Appendix A. Expert Panel Estimates of the Odor Threshold Concentration (OTC), Odor Recognition Concentration (ORC) and Odor Objection Concentration (OOC) for Crude 4-methylcyclohexanemethanol (MCHM) in Water

Michael J. McGuire, Inc.
469 25th Street
Santa Monica, CA 90402

TECHNICAL MEMORANDUM

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To: Jeffrey Rosen, Corona Environmental Consulting

From: Michael J. McGuire, PhD, PE

Subject: Expert Panel Estimates of the Odor Threshold Concentration (OTC), Odor Recognition Concentration (ORC) and Odor Objection Concentration (OOC) for Crude 4-methylcyclohexanemethanol (MCHM) in Water

EXECUTIVE SUMMARY

A spill of "Crude" 4-methylcyclohexanemethanol (MCHM) into the Elk River in West Virginia caused complaints by residents of odor problems in their tap water—predominantly a licorice odor. A team of experts was hired to understand the odor characteristics of the spilled chemical. The expert team developed a methodology based on ASTM Method E679 to estimate the Odor Threshold Concentration (OTC), Odor Recognition Concentration (ORC) and Odor Objection Concentration (OOC) for Crude MCHM in water during a single panel session.

A number of qualifiers must be attached to the findings of this report:

1. Small panel size: nine; two-thirds women and one-third men
2. Expert panelists more sensitive than consumers
3. Most panelists were young
4. Panelists were knowledgeable of MCHM odor
5. No chlorine in spiked samples
6. Determination of thresholds in a controlled environment

Table ES-1 summarizes the estimated OTC, ORC and OOC concentrations that were determined by the Expert Panel. The estimated OTC is in the realm of parts per trillion, an extraordinarily low concentration. The ability of the expert human nose to detect this compound is far greater than any analytical method available today.

Table ES-1. Summary of Expert Panel Odor Threshold Estimates

Odor Thresholds	Geometric Mean, ppb	Factor Greater than OTC
Odor Threshold Concentration (OTC)	0.16*	---
Odor Threshold Concentration (ORC)	1.6	10.1
Odor Threshold Concentration (OOC) Based on Degree of Liking	2.2	13.7
Odor Threshold Concentration (OOC) Based on Complaint	4.0	25.3

* Actual OCT for these panelists is likely <0.16 ppb

The estimated thresholds determined in the Expert 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 though the analytical reports were showing non-detect at a minimum reporting level of 10 ppb.

Recommendations for future work have been made including the convening of a larger panel to determine estimates of OTC, ORC and OOC for Crude MCHM using untrained consumers.

INTRODUCTION

On January 9, 2014, approximately 10,000 gallons of "Crude" 4-methylcyclohexane-methanol (MCHM) spilled into the Elk River from the property of Freedom Industries a short distance above the drinking water intake of the West Virginia American (WVA) water treatment plant. Shortly after the spill began, consumers located in the area served by WVA (Charleston, WV and environs) began complaining of a licorice odor in their drinking water. On February 9, I was hired as part of an expert team to help the state of West Virginia understand the odor characteristics of the spilled chemical and the reactions of the customers served by WVA.

It was urgent that the odor characteristics of the chemical be understood in a scientific context in a short period of time. Therefore, an Expert Panel study was planned which could give some answers in a matter of a few weeks.

The objectives of the work described in this technical memorandum were to:

1. Develop a methodology to estimate the Odor Threshold Concentration (OTC), Odor Recognition Concentration (ORC) and Odor Objection Concentration (OOC) for the licorice-smelling substance in water.

2. Work with an analytical laboratory to develop a spiking method to prepare samples of the licorice-smelling substance in a reference water that could be presented to a panel.
3. Convene a panel of experts to participate in a study using the methodology developed to determine concentrations of detection, recognition and objection/complaint for the licorice-smelling substance in water.
4. Understand how the Expert Panel results could be used to explain consumer observations in Charleston, WV where people smelled a licorice odor in their drinking water immediately after the spill and for many weeks following the spill even after repeated system flushing.
5. Make recommendations for additional work to supplement and confirm the Expert Panel findings.

DEFINITIONS OF DETECTION (THRESHOLD), RECOGNITION AND OBJECTION CONCENTRATIONS

Understanding how consumers react to off-odors in their drinking water is a complex problem that presents a unique set of challenges. To understand this phenomenon, it is important to appreciate the distinction between detectable odors and the concepts of recognizable and objectionable odors. Peer-reviewed scientific literature has recognized the concepts of detection, recognition and objection in drinking water and other substances.[1, 2, 3] Table 1 organizes the concentrations of odorants in drinking water into aesthetic response levels.

Table 1. Odor Response Levels for Concentrations of Chemicals 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 – ORC

The same principles in Table 1 apply to the sense of taste. For example, the taste thresholds for sodium chloride and calcium chloride are in the range of 200 to 300 mg/L.[4] At or above the taste threshold, panelists can describe the "salty" taste resulting in recognition. As the sodium chloride concentration is increased further, the salty taste becomes objectionable.

Concentrations of minerals (including sodium chloride) that are objectionable to consumers in actual drinking water distribution systems have been described by detailed surveys of households. Bruvold and Daniels found that total dissolved solids (TDS) concentrations above 450 mg/L resulted in a significant number of consumers to reject their water supply and to seek alternatives. This concentration is just below the Secondary Maximum Contaminant Level for TDS and is equivalent to the taste objection concentration for TDS.[5]

PANEL METHODOLOGY

Panelists were recruited for this study using the following criteria:

- Expert panelists trained in the Flavor Profile Analysis method[6, 7]
- Between the ages of 18 and 65
- Balance of women and men (approximately 50:50)
- Pregnant women could not participate
- Non-smokers only
- Anyone with a history of severe asthma or sinus problems was excluded
- Anyone currently suffering from a cold, the flu or any upper-respiratory disease at the time of testing was excluded
- No eating or drinking anything but water for one hour prior to testing

The Expert Panel was composed of nine individuals—three from the consulting engineering firm of Hazen and Sawyer (H&S) and six from the University of California, Los Angeles (UCLA). The H&S experts conduct assessments of water samples on a routine basis for their firm. The six panelists from UCLA were undergraduate and graduate students from various departments in the university. All six of the UCLA panelists had been trained in the FPA method, and they had participated in research studies on taste and odor for several months to several years prior to this study. The panel sessions were held on Friday, February 21 and Monday, February 24 at H&S and UCLA, respectively.

The gender split for the Expert Panel was 67:33, female to male. Figure 1 shows the distribution of ages of the panel. Because students made up most of the panel, it is not surprising that the 18 to 33 age category contains 56 percent of the panelists.

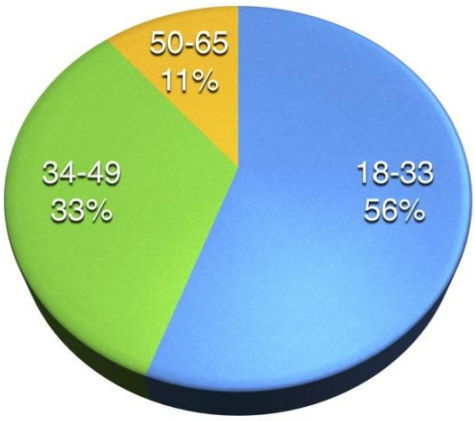

Figure 1. Age Distribution of Expert Panel Threshold Study

The H&S panel was held in a business office setting where the panelists were delivered the cups of water at their desks where they assessed them. There were no fugitive odors in the office that interfered with odor detection. The UCLA panel was held in a special odor panel room in the School of Public Health maintained by Dr. I. H. Suffet. Each UCLA panelist conducted his/her assessment of the samples in specially constructed booths that ensured privacy and independent determinations—see Figure 2.

Figure 2. Taste and Odor Testing Room at UCLA

Because of the limited health effects data on Crude MCHM, it was decided that only odor thresholds would be determined in the Expert Panel studies. Also, testing was focused on odor thresholds because the consumer complaints were primarily about a licorice odor in their drinking water.

Source of Crude MCHM

A 100 mL sample of the same Crude MCHM that spilled into the Elk River was collected by SGT Charles Cook of the West Virginia Army National Guard on February 12 and shipped overnight to my Santa Monica home. I transferred the sample to a fume hood at the UCLA laboratory the next day. The sample came from Tank SV35927LM at the Poca Blending Facility. The contents of that tank were transferred from the leaking tank on the property of Freedom Industries sometime after the leak was discovered.

Odor Assessment of Chemical to Spike into Water for Threshold Determinations

I assessed the odor characteristics of Crude MCHM and a pure standard of MCHM obtained from the chemical supply company TCI America. The 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. The MSDS form for Crude MCHM that accompanied the sample of the spilled tank contents showed that pure MCHM was the major component but other minor constituents were present. Figure 3 shows a chromatogram of Crude MCHM in methanol that was run on the Varian 450GC/220MS instrument in the UCLA laboratory showing MCHM and some of the minor constituents. We know from smelling a pure standard that dimethyl 1,4-cyclohexanedicarboxylate does have a licorice odor that is about the same characteristic and intensity as pure MCHM.

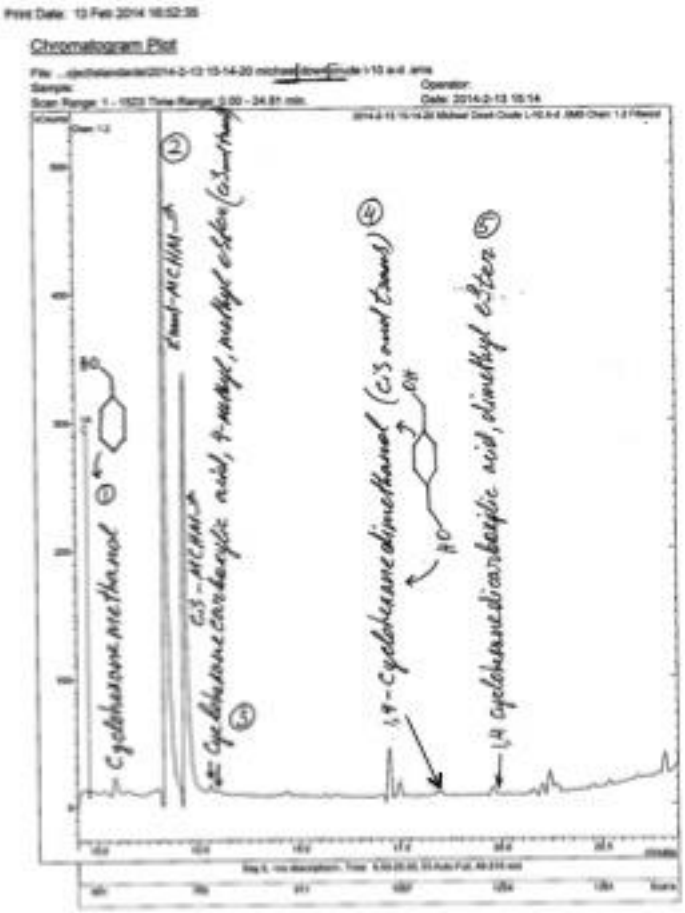

Figure 3. Chromatogram of Crude MCHM Showing Minor Components

Given the differences in the odor characteristics of the pure and Crude MCHM, it seemed plausible that one or more of the minor constituents of the Crude MCHM could be adding to the more obnoxious characteristics of the odor. Therefore, Crude MCHM was chosen as the chemical to spike into the water that would be presented for odor assessment to the panelists.

I also assessed the odor associated with the pure chemical propylene glycol phenyl ether (PPH), which was listed as one of the minor components of Crude MCHM. Pure PPH does not have a licorice odor of any kind. No further odor work with PPH has been conducted.

Selection of Matrix Water

We could not use treated water from the Elk River as the water for our tests because of the obvious problem that we did not know if the licorice problem was really absent from that source. Also, the goal was to conduct the threshold studies on water without chlorine. Chlorine interference with odor thresholds is well established and the impact of chlorine on the odor characteristics of MCHM in water is the subject of future research.

Based on several decades of experience in the field of taste and odor in water, I determined that we needed spring water with no off-flavors for the panel matrix water.[8, 9, 10] Arrowhead spring water was chosen because it is widely available in Southern California where the panel studies would take place. The odor quality of Arrowhead spring water is consistent, and in my experience, I have never detected any off-odors in that product.

Twenty-seven liters of Arrowhead spring water were purchased in several stores in Southern California in 3-L containers and used as the blank water in the Expert Panel threshold tests.

Preparation of Spiked Samples and Determination of Crude MCHM Concentrations

Eurofins Laboratory in Lancaster, PA was chosen as the site to prepare the spiked samples of Crude MCHM because it is the laboratory that is running the MCHM analytical method with a method detection level (MDL) of 0.5 ppb and a method reporting level (MRL) of 1.0 ppb. To the best of my knowledge, these concentrations are the lowest currently being determined by any laboratory in the U.S. Concentrations in the spiked samples were based on spiking 100% crude MCHM. The laboratory measured total peak area for the *trans* and *cis* isomers of MCHM and used this marker to determine the recovery of spiked concentrations in water.

The following is a summary of the Eurofins MCHM analytical method: A water sample is serially extracted with methylene chloride. The resulting extract is reduced in volume and an aliquot injected into a gas chromatograph equipped with a mass spectrometer detector (GC/MS). The GC/MS analytical system is tuned and calibrated following the principles outlined in SW-846, Method 8270D. This includes tuning the system to decafluorotriphenylphosphine (DFTPP) relative mass abundance criteria and calibration using a minimum of five calibration points from 1 ppb to 60 ppb. The analytical system is tuned and the calibration responses are checked every 12 hours.

As a routine part of the extraction procedure, a method blank, a laboratory control sample (LCS) and an MRL LCS are extracted along with every group of field samples that are analyzed. A method blank that is free of target compounds and an LCS and MRL LCS with acceptable recoveries of the target compounds is required for an extraction batch to be considered acceptable.

Unfortunately, Arrowhead spring water is not available in Lancaster, PA. Therefore, several gallons of Arrowhead spring water were purchased in Southern California and shipped to the Lancaster facility. The matrix water was spiked with Crude MCHM at eight levels with concentrations ranging from 0.164 to 100 ppb. Subsamples of the spiked water were analyzed immediately using the Eurofins analytical method. Two liters each of the eight levels of spiked samples were shipped overnight to the UCLA laboratory. On Wednesday, February 24 after the Expert Panels were complete, another subsample of the

spiked matrix water was analyzed by Eurofins and all of the results were sent electronically to me.

Reference Odor Descriptors from Each Panelist

Prior to conducting any of the Expert Panels, individual panelists were taken aside and told that they would be sniffing water that may have odors that were similar to a reference odor that I would be presenting to them. They were also told that they may not recognize any odors in the water samples that were anything like the reference odor. They were asked to carefully sniff a diluted sample of Crude MCHM and explain in their own words how they would describe the odor. Their descriptions of the reference odor were recorded on a form.

Panelist Instructions

After the reference odors were recorded, the panel moderator read a script to the assembled panels which described the methods and procedures that they would use and the way that they should record their observations and opinions, see Appendix A. While the panel was underway, the moderator walked around the panel testing area asking for any questions or clarifications and observing whether or not the panelists were following instructions. In a few cases, the moderator needed to repeat instructions to individual panelists.

Odor Threshold (Detection) Concentration Method

The well-known methodology referred to as ASTM E679-04 (2011) was used to estimate the OTC for Crude MCHM.[11] The same method was used in 1999 to determine the OTC for methyl *tert*-butyl ether (the gasoline additive MTBE) using a consumer panel.[12] For the UCLA study, three ounces of spiked and blank water were placed in nine-ounce odor-free plastic cups and covered with watch glasses, see Figure 4. Each panelist was presented with three cups at a time. One of the cups contained the spiked sample and the other two cups contained blank water. The panelists were asked to pick up each cup and watch glass, gently swirl the water in the cup, lift the watch glass and sniff the headspace above the water replacing the watch glass when they were finished. The panelists were instructed to then choose the odor in the cup that was different from the other two.

Figure 4. Sample Presentation to Panelists

Even if the panelists could not tell the difference between the three cups, they had to choose one of them as different. They could re-sniff the cups if they wished. The panelists received the lowest concentration of spiked water first. Subsequent groups of three cups contained one spiked sample with increasing concentrations of Crude MCHM to a maximum of 100 ppb. They recorded their observations by circling the code of the different cup on the score sheet. Appendix B shows the score sheet used in the Expert Panels.

Random numbers were used to code all of the cups. The location of the different cup containing the spiked sample was roughly split between the left, middle and right cup. This presentation and scoring methodology is generally referred to as a forced-choice triangle, ascending (concentration) series. Temperatures of the UCLA spiked and blank water in the cups ranged from 20 to 22 degrees Celsius.

The presentation method for the H&S panel was the same except five-ounce odor-free plastic cups were used and about two ounces of water was placed in each cup. Temperatures of the H&S spiked and blank water in the cups were 18 to 22 degrees Celsius.

Odor Recognition Concentration Threshold Method

Next, panelists were asked to record on the score sheet what they thought the water in the different cup smelled like. They were told that they should use any terminology that described the characteristic of the odor in the different cup, or they could use the terms that they provided for the reference odor if they recognized it. If the water smelled like nothing (had no odor), the panelists could write "nothing."

The ASTM E679 technique recognizes the determination of an ORC as part of its methodology. "…*recognition threshold*—the lowest concentration of a substance in a medium relating to the lowest physical intensity at which a stimulus is recognized as determined by the best-estimate criterion."[13] (italics in original)

Methods for Determining Odor Objection Concentrations

There is no generally accepted methodology for determining a level of objection to the odor of an organic compound in water. In this research, two methods were used to answer the question: When do we know that panelists object to something in the water they are testing?

The first approach used the widely-accepted methodology[14] of presenting a stimulus to a panelist and asking how much the panelist liked or disliked the stimulus using a hedonic scale for the panelist to score his/her judgments. The nine-point hedonic scale used for this work was taken from *Standard Methods*.[15]

The second approach is based on my experience determining when the concentration of a substance in water has reached the objection level in a water utility distribution system. When a significant number of consumers object to an odor in their drinking water, some of them will pick up the telephone and call to complain. Not all who object will complain, but it will be clear to water utility management when the telephone calls start rolling in that they have a problem.

From my experiences at the Metropolitan Water District of Southern California with earthy-musty odor problems, there is a clear "tipping point." Earthy-musty odors are generally caused by blue-green algae producing two compounds: geosmin and 2-methylisoborneol (MIB). Published OTCs for these compounds vary but they are generally around 4 parts per trillion (ppt). When 10 ppt of either compound (or both adding up to 10 ppt) is being served to consumers, some of them will definitely call and complain. For both of these compounds, 10 ppt is the Odor Objection Concentration. A number of water utilities have set 10 ppt as their treatment goal to avoid complaints. Other utilities that desire a more stringent goal have set 5 ppt for both geosmin and MIB.

Odor Objection Concentration Threshold Method—Degree of Liking

The panelists were asked to rate how much they liked or disliked the odor of the water in the different cup. Appendix C shows the degree of liking scale that was used by the

panelists to assess how much they liked or disliked the odor. They recorded their rating from the scale on the score sheet in the "Degree of Liking" column.

Odor Objection Concentration Threshold Method—Objection/Complaint

Finally, it was suggested to the panelists that they may find some of the odors in the different cups objectionable. If the odor was objectionable and the panelist would complain to their water utility or bottled water company, they were instructed to answer "Yes" in the "Object/Complain?" column.

Collection and Organization of Score Sheets

After the eighth sample set was completed, the moderator collected the score sheets and checked them to make sure that the panelists had followed all of the instructions properly, and that all of the descriptions and scores were filled in. The data from the panels were entered into an Excel spreadsheet and the best estimate thresholds for individuals and the panel as a whole were determined using the geometric mean calculation specified in ASTM E679.

RESULTS AND DISCUSSION

Analytical Results of Spiked Samples

Table 2 shows the concentrations of Crude MCHM recovered and the percent recoveries for samples analyzed before and after the Expert Panels were conducted. The data show good recoveries for spiked concentrations above the method MRL of 1 ppb ranging from 90.5 to 116 percent. Below the MRL, the recoveries are acceptable for the Pre-Panel analyses, but the Post-Panel recoveries are fairly low. None of these results indicate that the spiked concentrations of Crude MCHM degraded over the holding period. The data on Table 2 show the variability of the MCHM analysis and spiking processes, especially at concentrations below 1 ppb.

Table 2. Spiked Recoveries of Crude MCHM by Eurofins Laboratory

Spiked Crude MCHM, ppb	Crude MCHM Recovered, ppb		Percent Crude MCHM Recovered	
	Pre-Panel Analysis	Post-Panel Analysis	Pre-Panel Analysis	Post-Panel Analysis
0.164	0.12	0.073	74%	44%
0.41	0.33	0.27	81%	65%
1.024	0.91	0.77	89%	76%
2.56	2.6	2.3	103%	90%
6.4	7.0	6.6	109%	103%
16	17.8	17.7	111%	111%
40	44	46	110%	116%
100	99	104	99%	104%

Note: Pre-Panel analyses were conducted on 2/18/14; Post-Panel analyses on 2/24/14

Odor Threshold Concentration

Table 3 shows the results of the OTC determination for the nine panelists. The estimate of the individual odor thresholds is calculated as the geometric mean of the concentration where the last incorrect cup was chosen and the next higher concentration where the correct cup was chosen from there upward. An incorrect cup choice is recorded on the table as a "0" and a correct choice as a "+". Thus, the estimate of the OTC for Panelist 09 is the geometric mean of 1.024 and 2.56 or 1.62 ppb.

For those sensitive panelists who correctly chose the different cup at all eight concentrations, the estimate of their individual OTC is the geometric mean of the lowest concentration presented (0.164 ppb) and the concentration at the next lower step, which in this case would be 2.5 times lower or 0.0655 ppb. Thus, the estimate of the OTC for Panelist 02 is the geometric mean of 0.164 and 0.0655 or 0.104 ppb.

Table 3. Expert Panel Results for Odor Threshold Concentration

		Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
Panelists	Date Study Conducted	0.164	0.41	1.024	2.56	6.4	16	40	100	Value
02	2/21/14	+	+	+	+	+	+	+	+	0.104
03	2/21/14	+	+	+	+	+	+	+	+	0.104
04	2/21/14	+	+	+	+	+	+	+	+	0.104
07	2/24/14	+	+	+	+	+	+	+	+	0.104
08	2/24/14	+	+	+	+	+	+	+	+	0.104
09	2/24/14	+	+	0	+	+	+	+	+	1.62
10	2/24/14	0	+	+	+	+	+	+	+	0.259
11	2/24/14	+	+	+	+	+	+	+	+	0.104
12	2/24/14	+	+	+	+	+	+	+	+	0.104

Note: "0" indicates that the panelist selected the wrong sample of the set of three; "+" indicates that the panelist selected the correct sample; the individual OTC is the geometric mean of the two concentrations where there is a change from "0" to consistent answers of "+" which is noted by gray-shaded cells.

Geometric Mean, ppb = 0.16

The calculated estimate of the OTC for Crude MCHM determined by these panelists is the geometric mean of the nine individual geometric means, or 0.16 ppb. However, because seven of the nine panelists correctly identified the different cups at all eight concentrations, the true OTC for this group of sensitive individuals is most likely below 0.16 ppb. Therefore, for this study, the OTC for Crude MCHM in water will be reported as <0.16 ppb.

Based on the findings from this study, the lowest concentration presented to the Consumer Panel will be less than 0.164 ppb. While the expert panelists used in this study can usually detect OTC levels lower than consumers, lower concentrations must be presented to the consumer panelists to ensure that most of the correct responses are captured in the concentration range used.

Odor Recognition Concentration

Table 4 indicates that all expert panel members specified the reference odor in their odor descriptors. An ORC was only recorded for concentrations at or above the individual panelist's OTC. The best estimate of the individual panelist ORC is the geometric mean of the two concentrations where there is a change from "other" descriptors to the reference odor descriptor, which is noted with gray-shaded cells. For panelist 03 for example, the descriptor of "lemony" at 0.41 ppb changed to "anise" at 1.024 ppb. The panelist's individual ORC is the geometric mean of those two concentrations, 0.648 ppb.

Table 4. Expert Panel Results for Odor Recognition Concentration

		Concentrations of Crude MCHM Presented to Panelists, ppb									Best Estimate Threshold, ppb
Panelists	Date Study Conducted	0.164	0.41	1.024	2.56	6.4	16	40	100	Reference Odor Descriptor	Value
02	2/21/14	licorice	licorice, sweet	licorice, syrupy sweet	licorice, solvent, syrupy sweet	syrupy sweet, pineapple juice	syrupy sweet, pineapple juice	syrupy sweet, ripe fruit	syrupy sweet, ripe fruit	Licorice, sweet, woodsy	0.104
03	2/21/14		lemony	anise	anise	anise, lemony	anice, cough syrup	lemony, bile, anise	lemony, bile, anise	anise, sweet, vanilla	0.648
04	2/21/14	mehtanol	gasoline station	gasoline station	new leather, gasoline station	new leather, gasoline exhaust	paints, gasoline exhaust	sweet chemical	sweet chemical	flowery, sweet, hand wipes chemical	25.3
07	2/24/14	sweet, grassy (fades)	sweet, faint licorice, candy	faint sweet	faint sweet, licorice	sweet licorice	faint sweet licorice	faint sweet licorice	sweet licorice	sweet, licorice, candy	0.259
08	2/24/14		sweet	sweet, licorice	sweet, licorice	sweet, licorice	sweet, licorice	sweet, licorice	sweet, licorice	sweet, licorice	0.648
09	2/24/14				fruity, sweet	licorice, sweet	licorice, sweet	pine, licorice, sweet	licorice, sweet	fruity, pine, licorice	4.05
10	2/24/14					strong solvent, sweet	licorice, sweet	licorice, sweet	licorice, sweet	licorice, pine	10.1
11	2/24/14					sweet, refreshing	sweet, licorice	sweet, licorice	sweet, licorice	licorice	10.1
12	2/24/14					glue, rubbery	glue, rubbery, licorice	glue, rubbery, licorice	sweet, licorice, glue	sweet, licorice	10.1

Notes: The ORC was only recorded for concentrations at or above the OTC; the individual ORC is the geometric mean of the two concentrations where there is a change from other descriptors to the reference odor descriptor which is noted by gray-shaded cells. Panelist 04 was not assigned an individual ORC because he/she did not follow directions.

Geometric Mean, ppb = 2.2

One panelist was able to characterize the odor of the different cup as their reference odor of "licorice" at the lowest concentration presented, 0.164 ppb. The estimate of their individual ORC is the geometric mean of the lowest concentration presented (0.164 ppb) and the concentration at the next lower step, which in this case would be 2.5 times lower or 0.0655 ppb. Thus, the estimate of the ORC for Panelist 02 is the geometric mean of 0.164 and 0.0655 or 0.104 ppb.

Below the individual ORCs, many of the panelists noted that the correctly chosen different cup smelled "sweet." This was not sufficient to provoke a match with the reference odor descriptor. It is not unusual for organic chemicals to elicit a sweet odor description from expert panelists. In my own experience, the odor of MTBE has a sweet

odor characteristic at concentrations below the level where the reference odor (sweet solvent) is recognized.

The calculated estimate of the ORC for Crude MCHM determined by these panelists is the geometric mean of the nine individual geometric means, or 2.2 ppb. Most of the individual ORC concentrations were within the range of concentrations presented, 0.164 to 100 ppb. The ASTM method states: "If the concentration range has been correctly selected, all panelists should judge correctly within the range of concentration steps provided."

Odor Objection Concentration

As noted in the Methods section of this memorandum, two methods were used to estimate the OOC for Crude MCHM. Table 5 shows the results for the OOC determination based on the degree of liking scale used by the panelists. The OOC was only recorded for concentrations at or above the individual panelist's OTC. The best estimate of the panelist's individual OOC is the geometric mean of the two concentrations where there is a jump in the degree of liking score to 6 or above, which is noted by gray-shaded cells on the table.

Table 5. Expert Panel Results for Odor Objection Concentration—Degree of Liking

		Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
Panelists	Date Study Conducted	0.164	0.41	1.024	2.56	6.4	16	40	100	Value
02	2/21/14	3	7	4	8	9	9	9	9	0.259
03	2/21/14	4	3	1	6	7	8	7	6	1.62
04	2/21/14	6	6	6	6	6	6	6	6	0.104
07	2/24/14	2	3	1	1	4	3	4	4	158
08	2/24/14	3	3	4	5	6	7	7	8	4.05
09	2/24/14	3	4	2	4	6	6	5	4	4.05
10	2/24/14	5	5	4	5	7	8	8	8	4.05
11	2/24/14	2	1	2	4	6	7	7	7	4.05
12	2/24/14	5	5	6	6	7	8	8	8	0.648

Note: The OOC was only recorded for concentrations at or above the OTC; the individual OOC is the geometric mean of the two concentrations where there is a jump in the degree of disliking to a score of 6 or above, which is noted by gray-shaded cells.

Geometric Mean, ppb = 2.2

The same method as described above for OTC and ORC was used to calculate the individual OOC level when the panelist scored the lowest concentration of Crude MCHM as a degree of liking of 6 (panelist 04). For the panelists that did not score a 6 even at 100 ppb, the individual OOC was calculated as the geometric mean of 100 ppb and the next highest step, which in this case would be 2.5 times higher or 250 ppb. Therefore, the estimate of the OOC for panelist 07 is the geometric mean of 100 and 250 or 158 ppb.

The calculated estimate of the OOC for Crude MCHM using the degree of liking scale determined by these panelists is the geometric mean of the nine individual geometric

means, or 2.2 ppb. Most of the individual OOC concentrations were within the range of concentrations presented, 0.164 to 100 ppb.

Table 6 shows the results for the OOC determination based on objection/complaint. The OOC was only recorded for concentrations at or above the individual panelist's OTC. The best estimate of the panelist's individual OOC is the geometric mean of the two concentrations where there is a change to a consistent answer of "Yes" to the question: Would you object/complain about the odor in the different cup? The gray-shaded cells on the table note the two concentrations used to calculate the individual geometric means.

Table 6. Expert Panel Results for Odor Objection Concentration—Objection/Complaint

		Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
Panelists	Date Study Conducted	0.164	0.41	1.024	2.56	6.4	16	40	100	Value
02	2/21/14	N	Y	N	Y	Y	Y	Y	Y	1.62
03	2/21/14	N	N	N	Y	Y	Y	Y	Y	1.62
04	2/21/14	Y	Y	Y	Y	Y	Y	Y	Y	0.104
07	2/24/14	N	N	N	N	N	N	N	N	158
08	2/24/14	N	N	N	N	N	Y	Y	Y	10.1
09	2/24/14	N	N	N	N	Y	Y	Y	N	158
10	2/24/14	Y	Y	N	Y	Y	Y	Y	Y	1.62
11	2/24/14	N	N	N	N	Y	Y	Y	Y	4.05
12	2/24/14	N	N	Y	Y	Y	Y	Y	Y	0.648

Note: The OOC was only recorded for concentrations at or above the OTC; the individual OOC is the geometric mean of the two concentrations where there is a change to a consistent answer of Yes to the question: Would you object/complain about the odor in the different cup? Noted by gray-shaded cells.

Geometric Mean, ppb = 4.0

The same methods as described above for OTC, ORC and OOC (Liking) was used to calculate the individual OOC levels when the panelist scored the lowest concentration of Crude MCHM as a "Yes" or the highest concentration as a "No."

The calculated estimate of the OOC for Crude MCHM using the objection/complaint criterion determined by these panelists is the geometric mean of the nine individual geometric means, or 4.0 ppb. Once again, most of the individual OOC concentrations were within the range of concentrations presented, 0.164 to 100 ppb.

Limitations of the Methodology and Results

As with all research, there are limitations associated with this work that must be understood so that errors will not be made extrapolating the results to other applications.

- Only nine panelists were used in the study and two-thirds of the panelists are women as opposed to the 50:50 desired split
- Most of the panelists were young and not representative of the ages in Charleston, WV; younger people generally have lower individual thresholds than older people
- All nine of the panelists were experts who have been assessing taste and odor problems in drinking water for long periods
- Everyone on the panel knew that we were working with Crude MCHM from the spill in West Virginia; many of them had smelled Crude MCHM before the panel study as part of the method development at UCLA
- Arrowhead spring water was used as the matrix water which has different chemical characteristics compared to treated water from the Elk River
- No chlorine was in the water samples assessed by the panel

Applicability of Expert Panel Results to Understanding how Consumers Respond to Crude MCHM in Drinking Water

Table 7 summarizes the estimated OTC, ORC and OOC concentrations that were determined by the Expert Panel. Comparing the estimated OTC for Crude MCHM with thousands of others for a variety of organic compounds shows that Crude MCHM has an extremely low OTC.[16] As stated previously, the estimated OTC for Crude MCHM is likely less than 0.16 ppb. That means that the OTC is in the realm of parts per trillion, an extraordinarily low concentration. The ability of the expert human nose to detect this compound is far greater than any analytical method available today.

Table 7. Summary of Expert Panel Odor Threshold Estimates

Odor Thresholds	Geometric Mean, ppb	Factor: Greater than OTC
Odor Threshold Concentration (OTC)	0.16*	---
Odor Recognition Concentration (ORC)	1.6	10.1
Odor Objection Concentration (OOC) Based on Degree of Liking	2.2	13.7
Odor Objection Concentration (OOC) Based on Complaint	4.0	25.3

*Actual OTC for these panelists is likely <0.16 ppb

The OTC is limited in its ability to predict how consumers assess odors in their tap water. The OTC is determined in a controlled environment with no masking odors like chlorine present in the water. The panelists were striving under laboratory conditions to detect odor differences between three cups at eight concentration levels. That situation is far different than taking a glass of water from a kitchen faucet.

The ORC level determined in this study is higher than the OTC by a factor of 10.1. This finding is consistent with limited peer-reviewed literature comparing detection and recognition thresholds.[17] OOC levels are 13.7 to 25.3 times higher than the expert panel's OTC. Peer-reviewed literature does not provide much guidance on how high or low factors like this should be.

The OOC levels of 2.2 and 4.0 ppb are better values to use to gauge human response than the OTC. For example, setting a secondary standard for Crude MCHM would be best accomplished using estimates of the OOC, preferably with the results from a panel of untrained consumers. California did exactly this in 1999 when they set a 1 ppb secondary standard for Thiobencarb (a rice herbicide) that generated a bitter taste upon chlorination. Instead of using the expert panel findings they used the level of complaints from consumers objecting to the taste of the water.[18]

The ORC is a much better indicator than OTC for the point where consumers recognize an odor. Many of the panelists described the odor of the water containing Crude MCHM below the individual ORC concentrations as sweet, which was not an odor that many objected to. The Louisville odor panel used a distinctive sweet odor to note the presence of MCHM in the Ohio River as the plume from the Elk River chemical spill passed their intake.[19]

Minor components of the chemical compound mix called Crude MCHM could have an impact on the threshold concentrations experienced by panelists and consumers. We are still not certain if only the pure compound MCHM is responsible for the licorice odor in Charleston drinking water. More research is needed to determine the contribution of the minor components of Crude MCHM to the aesthetic responses experienced by Charleston residents.

It is not appropriate to look at only a portion of the responses by individual panelists in this study and extrapolate their determinations to the public at large. We have no idea if the individual responses of these nine expert panelists represent responses by any segment of the Charleston population. However the collective responses (with qualifiers) can give us guidance on consumer responses.

The most important finding of this work can be stated succinctly. The estimated thresholds determined in the Expert 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 though the analytical reports were showing non-detect at a minimum reporting level of 10 ppb.

The only appropriate use of the results of this work is to cite the geometric means of the data generated by the panelists, which resulted in estimates of the OTC, ORC and OOC concentrations. The fact that these composite numbers reflect the general experience of the consumers exposed to Crude MCHM contaminated tap water strengthens the appropriateness of this conclusion.

