses and health effects evaluations should be conducted for these minor components.
- Oxidation studies at higher MCHM concentrations to replicate the concentrations that may have been present in the KVWTP early in the event to assess the impact of treatment on crude MCHM and odors from treated waters.

- Determination of the concentration of MCHM in water that causes skin irritation for humans.
- Toxicological studies for pregnant animals exposed to MCHM.
- Characterization of the exposure (concentrations and durations) and reported health effects of the entire population impacted by the Elk River spill.

Many of these research objectives will advise approaches and decisions for future spills.

7.3 Recommendations to the Water Utility Community

Vulnerability Assessment

The Elk River spill is a call to action for all water utilities with hazardous chemicals in close proximity to their source water. Regardless of the regulations and responsibilities of the State and Federal regulators, water utilities have responsibilities and liabilities that should prompt initiative in the identification of possible chemical threats. WV TAP suggests that utilities should develop (i) an inventory of chemicals that are upstream of their raw water intakes, (ii) locations of the tanks, ponds and other appurtenances which contain these chemicals and (iii) methods for evaluating possible travel time for the chemicals from the tanks to the raw water intakes. For each chemical identified a dossier should be prepared that includes all chemical information including material safety data sheets, basic chemical characteristics, health effects information and likely approaches for water treatment, waste disposal and possible breakdown products. Additionally, utilities should develop sampling protocols for these chemicals including:

- The type of required sampling;
- The needed equipment;
- Safety precautions needed for personnel;
- Aesthetic response levels;
- Laboratories that could reliably analyze for the compounds, along with the methods they use and their detection levels; and
- Agencies that should be contacted and brought in to support the response.

Sampling plans should include details for rapid deployment of samplers to get samples as soon as possible to establish early exposure concentrations and contaminant distribution. Barriers to sampling need to be considered (e.g., difficulty of getting into people's homes). The inventory of chemicals, knowledge of health effects, treatability, key contacts, laboratories and sampling strategies all need to be updated on a regular basis.

The American Water Works Association (AWWA) has developed a robust Source Water Protection Standard (revised) (AWWA, 2014) and an operating guide for implementation of the standard (AWWA 2010). These documents present standard approaches for evaluating threats to source water used for drinking water. They contain effective guidance for the implementation of a comprehensive source water protection program. The operational guide to the AWWA standard G300 includes the creation of emergency response plans tied into the source water protection programs. It is essential that these emergency response plans not only be written, but tested through table top exercises and regular review and update.

Early Warning Systems

Utilities should consider deployment of water quality sensors in their source water, treatment plants and distribution systems. Completion and regular update of the vulnerability assessment would identify the contaminants of concern. Using the list of vulnerabilities, utilities could explore possible sensors that could act as early warning systems for the contaminants. Systems of this type are currently deployed by the Ohio River Valley Water Sanitation Commission (ORSANCO) along the Ohio River (Gullick et al., 2004). These sensors were used to effectively alert systems along the Ohio River of the crude MCHM plume as it approached water treatment plants along the river and allowed the water utilities and companies to take action to protect their water systems from contamination. (Schulte, J, personal communication[3]). Systems of this type have been deployed on the Ohio River for early warning since the 1980s.

Information Flow

During an event of this kind there is a need for collection and flow of a great deal of information via many different pathways. The organizations WVAW and AWWA along with the following agencies became the team that addressed this emergency: the WV DEP; the WVBPH; the WVDHHR; the West Virginia National Guard; the CDC; the US EPA; the National Science Foundation; and county and local authorities such as local departments of public health. Critical contacts within these agencies should be made long before there is another crisis. The agencies that may be critical and could help in an emergency of this type should be well understood by the utilities and the States. A plan should be in place for regular update of these contacts for each region and for each agency. Development of regional contact plans that can be shared among utilities, agencies and other stakeholders should be considered. The possible data needs of each agency that are required for the agency to support the local decision processes should be considered and methods for supplying these data should be planned in advance. Documentation of chronologies, communications and decision processes should also be planned.