Using the methodologies developed in this study, a group of untrained consumers should estimate the levels of OTC, ORC and OOC for Crude MCHM in water. We need to understand if the geometric mean values produced by the Expert Panel are significantly different from a group of untrained consumers.

Not surprisingly, many people in Charleston did not use tap water even after the "Do Not Use" restriction was lifted. They also did not start using tap water after they were told that the concentration of MCHM was non-detect. They stopped using tap water because their sense of smell recognized it and objected to its presence. For many people, smelling an off-odor in tap water means that it is not safe for them to drink.[20]

SUMMARY AND CONCLUSIONS

Based on the assessments in this report, the following points can be concluded:

1. A methodology was developed based on ASTM Method E679 to estimate the OTC, ORC and OOC concentrations for Crude MCHM in water during a single panel session.
2. Spiked concentrations of Crude MCHM were measured by a sensitive analytical method and found to be within acceptable percent recoveries.
3. The estimate of the Odor Threshold (Detection) Concentration for Crude MCHM in water determined by the Expert Panel was <0.16 ppb.
4. The estimate of the Odor Recognition Concentration for Crude MCHM in water determined by the Expert Panel was 1.6 ppb.
5. The estimates of the Odor Objection Concentrations for Crude MCHM in water determined by the Expert Panel were found to be 2.2 and 4.0 ppb when measured using the Degree of Liking and Objection/Complaint methods, respectively.
6. The estimated thresholds determined in the Expert Panel study support consumer observations in Charleston, WV that people could recognize and object to the licorice odor caused by Crude MCHM in their drinking water even though the analytical reports were showing non-detect at a minimum reporting level of 10 ppb.

RECOMMENDATIONS

As a result of the findings from this study, the following actions are recommended:

1. Convene a large panel comprised of untrained consumers and determine the OTC, ORC and OOC concentrations using the same methodology used in the Expert Panel Study.
2. Change the range of concentrations presented to the consumer panel to 0.027 to 60 ppb using eight concentration levels separated by a factor (step) of 3. This range will hopefully capture the correct OTC, ORC and OOC responses by the individual consumer panelists.
3. Conduct oxidation studies of Crude MCHM with chlorine and potassium permanganate and determine if the odor characteristic or intensity of the licorice odor is changed after oxidation.

ACKNOWLEDGMENTS

Many people are responsible for completing the Expert Panel tests in only 20 days after the task was assigned. Several graduate students at UCLA provided invaluable assistance. Michael Nonezyan was responsible for developing the GC/MS scan of crude MCHM. The graduate students are expertly guided by Dr. Mel Suffet who contributed a lot of thought and suggestions to the direction of the project. Thanks are due to the West Virginia Army National Guard for acquiring the samples of Crude MCHM used in this study. Andy Eaton and Duane Luckenbill of Eurofins Laboratory and Nicole Blute of Hazen and Sawyer consultants made major contributions to the success of this effort. Without the dedicated participation of the panelists, this study would not have been possible.

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Appendix B. Consumer Panel Estimates of the Odor Threshold Concentration, Odor Recognition Concentration and Odor Objection Concentration for Crude 4-methylcyclohexanemethanol (MCHM) in Water

Michael J. McGuire, Inc.
Santa Monica, CA 90402

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TECHNICAL MEMORANDUM

March 31, 2014

To: Jeffrey Rosen, Corona Environmental Consulting

From: Michael J. McGuire, PhD, PE
mike@michaeljmcguire.com; 310-560-0257

Subject: Consumer Panel Estimates of the Odor Threshold Concentration, Odor Recognition Concentration and Odor Objection Concentration for Crude 4-methylcyclohexanemethanol in Water

EXECUTIVE SUMMARY

On January 9, 2014, "Crude" 4-methylcyclohexanemethanol (MCHM) spilled into the Elk River in West Virginia, which contaminated the water supply treated by West Virginia American Water and resulted in licorice odor complaints by residents. A team of experts was hired to understand the odor characteristics of the spilled chemical. The team developed a methodology based on ASTM Method E679-04 (2011) to estimate the Odor Threshold Concentration (OTC), Odor Recognition Concentration (ORC) and Odor Objection Concentration (OOC) for Crude MCHM in water during a single panel session. An Expert Panel used the methodology and estimated these thresholds.[1] The same methodology was used in this study to estimate these thresholds using an untrained Consumer Panel.

Two qualifiers should be attached to the findings of this report:

1. Sixty consumer panelists with equal gender distribution were used in the study. The panelists were not a statistically representative sample of consumers from the area served by West Virginia American Water.
2. No chlorine was in the water samples assessed by the panel

Table ES-1 summarizes the estimated OTC, ORC and OOC concentrations that were determined by the Consumer Panel and compares them to the values determined in the Expert Panel study. The Consumer Panel study showed that panelists 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 to date (0.5 ppb).

Table ES-1. 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 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.

INTRODUCTION

On January 9, 2014, approximately 10,000 gallons of "Crude" 4-methylcyclohexane-methanol (MCHM) spilled into the Elk River from the property of Freedom Industries a short distance above the drinking water intake of the West Virginia American Water (WVAW) water treatment plant. Shortly after the spill began, consumers located in the area served by WVAW (Charleston, WV and environs) began complaining of a licorice odor in their drinking water. On February 9, an expert team was hired to help the state of West Virginia understand the odor characteristics of the spilled chemical and the reactions of the customers served by WVAW.

It was urgent that the odor characteristics of the chemical be understood in a scientific context in a short period of time. Therefore, an Expert Panel was convened within 15 days, which estimated the OTC, ORC and OOC values for Crude MCHM. The Expert Panel results were used to devise the concentration range for the Consumer Panel study that was held two weeks later.

The objectives of the work described in this technical memorandum were to:

1. Apply the Expert Panel methodology to a Consumer Panel study that would estimate the Odor Threshold Concentration (OTC), Odor Recognition Concentration (ORC) and Odor Objection Concentration (OOC) for the licorice-smelling substance in water.

2. Use the sample spiking methodology developed with Eurofins Laboratory to prepare samples of the licorice-smelling substance in a reference water for presentation to a Consumer Panel.
3. Understand how the Expert and Consumer Panel results could be used to explain consumer observations in Charleston, WV where people smelled a licorice odor in their drinking water immediately after the spill and for many weeks following the spill even after repeated system flushing.
4. Make recommendations for additional work to supplement and confirm the Consumer Panel findings.

DEFINITIONS OF DETECTION (THRESHOLD), RECOGNITION AND OBJECTION CONCENTRATIONS

Understanding how consumers react to off-odors in their drinking water is a complex problem that presents a unique set of challenges. To understand this phenomenon, it is important to appreciate the distinction between detectable odors and the concepts of recognizable and objectionable odors. Peer-reviewed scientific literature has recognized the concepts of detection, recognition and objection in drinking water and other substances.[2, 3, 4] Table 1 organizes the concentrations of odorants in drinking water into aesthetic response levels.

Table 1. Odor Response Levels for Concentrations of Chemicals 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 where 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

The same principles in Table 1 apply to the sense of taste. For example, the taste thresholds for sodium chloride and calcium chloride are in the range of 200 to 300 mg/L.[5] At or above the taste threshold, panelists can describe the “salty” taste resulting in

recognition. As the sodium chloride concentration is increased further, the salty taste becomes objectionable.

Concentrations of minerals (including sodium chloride) that are objectionable to consumers in actual drinking water distribution systems have been described by detailed surveys of households. Bruvold and Daniels found that total dissolved solids (TDS) concentrations above 450 mg/L resulted in a significant number of consumers to reject their water supply and to seek alternatives. This concentration is just below the Secondary Maximum Contaminant Level for TDS and is equivalent to the taste objection concentration for TDS.[6]

PANEL METHODOLOGY

Panel Recruitment

Panelists for this study had to meet the following criteria:

- Untrained consumers
- Between the ages of 18 and 65
- Balance of women and men (approximately 50:50)
- Pregnant women could not participate
- Non-smokers only
- Anyone with a history of severe asthma or sinus problems was excluded
- Anyone currently suffering from a cold, the flu or any upper-respiratory disease at the time of testing was excluded
- No eating or drinking anything but water for one hour prior to testing

The Atkins Research Group recruited the panelists for the Consumer Panel study. They randomly selected a group of people from their database of 85,000 respondents, targeting some of the selection criteria that were provided to them. They sent an email blast to the sample of potential panelists with several screening questions including smoking status and other factors. Based on the panelist responses to the email blast, the Atkins Research Group selected a short list of qualified respondents.

A week before the Consumer Panels were held, the Atkins Research Group sent an email to each respondent, invited the potential panelist to one of four specific sessions, and asked them to confirm their participation. As time for the panels drew closer, schedule conflicts arose and panelists dropped out. People on the short list were then contacted to fill in the needed places. For each panel of 15, a total of 18 panelists were invited to attend to cover no-shows and last minute attendance problems. Sixty consumer panelists participated in the study. Four Consumer Panel sessions were held at 5:30 and 7:30 pm on Monday, March 3 and Wednesday, March 5 at the Atkins Research Group facility at 4929 Wilshire Boulevard, Los Angeles, California.

The gender split for the Consumer Panel was 50:50, 30 females and 30 males. Figure 1 shows the distribution of ages of the panel. Most of the panelists (67%) were in the middle age range of 30 to 53.

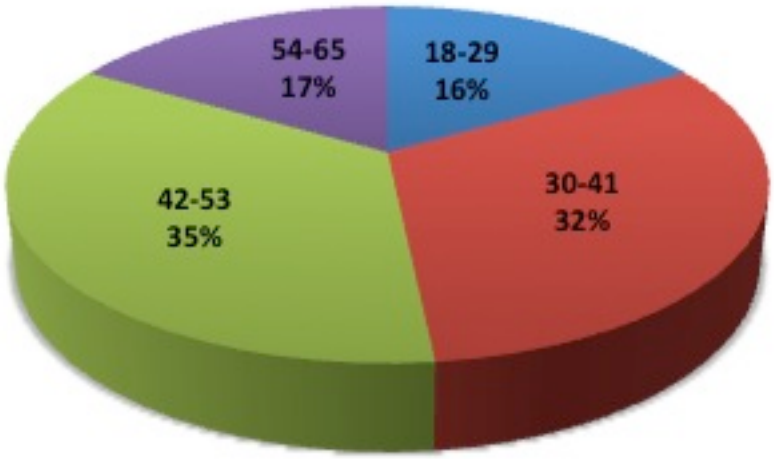

Figure 1. Age Distribution of Consumer Panel Threshold Study

The Consumer Panel was held in a market research room at the Atkins facility. There were no fugitive odors in the room that interfered with odor detection. On March 3, dividers separated the panelists to promote privacy—see Figure 2. Two moderators were in the room at all times and the panelists kept their worked covered with a sheet of paper assuring privacy and independent analysis. The head moderator decided that the dividers were not necessary for the March 5 panels.

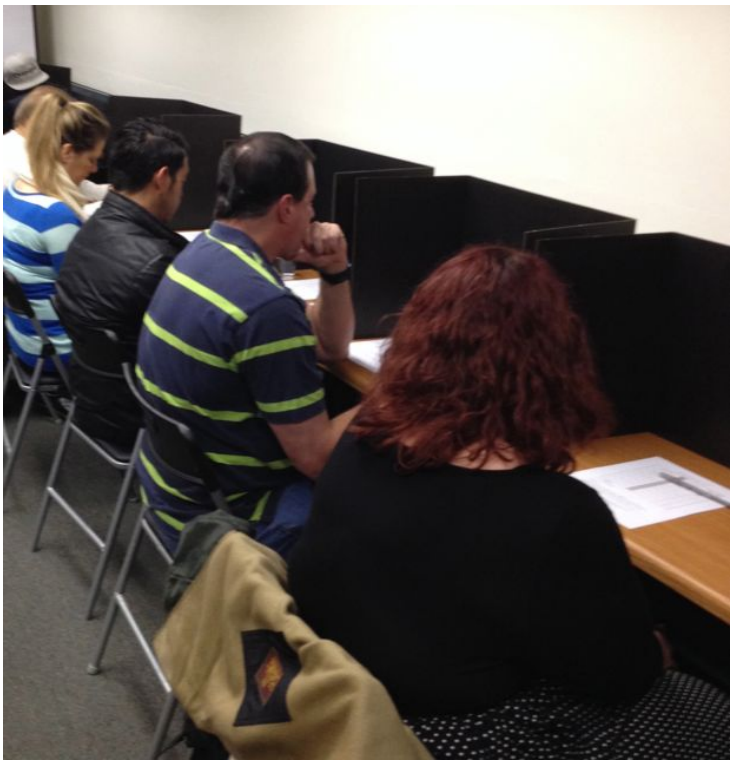

Figure 2. Consumer Testing Facilities

Source of Crude MCHM

A 100 mL sample of the same Crude MCHM that spilled into the Elk River was collected by SGT Brian Spotloe and SGT Charles Cook of the West Virginia Army National Guard on February 12 and shipped to the Los Angeles area the next day. The sample came from Tank SV35927LM at the Poca Blending Facility. The contents of that tank were transferred from the leaking tank on the property of Freedom Industries sometime after the leak was discovered. A subsample of this sample was shipped to Eurofins Laboratory for spiking purposes.

Odor Assessment of Chemical to Spike into Water for Threshold Determinations

I assessed the odor characteristics of Crude MCHM and a pure standard of MCHM obtained from the chemical supply company TCI America. The 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. The MSDS form for Crude MCHM that accompanied the sample of the spilled tank contents showed that pure MCHM was the major component but other minor constituents were present. Figure 3 shows a chromatogram of Crude MCHM in methanol that was run on the Varian 450GC/220MS instrument in the UCLA laboratory showing MCHM and some of the tentatively identified minor constituents. We know from smelling a pure standard that dimethyl 1,4-cyclohexanedicarboxylate does have a licorice odor that is about the same characteristic and intensity as pure MCHM.

On March 13, 2014, several experts assessed the odor characteristic of a pure standard of cyclohexanemethanol (CHM), the first peak to elute on the chromatogram shown on Figure 3). The experts characterized the odor as penetrating, irritating, medicinal, green grass, sweet and pine. The CHM odor is definitely not as sweet as Crude or pure MCHM. Even though CHM is present at a much lower concentration than MCHM, it appears that CHM is contributing to the sharp characteristic of the Crude MCHM odor that has been experienced in panel studies and by the consumers of water in the Charleston area. More work is needed with difficult-to-obtain pure standards before the contributions of all of the minor components of Crude MCHM to the overall odor can be stated with confidence.

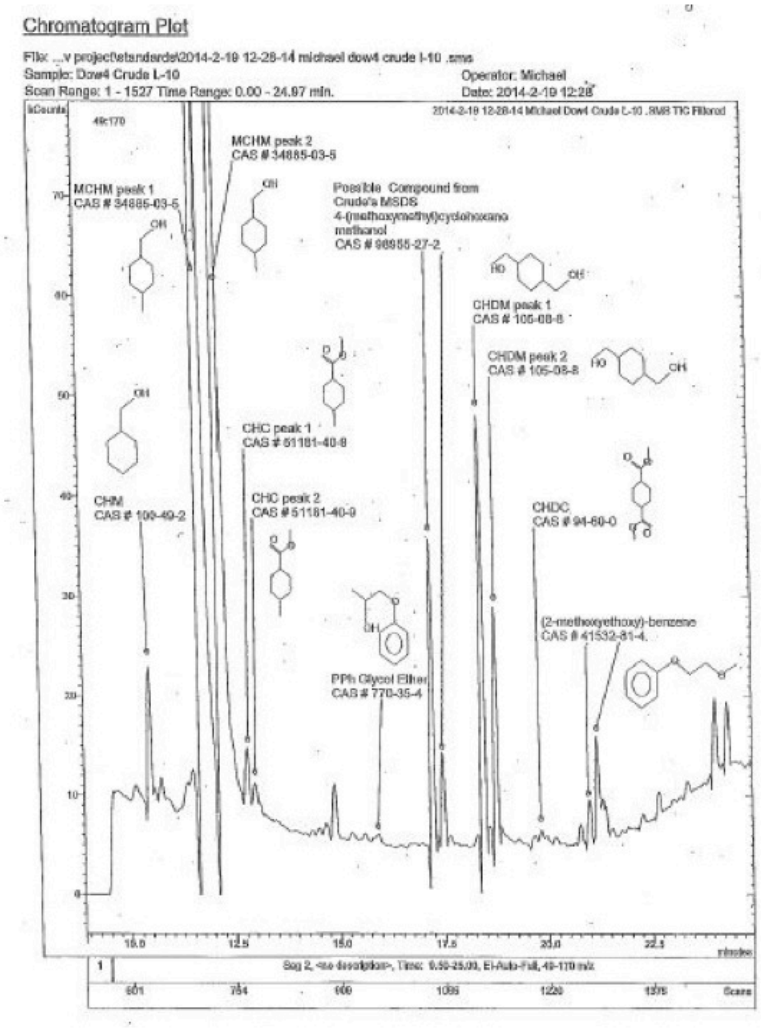

Figure 3. Chromatogram of Crude MCHM Showing Minor Components

To be certain that the Consumer Panel was presented with the same odor characteristics as experienced in the WVAW distribution system, Crude MCHM was spiked into the water that was presented to the consumer panelists. An odor assessment of propylene

glycol phenyl ether (PPH), which was listed as one of the minor components of Crude MCHM, showed that PPH does not have a licorice odor.[7]

Selection of Matrix Water

We could not use treated water from the Elk River as the water for our tests because of the obvious problem that we did not know if the licorice problem was really absent from that source. Also, the goal was to conduct the threshold studies on water without chlorine. Chlorine interference with odor thresholds is well established and the impact of chlorine on the odor characteristics of MCHM in water is the subject of future research.

For this study, a spring water was selected for the panel matrix water.[8, 9, 10] Arrowhead spring water was chosen because it is widely available in Southern California where the Consumer Panel studies would take place. The odor quality of Arrowhead spring water is consistent, and off-odors in that product have not been reported.

Table 2 shows the inorganic quality of Arrowhead spring water compared to a sample of water taken from the WVAW water treatment plant on March 11, 2014. While the total dissolved solids concentration of Arrowhead spring water is higher, neither water is highly mineralized. None of the minerals in the Arrowhead or WVAW treatment plant water would mask or interfere with consumers detecting, recognizing or objecting to levels of Crude MCHM in their tap water.

Table 2. Inorganic Water Quality of Arrowhead Spring Water and a Water Sample from the WVAW Treatment Plant

Parameter	Units	WVA Treatment Plant Effluent, March 11, 2014	Arrowhead Spring Water
pH	Std. Units	7.3	7.9
Total Dissolved Solids	mg/l	73	228
Specific Conductance	umhos/cm	157	453
Calcium	mg/l	12	50
Magnesium	mg/l	6	20
Potassium	mg/l	1.3	3.2
Sodium	mg/l	8	18
Chloride	mg/l	9	7
Nitrate-Nitrogen	mg/l	0.52	0.85
Sulfate	mg/l	34	23
Total Alkalinity	mg/l as CaCO3	16	195

Thirty-nine gallons of Arrowhead spring water were purchased directly from Arrowhead in 3-gallon containers, delivered to the Atkins Research Group facility and used as the blank water in the Consumer Panel threshold tests.

Preparation of Spiked Samples and Determination of Crude MCHM Concentrations

Eurofins Laboratory in Lancaster, PA prepared the spiked samples of Crude MCHM. Eurofins is using an MCHM analytical method with a method detection level (MDL) of 0.5 ppb and a method reporting level (MRL) of 1.0 ppb—the lowest MCHM concentrations currently being determined by any laboratory in the U.S. Concentrations in the spiked samples were based on spiking 100% crude MCHM. The laboratory measured total peak area for the *trans* and *cis* isomers of MCHM and used this marker to determine the recovery of spiked concentrations in water.

The following is a summary of the Eurofins MCHM analytical method: A water sample is serially extracted with methylene chloride. The resulting extract is reduced in volume and an aliquot injected into a gas chromatograph equipped with a mass spectrometer detector (GC/MS). The GC/MS analytical system is tuned and calibrated following the principles outlined in SW-846, Method 8270D. This includes tuning the system to decafluorotriphenylphosphine (DFTPP) relative mass abundance criteria and calibration using a minimum of five calibration points from 1 ppb to 60 ppb. The analytical system is tuned and the calibration responses are checked every 12 hours.

As a routine part of the extraction procedure, a method blank, a laboratory control sample (LCS) and an MRL LCS are extracted along with every group of field samples that are analyzed. A method blank that is free of target compounds and an LCS and MRL LCS with acceptable recoveries of the target compounds is required for an extraction batch to be considered acceptable.

Arrowhead spring water is not available in Lancaster, PA. Sixty-four liters of Arrowhead spring water were purchased in Southern California and shipped to the Lancaster facility. The matrix water was spiked with Crude MCHM at eight levels with concentrations ranging from 0.027 to 60 ppb. Subsamples of the spiked water were analyzed immediately using the Eurofins analytical method. Eurofins analyzed the top six concentrations. The bottom two concentrations (0.027 and 0.082 ppb) were so far below the MDL and MRL that no effort was made to detect them. The two low concentrations were assured by the results of the higher concentrations and careful dilution procedures used by Eurofins laboratory staff.

Six liters each of the eight levels of spiked samples were shipped to the Atkins Research Group facility for delivery on March 3. Two of the bottles were broken in transit. Eurofins shipped replacements overnight from the samples being held for later analysis.

On Thursday, March 6 after the Consumer Panels were complete, Eurofins analyzed surviving subsamples of the spiked matrix water. One of the spiked results was lost during the extraction procedure.

Panelist Procedures

Prior to conducting the Consumer Panels, individual panelists were taken into a separate room and told that they would be sniffing water that may have odors that were similar to a reference odor that I would be presenting to them. They were also told that they might not recognize any odors in the water samples that were anything like the reference odor. They were asked to carefully sniff a diluted sample of Crude MCHM and explain in their own words how they would describe the odor. Their descriptions of the reference odor were recorded on a form. To avoid prejudicing the consumer panelists, no mention was made of the relation of the odor to the chemical spill in West Virginia. Appendix A contains a script used to elicit reference odor responses from each of the panelists.

Each Consumer Panel only required 15 panelists. Because17-18 people were recruited for each panel, the moderator eliminated from the final panel people who were clearly anosmic (i.e., they could not smell anything in the dilute MCHM sample), people who had trouble describing the odor using reasonable descriptive terms and those who by their actions and attitude were not interested in participating.

When the 15 consumer panelists were assembled, the panel moderator read a script, which described the methods and procedures that they would use, see Appendix B. While the panel was underway, the moderator walked around the panel testing area asking for any questions or clarifications and observing whether or not the panelists were following instructions.

Odor Threshold Methodologies

The well-known methodology referred to as ASTM E679-04 (2011) was used to estimate the OTC for Crude MCHM.[11] The same method was used in 1999 to determine the OTC for methyl *tert*-butyl ether (the gasoline additive MTBE) using a Consumer Panel[12] and to determine four thresholds of Crude MCHM by an Expert Panel.[13]

For the Consumer Panel study, three ounces of spiked and blank water were placed in nine-ounce odor-free plastic cups and covered with watch glasses, see Figure 4. Each panelist was presented with three cups at a time. One of the cups contained the spiked sample and the other two cups contained blank water. The panelists were asked to pick up the cup and watch glass, gently swirl the water in the cup, lift the watch glass and sniff the headspace above the water replacing the watch glass when they were finished. The panelists were instructed to choose the cup containing the odor that was different from the other two.

Figure 4. Sample Presentation to Panelists

Even if the panelists could not tell the difference between the three cups, they had to choose one of them as different. They could re-sniff the cups if they wished. The panelists received the lowest concentration of spiked water first. Subsequent groups of three cups contained one spiked sample with increasing concentrations of Crude MCHM to a maximum of 60 ppb. They recorded their observations by circling the code of the different cup on the score sheet. Appendix C shows the score sheet used in the Consumer Panels.

Random numbers were used to code all of the cups. The location of the different cup containing the spiked sample was roughly split between the left, middle and right cup. This presentation and scoring methodology is generally referred to as a forced-choice triangle, ascending (concentration) series. Temperatures of the spiked and blank water in the cups during both nights of testing ranged from 19 to 21 degrees Celsius.

Next, panelists were asked to record on the score sheet what they thought the water in the different cup smelled like. They were told that they could use any terminology that described the characteristic of the odor in the different cup, or they could use the terms that they provided for the reference odor if they recognized it. If the water smelled like nothing (had no odor), the panelists could write "nothing."

The ASTM E679 technique recognizes the determination of an ORC as part of its methodology. "…*recognition threshold*—the lowest concentration of a substance in a medium relating to the lowest physical intensity at which a stimulus is recognized as determined by the best-estimate criterion."[14] (Italics in original)

There is no generally accepted methodology for determining a level of objection to the odor of an organic compound in water. In this research, two methods were used to answer the question: When do we know that panelists object to something in the water they are testing?

The first approach used the widely accepted methodology[15] of presenting a stimulus to a panelist and asking how much the panelist liked or disliked the stimulus using a hedonic scale for the panelist to score his/her judgments. The nine-point hedonic scale used for this work was taken from *Standard Methods*.[16] Using the nine-point hedonic scale to estimate the OOC was first reported by Suffet, Leavey and colleagues for determining odor and flavor objection concentrations in conjunction with a study of ethyl *tert*-butyl ether (ETBE) in drinking water.[17, 18, 19]

The panelists were asked to rate how much they liked or disliked the odor of the water in the different cup using the degree of liking scale shown in Appendix D. They recorded their rating of the odor in the different cup on the score sheet in the "Degree of Liking" column.

The second approach is based on water utility experience determining when the concentration of a substance in water has reached the objection level in a distribution system. When a significant number of consumers object to an odor in their drinking water, some of them will pick up the telephone and call to complain. Not all who object will complain, but it will be clear to water utility management when the telephone calls start rolling in that they have a problem.

Experiences at the Metropolitan Water District of Southern California with earthy-musty odor problems suggest that there is a clear "tipping point" (concentration) when consumers begin to complain. Earthy-musty odors are generally caused by blue-green algae producing two compounds: geosmin and 2-methylisoborneol (MIB). Published OTCs for these compounds vary, but they are generally around 4 parts per trillion (ppt). When 10 ppt of either compound (or both adding up to 10 ppt) is being served to consumers, some of them will definitely call and complain. For both of these compounds, 10 ppt is the Odor Objection Concentration. A number of water utilities have set 10 ppt as their treatment goal to avoid complaints. Other utilities that desire a more stringent goal have set 5 ppt for both geosmin and MIB.

It was suggested to the panelists that they might find some of the odors in the different cups objectionable. If the odor was objectionable and the panelist would complain to their water utility or bottled water company, they were instructed to answer "Yes" in the "Object/Complain?" column.

After the eighth sample set was completed, the moderator collected the score sheets and checked them to make sure that the panelists had followed all of the instructions properly and that all of the descriptions and scores were filled in. The data from the panels were entered into an Excel spreadsheet and the best estimate thresholds for individuals and the panel as a whole were determined using the geometric mean calculation specified in ASTM E679.

RESULTS AND DISCUSSION

Analytical Results of Spiked Samples

Table 3 shows the concentrations of Crude MCHM recovered and the percent recoveries for samples analyzed before and after the Consumer Panels were conducted. The data show good recoveries for spiked Crude MCHM concentrations (based on the sum of the *cis* and *trans* isomer peak areas for pure MCHM) above the method MRL of 1 ppb ranging from 90 to 116 percent (within the acceptable range of 80 to 120%). As expected, the one recovery below the MRL is outside the generally acceptable range. None of these results nor the results from the Expert Panel spiking[20] indicates that the spiked concentrations of Crude MCHM degraded over the holding period. These data do not indicate if any of the minor compounds in the Crude MCHM mixture are changing over time, because their peak areas were not quantified.

Table 3. Spiked Recoveries of Crude MCHM by Eurofins Laboratory

Spiked Crude MCHM, ppb	Crude MCHM Recovered, ppb		Percent Crude MCHM Recovered	
	Pre-Panel Analysis	Post-Panel Analysis	Pre-Panel Analysis	Post-Panel Analysis
0.027	(2)	(2)	---	---
0.082	(2)	(2)	---	---
0.25	ND	(3)	---	---
0.74	0.54	(3)	72%	---
2.2	1.9	2.3	83%	102%
6.7	7.0	7.4	104%	111%
20	22	(4)	112%	---
60	66	65	110%	109%

Notes:
(1) Pre-Panel analyses were conducted on 2/26 & 27/14; Post-Panel analyses on 3/6/14
(2) Not analyzed because concentration too low for MCHM analytical method
(3) Not analyzed due to broken bottle replacement
(4) Lost during extraction
ND = Not detected; All results rounded to two significant digits

Odor Threshold Concentration

Appendix E shows the results of the OTC determination for the 60 consumer panelists. The estimate of the individual odor thresholds is calculated as the geometric mean of the concentration where the last incorrect cup was chosen and the next higher concentration where the correct cup was chosen from there upward. An incorrect cup choice is recorded on Appendix E as a "0" and a correct choice as a "+". Thus, the estimate of the OTC for Panelist 02 is the geometric mean of 2.2 and 6.7 or 3.8 ppb.

For the 14 sensitive panelists who correctly chose the different cup at all eight concentrations, the estimate of their individual OTC is the geometric mean of the lowest concentration presented (0.027 ppb) and the concentration at the next theoretical lower

step, which in this case would be 3.0 times lower or 0.0091 ppb. Thus, the estimate of the OTC for Panelist 01 is the geometric mean of 0.027 and 0.0091 or 0.016 ppb.

The calculated estimate of the OTC for Crude MCHM determined by the Consumer Panel is the geometric mean of the 60 individual geometric means, or 0.55 ppb. The Consumer Panel study showed that consumers are able to detect Crude MCHM in water at concentrations at least as low as the most sensitive analytical method available to date for MCHM. Most of the individual OTC concentrations were within the range of concentrations presented, 0.027 to 60 ppb. However, 14 of the 60 panelist responses correctly chose the different cup for all eight concentrations.

Figure 5 shows the cumulative percentage plot for the 60 OTC responses. Using a log concentration scale, the plot shows good agreement with a straight line, which is similar to findings for the 57-panelist-OTC results for MTBE.[21]

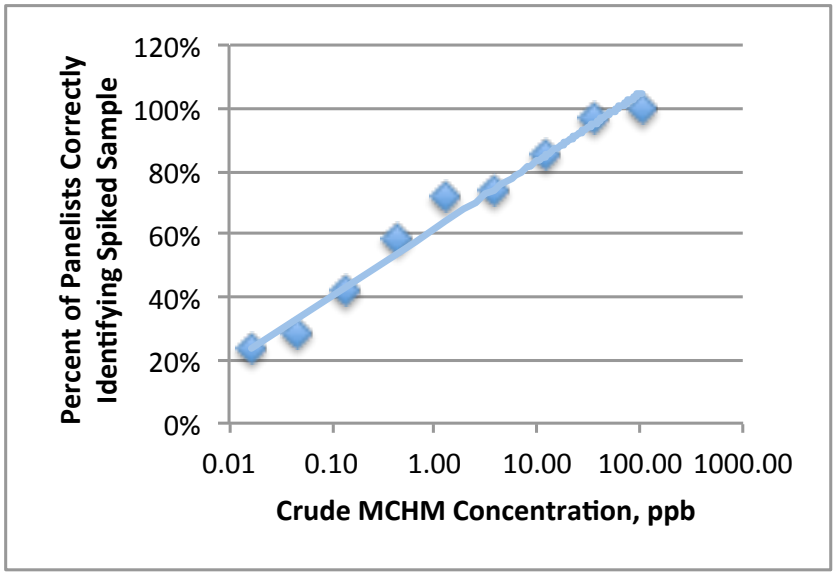

Figure 5. Cumulative Percentage Plot of Individual Odor Threshold Concentrations

The Expert Panel OTC for Crude MCHM was less than 0.15 ppb. It is not surprising that trained panelists are more sensitive to odors than untrained panelists. Nonetheless, the OTC of the Consumer Panel shows that the detection level is quite low when compared to other organic compounds.[22]

Figure 6 shows the estimated OTC values for individual panelists plotted against panelist age. For this study, there did not appear to be any relationship between age and odor sensitivity over four orders of magnitude of the Crude MCHM concentration. Other studies have shown an age-OTC relationship.[23, 24] However, Doty noted that the decrease in odor sensitivity was not severe below the age of 65.[25]

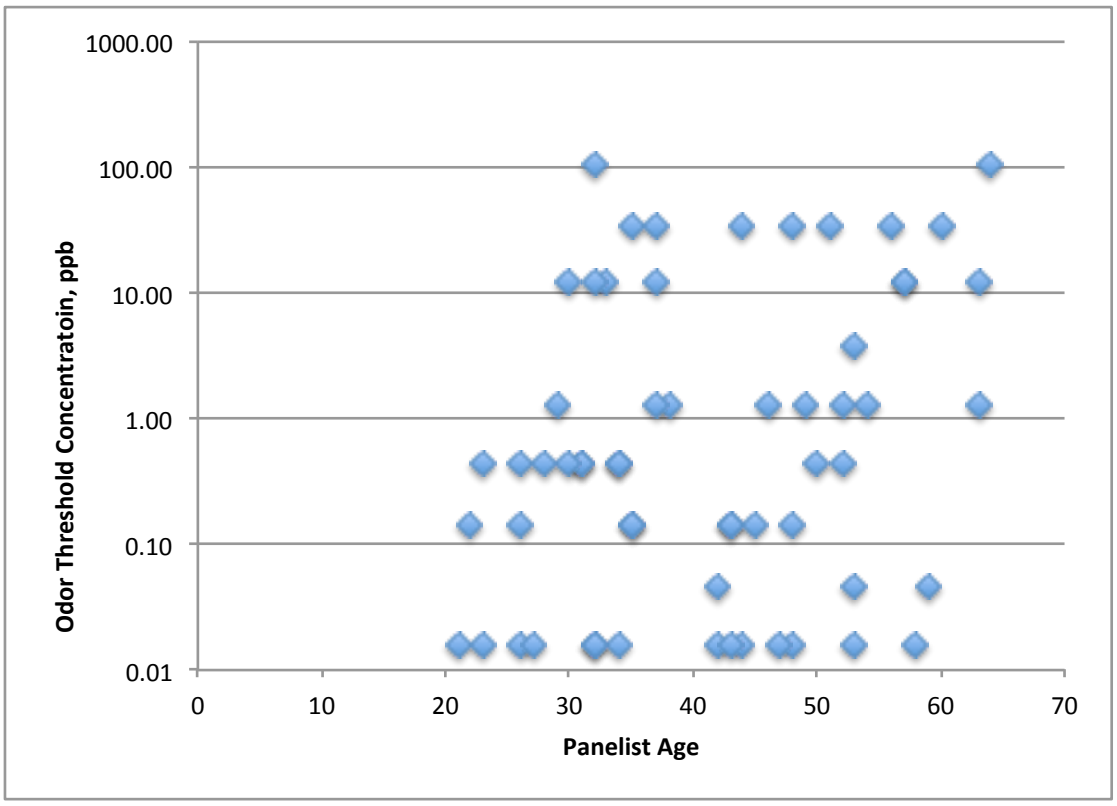

Figure 6. Plot of Consumer Panelist Age versus Estimated Individual OTC

Figure 7 indicates that OTC values for men and women on the consumer panel appeared to be different. A check of the gender OTC data sets showed that they were not normally distributed nor log normally distributed. Therefore, parametric statistics could not be used to check for differences. A nonparametric statistical test (Wilcoxon Rank Test) suggested that the two data sets were not statistically different. It appears that the variation in the data over four orders of magnitude make it difficult to determine differences as small as the one shown on Figure 7. Other studies have found inconsistent results comparing odor acuity comparisons between men and women.[26, 27, 28, 29]

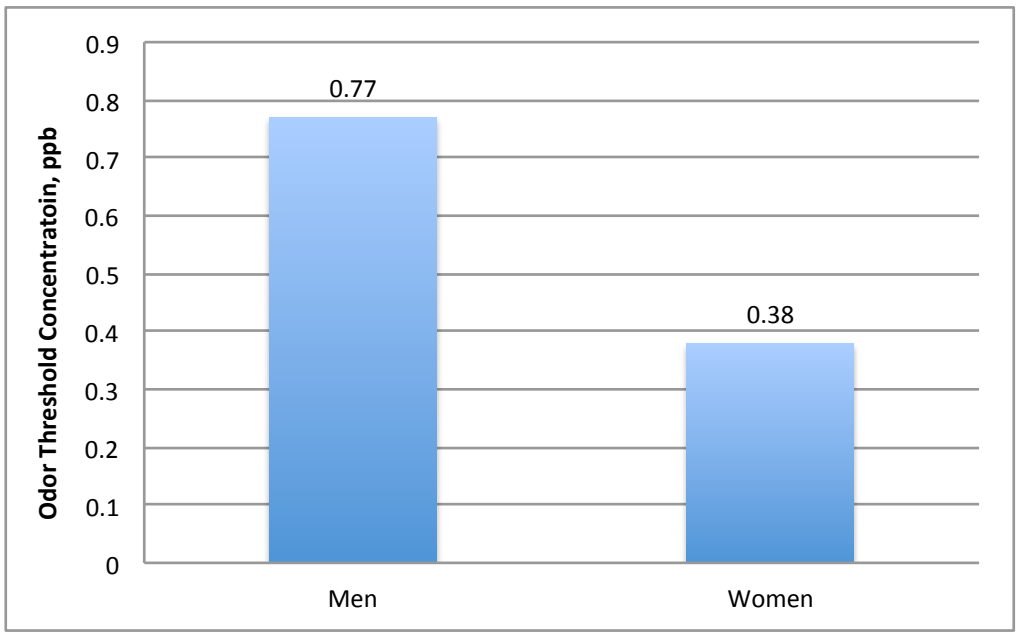

Figure 7. Odor Threshold Concentrations (Geometric Means) for Men and Women in the Consumer Panel

Odor Recognition Concentration

Appendix F shows the results of the ORC determination for the 60 consumer panelists. An ORC was only recorded for concentrations at or above the individual panelist's OTC. The best estimate of the individual panelist's ORC is the geometric mean of the two concentrations where there is a change from "other" descriptors to the reference odor descriptor and that change remains consistent to the highest concentration, which is noted with gray-shaded cells. For panelist 01 for example, the descriptor of "smelled fresh" at 0.74 ppb changed to "strawberry, fruity, familiar smell" at 2.2 ppb. The panelist's individual ORC is the geometric mean of those two concentrations, 1.3 ppb.

Two panelists were able to characterize the odor of the water in the different cup as their reference odor at the lowest concentration presented, 0.027 ppb. The estimate of their individual ORCs is the geometric mean of the lowest concentration presented (0.027 ppb) and the concentration at the theoretical next lower step, which in this case would be 3.0 times lower or 0.0091 ppb. Thus, the estimate of the ORC for Panelist 16 is the geometric mean of 0.027 and 0.0091 or 0.016 ppb.

For the panelists that did not describe their reference odor even at 60 ppb, the individual OOC was calculated as the geometric mean of 60 ppb and the theoretical next highest step, which in this case would be 3.0 times higher or 180 ppb. Therefore, the estimate of the OOC for panelist 02 is the geometric mean of 60 and 180 or 100 ppb.

Many of the panelists described their reference and descriptor odors using some variation of the term "sweet." Some judgment had to be applied to the many descriptors used by

the panelists to establish a continuum of odor descriptors up to the highest concentration of Crude MCHM presented. Appendix G lists the many sweet reference and descriptor odors used by the panelists.

The calculated estimate of the ORC for Crude MCHM determined by these panelists is the geometric mean of the 60 individual geometric means, or 7.4 ppb.

Odor Objection Concentration

As noted in the Panel Methodology section of this memorandum, two methods were used to estimate the OOC for Crude MCHM. Appendix H shows the results for the OOC determination based on the degree of liking scale. The OOC was only recorded for concentrations at or above the individual panelist's OTC. For this study, the best estimate of the panelist's individual OOC is the geometric mean of the two concentrations where there is a jump in the degree of liking score to 6 or above, which is noted by gray-shaded cells on Appendix H.

The previous studies that used the nine-point degree of liking scale chose the level 5 for objection and a level of 6 for rejection. It was not clear from those publications why two levels were chosen because a consumer who objects to an odor in water will most likely reject it. It was clear from their own data and the data from this study that the objection level in the nine-point degree of liking scale is 6. There was no need to determine an odor rejection concentration as was done in the other studies.[30]

The same methods as described above for OTC and ORC were used to calculate the individual OOC levels when the panelist scored the lowest concentration of Crude MCHM as a 6 or the highest concentration as a number less than 6. Therefore, the estimate of the OOC for panelist 39 is the geometric mean of 0.027 and 0.0091 or 0.016 ppb. The estimate of the OOC for panelist 01 is the geometric mean of 60 and 180, or 100 ppb.

The calculated estimate of the OOC for Crude MCHM using the degree of liking scale is the geometric mean of the 60 individual geometric means, or 7.7 ppb.

Appendix I shows the results for the OOC determination based on objection/complaint. The OOC was only recorded for concentrations at or above the individual panelist's OTC. The best estimate of the panelist's individual OOC is the geometric mean of the two concentrations where there is a change to a consistent answer of "Yes" to the question: Would you object/complain about the odor in the different cup? The gray-shaded cells on Appendix I note the two concentrations used to calculate the individual geometric means.

The same methods as described above for OTC, ORC and OOC (Liking) were used to calculate the individual OOC levels when the panelist scored the lowest concentration of Crude MCHM as a "Yes" or the highest concentration as a "No."

The calculated estimate of the OOC for Crude MCHM using the objection/complaint criterion is the geometric mean of the 60 individual geometric means, or 9.5 ppb.

Limitations of the Methodology and Results

As with all research, there are limitations associated with this work that must be understood so that errors will not be made extrapolating the results to other applications.

- Sixty consumer panelists with equal gender distribution were used in the study. The panelists were not a statistically representative sample of consumers from the area served by West Virginia American Water.
- No chlorine was in the water samples assessed by the panel

A substantial number of the individual ORC and OOC concentrations were at the highest concentration presented to the panelists, 60 ppb. While it would have been preferable to have more individual ORC and OOC values in the middle of the concentration range presented, it appeared that the panelists were already having trouble describing the odor and deciding if they objected to the odor at 60 ppb. There was evidence that the panelists were becoming fatigued at the highest concentration presented. Raising the upper end of the odor concentration range presented to the panelists would have aggravated that problem.

Applicability of Consumer Panel Results to Understanding how Consumers Respond to Crude MCHM in Drinking Water

Table 4 summarizes the estimated OTC, ORC and OOC concentrations that were determined by the Consumer Panel. The Consumer Panel study showed that panelists were able to detect this compound at a concentration in water (0.55) at least as low as the most sensitive analytical method available today (0.5 ppb).

Table 4. Summary of Consumer Panel Odor Threshold Estimates

Odor Thresholds	Geometric Mean, ppb	Factor: Greater than OTC
Odor Threshold Concentration (OTC)	0.55	---
Odor Recognition Concentration (ORC)	7.4	14
Odor Objection Concentration (OOC) Based on Degree of Liking	7.7	14
Odor Objection Concentration (OOC) Based on Objection/Complaint	9.5	17

The OTC is limited in its ability to predict how consumers assess odors in their tap water. The OTC is determined in a controlled environment with no masking odors like chlorine

present in the water. The panelists were striving under laboratory conditions to detect odor differences between three cups at eight concentration levels. That situation is far different than taking a glass of water from a kitchen faucet.

ORC is a much better indicator than OTC for the point where consumers recognize an odor. The ORC level determined in this Consumer Panel study is higher than the OTC by a factor of 14. OOC levels are 14 and 17 times higher than the Consumer Panel's OTC. Peer-reviewed literature does not provide much guidance on how high or low factors like this should be.

Figure 8 shows the cumulative percentage plots for all of the thresholds determined in the Consumer Panel studies. As shown before on Figure 5, the OTC plot appears to be a straight line with the Crude MCHM concentrations presented on a log scale. The other three plots are not linear and are indicative of cumulative percentages plotted for higher threshold concentration levels.

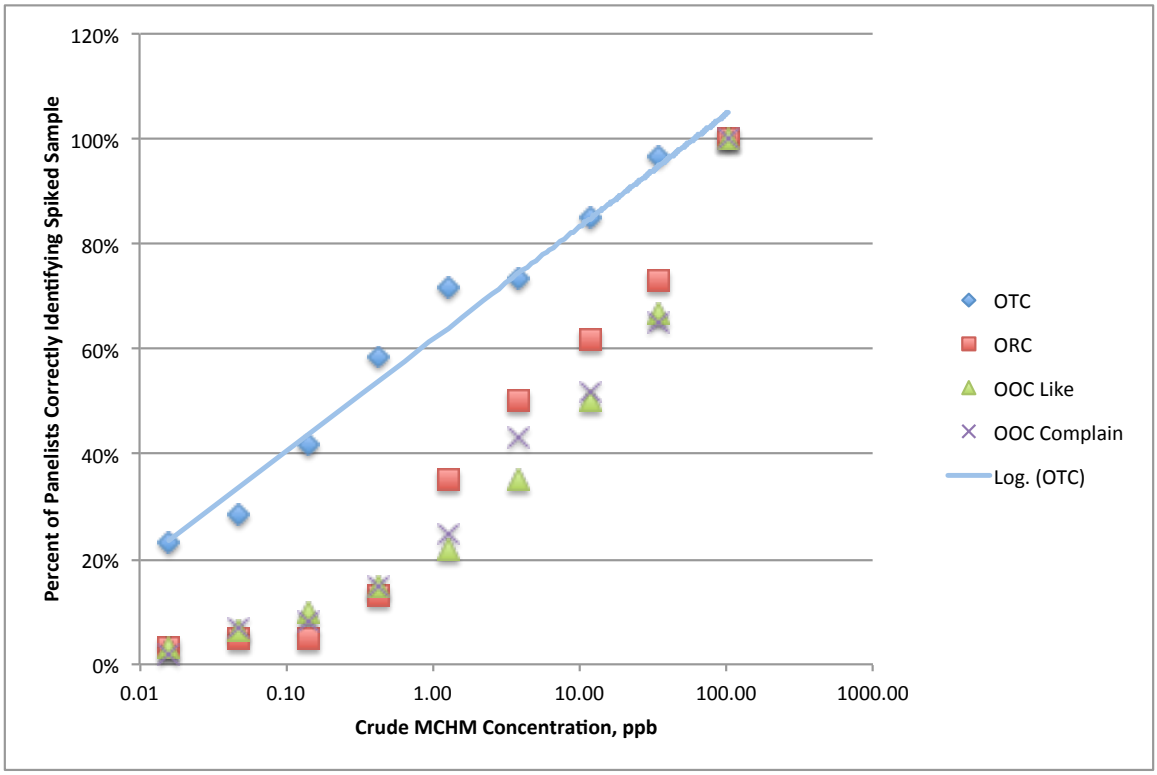

Figure 8. Cumulative Percentage Plots of Individual OTC, ORC and OOC Values

The ORC level of 7.4 and the OOC levels of 7.7 and 9.5 ppb are better values to use to gauge how consumers would respond to an odor event than the OTC. California used the taste objection concentration in 1999 when they set a 1 ppb secondary standard for Thiobencarb (a rice herbicide) that generated a bitter taste upon chlorination. Instead of using the Expert Panel findings they used the level of complaints from consumers objecting to the taste of the water.[31]

In the specific case of the Crude MCHM spill above the WVAW water intake, consumers would have been able to recognize and would have objected to concentrations of Crude MCHM in their tap water at low ppb concentrations (lower than those listed in Table 4) because they had become sensitized to it, they had the odor identified as licorice by the media and they had learned first hand how objectionable the licorice odor was when the first concentrations had been released into the water system at about 3,000 ppb.

Table 5 compares the OTC, ORC and OOC values for the Expert and Consumer Panels. While the Expert Panel determined lower values for all four thresholds, 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. Once again, the consumers 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 5. 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 5. 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

It is not appropriate to look at only a portion of the responses by individual panelists in this study and extrapolate their determinations to the public at large. We have no idea if the individual responses of these 60 consumer panelists represent responses by any segment of the Charleston population. However the collective responses (with qualifiers) can give us guidance to consumer responses.

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.

The only appropriate use of the results of this work is to cite the geometric means of the data generated by the panelists, which resulted in estimates of the OTC, ORC and OOC concentrations. The fact that these composite numbers reflect the general experience of the consumers exposed to Crude MCHM contaminated tap water strengthens the appropriateness of this conclusion.

Not surprisingly, many people in Charleston did not use tap water even after the "Do Not Use" restriction was lifted. They also did not start using tap water after they were told that the concentration of MCHM was non-detect. They continued not using tap water because their sense of smell recognized it and objected to its presence. For many people, smelling an off-odor in tap water means that it is not safe for them to drink it.[32]

SUMMARY AND CONCLUSIONS

Based on the assessments in this report, the following points can be concluded:

1. A methodology was used based on ASTM Method E679 to estimate the OTC, ORC and OOC concentrations for Crude MCHM in water during a single panel session. The methodology was tested using an Expert Panel and then applied to the Consumer Panel determinations.
2. Spiked concentrations of Crude MCHM were measured by a sensitive analytical method and found to be within acceptable percent recoveries.
3. The estimate of the Odor Threshold (Detection) Concentration for Crude MCHM in water determined by the Consumer Panel was 0.55 ppb. The Consumer Panel study showed that panelists were able to detect this compound at a concentration in water (0.55) at least as low as the most sensitive analytical method available to date (0.5 ppb).
4. The estimate of the Odor Recognition Concentration for Crude MCHM in water determined by the Consumer Panel was 7.4 ppb.
5. The estimates of the Odor Objection Concentrations for Crude MCHM in water determined by the Consumer Panel were 7.7 and 9.5 ppb when measured using the Degree of Liking and Objection/Complaint methods, respectively.
6. The estimated thresholds determined in the Consumer Panel study support consumer observations in Charleston, WV that people could recognize and object 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.

RECOMMENDATIONS

As a result of the findings from this study, the following actions are recommended:

1. Investigate the impact of free chlorine residuals on the ability of consumers to detect, recognize and object to the licorice odor of Crude MCHM in drinking water.

2. Conduct oxidation studies of Crude MCHM with chlorine and potassium permanganate and determine if the odor characteristic or intensity of the licorice odor is changed after oxidation.

ACKNOWLEDGMENTS

Many people are responsible for completing the Consumer Panel tests 25 days after the task was assigned. Several graduate students at UCLA provided invaluable assistance during the Consumer Panels. Yubin Zhou was particularly helpful both nights. Thanks to Dr. Mel Suffet who assisted in the experimental design of the study and the review of drafts of this report. Thanks are due to the West Virginia Army National Guard for acquiring the samples of Crude MCHM used in this study. Andy Eaton, Duane Luckenbill and Chuck Neslund of Eurofins Laboratory and Nicole Blute of Hazen and Sawyer consultants made major contributions to the success of this effort. Without the dedicated participation of the 60 consumer panelists, this study would not have been possible.

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Appendices

Appendix A

Script for Reference Odor Determination by Consumer Panelists

How are you? Thanks coming in. We're going to sniff water samples tonight. We will present water samples to you, have you sniff them and tell us in your own words what the water smells like. We are not looking for any particular answer. We are not digging for one way to describe the odors. There is certainly no right or wrong answer. We want to hear from you what the water smells like in your own words.

To begin with, I will present you with one sample and ask you to tell us in your own words what the sample smells like. (Moderator unscrews the cap of a small bottle containing a dilute solution of MCHM. Moderator sniffs the opening at the top of the bottle and then presents the bottle to the panelist.) Just lean forward and sniff.

So what does it smell like? (Panelist responds with odor descriptors. If the descriptors are not clear, the panelist is asked again how the sample smells. The panelist is given a second opportunity to sniff the contents of the bottle. All of the panelist's responses are written down on a form.)

(I then say the first name of the panelist and repeat the odor descriptors that he/she gave. For example:) Ok, Kevin. You said that the odor smells "sweet flowery." So, "Kevin's odor" is sweet flowery. That is your reference odor for this study. If you smell Kevin's odor in any of the samples we present to you, please call it sweet flowery. And if the odor doesn't then don't call it that. Please tell us in your own words what the samples smell like.

Thank you.

Appendix B

Procedure for Consumer Panel

Panelists check in. After they complete checkin, they are directed to another room. In that room, a person will hand them a cup of water and ask them to sniff it. After the panelist sniffs the example odor in the cup, the staff person will say, ***"The odors in the water samples may contain substances that smell like what is in this bottle. Please describe in your own words what you think this smells like."*** The panelist's response is marked on a score sheet by the staff person.

The panelist is then directed to the consumer panel testing room. Once all (15) of the panelists are seated, the panel session begins and the script is read.

Script for Consumer Panel

All 15 people are seated. In front of each person is:

1. Coding sheet
2. Pen (not a pencil)
3. Degree of Liking Scale
4. Cup of plain water (color of cup is different from the others)

Good evening. Thank you all for helping us out. Tonight we will be testing a compound that is sometimes found in drinking water. At very low concentrations some people find the aroma of the compound quite pleasant. At higher concentrations other people find it not so pleasant. Some people find nothing wrong with odor of the compound at all. We are trying to figure out how a large group of people in a controlled environment react to the odor of this compound.

We will present three cups of water to each of you 8 different times. For each cup, pick up the watch glass and cup just like this, swirl it gently, lift the watch glass and sniff the air above the water. Replace the watch glass. For each set of 3 cups, choose the cup that is different from the other two. Even if it is difficult for you to detect a difference in the three cups, you must select one cup that is different. If you want, you can re-sniff the cups. Circle the code on your score sheet representing the cup that is different. **Leader demonstrates.**

After you choose the cup that is different, write down the **Odor Description** representing the water in the different cup on the score sheet. Describe the smell of the water in your own words. If you smell the example odor that we presented to you in the other room, use that descriptor in the Odor Description blank. If the water in the cup smells like nothing, you can write ***"nothing."***

Next, we want you to tell us how much you **like or dislike** the water with the odor in the cup that was different. Use the Degree of Liking Scale at your place.

Finally, some of the odors we are presenting to you may be objectionable. If the odor is **objectionable** and you would complain to your water utility or the bottled water company about it, please mark "Yes" in the Object/Complain column. Otherwise, mark "No."

Please remember that there are no "wrong" answers here. We are trying to understand how you perceive the water samples.

The plain water is available for you to use at any time during the panel session.

Let's begin with the first set of three cups. (Three cups are delivered to each panelist.)

Are there any questions?

Leader walks around the room answering questions and making sure that everyone is filling in the coding sheets as the session continues.

After finishing the 8th and last set of three cups, all the panelists stay in their seats. The leader collects the coding sheets and makes sure that they are all filled out.
Then all the panelists can leave.

Appendix C

Score Sheet for Panelist Number _____

Sample Cup Codes			Office Use	Odor Description	Degree of Liking	Object/ Complain? Y or N
473	475	088				
298	332	649				
030	275	900				
874	503	301				
263	253	451				
547	152	636				
063	195	140				
827	841	607				

Date:_____

Start Time:_____

Instructions:

1. Circle the number of the sample cup that has a ***different*** odor from the other two cups.

2. Describe the odor in the cup that is different. Use your own words. If the odor is like the odor in the sample you smelled before the panel, use that descriptor.

3. Record how much you like or dislike the odor in the different cup using the Degree of Liking Scale provided.

4. Do you object to the odor in the different cup? Would you call your water utility or bottled water company to complain about the odor in the different cup?

Appendix D

Degree of Liking Scale

1. I would be very happy to accept this water as my everyday drinking water.

2. I would be happy to accept this water as my everyday drinking water.

3. I am sure that I could accept this water as my everyday drinking water.

4. I could accept this water as my everyday drinking water.

5. Maybe I could accept this water as my everyday drinking water.

6. I don't think that I could accept this water as my everyday drinking water.

7. I could not accept this water as my everyday drinking water.

8. I could never drink this water.

9. I can’t stand this water in my mouth and I could never drink it.

Appendix E. Consumer Panel Results for Odor Threshold Concentration

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
		0.027	0.082	0.25	0.74	2.2	6.7	20	60	Value
01	3/3/14	+	+	+	+	+	+	+	+	0.016
02	3/3/14	0	0	0	+	0	+	+	+	3.8
03	3/3/14	0	0	0	+	+	+	0	+	35
04	3/3/14	0	0	0	+	+	+	+	+	0.43
06	3/3/14	0	0	0	+	+	+	+	+	0.43
07	3/3/14	+	+	+	+	+	+	0	0	100
08	3/3/14	0	+	+	+	+	+	+	+	0.047
09	3/3/14	+	+	+	+	+	+	+	+	0.016
10	3/3/14	0	0	0	0	0	0	+	+	12
11	3/3/14	+	+	0	+	+	+	+	+	0.43
12	3/3/14	+	+	+	+	+	+	+	+	0.016
13	3/3/14	+	+	0	+	+	+	+	+	0.43
14	3/3/14	+	0	+	+	+	+	+	+	0.14
15	3/3/14	+	0	+	+	+	+	0	+	35
16	3/3/14	+	+	+	+	+	+	+	+	0.016
19	3/3/14	0	0	+	0	+	+	+	+	1.3
20	3/3/14	+	+	+	+	+	+	+	+	0.016
22	3/3/14	+	0	+	+	+	+	+	+	0.14
23	3/3/14	+	0	+	+	+	+	+	+	0.14
24	3/3/14	+	0	0	+	+	+	+	+	0.43
25	3/3/14	+	+	0	+	+	+	+	+	0.43
27	3/3/14	0	0	0	+	+	0	+	+	12
28	3/3/14	+	0	+	+	+	+	+	+	0.14
29	3/3/14	0	0	0	0	+	0	+	+	12
31	3/3/14	+	+	0	0	+	+	+	+	1.3
32	3/3/14	+	0	+	0	+	+	+	+	1.3
33	3/3/14	0	+	0	0	0	0	+	+	12
34	3/3/14	0	0	0	0	+	+	+	+	1.3
35	3/3/14	+	+	+	+	+	+	+	+	0.016
36	3/3/14	+	0	+	+	+	+	+	+	0.14
38	3/5/14	+	+	+	+	+	+	+	+	0.016
39	3/5/14	+	+	+	+	+	+	+	+	0.016
41	3/5/14	0	+	+	0	+	+	+	+	1.3
42	3/5/14	0	0	0	+	+	+	+	+	0.43
43	3/5/14	+	0	+	+	+	+	+	+	0.14
44	3/5/14	+	+	0	+	+	+	+	+	0.43
45	3/5/14	0	0	+	0	+	+	0	+	35
46	3/5/14	0	0	0	+	0	0	+	+	12
47	3/5/14	0	0	+	+	+	+	+	+	0.14
48	3/5/14	+	+	+	0	+	+	+	+	1.3
49	3/5/14	0	0	0	0	+	0	+	0	100
50	3/5/14	0	0	+	+	0	+	0	+	35
51	3/5/14	0	+	0	0	+	+	+	+	1.3
53	3/5/14	0	+	+	+	+	+	+	+	0.047
54	3/5/14	+	0	0	+	+	+	+	+	0.43
55	3/5/14	+	+	+	+	+	+	+	+	0.016
56	3/5/14	+	0	0	+	+	+	0	+	35
57	3/5/14	0	0	+	+	+	+	+	+	0.14
59	3/5/14	+	+	+	+	+	+	+	+	0.016
62	3/5/14	+	+	+	+	+	+	+	+	0.016
63	3/5/14	0	+	+	+	0	0	+	+	12

Appendix E. Consumer Panel Results for Odor Threshold Concentration

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
		0.027	0.082	0.25	0.74	2.2	6.7	20	60	Value
64	3/5/14	+	+	+	+	0	+	0	+	35
65	3/5/14	0	+	+	+	+	+	+	+	0.047
66	3/5/14	+	+	0	0	+	+	+	+	1.3
67	3/5/14	+	+	0	+	+	+	+	+	0.43
68	3/5/14	+	+	+	+	+	+	+	+	0.016
69	3/5/14	+	+	+	+	+	+	+	+	0.016
70	3/5/14	+	0	0	0	0	0	+	+	12
71	3/5/14	+	0	0	+	+	0	0	+	35
72	3/5/14	+	+	+	+	+	+	+	+	0.016

Note: “0” indicates that the panelist selected the wrong sample of the set of three; “+” indicates that the panelist selected the correct sample; the individual OTC is the geometric mean of the two concentrations where there is a change from "0" to consistent answers of "+" which is noted by gray-shaded cells.

Geometric Mean, ppb = 0.55

Appendix F. Consumer Panel Results for Odor Recognition Concentration

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Reference Odor	Best Estimate Threshold, ppb
		0.027	0.082	0.25	0.74	2.2	6.7	20	60		Value
1	3/3/14				Smelled fresh	strawberry, fruity, familiar smell	strawberry, fruity, familiar smell	strawberry, fruity, familiar smell (more like candy)	strawberry, fruity, familiar smell	strawberry, fruity	1.3
2	3/3/14								It's the one that smells different	perfumey, ocean breeze	100
3	3/3/14							Clear, clean, light, no odor	pepperminty, room freshner	floral, earthy, tan, minty	35
4	3/3/14					Nothing	Cut grass & vanilla	smells sweet like vanilla	smells sweet like cotton candy	sweet, vanilla, cut grass	3.8
6	3/3/14			chemicals	rubber, chemicals	Glue	Glue, chemicals	chemicals, glue, chlorine	chemicals, glue, rubber	licorice, chemical, not good	0.43
7	3/3/14								chemical smell	minty, basil	100
8	3/3/14				dewy	floral	sweet, fruity	sweet	sweet	fruity, flowery	1.3
9	3/3/14								plastic melted	Bubble bath, flowery	100
10	3/3/14						clean, fresh, pure	sweet, carbonated, fruity	sweet syrupy, cola: reminds me of the one I smelled before the panel	syrupy, coca cola	12
11	3/3/14						plastic	jolly rancher	jolly rancher	rosewater, candy (jolly rancher)	12
12	3/3/14					antiseptic wipe, cleaning agent	fruity	artificial grape, fruity	oranges, mixed fruit, fruity	fruity, licorice	3.8
13	3/3/14			sharp, cutting	mold-like, grassy, pungent	chemical, metal, pungent	gas-like, pungent, potent	chemical, dirty, potent	nail polish remover, varnish	medicine, pungent, rotten	0.43
14	3/3/14			clean, fresh, no smell	fruity	fruity	licorice	licorice, sweet	Jet fuel, medicine	medicine, fruity, perfumey	0.43
15	3/3/14							a bit smoky	licorice	licorice	35
16	3/3/14	fairly sweet, tangy, moutain dew, citrus	citrus, dewy, fruity	citrus, lemony	dull citrus, dull candy	mountain-dewy, monster energy drink	citrus, energy drink, almost lemony, jolly rancher	citrus, Pinesol	citrus, lemon, lemonhead candy	medicinal, neutral, sweet	0.016
19	3/3/14				seltzer	strawberry	fresh produce section of grocery store	old cantaloupe	lime, strawberry	cherry cough syrup, sweet	1.3
20	3/3/14								hair spray	medicinal, kids cough syrup	100
22	3/3/14							chemical detergent	wild cherry (Ludens) cough drops	cherry cough drops (Ludens)	35

Appendix F. Consumer Panel Results for Odor Recognition Concentration

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Reference Odor	Best Estimate Threshold, ppb
		0.027	0.082	0.25	0.74	2.2	6.7	20	60		Value
23	3/3/14						Fresh fruity	Similar to aroma during interview	Interview aroma, flowers, bathroom air freshner	Bathroom air freshner, flowery	12
24	3/3/14						vinegar, cleaner smell	cherry coke	cherry cough medicine, Robitussin	spicy, herb, fruity	12
25	3/3/14						Nothing	fruity, sweet	fruity, sweet	fruity, sweet, natural	12
27	3/3/14							chemical smell	medicine	mediciney	35
28	3/3/14		Fairly basic smell	sweet	flowery	coca cola, sugar cane syrup	cola, sugar cane syrup, sugary, sweet	sugary sweet	sweet soda	floral, brown sugar	0.14
29	3/3/14								mint-like, protein drink	algae fish tank, medicine	100
31	3/3/14					musty, chemical	grape, fruity	citrusy	chemical and artificial	citrusy, floral	3.8
32	3/3/14				clean air	floral, potpourri	lemon dish soap (sweet fruity)	cherry, Kool Aid fruit punch	cherry, Kool Aid fruit punch	dark cherry (floral and fruity)	1.3
33	3/3/14								garden hose, dirt and rubber	pine nut sage cookie	100
34	3/3/14				smells off	cherry cough syrup	cherry cough syrup	cherry cough syrup	cherry cough syrup	cherry cough syrup	1.3
35	3/3/14				fresh smell	smelled like reference sample	like ref sample, sage/pine	medicine	household cleaner	fruity, sage	1.3
36	3/3/14								hair spray	vanilla, baking flavoring	100
38	3/5/14				gas from the oven	sweet like test smell, slight perfumey acetone	perfumey acetone	sweet nail polish remover	sweet like a jelly bean	sweet candy, jelly bean, vanilla, watermelon	1.3
39	3/5/14	medicinal	medicine	medicinal	medicinal, chemical	chemical, medicinal	chemical, medicinal	chemical, medicinal	chemical, medicinal	Flower Bomb (perfume brand--floral, spicy, fruity), almond	0.016
41	3/5/14					Rum	licorice	berry, sweet	cherry	spicy, sweet	3.8
42	3/5/14				chemical	sweet, juicy fruit	sweet and surgary	sweet, hard candy	clean, fresh sweet smell like before the panel-licorice	licorice	1.3
43	3/5/14								garbage, sewer water	Candle vanilla, lavender, waxy flower	100

Appendix F. Consumer Panel Results for Odor Recognition Concentration

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Reference Odor	Best Estimate Threshold, ppb
		0.027	0.082	0.25	0.74	2.2	6.7	20	60		Value
44	3/5/14						chemical, jet fuel	perfumey, sweet, cloying	sweet, vanilla, sasparilla	tapioca, vanilla, sweet medicinal	12
45	3/5/14								7 Up	peppermint, pine (old tree)	100
46	3/5/14						Stephens flower paint thinner	perfumey flower	heavy plastic	flowery, terpentine, paint thinner	12
47	3/5/14			fruity	nutty	lemon (sweet fruity)	medicine like cherry Nyquil	almond	cherry, fruity	nutty, sweet, vanilla	0.43
48	3/5/14				hint of an actual aroma	citrus, sweetness	musky sweetness	sugary	perfumey, musty	floral, citrus	1.3
49	3/5/14								fruit	Sweet, fruity	100
50	3/5/14							sewage	sweet	medicinal, sweet candy	35
51	3/5/14					foul	minty chemical	watered down minty chemical	raspberry	minty chemical	3.8
53	3/5/14					dirty diaper, plastic	vinegar, plastic, fruity	ammonia, smog, vapor rub	sweet, chemical, ammonia	sweet cherry, menthol	3.8
54	3/5/14					cleaning solution	almond-like	almond-like	almond-like	almond extract	3.8
55	3/5/14							plastic, chemical	fruity, black licorice	fruity, black licorice	35
56	3/5/14								unpleasant	soapy, fruity, cough syrup	100
57	3/5/14								magic marker, gasoline	coconut, medicinal, nutty	100
59	3/5/14					nail polish	grape kids medicine	grape	mixed fruit Pedialyte	Nyquil medicine (licorice)	3.8
62	3/5/14							rubber glue	Blue Nyquil	Blue Nyquil (minty)	35
63	3/5/14								nothing	black licorice	100
64	3/5/14								water with no filtration	rose water	100
65	3/5/14				sewage	cleaning odor	cleaning agent	cleaning agent	cleaning agent	cleaning chemical	1.3

Appendix F. Consumer Panel Results for Odor Recognition Concentration

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Reference Odor	Best Estimate Threshold, ppb
		0.027	0.082	0.25	0.74	2.2	6.7	20	60		Value
66	3/5/14				no odor	licorice	licorice	licorice	licorice	Playdough (candy)	1.3
67	3/5/14								nothing	cough syrup, mediciney, Robutussin	100
68	3/5/14				pungent sulfur, sour, egg-like	sweet, acidic, orange or lime	organic, flowery	sweet raspberry, flowery, lavender, chemical	sweet raspberry chemical	sweet, carmelized brown sugar	1.3
69	3/5/14					boiled eggs	perfume	bubblegum, vanilla	peanuts (nutty)	bubblegum, vanilla, flowery	3.8
70	3/5/14						orange	nail polish remover (fruity)	fruity, grape	Robutussin, grape, vanilla	12
71	3/5/14								melted plastic	black licorice	100
72	3/5/14				nothing	flower	alcohol	flower	flower/alcohol	jasmine, flowery, alcohol	1.3

Notes: The ORC was only recorded for concentrations at or above the OTC; the individual ORC is the geometric mean of the two concentrations where there is a change from other descriptors to the reference odor descriptor which is noted by gray-shaded cells. Descriptors are not shown below individual ORC thresholds.