Customer complaints received by the water utility and state and local health officials are a valuable resource to early detection of problems. The crude MCHM event was first identified in the air near the spill site and conveyed to officials via a complaint by a citizen to the WV DEP. Customer odor complaints have been the first notification of other spills (see, e.g., Rink, 2011). For customer complaints to be an effective mechanism for event detection, there is a need for a baseline of the number and types of calls that are received by these authorities and there needs to be an established communications path and data flow to scientists, engineers and decision makers to provide for the best use of this critical data. The analysis of these data should be on-going and the results should be shared among entities to ensure early detection of departures from baseline conditions.

Similarly, monitoring of health effects in communities should be available and compared to baseline data using statistical processes established before any event occurs. The ability to do this needs to be set up prior to any crisis. Data that are relevant include the number of people admitted to hospitals, the number of emergency calls received, drug sales and aggregated

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[3] Grab samples collected along the Ohio River downstream of the confluence of the Ohio River and Elk River were analyzed by the Greater Cincinnati Water Works and other utilities in the path of the plume and used to track the plume of MCHM in the Ohio River. MCHM was detected in samples from the Ohio River. Significant attenuation of the peak concentration in the plume occurred between Huntington, WV, and Louisville, KY.

relevant symptoms from both hospitals and local medical offices and clinics. These data are useful to assess the severity of the health effects and are also important to help identify the end of the event. All of these data should be rapidly collected, interpreted, and reported so that decision makers can take steps based on the best available information.

Once sampling is started it is important that the data are properly managed, quality controlled, shared among the authorities and responders, and clearly understood before the results are communicated to the public. Data management and reporting are important tasks in any monitoring program but are critical when complex data are collected upon which important decisions will be made that could affect people's health. An important example of this requirement emerged during the WV TAP 10 home sampling program. The press put pressure on the WV TAP team to release all laboratory results as soon as the data were reported to the team by the laboratories. Parts of the data reports were chromatograms which are very complex data sets that require expert analysis and interpretation. Early chromatograms from the 10 homes sampled showed many unexpected peaks which were initially candidates for potential breakdown compounds. Subsequent research demonstrated that these peaks were artifacts of the analytical methods applied and were in no way related to the crude MCHM spill. Early release of these data would have caused unnecessary panic in the community and would then have taken major efforts to dispel the incorrect conclusions that there were breakdown products of crude MCHM. This would have resulted in wasted effort and loss of focus on the real health concerns.

Communications

When a spill occurs it is important that communications are well organized and coordinated to prevent the release of conflicting information. Decision makers and responders should have a well-considered and vetted communications plan in hand at the outset of a drinking water crisis. Such a plan minimizes the release of conflicting or incorrect information and reduces the amount of time responders must allocate to communication with the public.

Following a "Do not use" order the citizens affected by the incident are the most important audience. In the immediate aftermath of a spill, citizens must be quickly advised not to contact the water, where to seek alternate water sources, when the next update will be provided, and other essential information to help them properly respond and cope with the situation. During later stages of the response citizens must be provided very specific and easy to follow instructions on how they can protect themselves, decontaminate their premise plumbing (e.g., through flushing) and assess the safety of their water supply.

Regulators and other government officials both consume and collect data during a crisis and must communicate with both the technical community and the general public. Members of the public may have a general trust of government officials (or perhaps a general distrust) and government officials could partner with water utility representatives in disseminating information to the general public. WV TAP also showed the advantages of bringing in independent scientists and engineers to evaluate the problems following a crisis such as the Elk River chemical spill. The health community could also be involved in both information gathering and communication with the public. As noted above, the health community can collect potentially valuable information such as hospital admissions, doctor visits, patient symptoms, and over the counter drug sales that could indicate a health concern that might be related to a contaminated water supply. Those data would be valuable in identifying potential health effects associated with chemicals like MCHM that have very little toxicological data. Health care providers are also frequently the first place citizens turn to for information. Providing health professionals with information during a response could provide an effective strategy for helping disseminate important information to public.

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Appendices can be accessed on the WV TAP web site

http://www.dhsem.wv.gov/wvtap/test-results/Pages/default.aspx