Geometric Mean, ppb = 7.4

Appendix G. Sweet Reference and Descriptor Odors for MCHM

Reference Odor	Descriptor
strawberry, fruity	strawberry, fruity, candy
sweet, vanilla, cut grass	cut grass, vanilla, cotton candy
fruity, flowery	floral, sweet, fruity
syrupy, coca cola	sweet, carbonated, fruity, syrupy
rosewater, candy, jolly rancher	jolly rancher
fruity, licorice	artificial grape, fruity, oranges, mixed fruit
medicine, fruity, perfumey	fruity, licorice, sweet, jet fuel, medicine
licorice	licorice
medicinal, neutral, sweet	citrus, dewy, fruity, lemony, dull candy, mountain dew, monster drink, citrus, Pinesol, lemonhead candy
cherry cough syrup, sweet	strawberry, fresh produce section of grocery store, old cantaloupe, lime, strawberry
cherry cough drops (Ludens)	wild cherry (Lundens) cough drops
spicy, herb, fruity	cherry coke, cherry cough medicine, Robutussin
fruity, sweet, natural	fruity, sweet
mediciney	like medicine
floral, brown sugar	sweet, flowery, coca cola, sugar cane syrup, sugary sweet, sweet soda
citrusy, floral	grape, fruity, citrusy, chemical and artificial
dark cherry (floral and fruity)	floral, potpourri, lemon dish soap, cherry, Kool Aid fruit punch
cherry cough syrup	cherry cough syrup
fruity, sage	like reference sample, sage/pine, medicine, household cleaner
sweet candy, jelly bean, vanilla, watermelon	sweet like test smell, perfumey, acetone sweet nail polish remover, sweet like a jelly bean
Floral Bomb perfume, floral, spicy, fruity, almond	medicine, chemical
spicy, sweet	licorice, berry, sweet, cherry
licorice	sweet, juicy fruit, sweet, sugary, hard candy, fresh sweet smell like before the panel, licorice
tapioca, vanilla, sweet medicinal	sweet, vanilla, perfumey, sweet, cloying, sasparilla
nutty, sweet, vanilla	nutty, lemon, medicine like cherry Nyquil, almond, cherry, fruity
floral, citrus	citrus sweetness, musky sweetiness, sugary, perfumey, musty
sweet, fruity	fruit
medicinal, sweet candy	sweet
sweet cherry, menthol	vinegar, plastic, fruity, ammonia, smog, vapor rub, sweet, chemical, ammonia
almond extract	almond-like
fruity, black licorice	fruity, black licorice
Nyquil medicine, licorice	grape kids medicine, grape, mixed fruit Pedialyte
Blue Nyquil, minty	Blue Nyquil
Playdough, candy	licorice
sweet, carmelized brown sugar	sweet, acidic, orange, lime, organic, flowery, sweet raspberry, flowery, lavendar, chemical
bubblegum, vanilla, flowery	bubblegum, peanuts (nutty)
Robutussin, grape, vanilla	nail polish remover (non-acetone, fruity), fruity, grape
jasmine, flowery, alcohol	flower, alcohol,

Appendix H. Consumer Panel Results for Odor Objection Concentration Based on Degree of Liking

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
		0.027	0.082	0.25	0.74	2.2	6.7	20	60	Value
01	3/3/14	3	5	2	2	2	2	1	1	100
02	3/3/14	6	5	7	6	2	8	8	6	3.8
03	3/3/14	6	4	3	6	3	7	2	6	35
04	3/3/14	1	5	8	5	1	7	7	7	3.8
06	3/3/14	8	7	8	8	7	9	9	9	0.43
07	3/3/14	6	4	3	3	1	4	1	6	35
08	3/3/14	3	6	5	5	4	5	5	5	100
09	3/3/14	7	8	3	9	5	8	9	8	3.8
10	3/3/14	2	5	2	4	7	1	6	6	12
11	3/3/14	7	5	6	4	7	5	6	8	12
12	3/3/14	2	3	1	5	5	6	8	7	3.8
13	3/3/14	9	8	9	6	8	9	9	9	0.43
14	3/3/14	2	2	2	4	4	5	6	9	12
15	3/3/14	4	5	1	2	3	8	6	4	100
16	3/3/14	3	3	3	4	3	2	3	2	100
19	3/3/14	8	7	5	6	4	6	7	5	100
20	3/3/14	1	5	7	8	8	9	9	9	0.14
22	3/3/14	6	3	5	5	7	8	8	8	1.3
23	3/3/14	4	3	6	7	6	4	7	7	12
24	3/3/14	4	1	5	8	9	9	6	7	0.43
25	3/3/14	6	8	5	6	7	5	2	2	100
27	3/3/14	5	3	6	6	4	5	7	7	12
28	3/3/14	3	5	4	2	7	7	7	7	1.3
29	3/3/14	5	4	4	6	5	5	5	4	100
31	3/3/14	6	3	3	5	8	4	6	7	12
32	3/3/14	4	6	5	2	4	6	4	6	35
33	3/3/14	5	6	3	4	3	5	6	7	12
34	3/3/14	4	4	7	5	5	6	7	7	3.8
35	3/3/14	6	4	4	3	5	5	7	9	12
36	3/3/14	5	7	5	5	4	7	7	7	3.8
38	3/5/14	5	4	4	7	5	7	8	8	3.8
39	3/5/14	6	6	7	7	8	9	9	9	0.016
41	3/5/14	5	8	5	6	8	7	8	6	1.3
42	3/5/14	6	3	5	6	3	5	3	3	100
43	3/5/14	3	5	7	7	8	8	8	9	0.14
44	3/5/14	4	9	5	6	9	9	7	7	0.43
45	3/5/14	1	1	3	2	1	2	2	4	100
46	3/5/14	4	1	5	5	4	6	4	6	35
47	3/5/14	1	1	2	5	7	5	5	6	35
48	3/5/14	5	5	4	4	3	6	5	6	35
49	3/5/14	2	2	2	3	2	2	2	2	100
50	3/5/14	7	3	3	2	7	2	7	2	100
51	3/5/14	6	4	5	4	7	8	7	8	1.3
53	3/5/14	9	9	9	9	9	9	9	9	0.047
54	3/5/14	6	2	5	7	5	8	9	9	3.8
55	3/5/14	7	5	6	7	7	7	7	8	0.14
56	3/5/14	5	4	3	9	9	8	1	9	35
57	3/5/14	3	3	7	5	7	8	7	8	1.3
59	3/5/14	6	8	8	5	7	7	7	6	1.3
62	3/5/14	6	6	8	8	8	6	6	8	0.016
63	3/5/14	1	8	5	2	1	1	5	2	100

Appendix H. Consumer Panel Results for Odor Objection Concentration Based on Degree of Liking

		Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
Panelists	Date Study Conducted	0.027	0.082	0.25	0.74	2.2	6.7	20	60	Value
64	3/5/14	4	6	6	3	5	5	2	5	100
65	3/5/14	9	8	9	9	8	9	8	9	0.047
66	3/5/14	5	2	1	1	2	4	4	4	100
67	3/5/14	5	5	4	4	5	4	4	4	100
68	3/5/14	4	4	5	6	5	5	7	8	12
69	3/5/14	3	2	3	2	7	5	5	5	100
70	3/5/14	2	6	7	2	2	2	8	2	100
71	3/5/14	1	1	1	9	1	8	1	9	35
72	3/5/14	1	2	1	1	2	7	1	1	100

Note: The OOC was only recorded for concentrations at or above the OTC; the individual OOC is the geometric mean of the two concentrations where there is a jump in the degree of disliking to a score of 6 or above which is noted by gray-shaded cells.

Geometric Mean, ppb = 7.7

Appendix I. Consumer Panel Results for Odor Objection Concentration Based on Objection/Complaint

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
		0.027	0.082	0.25	0.74	2.2	6.7	20	60	Value
01	3/3/14	N	Y	Y	Y	Y	Y	Y	Y	0.047
02	3/3/14	Y	N	Y	Y	N	Y	Y	Y	3.8
03	3/3/14	Y	N	N	Y	N	Y	N	Y	35
04	3/3/14	N	N	Y	N	N	Y	Y	Y	3.8
06	3/3/14	Y	Y	Y	Y	Y	Y	Y	Y	0.43
07	3/3/14	Y	N	N	N	N	N	N	Y	100
08	3/3/14	N	Y	N	N	N	N	N	N	100
09	3/3/14	Y	Y	N	Y	N	Y	Y	Y	3.8
10	3/3/14	N	N	N	N	Y	N	N	N	100
11	3/3/14	Y	N	N	N	Y	N	N	Y	35
12	3/3/14	N	N	N	N	N	Y	Y	Y	3.8
13	3/3/14	Y	Y	Y	N	Y	Y	Y	Y	1.3
14	3/3/14	N	N	N	N	N	Y	Y	Y	3.8
15	3/3/14	N	Y	N	N	N	Y	Y	N	100
16	3/3/14	N	N	N	N	N	N	N	N	100
19	3/3/14	N	N	N	N	N	N	N	N	100
20	3/3/14	N	Y	Y	Y	Y	Y	Y	Y	0.047
22	3/3/14	N	N	N	N	Y	Y	Y	Y	1.3
23	3/3/14	N	N	N	Y	N	N	N	N	100
24	3/3/14	N	N	N	Y	Y	Y	Y	Y	0.43
25	3/3/14	Y	Y	N	Y	Y	N	N	N	100
27	3/3/14	N	N	Y	Y	N	N	Y	Y	12
28	3/3/14	N	N	N	N	Y	Y	Y	Y	1.3
29	3/3/14	N	N	N	Y	N	N	N	N	100
31	3/3/14	N	N	N	N	Y	N	Y	Y	12
32	3/3/14	N	Y	N	N	N	Y	N	Y	35
33	3/3/14	N	N	N	N	N	N	N	Y	35
34	3/3/14	N	N	Y	N	N	Y	Y	Y	3.8
35	3/3/14	N	N	N	N	N	N	Y	Y	12
36	3/3/14	N	Y	N	N	N	Y	Y	Y	3.8
38	3/5/14	N	N	N	N	N	Y	Y	Y	3.8
39	3/5/14	Y	Y	Y	Y	Y	Y	Y	Y	0.016
41	3/5/14	N	Y	N	Y	Y	Y	Y	Y	1.3
42	3/5/14	Y	N	N	Y	N	N	N	N	100
43	3/5/14	N	N	Y	Y	Y	Y	Y	Y	0.14
44	3/5/14	N	Y	N	Y	Y	Y	Y	Y	0.43
45	3/5/14	N	N	N	N	N	N	N	N	100
46	3/5/14	N	N	N	N	N	N	N	Y	35
47	3/5/14	N	N	N	N	Y	Y	N	Y	35
48	3/5/14	N	N	N	N	N	N	N	N	100
49	3/5/14	N	N	N	N	N	N	N	N	100
50	3/5/14	Y	N	N	N	Y	N	Y	N	100
51	3/5/14	Y	N	N	N	Y	Y	Y	Y	1.3
53	3/5/14	Y	Y	Y	Y	Y	Y	Y	Y	0.047
54	3/5/14	N	N	N	Y	N	Y	Y	Y	3.8
55	3/5/14	Y	N	N	Y	Y	Y	Y	Y	0.43
56	3/5/14	N	N	N	Y	Y	Y	N	Y	35
57	3/5/14	N	N	Y	N	Y	Y	Y	Y	1.3
59	3/5/14	N	Y	Y	N	Y	Y	N	N	100
62	3/5/14	Y	Y	Y	Y	Y	N	Y	Y	3.8
63	3/5/14	N	N	N	N	N	N	N	N	100

Appendix I. Consumer Panel Results for Odor Objection Concentration Based on Objection/Complaint

		Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
Panelists	Date Study Conducted	0.027	0.082	0.25	0.74	2.2	6.7	20	60	Value
64	3/5/14	N	N	N	N	N	N	N	N	100
65	3/5/14	Y	Y	Y	Y	Y	Y	Y	Y	12
66	3/5/14	N	N	N	N	N	Y	Y	Y	3.8
67	3/5/14	N	N	N	N	N	N	N	N	100
68	3/5/14	N	N	N	Y	N	N	Y	Y	12
69	3/5/14	N	N	N	N	Y	N	N	N	100
70	3/5/14	N	N	Y	N	N	N	Y	N	100
71	3/5/14	N	N	N	Y	N	N	N	Y	35
72	3/5/14	N	N	N	N	N	Y	N	N	100

Note: The OOC was only recorded for concentrations at or above the OTC; the individual OOC is the geometric mean of the two concentrations where there is a change to a consistent answer of Yes to the question: Would you object/complain about the odor in the different cup? Noted by gray-shaded cells.

Geometric Mean, ppb = 9.5

Appendix C. Assessment of Tentatively Identified Compounds in Tap Water Following the January 9 Chemical Spill from Freedom Industries

WV TAP
WEST VIRGINIA TESTING ASSESSMENT PROJECT

Assessment of Tentatively Identified Compounds in Tap Water Following the January 9 Chemical Spill from Freedom Industries

Charles Neslund, Duane Luckenbill, Richard Karam
Eurofins Lancaster Laboratories Environmental, Inc.

Andrew Eaton, PhD, BCES
Eurofins Eaton Analytical Inc.

Introduction

This report summarizes the development of a sensitive analytical method for 4-MCHM and PPH and the investigation of sources of additional peaks observed on chromatograms from samples collected as part of the WVTAP 10 home study.

Analytical Method Development

Eurofins Lancaster Laboratories Environmental, Inc. (ELLE) developed an analytical technique for the analysis of 4-methyl-1-cyclohexanemethanol (4-MCHM) CAS #34885-03-5 and propylene glycol phenyl ether (PPH) CAS #770-35-4 in potable water. In the absence of applicable toxicological evaluation and assessment with respect to concentrations that will result in negative human health effects, an analytical method that would be able to detect 4-MCHM and PPH at the lowest levels possible using commonly available instrumentation was desirable.

4-MCHM and PPH have very different characteristics. 4-MCHM (MW = 128.21 g/mole) is a colorless liquid with a density of 0.9074 g/ml and a boiling point of 202 °C. However, physiochemical property data for the contaminants spilled into the Elk River remains limited. The solubility of 4-MCHM was estimated by Dr. Kevin West at the University of South Alabama to range from approximately 2,500 mg/l (0°C) to 3,750 mg/l (100°C). This estimate was determined using COSMO-RS (Conductor like Screening Model for Realistic Solvents (3). Commercially available standards consist of a mix of the cis (axial substitution of the 4-methyl group) and trans (equatorial substitution of the 4-methyl group) isomers. The relative concentration of each isomer is not determined or provided in manufacturer's Certificate of Analysis information. PPH (MW = 152.19 g/mole) is a clear, colorless liquid with a density of 1.059 g/ml, a boiling point of 242.7 °C and a 11,000 mg/l water solubility (4).

Based on the aforementioned physical characteristics and chemical similarity to other compounds analyzed by this laboratory, an approach utilizing gas chromatography with mass spectrometry (GC/MS) and organic solvent extraction was used. The sample preparation step generally followed EPA SW-846 Method 3510. In summary, this method calls for the serial extraction of a water sample with methylene chloride or other suitable solvent. Due to the fact that 4-MCHM and PPH were similar to other compounds analyzed under a semivolatiles or extractable organics approach, methylene

chloride was used as the extraction solvent. The methylene chloride solvent fractions from the serial extractions of the water sample were combined and the total solvent volume reduced to a final volume (FV) of 1 milliliter (ml).

The instrumental analysis generally followed EPA SW-846 Method 8270. In summary, this method uses GC/MS instrumentation that is operated in the electron impact (EI) ionization mode. The GC/MS is tuned to decafluorotriphenylphospine (DFTPP) to "standardize" the consistency of the instrumental response. After tuning, the analytical system is then calibrated using a minimum of a 5-point calibration curve. The calibration curve/response is constructed using internal standard calibration. A calibration curve was considered acceptable if the percent relative standard deviation (%RSD) of the relative response factors (RRF) for the 5 or 6 calibration points was < 20%.

Experimental

For the work performed in preparation for the 10 Home Study under WV TAP, 1 liter of water was serially extracted with methylene chloride and the methylene chloride extracts were concentrated to a FV of 1 ml. Prior to the extraction with methylene chloride, a known volume and concentration of surrogate standards were added to each field sample and the associated quality control (QC) samples.

After extraction of the sample and after the methylene chloride extract is reduced to a volume of 1 ml, but prior to instrumental analysis, a known volume and concentration of internal standards were added to each 1 ml methylene chloride extract. The list of surrogate standards and internal standards added to the samples/extracts was the list of compounds typically used for Method 8270 analysis in the environmental industry. The compounds are listed in Table 1.

Table 1: Surrogate and Internal Standards initially used in 4-MCHM/PPH Method.

Surrogate Standards[1]	Internal Standards
2-Fluorophenol	1,4-Dichlorobenzene-d4
Phenol-d6	Naphthalene-d8
Nitrobenzene-d5 *	Acenaphthene-d10
2-Fluorobiphenyl *	Phenanthrene-d10
2,4,6-Tribromophenol	Pyrene-d10
Terphenyl-d14 *	Perylene-d12

Compounds designated with an asterix (*) are base/neutral surrogate standard compounds.

Early in the work it was recognized that one of the surrogate compounds, nitrobenzene-d5, impacted the detection and analysis of 4-MCHM at lower levels. Nitrobenzene-d5 has several secondary ions that are within an atomic mass unit (amu) of the quantification mass for 4-MCHM. This affected the detection of 4-MCHM at very low levels because nitrobenzene-d5 essentially coeluted with 4-MCHM under the chromatographic conditions of analysis and the mass loading of nitrobenzene-d5 was so substantial relative to 4-MCHM. Therefore, going forward into the 10 Home Study, the base/neutral surrogate standard compounds (those designated with an *) were eliminated from the surrogate standard spiking mixture. We also felt that the phenolic compounds remaining in the surrogate standard spiking solution better represented compounds like 4-MCHM and PPH, compounds that had free hydroxyl groups in the chemical structure.

The GCMS instrument was calibrated with six concentrations of calibration standard (Table 2).

Table 2: Calibration levels used for 4-MCHM and PPH.

Calibration Level	Concentration (µg/l)
1	1
2	5
3	10
4	20
5	40
6	60

Note: Concentration listed in µg/l is the concentration as it relates to the concentration in the water sample.

A relative standard deviation (%RSD) of < 20% for the Relative Response Factors (RRFs) of the initial calibration signified a valid, acceptable calibration. The performance of the analytical system was checked every 12 hours by passing a valid DFTPP tune and a continuing calibration check standard (CCV). A CCV was compliant and within specifications if the percent difference of the RRF in the CCV was < 20% of that of the average RRF observed in the initial calibration.

With every extraction group, the following Quality Control (QC) was run. Definitions of appropriate QC terms are shown below.

Extraction Batch – A group of field samples and associated QC extracted with methylene chloride and processed as a group. An extraction batch is not to exceed 20 field samples.

Method Blank – An aliquot of laboratory grade water that is processed through the entire extraction process and is handled (surrogates and internal standards) like a sample. It is used to monitor background contribution of analytical system and process to analytical results.

Laboratory Control Sample (LCS) – An aliquot of laboratory grade water that is spiked with a known quantity of the target compound(s) and processed through the entire extraction process. The spiking concentration is typically at or around the mid-point of the calibration curve. The recovery of the spiked target compound(s) is determined and the efficiency of the extraction process, as it relates to the specific batch, is assessed. Recoveries of 70%-130% were expected for MCHM and PPH. Recoveries outside of the 70%-130% window, particularly below 70% would be cause for the batch to be re-extracted.
Laboratory Control Sample Duplicate (LCSD) – Same as an LCS and when processed in conjunction with an LCS used to measure the precision of the analysis.

Minimum Reporting Limit LCS (MRL LCS) – An LCS for which the concentration at which the LCS is spiked is at or near (typically 1-2x) the minimum reporting limit for the analysis.

Matrix Spike and Matrix Spike Duplicate (MS/MSD) – additional aliquots of a field sample that are spiked, like the LCS, at the mid-point of the calibration curve.

Surrogate Standards – Compounds that are spiked into every sample and that are different from the target compound(s) but expected to extract similarly to the target compound(s). The recovery of the surrogate standards are determined in each sample, which becomes a measure of the efficiency of the extraction for that individual sample.

Internal Standard – Compounds added to the methylene chloride extract prior to instrumental analysis. Internal standards are used to a) monitor the effectiveness of each sample extract injection into the analytical system and b) calculate a response ratio with the target compound(s) in the initial calibration that can be used to quantify target compound(s) in subsequent sample analysis.

The results of the application of EPA Methods 3510 and 8270 towards the analysis of 4-MCHM and PPH are an analytical technique capable of reporting 4-MCHM and PPH to a limit of quantitation (LOQ) of 1 µg/l (ppb) and a method detection limit (MDL) of 0.5 µg/l as shown in Table 3.

Table 3: MDL determination for 4-MCHM and PPH.

Parameter	Compound	
	4-MCHM (µg/l)	**PPH (µg/l)**
MDL1	1.82	1.99
MDL2	1.83	2.00
MDL3	1.83	1.98
MDL4	1.79l	1.95
MDL5	1.83	2.02
MDL6	1.93	2.09
MDL7	1.90	2.03
Mean	1.85	2.01
Spike Level	2.0	2.0
Mean % Recovery	92.4 %	100.5 %
Standard Deviation	0.050	0.046
Statistical MDL	0.158	0.144

No preservation other than refrigeration (e.g. acidification or dechlorination) was used for the sample bottles for the 10 home study as it was not clear whether these could interfere with the analysis or react with the target analytes.

10 Home Study Data Review

Analysis of samples from hot and cold water taps at different points throughout each house in the WVTAP 10 Home Study indicated detections of 4-MCHM ranging from just below 1 µg/l to a high of approximately 6 µg/l. 4-MCHM was detected in all samples in all the houses. PPH was not detected in any of the samples collected from the 10 Home Study. An example chromatogram is shown in Figure 1.

The chromatographic peaks for the 6 internal standards and the 3 surrogate standards are listed on the chromatogram. However, a very distinct series of unknown peaks were also detected in the samples. The chromatogram presented in Figure 2 is an overlay of the chromatogram generated from the 4-MCHM analysis of a hot and cold water tap at 2 different houses in the 10 Home Study. The pattern of unidentified peaks detected in each sample was very similar if not the same.

A rough estimation from the visual observation of the chromatograms suggested concentrations for the unknown peaks/compounds in the range of 10 µg/l for many of the peaks to almost 200 µg/l for the significant peak observed at approximately 3.3 minutes (time is on the X axis of the chromatograms). Due to the high potential concentrations of these additional peaks it was deemed important to identify them and determine if they could be oxidation or other breakdown products of the 4-MCHM or if they could

represent additional compounds from the spill or were they coming from some other source.

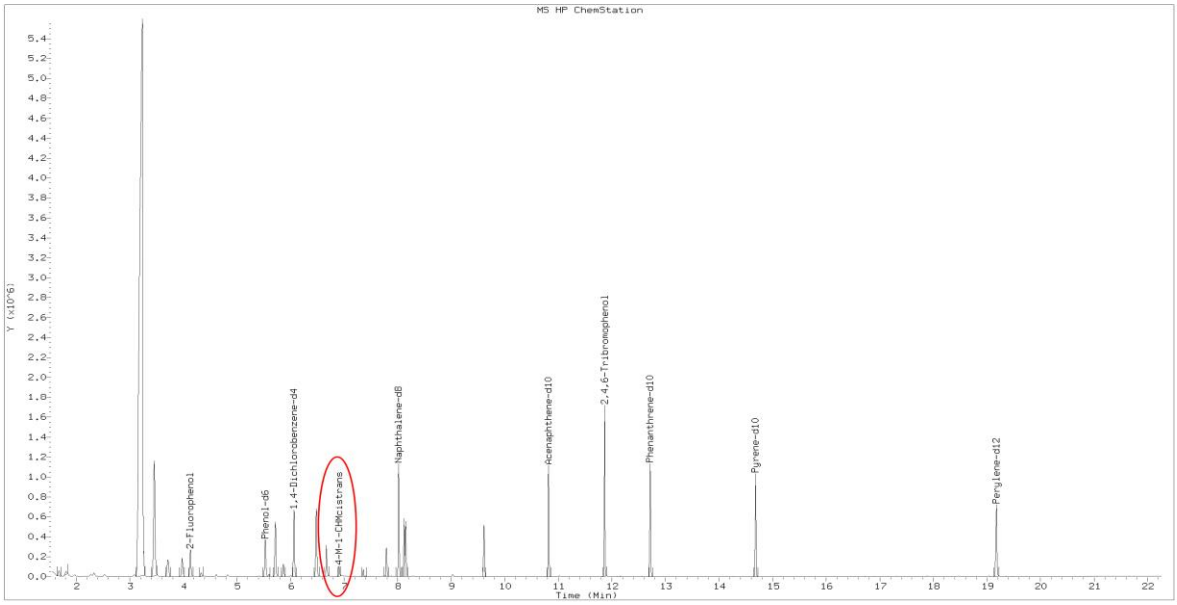

Figure 1: Example total ion chromatogram for one of the 10 house study samples. Red circle shows the peaks and location of 4 – MCHM. Peaks with names are surrogates and internal standards.

A close-up of the peak pattern that was observed is shown in Figure 3.

In an attempt to determine the identity of the unknown peaks, mass spectral library searches were performed on the chromatograms and GC/MS data files for the 10 Home Study samples. A mass spectral library search is a tool used by analytical chemists to attempt to tentatively identify and semi-quantitatively quantify the compound responsible for the observed chromatographic peak. Library search databases are available from standard reference sources like the National Institutes for Standards and Technology (NIST) and are typically part of most GC/MS data systems

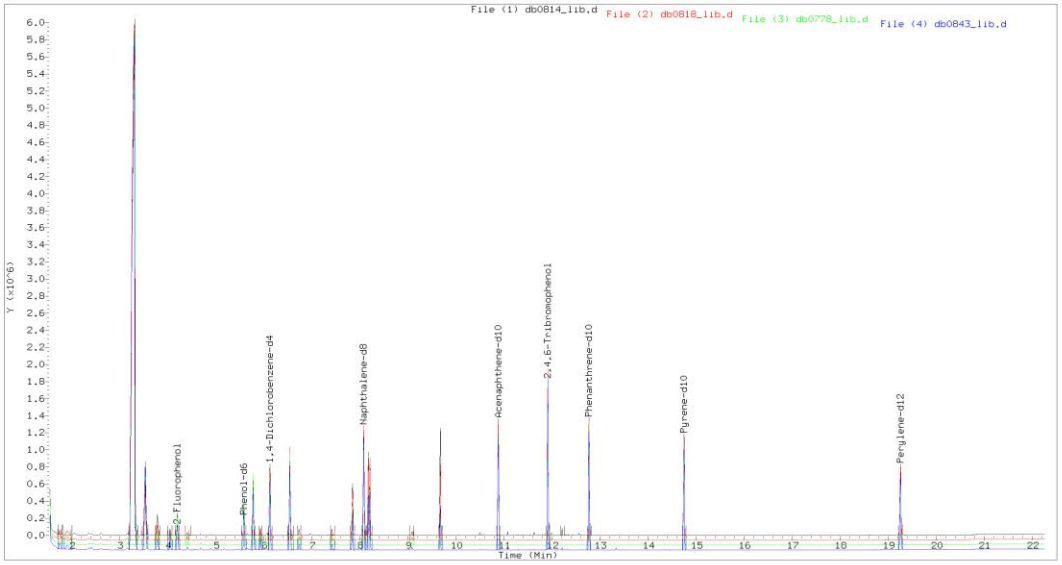

Figure 2: Overlay of chromatograms from multiple samples from 10 home survey. Peaks with names are surrogates and internal standards.

Library search data bases are generally useful when the analytical technique is EI (electron impact) ionization, which under controlled conditions fragments chemical compounds into predictable and relatively consistent ion fragment patterns. Because of the relative predictability of the ion fragment patterns, the ion fragment pattern from an unknown peak can be compared to the library's database of ion fragment patterns, with the intention of matching patterns and potentially identifying the compound responsible for the unknown peak. As the computer software that performs this function operates, it also assigns a quality of match number between the unknown compound ion fragment and the library database reference compound ion fragment. This quality of match indicator is typically on a scale of 0-100. The closer the number is to 100, the better the match between the unknown and the database reference compound.

The result of a library search on a given sample is a list of possible matches, called Tentatively Identified Compounds (TIC), a quality of match value and an estimated concentration. The estimated concentration is a very gross estimation in that it is calculated by using the response factor for an internal standard used in the sample analysis, to quantify the Tentatively Identified Compound (TIC).

For the 10 Home Study, library searches were performed on the GC/MS data file generated from the analysis of the cold water kitchen tap and the hot water kitchen tap for each house. Table 4 summarizes the most prevalent identifications listed in the TIC library search results. This is not a comprehensive list, but is presented as representative of what was "detected" and the tentative identifications assigned to them.

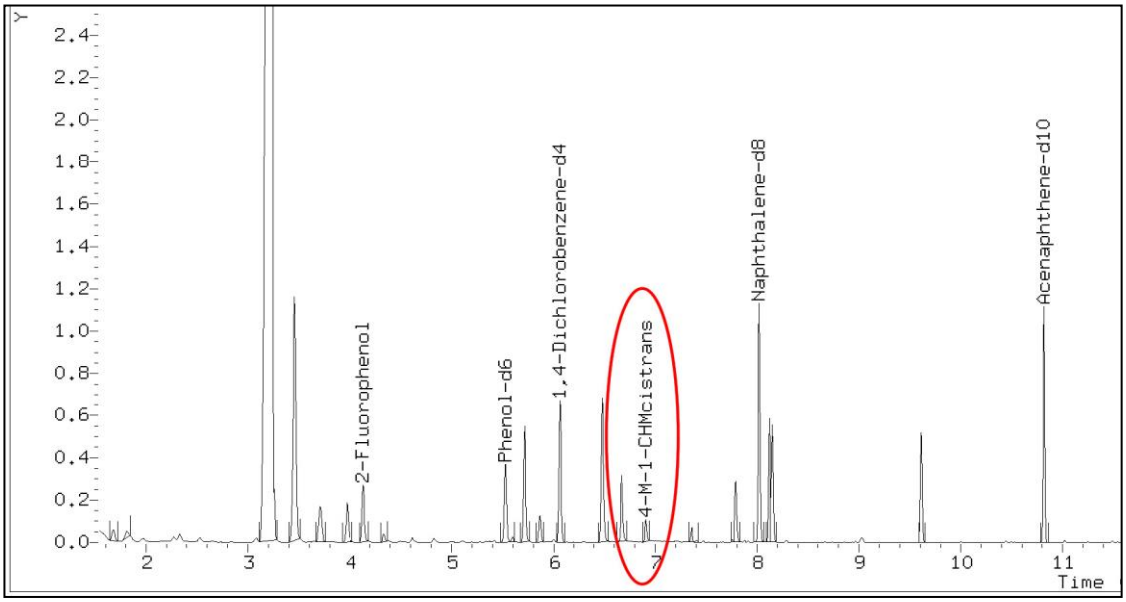

Figure 3: Expanded view of chromatogram showing additional peaks besides the surrogates, internal standards, and target compound. Peaks with names are surrogates and internal standard

Table 4: Most prevalent TIC identifications from library search of unknown compound peaks.

CAS Number	Compound Name	RT, min.	Estimated Conc., µg/l (rounded)
17773-64-7	1-Butene, 2-chloro-3-methly-	1.892	1.4
1985-88-2	1,1-Dimethyl-3-chloropropanol	3.309	200
507-45-9	Butane, 2,3-dichloro-2-methyl-	3.530	13.6
2419-74-1	2-Butanol, 1,4-dichloro-	3.781	3.7
74421-00-4	Butane, 2,3-dimethoxy-2-methyl	4.043	1.0
0-00-0	O-chlorophenol-d4	5.774	6.5
27639-93-9	Propanoic acid, 2-chloro-	6.538	9.3
77-73-6	4,7-Methano-1H-indene, 3a,4,7,7a-tetrahydro-	7.843	4.0
392-71-2	2,6-Dichloro-4-fluorophenol	8.170	5.8
21031-46-9	3-Butenenitrile, 3-chloro-	8.205	5.6
10025-67-9	Sulfur monochloride	9.674	9.3

We observed the following features for these TICS.

a. All of the houses tested showed these same unidentified peaks with the exception of one house that had low chlorine residual in field measurements. That house did not have any of the TICs
b. The TICs were processed against several different libraries that were available to the team and they generally produced the same identifications.
c. None of the TICs found in the house samples were observed in our analysis of the crude MCHM, supplied by Dr. Michael McGuire from samples obtained from the West Virginia National Guard from the material in the Freedom spill.
d. The TICs are really only presumptive positive detections, so to accurately designate the identity of a compound would require that an analytical grade standard of the presumptive compound be obtained and analyzed under the conditions of the GC/MS analysis. Only if the chromatographic retention time and the mass spectral ion fragmentation matched would chemists be able to positively identify the compound.
e. The TIC at 3.5 minutes, 2,3-dichloro-2-methylbutane, has been proposed to be a by-product of reactions between plastic pipes and chlorine by others[2] and therefore is likely not related to the crude MCHM.
f. At least two of the TIC peaks appeared to be deuterated chlorophenols, that is chlorophenols containing a different form of hydrogen, such as was found in the surrogates that are added by chemists as part of the sample preparation process for analysis.
g. The peak at 9.674 minutes, identified by the library search as sulfur monochloride, actually matched well with that of 2,4,6-trichlorophenol-d2, even though the library search database was not able to distinguish this compound.

The observation that two of the TICs appeared to be deuterated compounds was a concern. There was not an obvious scenario under which we would have expected to have detected deuterated compounds at the estimated concentrations listed. We subsequently confirmed the identities of the peak at 5.74 minutes (o-chlorophenol-d4) and the one at 9.674 minutes (2,4,6-trichlorophenol-d2) by obtaining standards of these compounds and matching retention times and spectra.

The only obvious source of deuterated compounds was from the surrogate standard mix mentioned previously. Since these two TICs were identified as phenolic type compounds and phenol-d6 and 2-fluorophenol are both phenolic type surrogates, we suspected these might be the source.

An experiment was performed to determine if these compounds, the deuterated ones in particular, were the result of a reaction with the surrogate compounds listed. To evaluate if this reaction was the cause, a sample of water from ones of the houses was spiked with surrogate compounds and extracted/analyzed under the normal set of analytical conditions. A second aliquot of water from the same house was not spiked with the surrogates and then extracted and analyzed.

The chromatograms are shown in Figures 4 and 5. Figure 4 shows the house sample that had the surrogate standard mix added prior to extraction. The chromatogram shows the surrogate standards and internal standards (all labeled) and the tentatively identified compound pattern that has been described previously. Figure 5 shows the internal standards (labeled), no surrogates (not added) and virtually all of the tentatively identified compounds are missing. The large peak at 3.3 minutes and the pipe reaction product at 3.5 minutes remain. Therefore, it appeared that the presence of the TICs was in fact a reaction between two of the surrogate standard compounds, phenol-d6 and 2-fluorophenol, and residual chlorine in the water. This was based on the tentatively identified compound names, which were in most cases some version of a chlorinated phenol.

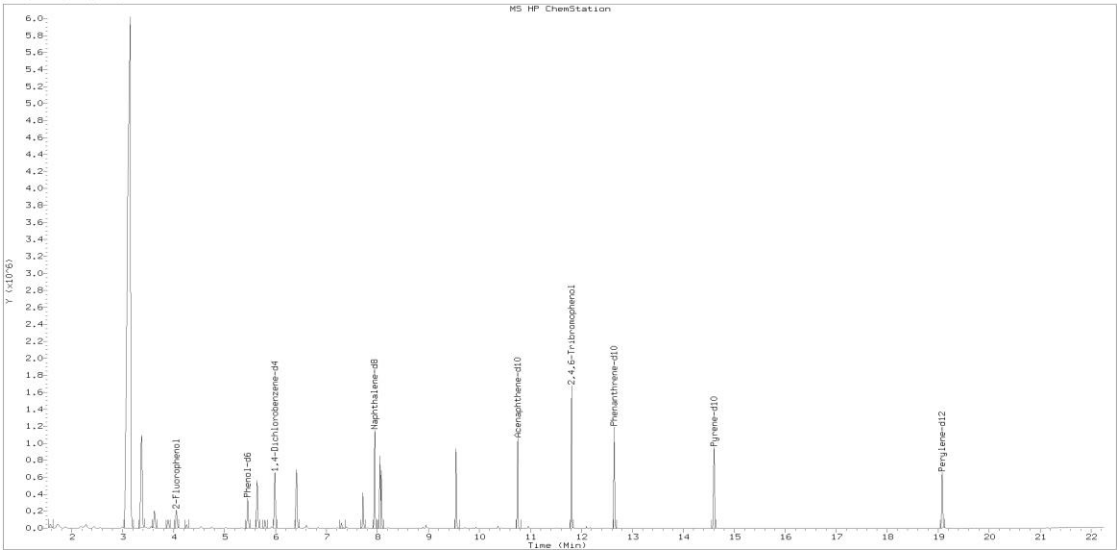

Figure 4: Chromatogram with surrogate standards added. Peaks with names are surrogates and internal standards.

This hypothesis was also consistent with the observation that these peaks were not present in the one house sample that had very low residual chlorine in the field testing. These peaks therefore are considered artifacts of the analytical process and are in no way related to the MCHM spill.

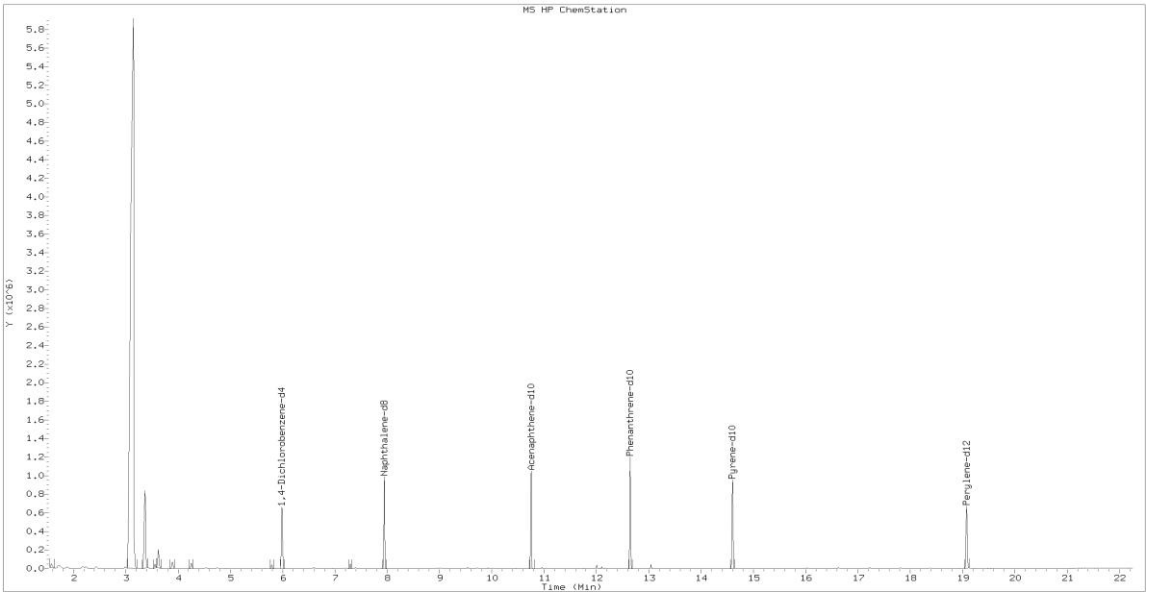

Figure 5: Chromatogram with surrogate standards not added. Peaks with names are internal standards.

To further validate this conclusion, two additional aliquots of water from one of the houses were obtained. One aliquot was dechlorinated with sodium sulfite and the other was not. Both aliquots had surrogate standards added to them prior to being extracted and analyzed by the 4-MCHM method. The chlorinated water displayed the TICs that had been observed in all of the 10 Home Study samples. The dechlorinated water (Figure 6) did not show any of the TICs. In fact, the dechlorinated water also did not exhibit the large peak at 3.3 minutes.

We also verified that the TICs were not related to the MCHM by taking an aliquot of Lancaster PA tap water, adding additional chlorine, and extracting and analyzing it using the method described here, including all of the surrogates. No 4-MCHM was detected, but the same tentatively identified compounds were observed. A second aliquot was dechlorinated and extracted. No tentatively identified compound peaks were observed.

Prior to the experiment with water dechlorination, efforts were undertaken to determine the identity of the large tentatively identified compound observed at approximately 3.3 minutes in all of the samples from the 10 Home Study. The presumptive identification of this peak when compared to several libraries consistently was identified as 1,1-dimethyl-3-chloropropanol. The analytical grade reference material was acquired and analyzed under the set of GC/MS conditions used for the analysis of 4-MCHM. The mass spectral

match was relatively good with that observed for the TIC, however, the retention time of the 1,1-dimethyl-3-chloropropanol was approximately 2 minutes later than that observed for the large tentatively identified compound, indicating that it could not be the compound identified in the library search. To further confirm that this was not some form of retention time shift, the extract of the house sample was spiked with the reference material and it showed as a clear second peak on the chromatograms.

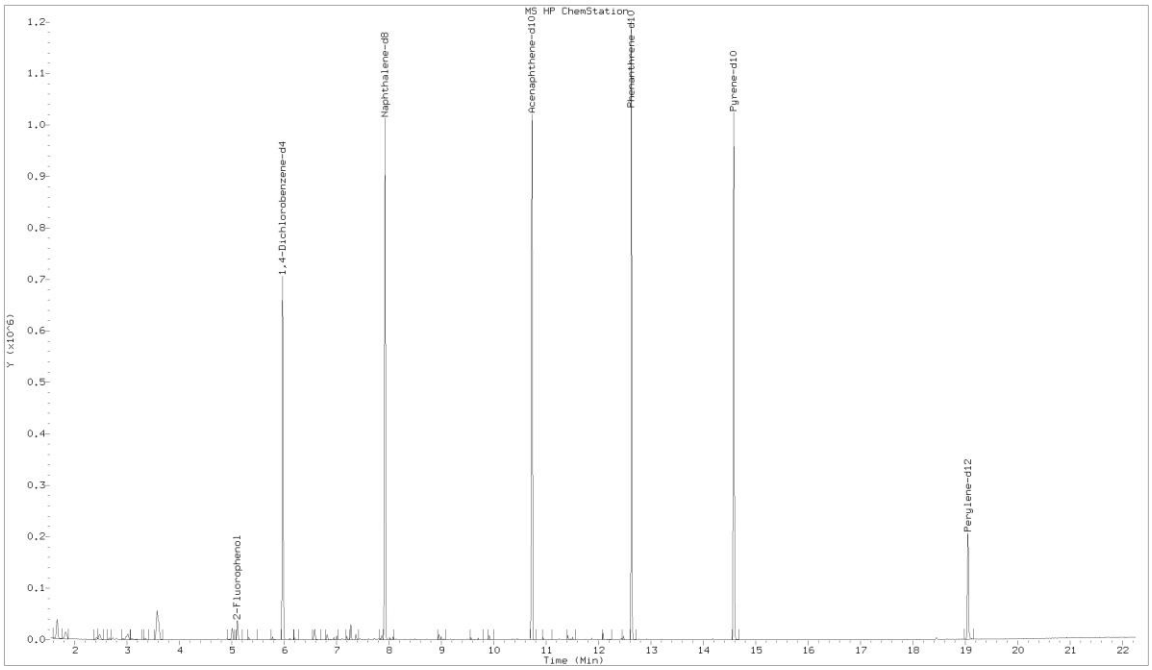

Figure 6: Dechlorinated house water – sodium sulfite added Peaks with names are internal standards.

This prompted an investigation as to whether or not there was something else in the water, unrelated to the crude MCHM which could be the source of the peak. To follow this line of reasoning, four (4) additional samples were collected upstream of the Freedom Industries spill site, at the West Virginia American Water (WVAW) facility influent, at the WVAW effluent, and from a house. An aliquot of water from each of these four sampling points was extracted and analyzed by the 4-MCHM analytical procedure. Neither 4-MCHM nor the large TIC at 3.3 minutes were detected in the upstream or influent sample, but both were detected in the effluent sample and the house sample. When this information was considered along with the results of the surrogate standard/chlorination work, it was postulated that the large TIC at 3.3 minutes was likely some sort of disinfection by-product.

A review of literature on disinfection by-products uncovered an article in the International Journal of Spectroscopy, by Karl J. Jobst and Johan K. Terlouw from

McMaster University in Ontario, Canada (1). In this article the authors identified some "disinfection" by-products that are actually the result of the reaction of chlorine in water samples with preservatives used in the manufacture of the methylene chloride which is used as part of the analytical method for extracting these water samples. The spectra and relative retention time information provided in the article matched what we observed in the 10 Home Study samples very well. We confirmed that the preservative suspected of reacting with the chlorine in the water, 2-methyl-2-butene, is in fact the stabilizer used in the methylene chloride used for analysis of samples in the 10 Home Study. Therefore, we would expect that if the water is dechlorinated prior to extraction, the large TIC at 3.3 minutes would not be present. That was confirmed in the dechlorination work mentioned previously.

We also examined chromatograms from the second laboratory participating in the 10 Home Study and saw that the large peak was also present in their chromatograms along with some of the other TICs we identified. This was initially a cause for concern as the lab reported that their sample bottles contained sodium thiosulfate, a dechlorinating agent, and we would therefore have expected to see no peaks that were related to chlorine. However upon query of the laboratory we determined that the amount of thiosulfate that was added to their bottles was 10 mg/l, which is well below the level normally used for dechlorination of drinking water samples (40-80 mg/l) for analysis of semivolatile compounds. The lab also reported low recoveries of some of their surrogates, which is consistent with reaction with chlorine. Thus we were confident that there was no inconsistency in TIC results between there chromatograms and ours.

Conclusion

Numerous tentatively identified compounds observed in the samples analyzed in the WVTAP 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.

There is no evidence presented here or in the course of the analysis of the 10 home study water samples, that would indicate that during mid-February, more than 1 month after the spill, the crude MCHM contributed to the creation or presence of the observed tentatively identified compounds. Our conclusions are that there were no breakdown compounds related to the MCHM spill that could be measured when these samples were collected, at the detection levels attained in this study (which were very low).

Additionally there is no evidence that the presence of chlorine in the samples interferes with the analysis of 4-MCHM or PPH. However, future sampling should include adequate amounts of dechlorinating agents to minimize the occurrence of tentatively identified compounds that are the result of reactions with chlorine.

References

(1) K. Jobst, V. Taguchi, R. Bowen, M. Trikoupis and J. Terlouw, "Identification of Halohydrins as Potential Disinfection By-Products in Treated Drinking Water," *International Journal of Spectroscopy*, Volume 2011, Article ID 949745.

(2) S.M. Mitroka, T.D. Smiley, J.M. Tanko, A.M. Dietrich. 2013. Reaction mechanism for oxidation and degradation of high density polyethylene in chlorinated water. *Polymer Degradation and Stability*, Volume 98, Issue 7, Pages 1369-1377

(3) K. West, Estimation of 4-MCHM Solvation Phenomena using COSMO-RS. "Personal Communication." Chemical Engineering Department, University of South Alabama, Mobile, AL USA.

(4) California Air Resources Board, Draft Interim Reference Exposure Level (REL), March 2010.

Appendix D. Oxidation Studies with Crude 4 methylcyclohexanemethanol in Water

Michael J. McGuire, Inc.
Santa Monica, CA 90402

WV TAP
WEST VIRGINIA TESTING ASSESSMENT PROJECT
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TECHNICAL MEMORANDUM

May 22, 2014

To: Jeffrey Rosen, Corona Environmental Consulting

From: Michael J. McGuire, PhD, PE
mike@michaeljmcguire.com; 310-560-0257

Subject: Oxidation Studies with Crude 4-methylcyclohexanemethanol in Water

EXECUTIVE SUMMARY

On January 9, 2014, "Crude" 4-methylcyclohexanemethanol (MCHM) spilled into the Elk River in West Virginia, which contaminated the water supply treated by West Virginia American Water and resulted in licorice odor complaints by residents. A Screening-level evaluation of Crude 4-methylcyclohexanemethanol (MCHM) was conducted using free chlorine and potassium permanganate (KMnO4).

Ten parts per billion 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 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 KMnO4 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. The 1.3 mg/L of KMnO4 appeared to reduce the MCHM concentration by approximately 20 percent. However, the 4.0 dose did not reduce the MCHM concentration. It is not clear if KMnO4 really oxidizes MCHM.

A trained panel conducted the flavor profile analysis of the oxidized, spiked samples. No difference in the odor characteristic or intensity was detected with chlorine oxidation. KMnO4 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.

A screening level evaluation of MCHM oxidation indicated that there was a possible minimal effect of KMnO4 oxidation of the compound and there was no effect with chlorine. More work is needed to confirm these findings.

INTRODUCTION

On January 9, 2014, approximately 10,000 gallons of "Crude" 4-methylcyclohexane-methanol (MCHM) spilled into the Elk River from the property of Freedom Industries a short distance above the drinking water intake of the West Virginia American Water (WVAW) water treatment plant. Shortly after the spill began, consumers located in the area served by WVAW (Charleston, WV and environs) began complaining of a licorice odor in their drinking water. Free chlorine and potassium permanganate (KMnO4) were used in the Kanawha Valley Water Treatment Plant (KVWTP) and had the potential to oxidize MCHM. The objectives of this task were to evaluate the potential for free chlorine and KMnO4 to oxidize MCHM and potentially change the odor characteristics and intensity of the compound.

KANAWHA VALLEY WATER TREATMENT PLANT

West Virginia American Water (WVAW) operates the Kanawha Water Treatment Plant (KVWTP) which is a conventional filtration facility that serves about 300,000 people. Figure 1 is a schematic of the treatment processes used in the plant. Figure 2 is a photo taken on February 24, 2014, of a computer screen that is part of the SCADA system showing the treatment processes at the treatment plant.

Turbidity removal is accomplished using the coagulant polyaluminum chloride and a polymer called Superfloc. Chemicals are combined with water in a mixing unit process followed by flocculation and solids removal in four sludge blanket clarifiers. The powdered activated carbon (PAC) used in the plant had a high residence time in the sludge blanket, which probably enhanced its effectiveness. At some point, the PAC was reported to remove 85 percent of the influent MCHM, but it is not clear under what circumstances that removal occurred.[1]

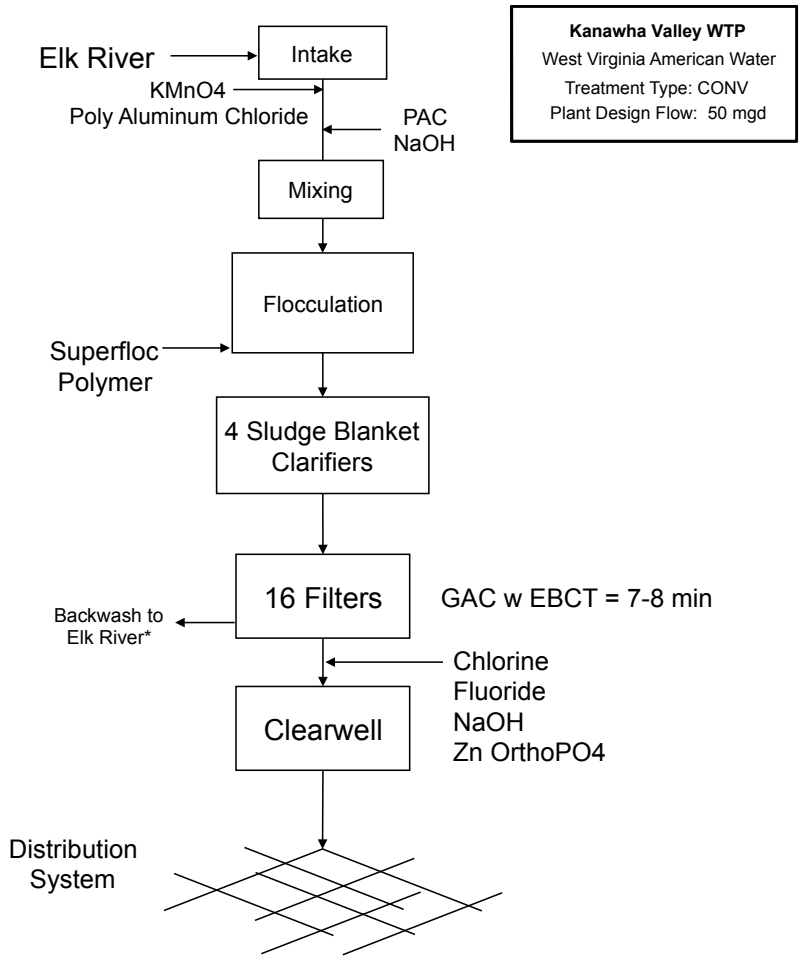
The treatment plant has 16 granular activated carbon (GAC, Calgon 8x30) filters with a reported empty bed contact time (EBCT) of 7 to 8 minutes and a depth of 36 inches. The filters are on a four-year regeneration/replacement cycle. Each year, one-quarter of the 16 GAC beds were taken out of service and the GAC was replaced.[2]

Backwash water from the GAC filters is usually settled and then recycled to the beginning of the treatment plant. However, during the MCHM contamination event, WVAW obtained permission from the West Virginia Department of Environmental Protection to discharge the filter backwash water into the Elk River so that they the odorous compound would not be recycled back into the treatment plant.

KMnO4 is added at the intake structure and is in contact with the water as the water is transported by pipeline until PAC (Watercarb 800) is added right before the mixing unit process. PAC reacts with KMnO4 and will remove any residual oxidant. If PAC is not being used, the GAC filters would remove any residual KMnO4. Figure 3 shows the doses of KMnO4 at the KVWTP during January. The graph shows that immediately after the discovery of the licorice odor, the KMnO4 does was raised from the usual dosage of

0.6 mg/L to 1.2 to 1.3 mg/L for two days. After these two days, the dosage was dropped back to about 0.6 mg/L. Mark LeChevallier of American Water provided all of the chemical addition data for this report.[3]

PAC was added in the treatment plant beginning on January 9, which was the same day the licorice odor was detected in the air around the Elk River and the same day that Freedom Industries was confirmed as the source of the chemical spill.[4] Figure 4 shows that the PAC dose was ramped up to 19 mg/L after which it was reduced over a two-week period to a continuing dose of 0.7 mg/L.



*Backwash water is normally settled and recycled to the head of the plant; river discharge temporary after spill event

Figure 1. Schematic of KVWTP Treatment Processes

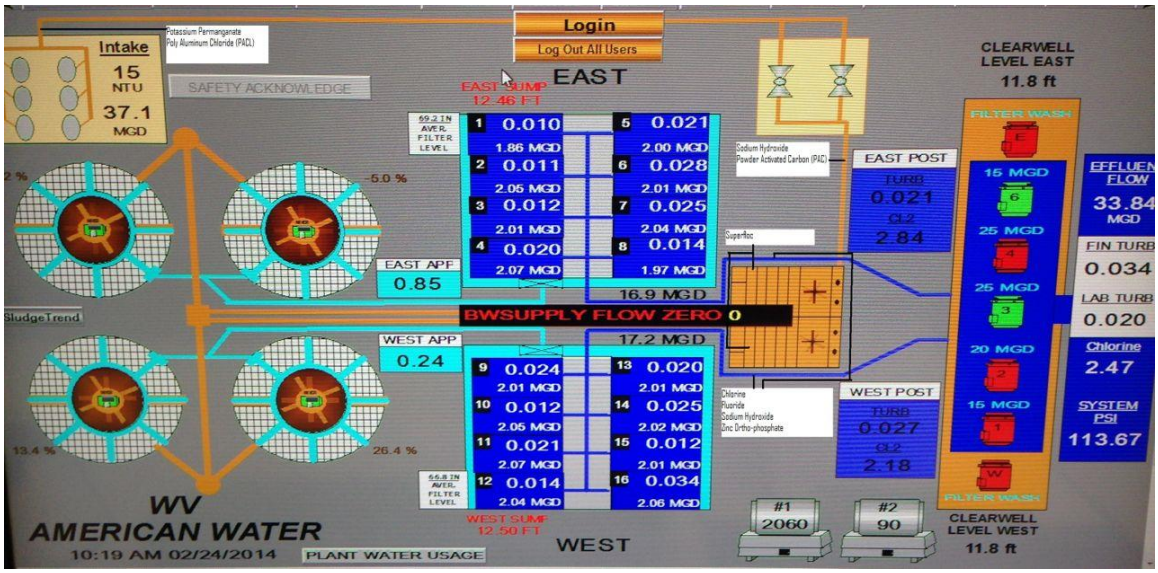


Figure 2. SCADA Screen Capture Showing Treatment Processes

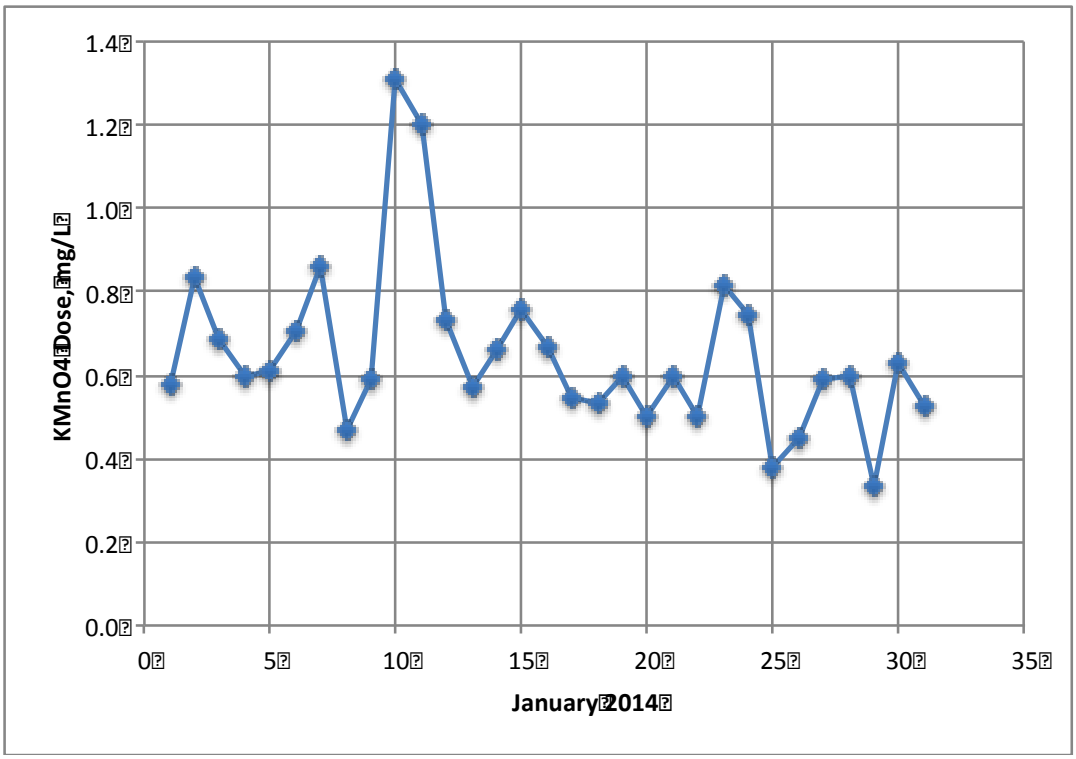


Figure 3. Potassium Permanganate Doses in the KVWTP During January 2014

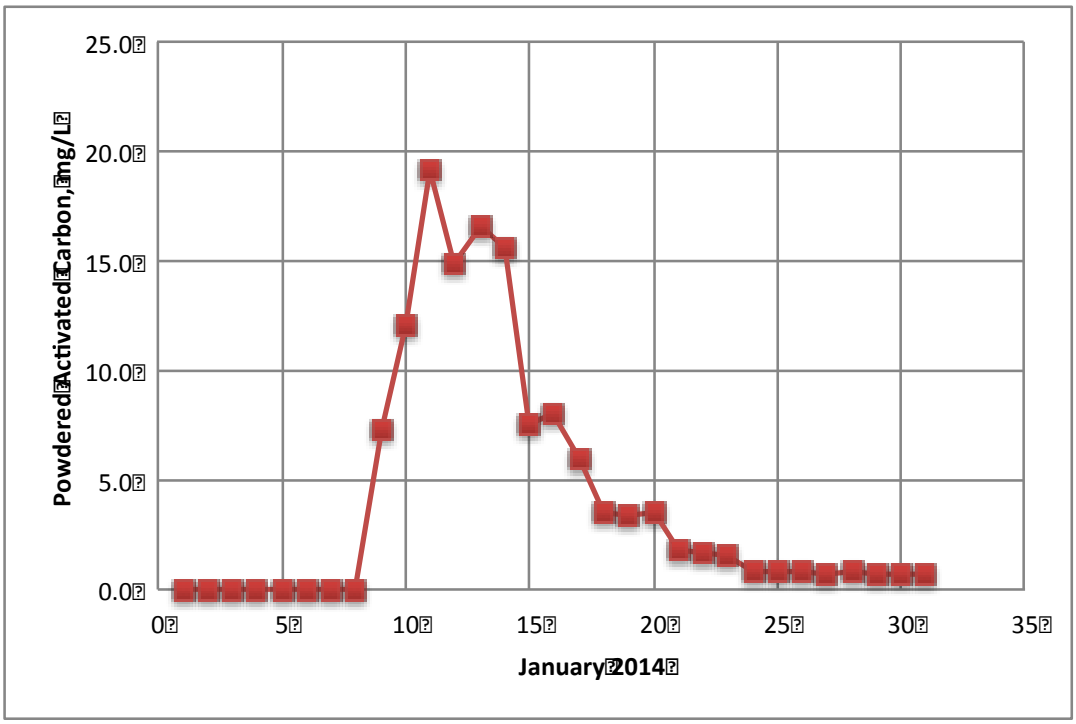


Figure 4. Powdered Activated Carbon Doses in the KVWTP During January 2014

Chlorine is added at two locations in the plant. A small prechlorination dose is added at an unknown location upstream of the GAC filters. The large dose of chlorine is added after the GAC filters to provide primary disinfection and to provide a secondary disinfectant in the distribution system. Figure 5 shows the chlorine doses used during January 2014 at the KVWTP.

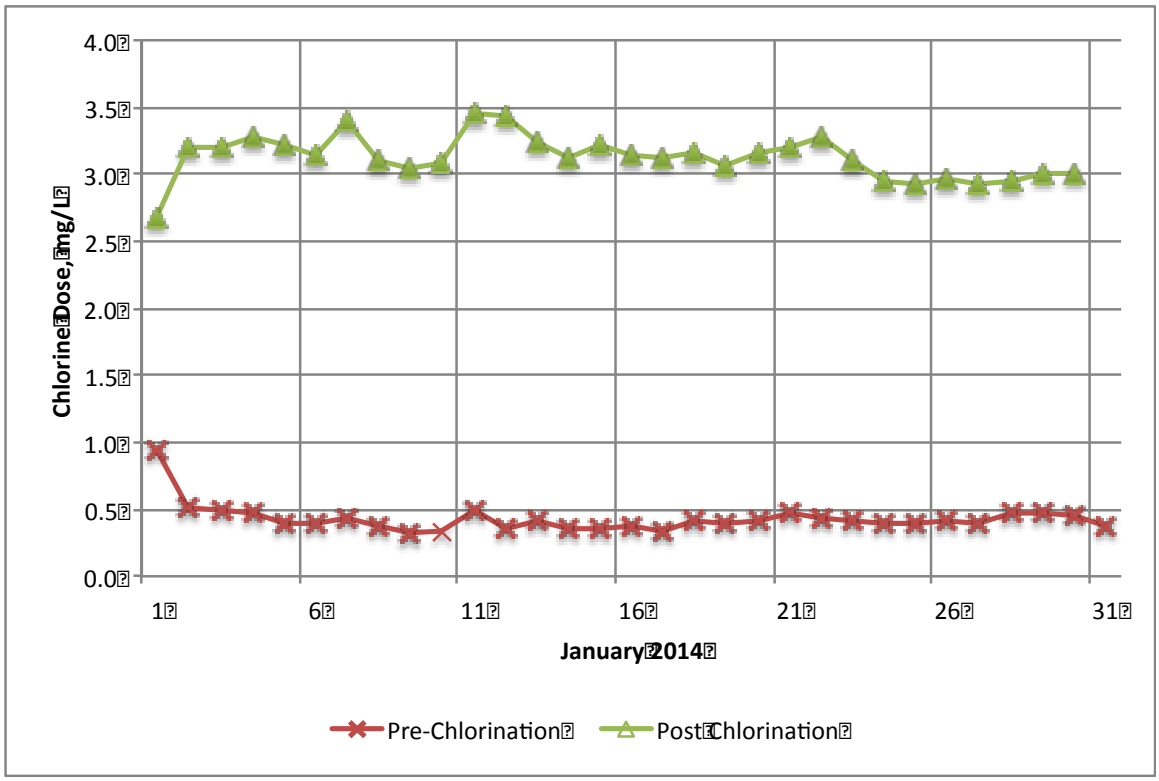


Figure 5. Free Chlorine Doses in the KVWTP During January 2014

The filtered water chlorine dose averaged 3.1 mg/L during January 2014. Chlorine residuals as high as 2.9 mg/L were measured in homes during the intensive 10-home sampling conducted February 13-18, 2014.

Figure 6 shows the MCHM concentration in the raw and treated water for the KVWTP during the six days after the chemical spill in January 2014. The maximum concentration of MCHM measured in raw or treated water was approximately 3.4 mg/L. Data plotted after January 13 are mostly reported as non-detect. Method reporting limits (MRLs) during this period varied widely resulting in confusion with the public about whether MCHM was present or not. Despite the use of KMnO4, PAC and GAC filters, it appears that during the first few days after the spill, MCHM in the raw water overwhelmed all of the removal processes and moved through the treatment plant without much change in its concentration.

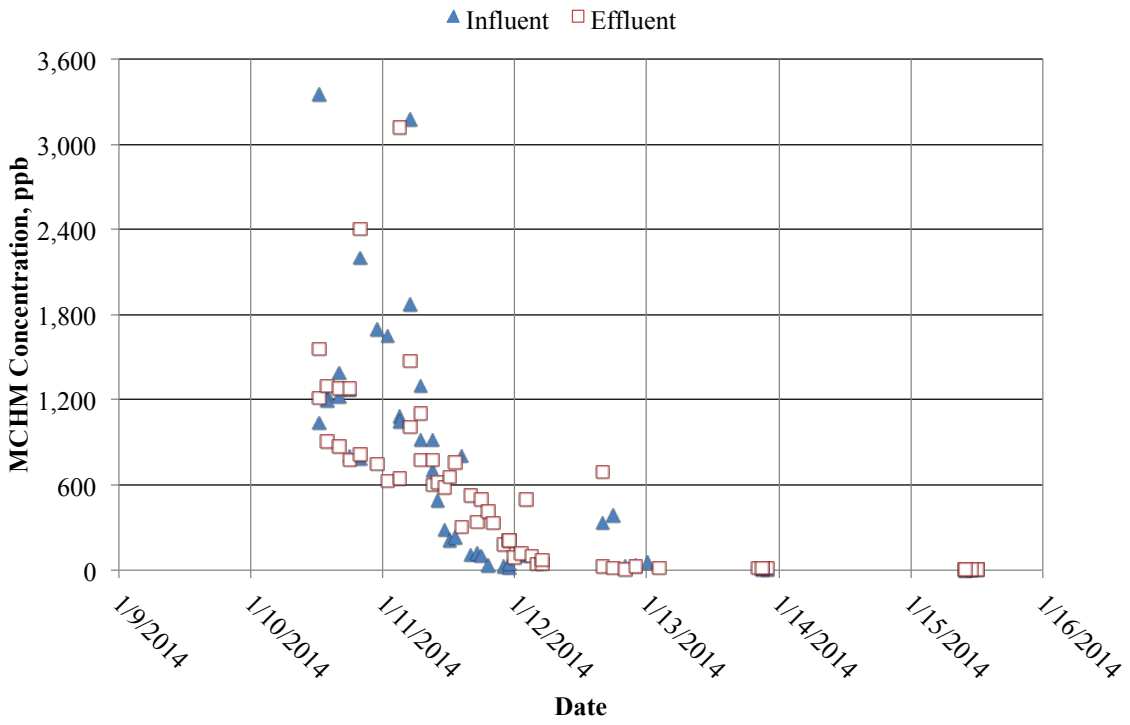


Figure 6. MCHM Concentrations in the KVWTP Influent and Effluent (Data Source: West Virginia Division of Homeland Security and Emergency Management)[5]

OXIDATION METHODOLOGY

Matrix Water

Arrowhead spring water was chosen as the matrix water for this study. Table 1 shows the inorganic quality of Arrowhead spring water compared to a sample of water taken from the WVAW water treatment plant on March 11, 2014. While the total dissolved solids concentration of Arrowhead spring water is higher that that from the treatment plant effluent, neither water is highly mineralized. Total organic carbon (TOC) concentrations in the Elk River have been reported to be about 1 mg/L. Concentrations of TOC in samples from the 10 house study ranged from 0.8 to 0.9 mg/L.[6] Such a low TOC is the only reason that WVAW is able to use high doses of free chlorine without producing concentrations of disinfection byproducts such as trihalomethanes that exceed state and federal standards.

Table 1. Inorganic Water Quality of Arrowhead Spring Water and a Water Sample from the WVAW Treatment Plant

Parameter	Units	WVAW Treatment Plant Effluent, March 11, 2014	Arrowhead Spring Water
pH	Std. Units	7.3	7.9
Total Dissolved Solids	mg/l	73	228
Specific Conductance	µmhos/cm	157	453
Calcium	mg/l	12	50
Magnesium	mg/l	6	20
Potassium	mg/l	1.3	3.2
Sodium	mg/l	8	18
Chloride	mg/l	9	7
Nitrate-Nitrogen	mg/l	0.52	0.85
Sulfate	mg/l	34	23
Total Alkalinity	mg/l as $CaCO_3$	16	195

Preparation of Spiked Samples and Determination of Crude MCHM Concentrations

The Eurofins laboratory in Lancaster, PA prepared the spiked samples of Crude MCHM used for the oxidation experiments. Eurofins is using an MCHM analytical method with a method detection level (MDL) of 0.5 ppb and a method reporting level (MRL) of 1.0 ppb—the lowest MCHM concentrations currently being determined by any laboratory in the U.S. Concentrations in the spiked samples were based on spiking 100% crude MCHM. The laboratory measured total peak area for the *trans* and *cis* isomers of MCHM and used this marker to determine the recovery of spiked concentrations in water.

The following is a summary of the Eurofins MCHM analytical method: A water sample is serially extracted with methylene chloride. The resulting extract is reduced in volume and an aliquot injected into a gas chromatograph equipped with a mass spectrometer detector (GC/MS). The GC/MS analytical system is tuned and calibrated following the principles outlined in SW-846, Method 8270D. This includes tuning the system to decafluorotriphenylphosphine (DFTPP) relative mass abundance criteria and calibration using a minimum of five calibration points from 1 ppb to 60 ppb. The analytical system is tuned and the calibration responses are checked every 12 hours.

As a routine part of the extraction procedure, a method blank, a laboratory control sample (LCS) and an MRL LCS are extracted along with every group of field samples that are analyzed. A method blank that is free of target compounds and an LCS and MRL LCS with acceptable recoveries of the target compounds is required for an extraction batch to be considered acceptable.

Oxidation Procedures

Spiked samples containing 10 ppb of Crude MCHM were treated with oxidants according to the matrix shown on Table 2. In addition process blanks were created and subjected to MCHM analysis and FPA evaluation. All of the oxidation treatments and blank manipulations were conducted at Eurofins.

Table 2. Oxidation Treatment Matrix Including Method Blanks

Sample No.	Description	Crude MCHM Spike, ppb	Oxidant Dose, mg/L	Hold Time	Other Actions
1	Blank Blank	0	0	3 days	None
2	Chlorine 1 day	10	3.5 Cl2	1 day	Dechlor w Na2SO3
3	Chlorine 3 day	10	3.5 Cl2	3 days	Dechlor w Na2SO3
4	Dechlor Blank	0	0	3 days	Same dechlor dose w Na2SO3
5	KMnO4 1.3 mg/L	10	1.3 KMnO4	3 hours	Remove KMnO4 w Na2SO3; filter 0.45 µm
6	Filter Blank	0	0	3 hours	Same dose to reduce KMnO4 w Na2SO3; filter 0.45 µm
7	Untreated Spike	10	0	0	None
8	KMnO4 4.0 mg/L	10	4.0 KMnO4	3 hours	Remove KMnO4 w Na2SO3; filter 0.45 µm
9	Filtration Treatment	10	0	0	Filter through 0.45 µm

Matrix water – Arrowhead Spring Water

Sodium hypochlorite was used as the chlorine source. The dose required for 3.5 mg/L was tested on MilliQ laboratory grade water before being used on the MCHM spiked samples. A stock solution of 1,730 mg/L was created using reagent grade KMnO4. Dosages were made to the spiked samples using the stock solution. A 15,750 mg/L solution of sodium sulfite was used to dechlorinate the chlorinated samples and reduce any active KMnO4 after the 3 hour contact time. After sodium sulfite reduction, KMnO4-treated solutions were filtered through a 0.45 um filter before being analyzed or shipped to UCLA for FPA analysis.

All oxidation experiments were conducted at room temperature. The pH of the chlorine treated solutions was 7.7 and the pH values of the KMnO4 treated solutions (1.3 and 4.0 mg/L) were 7.8 and 7.9, respectively.

One liter of each of the treated spiked samples and blanks were shipped to UCLA. Flavor profile analysis (FPA) panels evaluated the treated spiked samples and blanks during two panel sessions held on March 24 and April 8, 2014.

Flavor Profile Analysis Method

The FPA method was developed by the consulting firm Arthur D. Little in 1948.[7] The method is widely used in the food and beverage industries. In the early 1980s, the method was adapted to drinking water odor and flavor analysis at the Metropolitan Water District of Southern California.[8] Since then, hundreds of drinking water FPA panels have become operational around the world.

The FPA method is based on using panelists that are specifically trained using the procedure. Intensive training is followed by months of participation in panels with other experts. Each panelist develops a standard odor and taste vocabulary using specific chemicals that are responsible for causing odors in drinking water (e.g., geosmin and 2-methylisoborneol for earthy and earthy/musty odors). In addition, panelists are trained in the basic tastes (i.e., sweet, salt, sour, bitter) and they are calibrated to quantify odors and flavors using known concentrations of sucrose. A quantification scale of 0 to 12 is used in even steps with a "T" denoting detection of an odor or taste at threshold.

A panel session relies on the panelists independently determining the odor characteristic and intensity of each sample. After the independent evaluations, the panelists participate in a joint session where they present their individual findings. A panel leader compiles the individual results and determines which odor characteristics were determined by a majority of the panel. The intensity of that consensus odor or taste is calculated as the mathematical average of the individual findings. Any odor or taste characteristics that are not described by a majority of the panel are categorized as "notes" without any quantification. Mouthfeel and nosefeel reactions by the panelists are also recorded.

Samples were presented to the panelists in blind-coded cups. Three ounces of spiked samples or blanks were poured into nine ounce odor-free plastic cups. A watch glass was placed on top of each cup. The panelists were instructed to swirl the sample cup with the watch glass on top, lift the watch glass, sniff the odor in the headspace above the spiked water level and record their assessments of the odor characteristics and intensities on a score sheet.

Panelists then took a small sip of the contents of the cup and swirled it around their mouths forcing odors from the sample into the retronasal passage to assess the flavor. They then spit the sample into a container. Blank Arrowhead spring water was provided for the panelists to rinse their palates between samples. Samples 1 through 6 were evaluated by a panel on March 24. Samples 7 through 9 were evaluated by a panel on April 8. In addition, the April 8 panel performed another assessment of samples 5 and 6 that had been retained from the previous testing. The water samples assessed by the FPA panelists had a temperature of about 22 degrees Celsius.

RESULTS AND DISCUSSION

Analytical Results of Spiked Samples

Table 3 shows the analytical results for the spiked samples. The samples dosed with chlorine showed no decrease in MCHM concentration. The sample dosed with 1.3 mg/L of KMnO4 showed a possible 20 percent decrease in the MCHM concentration. However, the 4.0 mg/L dose of KMnO4 did not show a decrease in the MCHM concentration. Additional work will have to be done to determine if MCHM is susceptible to oxidation by KMnO4.

Table 3. Analytical Results from the Oxidation Study

Sample No.	Description	Crude MCHM, ppb	Percent Remaining After Oxidation
1	Blank Blank	ND	---
2	Chlorine 1 day	9.8	98%
3	Chlorine 3 day	9.6	96%
4	Dechlor Blank	ND	---
5	KMnO4 1.3 mg/L	8.0	80%
6	Filter Blank	ND	---
7	Untreated Spike	10.0	100%
8	KMnO4 4.0 mg/L	10.3	102%
9	Filtration Treatment	10.3	102%

Table 4 shows the relative peak areas for the *cis* and *trans* isomers of MCHM. The ratios of the *cis* and *trans* isomers of MCHM do not appear to be different for any of the oxidized samples. Neither isomer appeared to be preferentially oxidized or changed in concentration.

Table 4. Relative *Cis* and *Trans* Isomer Concentrations in Oxidized Samples

		MCHM Isomer Concentration, ppb			Ratio of Cis
Sample No.	Description	Trans 4-MCHM	CIS 4-MCHM	Total 4-MCHM	to Trans
2	Chlorine 1 day	5.0	2.8	7.8	0.56
3	Chlorine 3 day	4.9	2.8	7.7	0.57
5	KMnO4 1.3 mg/L	4.0	2.4	6.4	0.60
7	Untreated Spike	5.2	2.9	8.1	0.56
8	KMnO4 4.0 mg/L	5.3	2.9	8.2	0.55
9	Filtration Treatment	5.2	3.0	8.2	0.58

FPA Results of Spiked Samples and Blanks

Table 5 shows the FPA panel results. Comparing the results for samples 2 and 3 with sample 7, chlorine treatment of 3.5 mg/L over one and three days did not change or reduce the characteristic or intensity of the licorice odor. Comparing the results for sample 5 with 7 appears to indicate that there was an approximate 25 to 50 percent decrease in the licorice odor intensity. However, the result for sample 8, which was treated with 4.0 mg/L of KMnO4, was not different from the control (sample 7) indicating that KMnO4 did not oxidize the compounds causing the licorice odor.

As noted in the methods section, samples 5 and 6 were also presented to the second panel on April 8. Table 5 shows that the FPA results for the re-assessment of the 1.3 mg/L dose sample were inconsistent between the two FPA panels. It appears that the MCHM either degraded in or volatilized out of the one liter bottle in which it was stored for about 19 days.

Table 5. Oxidation Study Results from the FPA Panel

Sample No.	Description	Odor Characteristics and Intensities	Odor Characteristics and Intensities
1	Blank Blank	**Odor Free** Notes: turpentine, solvent, burnt, sweet	**Flavor Free** Notes: drying, plastic, salty, bitter
2	Chlorine 1 day	**Licorice 4** Notes: plastic, chemical	**Licorice 4** Notes: plastic, bitter, drying
3	Chlorine 3 day	**Licorice 4** Notes: plastic, sweet, fruity	**Licorice 4** Notes: plastic, bitter, fruity, sweet, oily mouth feel
4	Dechlor Blank	**Odor Free** Notes: anise, sweet	**Flavor Free** Notes: drying, salty
5	KMnO4 1.3 mg/L	**Licorice 3** Notes: plastic, paint, sweet, chemical, fruity	**Licorice 2** Notes: plastic, bitter, fruity, sweet, oily mouth feel
6	Filter Blank	**Odor Free** Notes: turpentine, sweet, fruity	**Flavor Free** Notes: drying, bitter
7	Untreated Spike	**Licorice 4** Notes: sweet, fruity, juicy fruit	**Licorice 4** Notes: chalky, bitter, juicy fruit
8	KMnO4 4.0 mg/L	**Licorice 4** Notes: sweet chemical, juicy fruit	**Licorice 4** Notes: juicy fruit
9	Filtration Treatment	**Licorice 4** Notes: sweet chemical, sweet, bile, turpentine, juicy fruit	**Licorice 4** Notes: juicy fruit
5	Repeat: KMnO4 1.3 mg/L	**Odor Free** Notes: licorice, sweet, fruity	**Flavor Free** Notes: licorice, chalky, drying
6	Repeat: Filter Blank	**Odor Free** Notes: musty	**Flavor Free** Notes: drying, chalky

Chlorine residuals were determined at UCLA prior to the FPA analysis on March 24 using a Hach DPD field kit. No chlorine residual was measured for sample 2 (Chlorine 1 day). However, for sample 3 (Chlorine 3 day), a 0.23 mg/L free chlorine residual was measured indicating that the dechlorination step by Eurofins was not complete. Interestingly, the FPA panel did not detect a chlorine odor or flavor in that sample. The odor and flavor thresholds for free chlorine were determined by Krasner and Barrett to be 0.24 to 0.36 mg/L.[9] Therefore, the MCHM concentration that was above the OTC, ORC and OOC determined by both the expert and consumer panels appeared to mask the chlorine concentration that was just at its OTC.

More work is needed to determine if KMnO4 will significantly oxidize MCHM and produce oxidation byproducts. Further experiments with higher concentrations of Crude MCHM and KMnO4 would be needed to produce potential byproducts at sufficient concentrations that could be identified using the existing analytical methodology.

Limitations of the Methodology and Results

As with all research, there are limitations associated with this work that must be understood so that errors will not be made extrapolating the results to other applications.

- Only one chlorine dose over two holding periods was tested in this study.
- Only two KMnO4 doses were tested.
- At higher doses, it is possible that these oxidants could have an impact on both the concentration of Crude MCHM and its odor characteristics.

Applicability of Oxidation Results to What Transpired at the KVWTP During January 2014

These preliminary evaluations of MCHM oxidation indicate that there was minimal, if any, effect of KMnO4 oxidation on Crude MCHM and there was no effect with chlorine. Therefore, the only impact of the oxidation processes was a possible slight decrease in the concentration and odor characteristics of MCHM at a 10 ppb concentration. When the concentration of MCHM was at levels of 1 to 3 mg/L during the first few days of the chemical spill, the possible slight impact of KMnO4 oxidation would have had no impact on the MCHM concentration delivered to the distribution system. Also, it does not appear that oxidation with KMnO4 changed the odor characteristic of MCHM.

A separate study at the University of California, Los Angeles (UCLA) investigated the oxidation of Crude MCHM with similar concentrations of chlorine and potassium permanganate. Using a different analytical method, the UCLA study found no changes in the MCHM concentration after contact with the oxidants.[10]

SUMMARY AND CONCLUSIONS

Based on the assessments in this report, the following points can be concluded:

1. Free chlorine did not appear to cause any reduction of the MCHM. The 1.3 mg/L of KMnO4 appeared to reduce the MCHM concentration by approximately 20 percent. However, the 4.0 dose did not significantly reduce the MCHM concentration.
2. A trained panel conducted the FPA of the oxidized, spiked samples. No difference in the odor characteristic or intensity was detected with chlorine oxidation. KMnO4 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.
3. It does not appear that oxidation with free chlorine and KMnO4 changed the concentration or odor characteristic of MCHM at doses consistent with those used by WVAW at the KVWTP.

RECOMMENDATIONS

As a result of the findings from this study, the following actions are recommended:

1. Conduct more intensive oxidation studies at higher concentrations of Crude MCHM with KMnO4 to determine the kinetics of the reaction.
2. Further experiments with higher concentrations of Crude MCHM and KMnO4 are needed to produce potential byproducts at sufficient concentrations that could be identified using the existing analytical methodology.

ACKNOWLEDGMENTS

Thanks are due to the West Virginia Army National Guard for acquiring the samples of Crude MCHM used in this study. Andy Eaton, Duane Luckenbill and Chuck Neslund of Eurofins Laboratory made major contributions to the success of this effort. Many thanks to Mark LeChevallier of American Water for providing the treatment information and chemical dosage data. I am grateful to the FPA panelists for their attention and diligence in examining these samples.

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Appendix E. Report of Expert Panel Review of Screening Levels for Exposure to Chemicals from the January 2014 Elk River Spill

TERA
TOXICOLOGY EXCELLENCE FOR RISK ASSESSMENT

WV TAP
WEST VIRGINIA TESTING ASSESSMENT PROJECT

Report of Expert Panel Review of Screening Levels for Exposure to Chemicals from the January 2014 Elk River Spill

Expert Panel:
Michael Dourson, Shai Ezra, James Jacobus,
Stephen Roberts, Paul Rumsby

Report Prepared for the Expert Panel by:
Toxicology Excellence for Risk Assessment

May 12, 2014

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NOTE

This report was drafted by scientists of Toxicology Excellence for Risk Assessment (TERA) and then reviewed and finalized by the panel members. The members of the panel served as individuals, representing their own personal scientific opinions. They did not represent their companies, agencies, funding organizations, or other entities with which they are associated. Their opinions should not be construed to represent the opinions of their employers or those with whom they are affiliated.

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

An 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 storage tank. The expert panel and meeting were organized by Toxicology Excellence for Risk Assessment (TERA) under contract to Corona Environmental Consulting for the West Virginia Testing Assessment Project (WV TAP). The panel discussed the initial screening value of 1 ppm (or 1,000 ppb) for 4-methyl-1-cyclohexanemethanol (MCHM), which was developed by the United States (US) Centers for Disease Control and Prevention (CDC) for the State of West Virginia. The panel evaluated the currently available data and developed short-term health advisories for MCHM, propylene glycol phenyl ether (PPH) and dipropylene glycol phenyl ether (DiPPH). They also identified data gaps and made recommendations for additional studies and analyses to reduce uncertainty.

The WV TAP mission is to provide an independent scientific assessment of the spill of crude MCHM into the Elk River and its distribution throughout the nine counties served by West Virginia American Water (WVAW). The project consists of four tasks: (1) an in-depth analysis to determine the odor threshold for MCHM; (2) an initial assessment of the concentration and variability of MCHM at the taps in homes, to be used to design a statistically robust sampling plan for the entire affected area; (3) establishment of an independent panel of experts to evaluate the screening level for MCHM (this expert panel); and, (4) 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. Members of the WV TAP team provided the expert panel with a brief description of their findings to provide context for the panel.

In preparation for the meeting, the expert panel reviewed the available toxicological data in order to discuss 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 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 their screening levels for MCHM and PPH. They 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, however, 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 have been exposed to MCHM through their community water supply and use this water for multiple purposes. People were exposed to the contaminated water through direct ingestion, but also on the skin, and through inhalation. The panel thought that these other routes of exposure should be considered in setting short-term health advisories, to the extent possible.

The panel reviewed the available data on crude and pure MCHM and recognized that there were limited toxicology data for MCHM. They 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- 3 months.

For MCHM, the panel recommended a short-term health advisory of 120 ppb (120 µg/L). This value was recommended for public health use with the 2014 Elk River spill and the subsequent contamination of the local water supply. The advisory is based on the following calculations:

- Use the NOEL of 100 mg/kg-day from the 4 week study of MCHM dated April 3, 1990 by Eastman Kodak (Eastman, 1990).
- Adjust this NOEL to 72 mg/kg-day by multiplying by a factor of 21 days/29 days (0.72) to account for the fact that the rats were only dosed for 5 days per week.
- Divide this adjusted NOEL by a 1000-fold uncertainty factor to estimate a short-term reference dose of 0.07 mg/kg-day (rounded from 0.072); this factor consists of factors of 10 for interspecies adjustment, intraspecies adjustment, and database deficiencies (i.e., missing developmental and reproductive toxicology studies and a second species repeat dose study monitoring systemic toxicity).
- Divide this short-term reference dose by consumption of 0.285 liters of water per kg of body weight per day (US EPA 2011b), representing the 95th percentile of water intake for formula-fed infants (the most exposed population); and then multiply this by 0.5 (Relative Source Contribution, RSC) to allow for other possible sources and routes of exposure, such as dermal and inhalation.
- The resulting short-term health advisory is 120 ppb (rounded to two significant digits).

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. They considered the prenatal developmental toxicity study using gavage administration that was used by the CDC, but also considered two other studies: a 90-day drinking water study in rats and a two-generation

drinking water study in rats. The panel thought that the no effect levels from each of these three studies should be considered as potential points of departure to derive a short-term health advisory. The panel selected the no observed adverse effect level (NOAEL) of 146 mg/kg-day from the 90-day drinking water study (ECHA, 2014a) to be the best estimate of the boundary between effect and no effect when assessing the available studies as a group. Even though this NOAEL of 146 mg/kg-day is greater than the NOAEL of 40 mg/kg-day identified in the developmental toxicology study used by CDC, the panel thought it was the better choice for the point of departure because the combination of experimental no effect level with the appropriate water intake for infants resulted in a lower value upon which to apply the uncertainty factors. As with MCHM, the toxicological data did not provide evidence that a particular life stage was more or less sensitive or susceptible to adverse effects from exposure to PPH than other life stages, and so the panel used the life stage with the greatest water consumption on a per kilogram body weight basis, that is the formula-fed infant.

The panel recommended a short-term health advisory of 880 ppb (880 µg/L) 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.

- Use the NOAEL of 146 mg/kg-day from the 90-day drinking water study (ECHA, 2014a).
- Divide this NOAEL by a 300-fold uncertainty factor to estimate a short-term reference dose of 0.5 mg/kg-day (rounded from 0.487). This factor consisted of multiples of 10 for interspecies adjustment and intraspecies adjustment, and a factor of 3 to account for data deficiencies (i.e., incomplete database, e.g., missing a second repeat dose toxicology study).
- Divide this short-term reference dose of 0.5 mg/kg-day by consumption of 0.285 liters of water per kg of body weight per day, which represented the 95th percentile of water intake for formula-fed infants (the most exposed population); and then multiply this by 0.5 (RSC) to allow for other possible sources and routes of exposure, such as dermal and inhalation. The resulting short-term health advisory for PPH is 880 ppb (rounded to two significant digits).

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 database (UF_D) 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 (260 µ/L) 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.

- Use the NOAEL of 146 mg/kg-day from the 90 day drinking water study of PPH (ECHA, 2014a);
- Divide this NOAEL by a 1000-fold uncertainty factor. This factor consists of multiples of 10 for interspecies adjustment, intraspecies adjustment, and to account for data deficiencies (e.g.,

missing many studies); then divide by consumption of 0.285 liters of water per kg of body weight per day, which represented the 95th percentile of water intake for formula-fed infants (the most exposed population); then multiply this by 0.5 (RSC) to allow for other possible sources and routes of exposure, such as dermal and inhalation.

- The resulting short-term health advisory for DiPPH is 260 ppb (rounded to two significant digits).

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.

Charge Question 4 addressed people using contaminated water for multiple purposes and through multiple routes of exposure. 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. They 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, water plant and 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 long-term health effects study. 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.

5. Determine chemical fate and transport within the treatment plant and water distribution system. The panel recommended 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.

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 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 28-day rodent study and with the appropriate uncertainty factors is appropriate to use for human exposure situations of one day up to approximately 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 concluded that the CDC used traditional methods and reasonable assumptions of the US EPA Health Advisory program to develop their screening levels. This expert panel's conclusions are 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 panel's advisories each have two digits of precision. While guidance is often provided to express these advisories at the level of one significant digit, the panel chose to include two digits to aid in the reader following the calculations and understanding the results.

This meeting report is a summary, not a transcript of the discussions. This 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.

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Report of Expert Panel Review of Screening Levels for Exposure to Chemicals from the January 2014 Elk River Spill

PARTICIPANTS

Expert Panel Members[1]

Michael Dourson, Ph.D., DABT, ATS
Toxicology Excellence for Risk Assessment (TERA)
Shai Ezra, Ph.D.
Mekorot, Israel National Water Company Ltd.
James Jacobus, Ph.D.
Minnesota Department of Health
Stephen Roberts, Ph.D.
University of Florida
Paul Rumsby, Ph.D., ERT
National Centre for Environmental Toxicology at WRc plc

WV TAP Team

Craig Adams, Ph.D.
Utah State University
Michael McGuire, Ph.D., PE
Michael J. McGuire, Inc.
Jeffrey Rosen, M.S.
Corona Environmental Consulting
Andrew Whelton, Ph.D.
University of South Alabama

TERA Staff

Patricia Nance, M.A., M.Ed.
Jacqueline Patterson, M.En.

[1] Affiliations listed for identification purposes only. Panel members served as individuals on this panel, representing their own personal scientific opinions. They did not represent their companies, agencies, funding organizations, or other entities with which they are associated. Their opinions should not be construed to represent the opinions of their employers or those with whom they are affiliated.

INTRODUCTION

This meeting of an independent expert peer review panel has been organized by Toxicology Excellence for Risk Assessment (TERA*)*. TERA is an independent non-profit organization whose mission is to support the protection of public health by developing, reviewing, and communicating risk assessment values and analyses, improving risk methods through research, and educating risk assessors and managers and the public on risk assessment issues. TERA has organized and conducted peer reviews for private and government sponsors since 1996 (see http://www.tera.org/Peer/index.html for information about TERA's program). TERA organized and conducted this expert review under contract to Corona Environmental Consulting for the West Virginia Testing Assessment Project (WV TAP).

TERA independently selected and convened a panel of five experts to review and discuss the available toxicology data and the scientific support for the West Virginia (WV) Screening Level established at 10 parts per billion (ppb). The panel discussed the initial starting value of 1 part per million (ppm), or 1,000 ppb, established by the United States (US) Centers for Disease Control and Prevention (CDC) and the currently available data. They identified data gaps and made recommendations for additional studies or analyses that could strengthen the screening level and reduce uncertainty. The expert panel sought to reach consensus or common agreement on the scientific issues and conclusions.

The panel drew upon the scientific review document authored by Utah State University Professor Craig Adams. The document can be found on the WV TAP website (http://www.dhsem.wv.gov/wvtap/Pages/default.aspx) and is entitled *Health Effects for Chemicals in 2014 West Virginia Chemical Release: Crude MCHM Compounds, PPH and DiPPH. Version 1.5.* The document provides a literature review summarizing toxicity information on the chemicals involved in the spill into the Elk River in January 2014 from the Freedom Industries facility. The chemicals included 4-methyl-1-cyclohexanemethanol (MCHM) (CAS 34885-03-5), propylene glycol phenyl ether (PPH) (CAS 770-35-4), and dipropylene glycol phenyl ether (CAS 51730-94-0) (DiPPH). Crude MCHM is the mixture of MCHM and other compounds.

The independent expert panel included five scientists with expertise in the key disciplines and areas of concern for toxicology evaluation. Each panelist is a well-respected scientist in his field. The panel members have training and experience in the various scientific disciplines involved in evaluating the safety of chemicals in water. Collectively, the panel members are experts in toxicology, derivation of health advisories, human health risk assessment, and water contaminants and systems. They have experience in academia, government, research, and non-profit sectors, which provided a diversity of perspectives for the discussions. TERA questioned each candidate on his current and past relationships with potentially interested parties to identify any potential conflicts of interest. TERA was solely responsible for the selection of the panel members. The experts served as individual scientists and represented their own personal scientific opinions. They did not represent their companies, agencies, funding organizations, or other entities with which they are associated. Short biographical sketches and conflict of interest statements for panel members are provided in Appendix A.

In preparation for the meeting, the expert panel reviewed the Adams et al. literature review and other pertinent information. TERA provided the panel with a list of key questions (the "charge to peer reviewers") to help focus the discussions. The charge questions are briefly described below. A copy of the full charge is found in Appendix B, along with other meeting materials:

- 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 meeting opened with a welcome by Ms. Jacqueline Patterson of TERA. She described the background and purpose of the expert review and the agenda for the meeting. The panel members then introduced themselves and noted whether they had additions or changes in their conflict of interest statements. None of the panel members had any questions regarding one another's' conflict of interest statements or substantive changes to their own statements.

Dr. Dourson, the panel chair, then described how the meeting would be conducted. He explained that discussions would be organized around the charge questions and would follow the order in the agenda (see Appendix B). He noted that panelists were expected to share their scientific opinions on the discussion questions and panel members were encouraged to question one another to make sure that they understand the scientific basis for one another's opinions. The panel was asked to seek agreement, but if agreement was not possible, the meeting report would note this. He explained that the WV TAP representatives would make a brief presentation on the WV TAP project and results, and answer clarifying questions from the panel. The WV TAP representatives would also be permitted to ask clarifying questions of the panelists to ensure clarity and understanding of the panel conclusions.

TERA drafted this meeting report to provide a summary of the expert panel's discussions and conclusions, and to serve as the official record of the expert review. The draft report was reviewed and revised by the panel members and the final report was approved by the panel. The meeting report is a summary, not a transcript of the discussions. Opinions and comments of panel members are summarized to describe the scope and breadth of the discussions. Individual panelist comments are not identified by name, as it is the conclusions of the panel as a whole that is the value of a peer review meeting. When the panel did not reach consensus on a recommendation, this has been noted. Preliminary conclusions from the panel's discussions were reported on April 1, 2014 in a public meeting in Charleston, West Virginia (see Appendix C for slides used in that presentation). This 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.

PRESENTATION

Mr. Jeffrey Rosen, Dr. Andrew Whelton, and Dr. Michael McGuire of the WV TAP team began the meeting with a short overview presentation to explain the WV TAP project and present a summary of their findings. Slides from their presentations are found in Appendix D. The WV TAP project mission is to provide an independent scientific assessment of the spill of MCHM into the Elk River and its distribution throughout the nine counties served by West Virginia American Water (WVAW). The project consisted of four tasks: (1) an in-depth analysis to determine the odor threshold for MCHM; (2) an initial assessment of the concentration and variability of MCHM at the taps in homes, to be used to design a statistically robust sampling plan for the entire affected area; (3) establishment of an independent panel of experts to evaluate the safety factor for MCHM; and, (4) 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. Figure 1 below shows how the four parts of the project fit together. The team members presented results from the first two tasks and preliminary results of the fourth task.

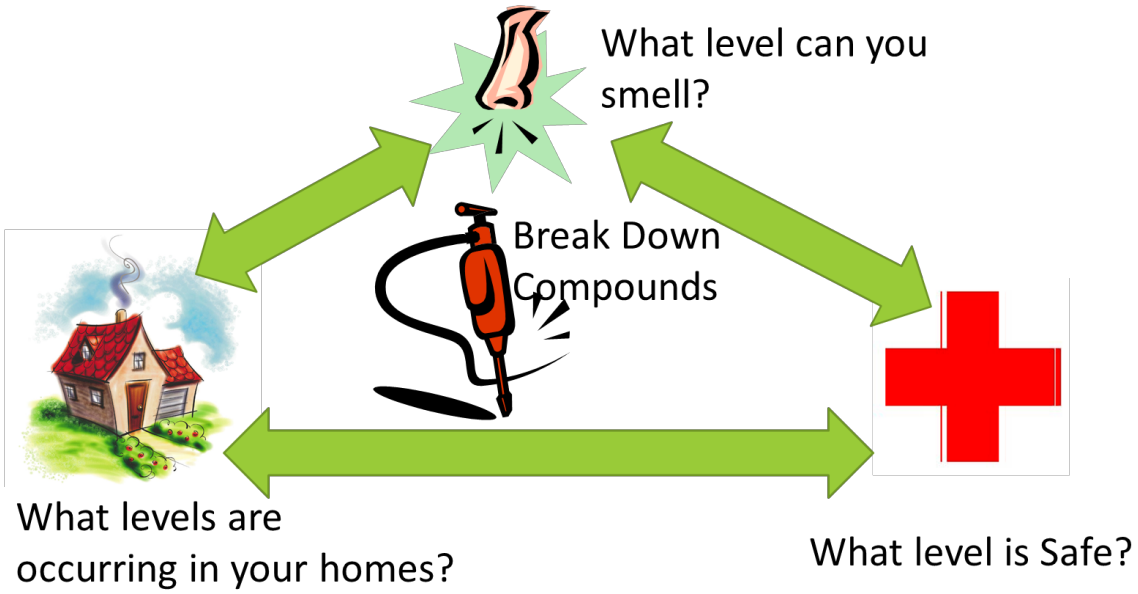

Figure 1. WV TAP Program Mission

Research on an odor threshold for MCHM was designed and conducted by Dr. Michael McGuire of Michael J. McGuire, Inc, along with Dr. I. H. (Mel) Suffet of the University of California, Los Angeles. The objectives of this task were to develop a method to estimate odor thresholds and convene a panel of odor experts to estimate threshold concentrations of detection, recognition, and objection (complaint). The results will be used to understand and explain consumer observations. Dr. McGuire's team used samples of crude MCHM that came from the tank that was the source of the spill. They used ASTM

E679-04 method (ASTM 2011) and trained experts to determine the three thresholds (calculated using geometric mean):

- Odor Threshold Concentration (OTC) - less than 0.15 ppb
- Odor Recognition Concentration (ORC) - 2.2 ppb
- Odor Objection Concentration (OOC) (Based on Degree of Liking) - 4.0 ppb and Odor Objection Concentration (OOC) (based on Objection/Complaint) - 4.0 ppb

The estimated thresholds support consumer observations in Charleston, WV that people could recognize and objected to the licorice odor caused by crude MCHM in their drinking water even though the analytical reports were showing non-detect at a minimum reporting level of 10 ppb.

The second task 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. Dr. Andrew Whelton of the University of South Alabama led this project. Ten homes were identified through assistance with local nonprofit organizations and word of mouth. Eight of the nine counties were represented. The sampling was conducted from February 11 – 18, 2014. Eight of the 10 households reported symptoms such as rash, dizziness, headaches, and nausea, with four of the households seeking medical assistance for symptoms. A complete description of the water testing methods and results can be found in a companion WV TAP report related to the 10 home study (WV TAP 2014). All ten houses' tap water contained 4-MCHM with 90% of the samples measured at less than or equal to 2.2 ppb. The highest level measured was 6.1 ppb. No trends were found between 4-MCHM detection and location within the house or water temperature.

In addition to the ten home samples, the WV TAP team developed analytical methods to detect and measure 4-MCHM and to identify breakdown products. Eurofins Laboratory and ALS Laboratories conducted all the tap water characterizations for the ten homes. They adapted EPA Method 3510 (US EPA 1996) for the extraction and EPA Method 8720D (US EPA 2007) for the chemical analysis. Eurofins was able to analyze the samples with a method detection level of 0.5 ppb and a method reporting level of 1.0 ppb; these levels were lower than the lowest attained by any other laboratory in the US. The laboratories carefully evaluated the results of the GCMS analyses to determine if any possible breakdown compounds were present in the samples. No breakdown products were observed. No PPH was detected in any of the ten house's water samples; 4-MCHM was observed in all ten homes sampled. Sampling done by the WV TAP team demonstrated that as of March 22, 2014 low levels of 4-MCHM were still present in the finished water produced by the West Virginia American Water (WVAW) treatment plant. Subsequent sampling performed by WVAW showed that MCHM was desorbing from the granular activated carbon (GAC). The team noted that all of the sample results and analyses are posted on the WV TAP website (http://www.wvtapprogram.com) and that in the coming weeks they would be finalizing a design for a larger home study. They anticipated delivering their final report to the State of West Virginia by May 15 and it would include recommendations for short- and long-term activities.

Clarifying Questions from the Panel

Panel members asked the presenters clarifying questions regarding their presentations and the WV TAP program.

Question 1. How confident is Eurofins on identification of all the compounds contained in crude MCHM in the environmental samples?

Dr. McGuire responded that Eurofins and Mel Suffet's laboratory at UCLA each analyzed the crude MCHM and tentatively identified the constituents as compared to what was listed in the Material Safety Data Sheets (MSDS). The identifications were made from library search results generated on the GC/MS systems used for the analysis, but not confirmed with the analysis of known, independent standards. Only the two isomers of MCHM (4-methylcyclohexane methanol) were confirmed with analysis of an independent standard material. Additional peaks were observed in the chromatograms for all the samples taken in the 10-home samples. Initially these peaks were considered candidates for breakdown compounds that might have been caused by treatment of the drinking water with chlorine and with potassium permanganate. Detailed analysis demonstrated that all of the extraneous peaks were results of the breakdown of surrogates added to the samples as part of the laboratory quality control for analyzing for the constituents of the crude MCHM. One particularly confusing tentatively identified compound was finally tracked down to a reaction with a preservative in methylene chloride.

Question 2. The 10-home study did not find any PPH in the household water. Is there any in the distribution system?

Mr. Rosen stated that two samples collected by the West Virginia National Guard and analyzed at REIC laboratories were positive for PPH on January 10th at concentrations of 10 and 11 ppb in the finished water from WVAW. There were very few other samples taken throughout the water system supplied by WVAW where PPH was detected above the method reporting limit of 10 ppb.

Question 3. How many days were the water samples held before the analysis was done and how many follow up samples?

Dr. Whelton responded water samples were collected and shipped daily to the designated laboratory that night. Water samples then underwent analysis within 24 hours. The holding times for all samples were 7 days and all sample analyses were completed within the designated hold times. Some samples were broken in shipping.

Question 4. It is thought that crude MCHM has another constituent that might contribute to the sharp odor, but this constituent is a small percentage of the crude MCHM and too low to detect in the homes that were sampled. How would such a low concentration of the minor component affect the odor of crude MCHM?

Dr. McGuire answered that even if the minor component thought to cause the sharp odor characteristic (cyclohexanemethanol) is in low part per trillion concentrations, it could still affect the odor of crude MCHM.

Question 5. There are CDC documents that describe the 1 ppm screening value. Is there any document describing how the West Virginia 10 ppb level was derived?

Dr. Adams explained that reference to the state's 10 ppb level is found in Governor Tomblin's proclamation of February 28, 2014 (Tomblin, 2014), wherein the state established a more stringent testing threshold of 10 ppb. The proclamation does not explain how this screening level was reached.

Question 6. Appendix M mentions an interagency review of the CDC work, is there a report or documentation of this review that we can use?

Dr. Adams indicated that previously Dr. Kapil of the CDC had told him that there was no report issued by the interagency panel. Additionally, the screening level and its basis reported by the CDC were developed by consensus and vetted within the interagency panel. The interagency panel included the National Institute of Environmental Health Sciences (NIEHS), the National Toxicology Program (NTP), the National Library of Medicine (NLM), the US Environmental Protection Agency (US EPA), and CDC/ATSDR (Agency for Toxic Substances and Disease Registry).

Question 7. – Has there been any central collection or synthesis of public health complaints?

Dr. Whelton explained that he was aware that various groups, including the poison control center, the WV Bureau for Public Health, local emergency departments, and the Kanawha-Charleston Health Department had collected data, but he was not aware of any central collection or any group synthesizing the data. Dr. Rahul Gupta, Director of the Kanawha-Charleston Health Department, provided data from their department for use by the WV TAP and the expert panel. The Kanawha-Charleston Health Department had conducted syndromic surveillance in the two largest counties affected (Kanawha and Putnam). The Health Department shared a description of its work and a summary of results for the panel to use (see Appendix E). The Kanawha-Charleston Health Department collected and compiled data on "frequency of illnesses with a specified set of clinical features not identified with a specific diagnosis" from ten sentinel multi-provider and multi-location medical practices, following standard practice and international and national protocols. These ten providers reported information on more than 200 patients who sought medical attention and who "presented with self-reported symptoms related to exposure to MCHM" with onset after January 9, 2014. The list of symptoms reported included multisystem symptoms (respiratory, digestive, integumentary [skin], neurological); respiratory: cough, sore throat; digestive: nausea, vomiting, diarrhea; skin: rash, skin irritation; neurological: Headache; and "other symptoms" for symptoms that had not been defined. Some patients reported multiple symptoms (e.g., rash, nausea, etc.). The providers did not report names, addresses or other identifying information on the patients beyond gender and age. Graphs created by the Kanawha-Charleston Health Department showed the number of patients by date of symptom onset and of number of illnesses for each self-reported syndrome.

Panel members observed that following the initial spike of symptoms after the contamination event, a further spike in reported symptoms occurred, which coincided with the period of system flushing. They

asked whether there were data to tie the reports of symptoms to the areas being flushed at that time. Dr. Whelton explained that there were not data to do that analysis and noted that some people flushed outside their area's assigned time/permission. Dr. Whelton also relayed to the panel his personal experience of having experienced dizziness while witnessing a flushing in a small, poorly ventilated, bathroom on January 17 or 18. The panel also asked whether it was known if the patients were drinking the water at the time of symptoms, Dr. Whelton indicated that there were no additional data available to answer that question.

PANEL DISCUSSION

Available Data

The panel evaluated the available toxicological data on crude and pure MCHM, utilizing the Adams et al. (2014) literature review and associated references. Panel members noted that although additional and more appropriate studies would allow for a more robust risk evaluation, such studies were not available. They identified a few additional references and other resources that they drew upon, including the development of quantitative structure activity relationship (QSAR) information for the various chemicals in the spill. The QSAR results, while preliminary, suggested that the chemicals were not likely to be mutagenic and one panel member thought that none of the chemicals was likely to be more toxic than MCHM. Several panel members mentioned that because of the limited toxicological data available, the use of such QSAR programs and tools (such as the Organisation for Economic Co-operation and Development [OECD] Toolbox) to gain additional insights into the potential toxicity of these chemicals was reasonable.

Methodology

The expert panel members brought a diversity of backgrounds and experience with toxicology and risk assessment from government, university, and non-profit sectors of Europe, Israel, and the US to the meeting. The panel recognized that the CDC used the US Environmental Protection Agency (US EPA) Health Advisory method (as described in Donohue and Lipscomb 2002) to develop their screening levels for MCHM and PPH. They 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 such advisories for the Elk River spill. Panel members discussed their experience and knowledge of various organizations' approaches, but used their own personal best scientific judgment to evaluate and develop their opinions and conclusions for this expert panel.

Several panel members explained how their organizations would approach calculation of a short-term health advisory. All described a similar basic approach, which includes the identification of a point of departure in the dose-response relationship for toxicity and division by uncertainty (safety) factors

(UFs). UFs reflect both variability in biological response between species and within humans, and the lack of knowledge of the toxicity of the chemicals being assessed. Differences in the approaches were seen with regard to the preferred duration of experimental studies, conversion of intermittent dosing to a continuous dose, dosimetric adjustment for species differences, use of a relative source contribution or water ingestion allocation factor with short-term advisories, and selection of the most sensitive (or most exposed) receptor. These differences reflect differences in professional judgment and consideration of more recently adopted approaches, including technical guidance provided by the US EPA, that further refine the basic approach. Key differences in approaches from the United Kingdom (UK), Israel, and Minnesota were discussed.

When providing advice to water companies, the National Centre for Environmental Toxicology (NCET) in the UK prefers to use longer duration studies where available to provide additional protection and precaution. NCET generally uses standard 10-fold uncertainty factors and generally follows the body weights and consumption values for adults and children as used by the World Health Organization (WHO) (WHO, 2011). For spill situations such as the Elk River, they would use the same water consumption and body weight for a child as the US EPA 1- and 10-day health advisory method. NCET would also include a water allocation factor of 50% to account for other routes of exposure.

In Israel there is no specific policy regarding the methodological procedures for determining the advisory level for compounds without existing international reference levels for drinking water thresholds. In cases of water source contamination, the Israeli Ministry of Health would seek an international drinking water threshold-reference or published drinking water threshold from a western country. Any contaminated water source would be closed until the drinking water threshold was achieved. When there is no known threshold, the water source would remain closed until a complete elimination is achieved. In an event where closing the water source is not an option, Israel would use the same traditional and widely accepted methods that were used by the CDC to develop a threshold value for the situation.

The Minnesota Department of Health (MDH) developed risk assessment guidance in 2008 for its health risk assessment program (MDH 2008). These risk assessment methods incorporate recent enhancements for the derivation of toxicity values, much of which comes from guidance issued by the US EPA, including use of dosimetric adjustments. Timing and duration of exposure are carefully considered by Minnesota in deriving reference doses (RfDs) for multiple durations, as well as life stage sensitivity. A panelist explained that the MDH methods have incorporated recently updated recommendations from US EPA that differ in several ways from the 2002 US EPA Health Advisory guidance (i.e., Donohue and Lipscomb 2002). A panelist explained that the differences in methodology, applicable to MCHM, are focused in five areas: (1) the acute and short-term duration receptor of first consideration, when relevant, is the most highly exposed on a water intake per body weight basis (a 1-3 month old formula-fed infant [based on EPA Exposure Factors Handbook (US EPA 2011)]); (2) adjustment of the experimental dose by 5/7 because the animals were only given the MCHM 5 days per week; (3) calculation of a human equivalent dose/concentration by adjusting the animal body weight by a default factor of body weight scaled to the ¾ power; (4) refinement of the uncertainty factor for interspecies adjustment (UF_A) to account for the scaling done in #3; and, (5) consideration of a relative

source contribution to account for other chemical exposures that occur beyond the ingestion of drinking water containing the subject chemical.

Another panelist asked if the MDH methods would be applied to spill situations. The first panelist noted that the MDH's risk assessment methods comprise multiple durations, including shorter-term exposures such as this, and one of the strengths in developing multi-duration guidance is that it can be applied to a wider range of scenarios. He noted that the duration of the 4-week MCHM study fit well with the MDH short-term duration methodology. A panelist asked if US EPA was aware of Minnesota's methodology. The first panelist explained that the MDH methods are based on current US EPA technical guidance, and have their foundation in published US EPA-based technical guidance documentation.

The panel discussed the differences in the MDH methodology and the US EPA Health Advisory approach and that the implications of these alternatives on a short-term health advisory would be to lower the concentration. Because the MDH methods incorporate an adjustment of the animal dose to a human equivalent dose (HED), they also use a more refined approach for the interspecies uncertainty factor for animal to human extrapolation (UF_A) that breaks the UF into two components to adjust for toxicokinetic difference and toxicodynamic differences. The panel discussed that this type of adjustment is largely based on the work of Dr. Andy Renwick and the International Programme on Chemical Safety (IPCS, 2005). MDH has adopted US EPA guidance (US EPA 2011) for using body-weight scaling factors, called dosimetry adjustment factors, in the absence of study-specific time-weighted average animal weights to derive the HED. As the HED is meant to account for the toxicokinetic extrapolation from animals to humans, the UF_A is reduced to 3, with the remainder left to account for toxicodynamic uncertainty in the absence of chemical-specific information. MDH methods are consistent in this approach with the US EPA (US EPA 1988). Other groups apportion this uncertainty factor slightly differently. For example, the IPCS would use a default factor of 4.0 for kinetics and 2.5 for dynamics (IPCS, 2005), rather than the two factors of 3 used by MDH and US EPA.

Charge Question 1: MCHM

The expert panel was provided with a summary of the available health effects data (Adams et al., 2014) as well as copies of the studies and references, prior to the meeting. They used a number of charge questions to help focus their review and discussions (see Appendix B).

Charge Question 1 asked the panel to evaluate and discuss the data and information currently available on crude MCHM, along with the screening levels reported by the State of West Virginia and the US Centers for Disease Control and Prevention (CDC):

- Given the current knowledge, what would be an appropriate screening level for MCHM in drinking water? In your expert opinion, based on the data that are available, do you think that the screening levels are appropriate for the intended uses of the water?
- Discuss the scientific uncertainties and what additional data, analyses, or studies might reduce uncertainty and provide greater confidence.

The panel discussion and conclusions on MCHM are summarized below.

Selection of Study and Point of Departure

The panel reviewed the available studies on crude and pure MCHM (see Adams et al. 2014 for a summary of the literature). They recognized that there were limited data for crude MCHM and agreed with the judgment of CDC that the 4-week oral study in rats with pure MCHM (Eastman, 1990) was the most appropriate study available to establish a short-term health advisory.

The following is a description of this study from the Eastman study report (Eastman, 1990):

> "Groups of two male and two female rats were given doses of 200, 400, or 800 mg/kg/day of 4-methylcyclohexane methanol in corn oil for five days as part of a probe study conducted to establish dose levels for the four-week toxicity study. Rats dosed with 800 mg/kg showed signs of narcosis resulting in decreased activity levels (one male and two females) and ataxia (one female). One of the female rats was subsequently euthanatized. One of the 400 mg/kg/day females had decreased activity on Days 2 and 3 of the study. The remaining animals did not exhibit clinical abnormalities related to exposure to the test article. Dose levels of 0, 25, 100, and 400 mg/kg/day were chosen for the four-week study based on these results.
>
> In the four-week study, the test article was administered five days per week by gavage in corn oil to groups of five male and five female rats. No mortality was observed during this study. Minimal reductions in body weight growth were present for both male and female rats given the high-dose of the test article. These differences were not statistically significant. At lower dose levels, no consistent effect was noted. Males given the lower doses weighed slightly less than their control group while females weighed slightly more. Feed consumption was unaffected by administration of the test material.
>
> Sialorrhea after dose administration occurred frequently in the 400 mg/kg male and female dose groups from Days 14 to 28. Transient depression of activity occurred in one 400 mg/kg female animal on Day 3 of the study. These were the only two treatment-related clinical observations noted.
>
> Hematologic changes indicative of minimal anemia were observed in the 400 mg/kg female group. These changes included a significantly decreased mean red blood cell count relative to the control group, and lower mean values for hemoglobin and hematocrit. In the absence of evidence of increased red blood cell destruction or turnover, these results suggest an interference with erythropoiesis rather than a direct effect on circulating red blood cells. Male and female rats from the 400 mg/kg dose group had significant increases in mean serum creatinine levels relative to their respective control groups, although the differences were not clearly of biological significance as urea nitrogen levels were not similarly increased. Microscopic examination of the kidneys of the 400 mg/kg animals revealed scattered areas of degeneration of the proximal convoluted tubules in 2 out of 5 animals of each sex. While mean relative kidney

weights of all male treatment groups were statistically significantly heavier than their control group, the differences did not fit a dose-related pattern.

Male rats from the 400 mg/kg dose group had significantly higher mean serum aspartate transaminase (AST) and sorbitol dehydrogenase (SDH) levels when compared to their control group. While the high-dose female group did not exhibit similar increases, one of the high-dose females did have an elevated SDH level and the mean relative liver weight for the female high-dose group was statistically significantly increased at the 400 mg/kg dose level. Microscopic examination of the livers from the 400 mg/kg animals of both sexes revealed increased severity and wider distribution of chronic focal inflammation in three males and two females when they were compared to their control groups.

In summary, administration of 400 mg/kg/day of the test article for four weeks was associated with erythropoietic, kidney, and liver effects. None of the effects were indicative of more than minor toxicity, and all were most likely reversible. The no-observed-effect level for this subacute toxicity study was 100 mg/kg/day."

Panel members noted that the study used an appropriate OECD method and was conducted under Good Laboratory Practice (GLP).

The panel agreed that a 4-week rodent study was of a reasonable duration to use for deriving a short-term health advisory. One member noted that in his organization in the UK a longer duration study would be used if available to be more conservative; however, in the absence of a longer study (and this is often the case with uncommon chemical contaminants), the use of this study with relevant UFs would be appropriate. Another panelist explained that the 1- and 10-day health advisories would fall under acute and short-term durations, respectively, as outlined by MDH multi-duration methods. MDH would derive acute guidance from a 1-day study and short-term guidance from a multiple dose study lasting longer than 1 day and up to 30 days. In the absence of an appropriate acute study, acute guidance would not be derived. However, if acceptable short-term studies were available, then short-term guidance could be developed. The inclusion of reproductive/developmental studies is preferred for deriving health-protective guidance for all durations, as these types of studies assess life-stage sensitivity. In the case where reproductive/developmental studies are not available, but a study conforming to the short-term duration is available and of sufficient quality to derive guidance, a 10x database uncertainty factor (UF_D) would be applied to the point of departure derived from the available study. The use of this factor is consistent with that used by the CDC.

The Eastman 4-week study was conducted using oral gavage as the route of MCHM administration to the animals. Panel members noted that a study that administered MCHM to the test animals in drinking water would be preferable to gavage dosing for use in setting a drinking water advisory level. In gavage dosing studies, the full daily amount of the chemical is put in the animal's stomach at one time through a gastric tube. One panel member noted that gavage administration often results in higher acute toxicity due to the bolus dosing that causes a higher initial body burden of the test chemical as compared to drinking water studies. Panel members recognized that because of MCHM's strong odor,

conducting drinking water studies could be problematic in that the animals may avoid drinking the water. For MCHM drinking water studies were not available but panel members noted that results of gavage studies are routinely used in risk assessment.

The panel discussed the hematuria findings in the two acute studies (Eastman 1998; Eastman 1999a) with crude MCHM. The first acute study (Eastman 1998) used male and female Sprague-Dawley (SD) rats [SAS:VAF/(SD)] and single gavage doses of 250, 500 or 1000 mg/kg-day. Red discoloration in the urine was reported in some animals and all the animals' urine was then measured for presence of blood using a semi-quantitative dipstick (N-Multistix); all the rats with visible red urine tested positive, as did half of those that did not have visible red urine. The authors considered the positive N-Multistix result in the absence of visible red coloration to indicate "blood in the urine too low to produce visible color changes." (page 6) Eastman conducted a second acute oral study (Eastman 1999) because of problems the laboratory had using the SAS:VAF/(SD) strain of rat (Dyer 2000). The second study used the Crl:CD(SD)IGS BR strain of CD rat. Five female rats were administered a single dose of 500 mg/kg-day. One panel member pointed out that as the animal numbers are low and there was only one dose, this would not be used as a regulatory test, but only as confirmation of a larger study. There were no observations of blood in urine or hematuria in the second study, but the study report did not mention or report on the use of a dipstick to measure blood in the urine directly. Panel members did not think that the second study could rule out hematuria as an effect; they questioned the choice of doses tested and why the more sensitive dip stick was not used. Moreover, the 4-week study showed anemia and kidney lesions at 400 mg/kg-day. Thus, the possible hematuria in the first acute study is consistent with kidney lesions and anemia findings in the 4-week study.

In summary, the panel concluded that, in the absence of other available studies, the oral rat study of 4-week duration was acceptable to use in this assessment for deriving a short-term health advisory for MCHM, although the panel recognized that other organizations might not use this duration study for deriving short-term advisories. The critical effects were anemia in the female animals at 400 mg/kg-day, and histopathology indicating liver and kidney effects in males and females at 400 mg/kg-day. The clinical chemistry findings supported the kidney and liver effects. Two panel members noted that the study report included a substantial discussion of effects seen in the 400 mg/kg-day dose group, but fewer details for the 100 mg/kg-day dose. The panelists thought that this increased the difficulty to critically determine from the study report whether the 100 mg/kg-day is a No Observed Effect Level (NOEL). The panel thought that the individual animal data from the study report would be useful to verify the NOEL of 100 mg/kg-day and asked if these data were available. The receipt of individual experimental animal data from the 4-week study of MCHM would allow confirmation of the study summary and thus afford more confidence in the study's conclusions. A panel member noted that if the individual animal data were available, benchmark dose modeling could be considered to utilize all the dose-response data to better estimate a point of departure. TERA contacted Eastman during the meeting, but was not able to obtain the individual data. The panel concluded that, in the absence of any

further data, the 100 mg/kg-day NOEL from the 4-week oral study in rats with pure MCHM (Eastman, 1990) was the most appropriate to establish a short-term health advisory for MCHM. [2]

Dose Adjustment

The CDC (CDC, 2014a) used the 100 mg/kg-day dose from the Eastman 4-week oral gavage study (Eastman, 1990) as the point of departure for their screening level. The expert panel agreed that this dose was appropriate to use as a starting point, but discussed adjusting it to account for the dosing regimen of 5 days per week. The study used a bolus dose delivered in corn oil by gavage to the experimental animals five days each week with no dosing on the weekends. The study reported a total of 21 doses.

In cases like this, where people are exposed to the chemical in their drinking water for more than a few days, the experimental dose is often adjusted to a continuous dose, to account for anticipated human exposure via drinking water. This is done by multiplying the dose of 100 mg/kg-day by 21 days/29 days, to approximate a continuous dose of 72 mg/kg-day (21 doses multiplied by 100 mg/kg body weight per day, divided by 29 days, equals 72 mg/kg-day). Panel members noted that adjustment to a continuous dose is a common practice and used by the US EPA and others when calculating risk values for lifetime exposures.

Some organizations (e.g., MDH in their health risk assessment program and the US EPA in its Integrated Risk Information System [IRIS] program) would further adjust this dose to calculate a human equivalent dose (HED) or human equivalent concentration (HEC) to account for the toxicokinetic differences between the experimental animal and humans. These adjustments are based on chemical-specific toxicokinetic data and modeling or use generic adjustments based on the animal body weights. For example, using the US EPA (2011a) guidance, dosimetric adjustment factors (e.g., adjusting the animal body weight by a default factor of body weight scaled to the ¾ power) or study specific time-weighted average animal weights could be used to derive an HED. The HED accounts for the toxicokinetic differences between the experimental animal and humans, and therefore the interspecies uncertainty

[2]Post-meeting, the chair of the panel, Dr. Dourson received questions on the panel's selection of critical effect, specifically whether the low dose of 25 mg/kg was a Lowest Observed Adverse Effect Level (LOAEL), based on relative and absolute kidney weights that were statistically significantly greater at the male low dose. Since both relative and absolute changes are normally required for a judgment of adverse effect in the kidney, this dual change appeared to represent an adverse effect. However, the study report noted that:

- higher doses did not show statistically significant increase in absolute kidney weights;
- kidney weights, both relative and absolute, did not show a dose-related trend; and
- these low dose effects did not have matching clinical changes or histopathology, which when compared with organ weight changes, are more definitive.

Toxicology studies often find various effects that are statistically significant at the 5% level, since many more than 20 tests on different organs and systems are monitored. We expect at least 1 in 20 endpoints to show statistically significant results due to chance alone, that is, such results are strictly artifacts of the testing (1/20 = .05 = 5%). Furthermore, experimental animals sometimes adapt to the exposure by specifically increasing the size of the liver and kidney to handle the extra metabolism work that results in elimination and excretion of the chemical. Moreover, the hallmark of adversity is dose- related responses, which did not happen with the kidney weights. The judgment of many, if not all, board certified toxicologists would be that these kidney weight effects at the low dose are either due to chance or due to adaptation.

factor for extrapolation from animals to humans (UF_A) is reduced from 10 to 3 to reflect the remaining uncertainties in toxicodynamics.

In contrast, the CDC used a value of 10 for the UF_A in derivation of their MCHM screening value (CDC 2014a). Such a 10-fold default uncertainty factor is traditionally used by most organizations for interspecies extrapolation. Some panel members noted that groups they work with would use the same approach as CDC for a short-term exposure value. The panel stated that while the CDC approach is traditional and not incorrect, the newer practices mentioned above, specifically, a dosimetric adjustment for the toxicokinetic portion of the UF_A, could also be considered (see Uncertainty Factor discussion below).

Uncertainty Factors

The panel agreed that the 100 mg/kg-day adjusted for the dosing schedule of 21 doses in 29 days (72 mg/kg-day) was the appropriate point of departure to calculate a short-term advisory for MCHM. They agreed that 72 mg/kg-day should then be divided by a 1000-fold uncertainty factor to estimate a short-term reference dose (RfD) of 0.07 mg/kg-day (0.072 rounded to one significant figure for 0.07). This factor consisted of a factor of 10 for interspecies adjustment for extrapolation from experimental animals to humans (UF_A), another 10 for intraspecies adjustment for within human variability in susceptibility (UF_H) and a factor of 10 to account for data deficiencies for an incomplete database that lacked developmental and reproductive toxicology studies and a second species repeat-dose study that monitored systemic effects (UF_D).

The use of a dosimetrically adjusted UF_A would yield a short term RfD of 0.06 or 0.07 mg/kg-day, depending on the method chosen to develop the adjusted UF_A (either the US EPA method used by the Minnesota Department of Health or the IPCS, respectively). These alternative approaches would reduce the toxicokinetic portion of the UFA, but would also lower the POD based on species body weight ratios. Thus, the net effect of these alternatives yields only a slight difference in the short-term reference dose.

Water Consumption

The CDC followed the US EPA Health Advisory method for one and ten-day advisories, with the use of 10 kg for body (approximately 22 pounds) and water consumption of 1 liter/day (approximately one quart). Using these values for a child results in a lower health advisory (more health protective) than if the value were based upon adult weight and water consumption values. The panel recognized that these are common assumptions and represent the high end of the range for a one-year-old child's drinking water intake (US EPA 2011b).

The panel discussed which life stage or subpopulation was most sensitive to MCHM. Panel members noted a lack of toxicological data for MCHM that could provide evidence that a particular life stage is more sensitive or susceptible to adverse effects from exposure to MCHM than other life stages. The rest of the panel agreed. When a most sensitive life stage cannot be identified, the most exposed relevant life stage is often selected for the duration of interest; that is the life-stage specific water intake rates need to match with the duration of the advisory. A panel member noted that on a drinking water intake

per body weight basis, the 1-3 month old infant being fed infant formula made with tap water has a higher consumption per body weight than the 1-year-old infant consumption used by the CDC. Water intake data have been published by US EPA since the 2002 Health Advisory framework was published, and can be found in their Exposure Factors Handbook (US EPA 2011b). These data can be used to match or calculate the appropriate water intake to the duration of interest. For instance, the MDH would consider the formula-fed infant to be the most exposed in the acute (1-day) and short-term (up to 30 days) exposure durations. For a longer duration (>30 days to <10% of lifespan) a young child's time-weighted average intake calculated from the US EPA water intake values from birth to 8 years of age would be used and for a lifetime duration guidance, a time-weighted average from birth to approximately 70 years of age would be used. The panel agreed that, lacking toxicological information on which life stage would be most sensitive to MCHM, consumption for the most exposed relevant life stage should be used. The panel chose to use a consumption rate of 0.285 liters of water per kg of body weight per day. This represents the 95th percentile of water intake for formula-fed infants (see Table Ref 3-19 on page 3-40 of US EPA, 2011b).

Routes of Exposure

People in the affected area have been exposed to MCHM through their community water supply. This water is used for multiple purposes, including direct ingestion from drinking and through foods prepared with water; along with additional routes of exposure such as bathing, brushing teeth, and household uses. People are exposed to the contaminated water through direct ingestion, but also on the skin, and probably through inhalation during showering. The panel discussed whether and how these other routes of exposure could be considered in setting a short-term health advisory.

The information provided by Dr. Gupta and the Kanawha-Charleston Health Department on the frequency of self-reported symptoms related to exposure to MCHM included reports of skin irritation and rashes. The panel noted these general symptoms were not specifically attributed to the contaminated water, but the symptoms appeared to correspond with the first days of the incident and again during the time when water systems in the affected homes were being flushed. The surveillance data, which listed respiratory symptoms, along with Dr. Whelton's reported experience of dizziness while flushing a home's hot water system, led the panel to conclude that inhalation exposures might also be of concern. One panel member noted that in his experience, flushing of water systems is sometimes accompanied by consumer complaints on water quality and in some cases, people link skin irritation to poor water quality. Another panelist noted that the chemicals in crude MCHM are clearly volatile, and their physical-chemical properties can allow them to escape from water and enter the air. Typically, this occurs to the greatest extent when water is heated (e.g., in the home, from cooking or running the dishwater) or sprayed (e.g., during showering). Consequently, household use of contaminated water could result in inhalation exposure in addition to ingestion and dermal exposure. However, without a better understanding of air concentrations of MCHM in homes and the concentrations in air that cause effects, it is difficult to relate inhalation exposure to specific consumer complaints.

The animal toxicological studies showed dermal and eye irritation for both crude and pure MCHM at all concentrations tested, although these concentrations were generally high and the skins of the experimental animals were generally occluded. After additional discussion, the panel agreed that the short-term advisory level should consider potential dermal and inhalation effects from exposure to the contaminated water to the extent possible.

The panel discussed approaches that are used by other agencies and organizations to account for other exposures beyond drinking the contaminated water. A relative source contribution (RSC) is commonly used in risk assessment to address potential exposure from sources and pathways other than ingestion of drinking water. For example, MDH describes the relative source contribution, or RSC, as "a factor used in drinking water risk assessment to allocate only a portion of the RfD to exposure from ingestion of water, and reserves the remainder of the RfD for other exposures, such as exposures from non-ingestion routes of exposure to water (e.g., inhalation of volatilized chemicals, dermal absorption) as well as exposures via other contaminated media such as food, air, and soil." (MDH, 2008)

The US EPA in its drinking water health advisory program also uses an RSC to adjust for other sources and pathways of exposure to the chemical. A default value of 0.2 is used in the absence of sufficient data to the contrary for the lifetime advisory; but the RSC concept is not applied to the calculation of the one day, 10-day, or longer-term drinking water health advisories (Donohue and Lipscomb, 2002). The 0.2 RSC default adjustment assumes that only 20% of a person's exposure to the chemical of interest comes from drinking water and 80% comes from other sources. US EPA guidance on relative source contributions is found in the Ambient Water Quality Program guidance, which contains a decision tree for determining the RSC allotment (20, 50, or 80%) to be used (US EPA, 2000a). The percentage is dependent upon the availability of exposure data to identify and quantify other sources of exposure. In the case of MCHM, there are very limited uses of the chemical, and the potential for people to be exposed to MCHM from sources other than their water supply, such as foods, is not likely.

In the UK, advice to water companies would contain an "allocation to water" of 100% for a one-day exposure, and 50% would be used for a seven-day exposure period. For longer exposure periods (on the order of months rather than years), when there are little data on other sources, an allocation of 50% would also be used. This factor accounts for other sources mainly and other routes of exposure where relevant.

Other authoritative bodies recommend a 50% reduction in the drinking water advisory level as a protective "rule of thumb" to address exposures from a contaminated water source that are other than direct consumption of water. For example, the Superfund program in US EPA Region IV (US EPA, 2014) recommends that dermal and inhalation exposure to volatile chemicals in water while showering is equal to the exposure from direct ingestion, in effect using a factor of 0.5. The logic is that exposure through other exposure pathways not captured from the oral dosing studies (exposures such as showering and bathing) need to be considered in deriving acceptable water concentrations. Although there are limited data, work on volatile chemicals such as chloroform (which is a disinfectant by-product), indicate that uptake of a chemical present in drinking water could double (or more) when inhalation as well as ingestion is considered (WHO, 2004).

A panel member explained that unless the chemical was extremely volatile, or there were data to indicate otherwise, MDH would use a factor of 0.5 for other sources of exposure for the bottle-fed infant scenario. Even if exposure is from a single source (e.g., water), there are other routes of exposure to be considered that in total should not exceed the reference dose established when combined with exposure from ingestion of drinking water. When MDH bases an advisory value on the formula-fed infant, the factor of 0.5 is used as a default value based on the narrow range of environments young infants encounter in the first few months of life. This default of 0.5 RSC for 1-3 month old formula-fed infant is only valid for acute and short-term guidance, for this life stage is very short and therefore the exposure assumption is only relevant to those shorter durations. For longer exposure durations, MDH uses a time-weighted average or adult water intake and the default RSC is 0.2, based on US EPA guidance unless exposure data are available to refine the RSC. Note that a default factor of 0.5 by MDH when using an infant exposure scenario is the same as suggested by US EPA's Superfund guidance.

The panel recognized that different groups have different approaches to adjust short-term health advisories to account for other routes and/or sources of exposure. They range from no adjustment as in the case of the CDC health advisory utilizing US EPA Health Advisory methods, up to reducing the advisory level by up to 80% (multiply by an RSC of 0.2 or divide by a factor of 5). The panel thought that since MCHM can volatilize and surveillance data of Dr. Gupta and the Kanawha-Charleston Health Department indicated that dermal and inhalation exposures to the contaminated water may be having effects, the use of a 0.5 adjustment was reasonable to apply to this situation. A factor other than 0.5 was not selected, since non-water sources of contamination are not expected, and specific data do not exist to inform selection of an alternate RSC. Thus, the panel recommended that a 50% adjustment (i.e., a factor of 0.5) be used for sources and exposures of MCHM from other water uses.

Summary of Calculation of MCHM Short-Term Health Advisory

The panel recommended a short-term health advisory of 120 ppb (120 µg/L) for MCHM. This value was recommended for public health use with the 2014 Elk River spill and the subsequent contamination of the local water supply. The advisory is based on the following calculations:

- Use the No Observed Effect Level (NOEL) of 100 mg/kg-day from the 4 week study of MCHM dated April 3, 1990 by Eastman Kodak (Eastman, 1990).
- Adjust this NOEL to 72 mg/kg-day by multiplying by a factor of 21 days/29 days (0.72) to account for the fact that the rats were only dosed for 5 days per week.
- Divide this adjusted NOEL by a 1000-fold uncertainty factor to estimate a short-term reference dose of 0.07 mg/kg-day (rounded from 0.072); this factor consists of factors of 10 for interspecies adjustment, intraspecies adjustment, and database deficiencies (i.e., missing developmental and reproductive toxicology studies and a second species repeat dose study monitoring systemic toxicity).
- Divide this short-term reference dose by consumption of 0.285 liters of water per kg of body weight per day (US EPA 2011b), representing the 95th percentile of water intake for formula-fed infants (the most exposed population); and then multiply this by 0.5 (RSC) to allow for other possible sources and routes of exposure, such as dermal and inhalation.

- The resulting short-term health advisory is 120 ppb (rounded to two significant digits).

The panel briefly discussed whether the short-term health advisories constituted a safe level of exposure. The majority of the panel expressed agreement with using the term "safe" for the short-term health advisories the panel derived for use in this situation. However, one member preferred to not use "safe," but rather to indicate that the advisories are at levels "not likely to be of concern to human health including the most sensitive individuals" as is used in advice to water companies in the UK. The panel agreed that both of these expressed the panel's intended meaning that the concentrations in water below this level are without appreciable risk to public health.

Chronic Value for MCHM

Development of a chronic guidance for MCHM was briefly discussed in response to a clarifying question. The development of a lifetime 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. The panel provided some thoughts in response to the question, "Can a chronic screening level be developed based on the available data?" A preliminary assessment could be done by considering the use of an additional uncertainty factor to adjust the study results from a short-term to longer-term exposure. Alternatively, additional longer-term studies could be conducted so that a chronic health advisory can be developed without the need for these additional factors.

Charge Question 2: PPH and DiPPH

Sometime after the spill, it was reported that the tank that leaked crude MCHM contained 88.5% MCHM, 7.3% PPH Stripped basic and 4.2% water (CDC, 2014b). According to the CDC (2014b) the PPH Stripped basic is primarily DiPPH and PPH. The relative proportions of DiPPH and PPH, and whether there were other ethers present in the tank is not clear, as several commercial products with varying compositions are available. Dr. Whelton explained that PPH was first measured in water treatment plant effluent in January 2014 at a concentration of 11 ppb concentration. No PPH was detected (detection limit of 0.5 ppb) in the 10 houses sampled. CDC developed a short-term screening level of 1200 ppb for PPH and indicated that this level would also be protective for DiPPH.

As noted earlier, the expert panel was provided with a summary of the available health effects data (Adams et al., 2014), as well as copies of the available studies and references, prior to the meeting. They were given a number of charge questions to help focus their discussions and review (see Appendix B). Charge Question 2 asked them to evaluate and discuss the data and information now available on PPH and DiPPH, along with the screening levels reported by the State of West Virginia and the US CDC.

- Given the current knowledge, what would be an appropriate screening level for PPH and DiPPH in drinking water? In your expert opinion, based on the data that are available, do you think that the screening levels are appropriate for the intended uses of the water?
- Discuss the scientific uncertainties and what additional data, analyses, or studies might reduce uncertainty and provide greater confidence.

The panel discussion and conclusions on PPH and DiPPH are summarized below.

Selection of Study and Point of Departure

The panel reviewed the available information on PPH and DiPPH. Panel members identified additional information, including:

- One panel member noted that the 2011 information the manufacturers provided to the European Chemicals Agency (ECHA) for the REACH program can be found on the ECHA website (available at http://echa.europa.eu). He briefly described REACH (Registration, Evaluation and Authorisation of Chemicals) as a European regulation by which all chemicals produced or used in the European Union are registered and, according to tonnage produced per year, a dossier of information (including toxicology) is submitted. This process is ongoing and administered by the ECHA. A dossier was available on the ECHA website for PPH (CAS number 770-35-4), but not for MCHM or DiPPH.
- WV TAP sent a request to Dow and they provided the panel with a copy of Dow Chemical Company's Chemical Safety Report, Substance Name 1-phenoxypropan-2-ol, July 9, 2010 (Dow Chemical 2010-09-07 CSR-PI-5.2.1) during the meeting.
- The interim California REL for PPH (available at http://www.arb.ca.gov/consprod/regact/2010ra/pph770354.pdf) was also identified and provided to the panel.

Oral toxicological data on PPH included acute studies and *in vitro* and *in vivo* genetic toxicity tests, as well as several key studies that the panel evaluated

- A 90-day drinking water study (and 28-day range finding study) in rats (ECHA, 2014a)
- A two-generation study drinking water study in rats (ECHA, 2014b)
- Prenatal developmental toxicity studies using gavage with rats (ECHA, 2014c) and rabbits (ECHA, 2014d)

Details of these studies, which all used OECD test guidelines and were conducted under GLP, are found in various reports. An OECD document on PPH (OECD 2006) describes much of the data; however, the SIDS document does not include a description of the study in rats that was used by CDC to derive their screening value. This key study (ECHA, 2014c) is included in the REACH submission on PPH, which the panel accessed during the meeting for additional details. Full study reports for the key studies noted above were not available for the panel to review but they utilized the secondary sources including the OECD document and the REACH information found on the ECHA website.

The CDC used results of a rat oral gavage developmental study (ECHA, 2014c) to derive their screening level for PPH. Wister rats (25/sex/dose) were gavaged with PPH emulsified in 0.5% Tylose to 0, 40, 160, and 640 mg/kg-day for 7 days a week on days 6-19 *post coitum*. Details about this study and results are found in the REACH information on the ECHA website. Overt signs of maternal toxicity (reduced food intake and body weight) were seen at the 160 mg/kg-day dose level; the next lowest dose of 40 mg/kg-day was the maternal NOAEL. Fetuses from dams receiving 640 mg/kg-day showed developmental

toxicity (reduced fetal weight and increases in skeletal variations); the next lowest dose of 160 mg/kg-day was the NOAEL for prenatal developmental toxicity. "No substance-induced teratogenicity was seen up to 640 mg/kg per day. Thus, prenatal toxicity was seen at a dose that was severely toxic to the dams. No teratogenic effects were noted at any dose." (ECHA, 2014c)

Panel members thought that this study (ECHA, 2014c) used by CDC was of appropriate quality, in that it used an appropriate OECD method (i.e., OECD method 414), was conducted under GLP, and the REACH dossier assigned it a Klimisch score of 1 (reliable without restrictions).

The panel discussed two other studies: a two-generation drinking water study (ECHA, 2014b) and a 90-day drinking water study in rats (ECHA, 2014a). In the two-generation drinking water study (ECHA, 2014b), Wistar rats (25/sex/group) were administered PPH in drinking water for 26 weeks at concentrations of 0, 100, 1000, or 5000 ppm (0, 11.3, 113.9, 477.5 mg/kg-day). The NOAEL was 1000 ppm (113.9 mg/kg-day), based on signs of systemic toxicity in the parental generations (F0 and F1) seen in the next highest dose group, which was the highest tested dose (5000 ppm, 477.5 mg/kg-day). In the 5000 ppm (477.5 mg/kg-day) group observed effects were: decreased water and food consumption, decreased body weight and body weight gain. Gross and histopathology did not see any substance related adverse effects at any dose.

In the 90-day drinking water study (ECHA, 2014a), Wistar rats were continuously administered PPH in drinking water for 90 days at concentrations of 0, 500, 2000, and 6000 ppm (0, 35/46, 146/177, and 429/486 mg/kg-day bw in males/females). The NOAEL in this study was 146 mg/kg-day (2000 ppm group), based on body weight changes in males and discoloration of urine in both males and females seen in the next highest dose group of 6000 ppm (429/486 mg/kg-day bw in males/females), which was the highest dose tested. Panel members noted that both of these additional studies are of high quality and utilized relevant test guidelines and GLP.

Panel members discussed how other groups would approach this risk assessment and examined other available data to evaluate whether even shorter-term studies were available that might be used to calculate a short-term health advisory. The panel did not find any shorter-term studies to use. Panel members noted that the preference in the MDH methodology would be to use the 90-day study for sub-chronic guidance and the 28-day study for short-term guidance (if this range-finding study was of sufficient quality). The UK's NCET would prefer a 90-day or 26-week study as they feel that the longer duration provides additional protection for exposed populations. However, in the absence of such studies, NCET would consider the above studies in their risk assessment.

The panel thought that the no effect levels from each of these three studies (ECHA, 2014a; ECHA, 2014b; ECHA, 2014c) should be considered as potential points of departure to derive a short-term drinking water health advisory. The panel evaluated the calculations and results for each of the studies in order to reach their recommendation for a short-term health advisory for PPH.

Even though the 90-day drinking water NOAEL (146 mg/kg-day) (ECHA, 2014a) is greater than the NOAEL (114 mg/kg-day) identified for maternal toxicity in the 2-generation study (ECHA, 2014b), and also greater than the NOAEL (40 mg/kg-day) identified in the developmental toxicology study used by

CDC), the panel thought that 146 mg/kg-day was the better choice for the point of departure for a number of reasons. The combination of the 146 mg/kg-day experimental no effect level with the appropriate water intake for infants, resulted in the most conservative water guidance value. The 90-day study used a drinking water exposure route that better represented the human exposure scenario under consideration, when compared to the bolus dosing of the lone gavage study. The 160 mg/kg-day (gavage) LOAEL for maternal toxicity in the 2-generation study was just slightly above the panel's selected point of departure (NOAEL of 146 mg/kg-day), but the nature of gavage bolus dosing reduced confidence in using this study when two other drinking water based studies were available, one of which examined maternal toxicity and found no effects at a nearly equivalent dose level. Moreover, the three studies under consideration were all conducted using the same strain of rodent (Wistar rats), increasing the direct comparability of the endpoints and dose levels under consideration. The panel's choice also represented the highest NOAEL that was also below the lowest LOAEL among these studies. In addition, the panel members thought that the variation in NOAELs among these studies appeared to represent more the variation in the choice of doses used in the studies rather than differences in toxicity. Thus, the panel considered the NOAEL of 146 mg/kg-day to be the best estimate of the boundary between effect and no effect when assessing the available studies as a group. As the 90-day study was conducted in young animals, and no direct-dosing neonatal exposure studies were available to assess the sensitivity of very young animals to PPH, the panel used water intake for the relevant and most exposed population, the formula-fed infant. This combination of NOAEL and intake resulted in a lower value than that derived by CDC (based on a pregnant woman's intake rate and the NOAEL from the developmental study).

Dose Adjustment

The experimental doses from the drinking water studies represented a continuous exposure and did not need to be adjusted further.

Uncertainty Factors

In reviewing the CDC calculations for MCHM and PPH, one panel member observed that CDC used a factor of 10 to account for data base deficiencies, or limitations in the database (UF_D), for both MCHM and PPH. For MCHM, CDC explained the 10 for UF_D "for weaknesses in the toxicological database (10X). For example there are no developmental, neonatal, or transplacental studies available" (CDC 2014a). The panel also judged this appropriate for MCHM. For PPH, CDC used the same 1000-fold uncertainty factor, noting use of 10x "to account for weaknesses in the toxicological database" (CDC 2014b). Panel members noted that there were more studies available for PPH and questioned the use of a full 10-fold database deficiency factor (UF_D) for PPH. However, the available information from the CDC did not provide any further details or rationale for the uncertainty factor selections and the panel did not think it would be appropriate for them to speculate on the CDC's rationale.

Several panel members thought that a case could be made to use a smaller UF_D (e.g., 3X) for PPH. The database for PPH was more robust than MCHM and included several repeat dose studies, a range of genotoxicity tests, and developmental and reproductive toxicology studies. Other panel members

agreed. Thus, the panel determined that a UF of 300 would be appropriate to estimate a short-term reference dose for PPH. This factor consisted of multiples of 10 for interspecies adjustment and intraspecies adjustment, and a factor of 3 to account for data deficiencies.

Water Consumption

The CDC used the body weight (75 kg) and water consumption (2.5 L/day) values for a pregnant woman. It is standard practice to use values for a pregnant woman when the critical effect is maternal toxicity and the panel thought that these values would reasonably protect pregnant women. In developing its three alternative options, the panel considered the most appropriate life stage to use for each of the options as described below.

There were more studies available for PPH than MCHM, including the two-generation studies that dosed parents and young animals with drinking water, a gavage study that dosed pregnant animals, and a 90-day study that tested younger animals. The panel did not find data to determine any particular life stage more sensitive, and thought that differences in NOAELs among the studies appeared to be due more to dose selection. As with MCHM, when toxicological data did not provide evidence that a particular life stage was more or less sensitive or susceptible to adverse effects from exposure than other life stages, the life stage that would be most exposed was used as a default for a short-term health advisory; for PPH this would be the formula-fed infant. Similarly to MCHM, and for the same reasons, the panel used the water consumption rate of 0.285 L/day and a relative source contribution, or water allocation, of 0.5 with the formula-fed infant scenario.

Panel members also noted that at the time of the expert panel meeting (March 31, 2014) no PPH was being detected in the water. Dr. Whelton confirmed that the last time PPH was detected in any water samples was two days after the spill and it was at a low level.

Routes of Exposure

For the same reasons as explained above for MCHM, the panel recommended that a 50% adjustment (i.e., a factor of 0.5) be used for sources and exposures of PPH from other water uses.

Summary of Calculation of PPH Short-Term Health Advisory

The panel recommended a short-term health advisory of 880 ppb (880 µg/L) 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.

- Use the No Observed Adverse Effect Level (NOAEL) of 146 mg/kg-day from the 90-day drinking water study (ECHA, 2014a).
- Divide this NOAEL by a 300-fold uncertainty factor to estimate a short-term reference dose of 0.5 mg/kg-day (rounded from 0.487). This factor consisted of multiples of 10 for interspecies adjustment and intraspecies adjustment, and a factor of 3 to account for data deficiencies (i.e., incomplete database, e.g., missing a second repeat dose toxicology study).

- Divide this short-term reference dose of 0.5 mg/kg-day by consumption of 0.285 liters of water per kg of body weight per day, which represented the 95th percentile of water intake for formula-fed infants (the most exposed population); and then multiply this by 0.5 (RSC) to allow for other possible sources and routes of exposure, such as dermal and inhalation. The resulting short-term health advisory for PPH is 880 ppb (rounded to two significant digits).

DiPPH

CDC noted in its document on PPH that, "Very limited specific toxicological information is available for DiPPH at this time. However the LD50 of >2000mg/kg and chemical structure suggest similar or lower toxicity, and the screening value calculated for PPH would also be protective for DiPPH" (CDC 2014b). The panel agreed with CDC and noted that the available manufacturers' information indicated that DiPPH is the major constituent of PPH Stripped. The panelists discussed whether there were sufficient data currently available to estimate a short-term advisory for DiPPH. One panel member noted that the LD50 values for PPH and DiPPH are greater than 2000 mg/kg-day, this was one piece of information to support that they are similar, but not sufficient alone. Others thought that the two are structurally similar and with LD50 values greater than 2000 mg/kg for both chemicals, that it would be appropriate to use the PPH results to estimate a DiPPH value. Other panel members agreed, with the stipulation that the UF_D uncertainty factor should be 10, rather than 3, to reflect the greater uncertainty in the DiPPH database.

The panel recommended a short-term health advisory of 260 ppb (260 µ/L) 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.

- Use the No Observed Adverse Effect Level (NOAEL) of 146 mg/kg-day from the 90 day drinking water study of PPH (ECHA, 2014a);

- Divide this NOAEL by a 1000-fold uncertainty factor. This factor consists of multiples of 10 for interspecies adjustment, intraspecies adjustment, and to account for data deficiencies (e.g., missing many studies); then divide by consumption of 0.285 liters of water per kg of body weight per day, which represented the 95th percentile of water intake for formula-fed infants (the most exposed population); then multiply this by 0.5 (RSC) to allow for other possible sources and routes of exposure, such as dermal and inhalation.

- The resulting short-term health advisory for DiPPH is 260 ppb (rounded to two significant digits).

Note that the panel did not develop a short-term reference dose for DiPPH because the assessment was based on the toxicity of PPH.

Charge Question 3: Mixtures

Charge Question 3 addressed the presence of multiple chemicals from the tank that spilled into the Elk River. The panel was asked:

> How should the presence of multiple chemicals in the release to the Elk River (i.e., crude MCHM, PPH and Di-PPH) be considered in the derivation or application of the screening values?

Panel members discussed that the mixture of concern is the contents of the tank that spilled in the river: crude MCHM and PPH Stripped basic. The CDC reported that the tank contents were 88.5 % MCHM, 7.3 % PPH Stripped basic and 4.2 % water. Both crude MCHM and PPH Stripped are commercial products that are mixtures of chemicals and these commercial products may have varying compositions.

Panel members began their discussion by briefly reviewing how chemical mixtures are generally assessed. They noted there is no single approach used by all authorities and groups. The US EPA approach to mixtures risk assessment is found in the US EPA *Guidelines for Health Risk Assessment of Chemical Mixtures* (US EPA 1986 and 2000b). These guidelines describe a commonly accepted approach in the US and elsewhere for assessing risk to humans from chemical mixtures. US EPA (US EPA 1986 and 2000b) recommends first looking for toxicity information on the actual mixture of concern, in the absence of this information, data on similar mixtures are sought. If data on similar mixtures are unavailable, one considers the toxicity of the individual components in the mixture and how the toxicity of the components might interact to affect the toxicity of the mixture. In determining how best to consider the cumulative activity of the individual chemicals in a mixture, the risk assessment scientist considers the individual chemical's mode or mechanism of action as well as any information on interactions among the components.

Data on toxicity of specific chemical mixtures are rarely available and data on sufficiently similar mixtures are often lacking as well. Thus, the most commonly used approach is to assess the potential hazards for each chemical and then sum the hazards after considering potential for interactions in the exposure or toxicity of the chemicals. This process considers any experimental toxicology data on interactions between or among chemicals.

The quantification of MCHM in water is based on pure MCHM (a mixture of cis and trans isomers). The panel noted that there are few or no data on some components in crude MCHM and discussed how one could best address the toxicity of the crude MCHM mixture when it includes components for which there are no toxicity data or risk values. One panelist said that given pure MCHM makes up the bulk of the crude MCHM, he would focus on the toxicity of pure MCHM. Others suggested that a systematic look for information on similarly-structured chemicals might be helpful, although several panelists stated that their informal review of structure-activity-relationships did not suggest unsuspected toxicity.

The panel discussed 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. The panel recommended assuming additivity for the components of the mixture that work on the same mode of action or have similar critical effects.

One panelist explained that the US Superfund approach (US EPA, 2001) to this situation one would need to estimate how much exposure people have to each chemical and identify risk values for each of the chemicals (e.g., "safe" or acceptable levels such as reference doses or tolerable daily intakes). A hazard quotient (HQ) is calculated for each chemical by dividing a person's expected daily exposure to the chemical by the risk value. An HQ of one or less than one indicates the exposure is not likely to be a risk to human health. One then adds together all of the HQs for similar-acting compounds (same mode of action or critical effect). A total HQ equal to or less than one would indicate the total exposure of the chemicals combined is not likely to be a risk to human health. Alternatively, one could add each of the chemical's daily exposures together and compare this total daily dose with the short-term health advisory for MCHM. Again, if the HQ is equal to or less than one, then the exposure is not likely to be a risk to human health. For a mixture of PPH, DiPPH and MCHM, MCHM is the most potent and also makes up a large percentage of the tank contents that spilled. The panel thought that for these chemicals, evaluating the toxicity of the mixture could be approached by a simple additivity of each component toxicity. 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 also briefly discussed that there may be other chemicals in the drinking water; perhaps disinfectant by-products that acted on the same toxic endpoint that might need to be considered when using an additivity approach. In addition, it is not known how the spilled chemicals interact with the environment, the water treatment plant, the distribution system, or the plumbing and fixtures in buildings and homes. The panel recommended that research be done to determine the chemical fate and transport of the spilled chemicals of major concern within the treatment plant and water distribution system.

The panel agreed that an appropriate approach to consider the mixture of chemicals in this spill would be to do a constituent-specific analysis and use dose addition following US EPA's mixtures guidelines (US EPA 1986 and 2000b). Surrogates could be chosen for those chemicals without adequate toxicity information, or they could be excluded from the calculation.

Charge Question 4: Multiple Uses of Water

Charge Question 4 addressed people using contaminated water for multiple purposes:

> Residents use water for drinking, bathing, showering, brushing teeth, cooking, baby formula, pets, washing dishes, water plants, etc. Are the reported screening values protective for all potential routes of exposures (i.e., ingestion, dermal and inhalation)? If not, how can these other routes of exposure be addressed?

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 (e.g., relative source contribution or water allocation factor) in the calculation of the short-term health advisories discussed in this report. This factor helps account for exposures from contaminated water other than drinking and preparing foods and beverages; these other exposures may include bathing, showering, brushing teeth, washing dishes, and watering plants.

Research and Data Needs

The panel discussed what additional data, analysis, or research might help reduce uncertainty. They 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 made five recommendations for additional data, analyses, or research:

1. **Undertake research to determine what level of MCHM in water would cause skin irritation in humans**.

   Panel members noted that there were anecdotal reports of dermal symptoms (irritation, rash), which may or may not be attributable to the water. Dermal toxicology studies indicated MCHM is a strong irritant, with a low potential for systemic toxicity (through dermal exposure) and dermal LD50 values are greater than the oral LD50 values. The dermal studies were conducted to identify hazard and not dose-response, and experimental protocols, such as skin occlusion, would not be expected to be part of the human experience. In the experimental animal studies, 100 mg/kg-day was the lowest dose with dermal irritation reported (Eastman, 1999b). The panel recognized that the experimental animal results might be consistent with the surveillance reports. However, a threshold for dermal irritation was not known and the available data were not sufficient to estimate a threshold. 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 discussed the types of toxicological studies that were not available for MCHM. The 10-fold uncertainty factor was applied for an incomplete database due to lack of several studies including a two generation reproductive study, two developmental toxicity studies in separate species, a repeat dose toxicity study in a second species, and genotoxicity studies (beyond the Ames test results). The panel was most 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. This could be combined into a two-generation reproductive/developmental toxicity study, if sufficient funds were available. A repeat dose study in a second species was of lesser importance, although one panelist noted that a continuous exposure drinking water-based study would be beneficial. With regard to potential genotoxicity, several panel members ran the chemicals through QSAR programs and they reported that all predictions were negative for genotoxicity. The missing studies are currently covered in the screening level calculation with use of a 10-fold uncertainty factor (UF_H). Availability of an additional developmental/reproductive study could result in a reduction of this UF_D to 3-fold. In addition, further studies may identify a better point of departure (POD), which may also have the impact of changing the short-term health advisory, depending upon the POD and selection of appropriate corresponding UFs.

3. Organize all available data on exposures and health effects (from immediately following the spill) to facilitate the estimation of initial conditions.

The panel members did not have information on what people were actually exposed to in the initial days after the spill. They understood that multiple parties measured concentrations of the chemicals in the river, water plant and finished water. The panel recommended that data be collated and analyzed to better understand and estimate exposure.

In addition, air levels resulting from water use in the home would help the understanding of potential inhalation risks from water usage. Data on inhalation exposure would help refine the evaluation of this exposure route that the panel was only able to address through application of a relative source contribution/water allocation factor.

Multiple parties have collected data related to symptom reports. These should also be collated and all of this data should be analyzed together to better understand exposure and effects.

4. Pending results of #2 and #3, consider the need for long-term health effects study.

The panel recommended in #2 that developmental toxicology studies be conducted with MCHM to determine the potential for effects on the fetus or on development. If these studies show developmental effects that are specific to MCHM and not due to maternal toxicity (#2) 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.

5. Determine chemical fate and transport within the treatment plant and water distribution system.

The panel discussed reports in the media (published around the time of the expert panel meeting) of MCHM being captured in the water treatment plant's activated carbon filters and the hypothesis that some of the captured chemical may still be washing off the filters and entering the finished water. In addition, panel members understood that it is not known whether the spilled chemicals might interact with other chemicals in the water (e.g., disinfectant chemicals or disinfectant byproducts) or how they might interact with the distribution system pipes and materials, as well as fixtures in the home. The panel recommended additional research be done on chemical fate and transport.

QUESTIONS FROM PUBLIC MEETING OF MARCH 28, 2014

The WV TAP team asked the panel to consider several of the questions raised by members of the public at the March 28 public briefing. The panel briefly discussed these and provided the following thoughts.

- *Will the panel consider health impacts on women and particularly pregnant women?* The panel developed the short-term health advisory levels to be protective for all people, including pregnant women.
- *Can MCHM exposure in steam be tied to headaches or irritated throat?* The panel noted that there are no toxicology data for MCHM that can answer this question directly. The panel reduced the advisory level by half to be protective for the potential exposures of contaminated water from inhalation and skin contact.
- *What about interaction with pharmaceuticals taken for diabetes or sleep apnea*? The panel members do not know of specific information or basis to predict interactions of the contaminated water with pharmaceuticals in the human body. The panel recommended that concerned individuals should consult their physician.
- *Is this stuff going to kill us and at what level? What is the difference between the fear and the actuality?* The panel estimated short-term health advisory levels for MCHM, PPH and DiPPH. Exposures to concentrations in water at or below these levels are without appreciable risk to public health, including sensitive subgroups.
- *Is the water safe for pets?* The panel thought that the safe levels established for people should also be safe for pets. This is because the main experimental studies used for the derivation of the drinking water advisories for people were carried out in rats. Large uncertainty factors were then used to set a much more precautionary level for humans. Therefore, these drinking water advisories will be safe for pets; the pets' response to the chemicals is likely to be similar to the experimental animals.
- *Do the chemicals leach into hard skin vegetables?* The panel did not have specific information to answer this question, but believed that the additional factor of 0.5 for other routes and exposures would protect people from any additional exposures via washing vegetables.
- *Everything is based on the CDC screening level recommendation. We don't even know if that is a valid safety threshold.* The panel reviewed the CDC screening values. The CDC used traditional methods and reasonable assumptions of the US EPA Health Advisory program to develop their screening levels. This expert panel's conclusions are 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).

CONCLUSIONS

The panel reviewed available data for MCHM, PPH, and DiPPH and developed short-term health advisories for each that are appropriate for the intended uses of the water supply. Each of the

screening values was intended to protect all portions of the population, including infants, children and pregnant women. Each value was 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 panel evaluated the available toxicological data on crude and pure MCHM utilizing the Adams et al. (2014) literature review and associated references. Panel members noted that although additional and more appropriate studies would allow for a more robust risk evaluation, such studies were not available. They identified a few additional references and other resources they drew upon, including the development of QSAR information for the various chemicals in the spill.

The expert panel was made up of independent experts from the US, UK and Israel; they were not constrained to use any particular method. The panel thought that the CDC used traditional methods and reasonable and common assumptions of the US EPA Health Advisory program to develop their screening levels to develop their screening levels. The use of an RSC and 1-3 month old infant intake are not included in the US EPA Health Advisory methodology from 2002. This expert panel's conclusions were not incompatible with the CDC values; however, this panel chose to adjust their advisory levels further to account for additional routes and pathways of exposure (dermal and inhalation). In addition, the panel used intake levels for what it deemed to be the most exposed life stage (i.e., the formula-fed infant). 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 panel recommended a short-term health advisory of 120 ppb (120 µg/L) for MCHM.
- The panel recommended a short-term health advisory of 880 ppb (880 µg/L) for PPH.
- The panel recommends a short-term health advisory of 260 ppb (260 µg/L) for DiPPH.
- The panel derived short-term health advisories for MCHM, PPH and DiPPH.

The MCHM advisory is based upon a 28-day rodent study, and with the appropriate uncertainty factors is applicable for human exposure situations of one day up to approximately 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's advisories each have two digits of precision. While guidance is often provided to express these advisories at the level of one significant digit, the panel chose to include two digits to aid in the reader following the calculations and understanding the results.

The panel agreed that an appropriate approach to consider the mixture of chemicals in this spill would be to do a constituent-specific analysis and use dose addition following US EPA's mixtures guidelines (US EPA 1986 and 2000b). Surrogates could be chosen for those chemicals without adequate toxicity information, or they could be excluded from the calculation.

The panel discussed the scientific uncertainties and what additional data, analyses, and studies might reduce uncertainty and provide greater confidence. They recommended five areas for further work:

1. Undertake research to determine what level of MCHM in water would cause skin irritation in humans.
2. Conduct toxicology studies for MCHM in pregnant animals.
3. Organize all available data on exposures and health effects (from immediately following the spill) to facilitate the estimation of initial conditions.
4. Pending results of #2 and #3, consider the need for long-term health effects study.
5. Determine chemical fate and transport within the treatment plant and water distribution system.

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APPENDIX A: PANEL BIOGRAPHICAL SKETCHES AND CONFLICT OF INTEREST

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Expert Panel Bios

Dr. Michael Dourson, Toxicology Excellence for Risk Assessment, Cincinnati, Ohio, USA
Since 1995, Dr. Dourson has served as President for Toxicology Excellence for Risk Assessment (TERA). Dr. Dourson will Chair the Expert Panel and has over 30 years experience in toxicology, risk assessment and derivation of risk values. While with the US Environmental Protection Agency (EPA) he chaired the EPA's Reference Dose (RfD) Work Group, was a charter member of the US EPA's Risk Assessment Forum, and chief of the group that helped create the Integrated Risk Information System (IRIS). Dr. Dourson received his Ph.D. in toxicology from the University of Cincinnati and is a Diplomate of the American Board of Toxicology (DABT) and a Fellow of the Academy of Toxicological Sciences. He has served on or chaired many expert panels in the US EPA, Food and Drug Administration (FDA), National Sanitation Foundation International, and independent organizations. He served as President of the American Board of Toxicology and Secretary for the Society for Risk Analysis (SRA), and has published more than 100 papers on risk assessment methods.

Dr. Shai Ezra, Mekorot, Israel National Water Company Ltd, Tel Aviv, Israel
Dr. Ezra is the Director of the Water Security Department at the Water Quality Division of Mekorot. Dr Ezra's department is responsible for optimizing contaminant detection efficiency, and applying advanced online monitoring systems and response strategies in Mekorot's water systems. He is continually engaged in examining and developing state of the art technologies for early warning detection systems. Dr. Ezra received his Ph.D. and M.Sc. from the Geological and Environmental Sciences Department of Ben Gurion University of the Negev, Israel. Dr. Ezra has investigated water quality issues in water distribution systems and has lectured in environmental organic geochemistry. He has published on water contamination issues, including chemical transformation and degradation of organic contaminants in aquifers, and decontamination methods of water pipe systems after contamination events.

Dr. James Jacobus, Minnesota Department of Health, Saint Paul, Minnesota, USA
Dr. James Jacobus is a research scientist and risk assessor in the Health Risk Assessment Unit at the Minnesota Department of Health (MDH) in St. Paul Minnesota. Dr. Jacobus derives multi-duration health-based guidance for drinking water contaminants of special concern. In his position at MDH, Dr. Jacobus has authored or reviewed toxicological assessments on approximately 15 contaminants of emerging concern, evaluating the available toxicity data to derive drinking water guidance values for acute, subchronic and chronic durations and addressing different life stages. Dr. Jacobus has worked as an environmental scientist engaged in the remediation of leaking underground storage tanks and performed basic science research on the genotoxicity of semi-volatile polychlorinated biphenyls and the biological effects of ionizing radiation. He earned his doctorate in human toxicology from the University of Iowa, trained as an NIH T-32 postdoctoral fellow, and holds an adjunct faculty appointment at the University of Minnesota.

Dr. Stephen Roberts, University of Florida, Gainesville, Florida, USA

Dr. Steve Roberts is Director of the Center for Environmental & Human Toxicology at the University of Florida, and is a Professor in the College of Veterinary Medicine, College of Medicine, and the College of Public Health and Health Professions. He received his Ph.D. from the University of Utah, College of Medicine, and subsequently completed a National Institutes of Health (NIH) individual postdoctoral fellowship in pharmacokinetics at SUNY Buffalo. He has previously served on the faculties of the College of Pharmacy at the University of Cincinnati and the College of Medicine at the University of Arkansas for Medical Sciences. Dr. Roberts conducts research in a number of areas of toxicology, including mechanisms of toxicity, toxicokinetics, nanotoxicology, and risk assessment. His research has been funded by several federal agencies, including the National Institutes of Health (NIH), the U.S. Environmental Protection Agency (EPA), and the Department of Defense (DOD). Dr. Roberts currently serves as an advisor to the Florida Department of Environmental Protection and is on the Chemical Assessment Advisory Committee of the Science Advisory Board for the U.S. EPA.

Dr. Paul Rumsby, National Centre for Environmental Toxicology at WRc plc, United Kingdom

Dr. Paul Rumsby is a Principal Toxicologist and Technical Manager of the National Centre for Environmental Toxicology (NCET) at WRc plc (formerly the Water Research Centre), in Swindon, United Kingdom. He received his Ph.D. in biochemical pharmacology from the University of Dundee and is a European Registered Toxicologist (ERT). He serves as the project manager and overseeing scientist for a 24-hour toxicology advisory service and conducts scientific evaluations of data on occupational and environmental chemicals for risk assessment and drinking water monitoring studies on chemicals of regulatory importance. He has conducted reviews of toxicological data for human health risk assessments from drinking water contamination incidents and the setting of short-term guidance values. He has 25 years' laboratory research experience in molecular toxicology and cancer research and is an expert in mechanisms in toxicology including carcinogenesis, mutagenesis, neurotoxicity, and endocrine disruption. Dr. Rumsby has authored numerous peer-reviewed publications on drinking water contaminants.

Conflict of Interest Screening

To facilitate the evaluation of potential conflict of interest (actual and perceived) and bias situations for the peer review candidates, TERA identified a list of *potentially* affected or interested parties and sectors for this peer review. The candidates were asked to consider their financial and other relationships with these parties when completing the conflict of interest questions and to report any relationships they may have with these parties. The candidates were also questioned about current and past activities or interest for the list of chemicals involved.

Potentially Affected or Interested Parties:

- State of West Virginia
- Centers for Disease Control and Prevention
- Freedom Industries
- Eastman Chemical
- DOW Chemical [PPH (one of the chemicals in the Crude MCHM and spilled) is manufactured by DOW, although the source of PPH in the tank is not clear]
- West Virginia American Water
- American Water Works Service Company [Parent company of West Virginia American Water]
- Coal mining industry (including mining, processing, storage, and transport)

Expert Panel:

Michael Dourson is President of TERA. TERA conducts work under contract for government and private sector sponsors on chemicals and risk assessment issues. He has no conflicts of interest for this peer review.

Shai Ezra is the Director of the Water Security Department at the Water Quality Division of Mekorot. He participated in an Israeli delegation to West Virginia hosted by the WV National Guard in January of this year to learn about the spill situation. He has no conflicts of interest for this peer review.

James Jacobus is a research scientist and risk assessor in the Minnesota Department of Health. He has no conflicts of interest for this peer review.

Stephen Roberts is Director of the Center for Environmental & Human Toxicology at the University of Florida, and is a Professor in the College of Veterinary Medicine, College of Medicine, and the College of Public Health and Health Professions. He has no conflicts of interest for this peer review.

Paul Rumsby is a principal toxicologist and technical manager of the National Centre for Environmental Toxicology (NCET) at WRc plc (formerly the Water Research Centre. He has no conflicts of interest for this peer review.

Toxicology Excellence for Risk Assessment (TERA)

TERA evaluates the potential for conflict of interest for each potential new project. The following is a summary of information for this project that TERA is disclosing in the interests of transparency.

TERA has no current financial or other interest with any of the chemicals identified in the spill. In the past, TERA compiled toxicity data and a hazard summary on one of the chemicals, methanol, for the U.S. EPA and organized a letter peer review of methanol toxicology studies for the Methanol Institute. TERA currently has projects with Dow AgroSciences and Dow Corning (a subsidiary, and joint venture, respectively of Dow Chemical) to evaluate chemical toxicity for several chemicals that are not related to this project. TERA has done work in the past for Dow Chemical and Eastman Chemical on other chemical toxicity evaluations, but not on any of these chemicals. TERA assisted the State of West Virginia in organizing a peer panel to conduct a risk assessment and toxicology evaluation of Ammonium, perfluorooctanoate (PFOA) in 2002. None of these projects involved the spill chemicals and the projects are not related in any way to this peer review, and therefore there is no conflict of interest for this peer review or reason for TERA or Dr. Dourson not to be objective in this matter.

APPENDIX B: MEETING MATERIALS

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Fact Sheet on WV TAP Expert Panel

Background

This meeting of an independent expert peer review panel has been organized by Toxicology Excellence for Risk Assessment (TERA*)*. TERA is an independent non-profit organization whose mission is to support the protection of public health by developing, reviewing, and communicating risk assessment values and analyses, improving risk methods through research, and educating risk assessors and managers and the public on risk assessment issues. TERA has organized and conducted peer reviews for private and government sponsors since 1996 (see http://www.tera.org/Peer/index.html for information about TERA's program).

Peer review is an essential part of science– peer review is the evaluation of scientific, work by others working in the same field. Evaluation by a diverse group of independent "peers," provides for a scientifically robust and objective appraisal of the work.

TERA has selected and convened a panel of five experts to review and discuss the available toxicology data and the scientific support for the West Virginia Screening Level established at 10 parts per billion (ppb). The panel will discuss the initial starting value of 1 part per million (1,000 ppb) established by the US CDC and then consider if the additional safety factor applied by the State of West Virginia was protective of public health, based on available data. The panel will identify data gaps and make recommendations for additional studies or analyses that could strengthen the screening level and reduce uncertainty. The expert panel will seek to reach consensus or common agreement on the scientific issues and conclusions.

The panel will draw upon the scientific review document authored by Utah State University Professor Craig Adams. The document can be found on the WV TAP website and is entitled *Health Effects for Chemicals in 2014 West Virginia Chemical Release: Crude MCHM Compounds, PPH and DiPPH. Version 1.5.* The document provides a literature review summarizing toxicity information on the chemicals that were spilled into the Elk River in West Virginia in January 2014 from the Freedom Industries facility.

In the spirit of the Expert Panel's independence and mission, it would not be appropriate for the experts to discuss the subject of this review publically before they deliberate as a group and finalize their report.

Independent Expert Review Panel

The independent peer review panel includes five scientists who have expertise in the key disciplines and areas of concern. Each panelist is a well-respected scientist in his or her field. The panel has training and experience in the various scientific disciplines involved in evaluating the safety of chemicals in water. Collectively, the panel members are experts in toxicology, derivation of screening levels, human health risk assessment, and water contaminants and systems. They have experience in academia, government, research, and non-profit sectors, which will provide a diversity of perspectives in the discussions. TERA questioned each candidate on their relationships with interested parties, to identify

any potential conflicts of interest. TERA was solely responsible for the selection of the panel members. The experts serve as individual scientists and will represent their own personal scientific opinions. They are not representing their companies, agencies, funding organizations, or other entities with which they are associated. Affiliations are for identification purposes only.

- Dr. Michael Dourson, Toxicology Excellence for Risk Assessment, Cincinnati, Ohio USA
- Dr. Shai Ezra, Mekorot, Israel National Water Company Ltd, Tel Aviv, Israel
- Dr. James Jacobus, Minnesota Department of Health, Saint Paul, Minnesota USA
- Dr. Stephen Roberts, University of Florida, Gainesville, Florida USA
- Dr. Paul Rumsby, National Centre for Environmental Toxicology at WRc plc, United Kingdom

Review Package and Charge to Peer Reviewers

In preparation for the meeting, the expert panel reviewed the Adams et al. literature review and pertinent references. TERA provided the panel with a list of key questions (the "charge to peer reviewers") to help focus the discussions. The charge questions are briefly described below:

- 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.

Meeting Report

The consensus opinion of the panel as a whole is the valuable result of this expert review. Preliminary conclusions from the panel's discussions will be reported on April 1. TERA will draft a meeting report that summarizes the expert panel's discussions and conclusions, and this report will serve as the record of the peer review. The draft report will be reviewed by the panel members for accuracy and completeness and the final report will be approved by the panel before it is released. The goal is to have the final report complete by the end of April.

Press Conference, April 1, 2014

A press conference to present preliminary conclusions will be held Tuesday, April 1 at West Virginia State University in Institute, West Virginia. Similar to the March 28 public meeting, the Expert Panel press conference will be held in the Ferrell Hall Auditorium. The auditorium, on the 2nd floor of Ferrell Hall, has theatre style audience seating for 400 persons on the lower level and 200 persons in the balcony. The event will begin at 10:00 AM EDT and conclude at approximately 11:00 AM EDT.

Agenda

Charleston, West Virginia

Monday, March 31, 2014

8:00	**Arrival, coffee**
8:30	**Meeting Convenes**[3]
	Welcome, Ms. Jacqueline Patterson, TERA
	Panel Introductions and Conflict of Interest/Bias Disclosures, Panel
	Meeting Process and Ground Rules, Dr. Michael Dourson, Chair
9:00	**Background**
	WV TAP Team
	Clarifying Questions from the Panel
9:30	**Panel Discussion of Data and Charge Questions**
12:00`	**Lunch (provided)**
1:00	**Panel Discussion of Data and Charge Questions, continued**
5:00	**Meeting Adjourns**

[3] The Chair will call a break mid-morning and mid-afternoon.

Charge Questions

Introduction

The expert panel will review and discuss the available toxicology data and the scientific support for the West Virginia Screening Level established at 10 parts per billion. They will discuss the initial starting value of 1 ppm established by CDC and then consider if the additional safety factor applied by the State of West Virginia is protective of public health, based on the data that are currently available. The panel will identify data gaps and make recommendations for additional studies or analyses that could strengthen the screening level and reduce uncertainty.

The panel will then be asked to consider whether any additional data are available on the chemicals that were released from the tank: pure-MCHM and the chemicals found in crude-MCHM, PPH, and Di-PPH. The Review Package includes the literature available to both the State of West Virginia and the CDC, as well as a literature review put together by Craig Adams and related references.

1. Evaluate and discuss the data and information now available on crude-MCHM, along with the screening levels reported by the State of West Virginia and the US Centers for Disease Control (CDC).
    - Given the current knowledge, what would be an appropriate screening level for MCHM in drinking water? In your expert opinion, based on the data that are available, do you think that the screening levels are appropriate for the intended uses of the water?
    - Discuss the scientific uncertainties and what additional data, analyses, or studies might reduce uncertainty and provide greater confidence.

2. Evaluate and discuss the data and information now available on PPH and DiPPH, along with the screening levels reported by the State of West Virginia and the US Centers for Disease Control (CDC).
    - Given the current knowledge, what would be appropriate screening levels for PPH and Di-PPH in drinking water? In your expert opinion, based on the data that are available, do you think that the screening levels are appropriate for the intended uses of the water?
    - Discuss the scientific uncertainties and what additional data, analyses, or studies might reduce uncertainty and provide greater confidence.

3. How should the presence of multiple chemicals in the release to the Elk River (i.e., crude-MCHM, PPH and Di-PPH) be considered in the derivation or application of the screening values?

4. Residents use water for drinking, bathing, showering, brushing teeth, cooking, baby formula, pets, washing dishes, water plants, etc. Are the reported screening values protective for all potential routes of exposures (i.e., ingestion, dermal and inhalation)? If not, how can these other routes of exposure be addressed?

5. Please identify any additional scientific issues or questions that the panel should discuss.

Summary Table: MCHM **DRAFT v2.0** **DRAFT v2.0**

	Crude												Pure	
	MSDS for Crude MCHM 1998	Eastman MSDS for Crude MCHM, 2005	Eastman MSDS for Crude MCHM, 2011	Eastman TX-97-306 (1st Oral Tox Rat 14 day)	Eastman TX-99-188 (2nd Acute Oral Tox Rat)	Eastman TX-97-271 (Skin Sensitization)	Eastman TX-97-241 (Ames)	Eastman TX-98-129 (14 day dermal)	Eastman TX-97-308 (Acute dermal tox)	Eastman TX-97-256 (Acute dermal irrit)	Eastman TX-98-004 (Fathead minnow)	Eastman TX-98-005 (Acute daphnid)	The 28-day oral feeding study on pure MCHM (Eastman TX-89-296)	Acute toxicity battery (containing 5 study reports (Eastman TX-90-5)
Ingestion														
Acute oral LD50 (rat)	825 mg/kg	825 mg/kg	825 mg/kg	825 mg/kg	---	---	---	---	---	---	---	---	---	---
Acute oral tox (male rat) LD50	---	---	---	933 mg/kg	---	---	---	---	---	---	---	---	---	---
Acute oral tox (female rat) LD50	---	---	---	707 mg/kg	---	---	---	---	---	---	---	---	---	---
Acute oral LD50 (rat)				---	---	---	---	---	---	---	---	---	---	---
Ingestion	Blood disorders	---	---	---	---	---	---	---	---	---	---	---	---	---
acute oral toxicity in rats testing, LD50 (male)	---	---	---	---	---	---	---	---	---	---	---	---	---	1,768 mg/kg
acute oral toxicity in rats testing, LD50 (female)	---	---	---	---	---	---	---	---	---	---	---	---	---	884 mg/kg
rats for acute oral toxicity,	---	---	---		---	---	---	---	---	---	---	---	---	"slightly toxic by the oral route"
NOEL subacute tox (rat)	---	---	---	---	---	---	---	---	---	---	---	---	100 mg/kg/d	---
Erithropoeitic, kidney, liver tox	---	---	---	---	---	---	---	---	---	---	---	---	400 mg/kg/d minor	---
Dermal					---	---	---	---	---	---	---	---		
Dermal LD50 (rat)	>2000 mg/kg (only dose tested)	>2000 mg/kg (only dose tested)	>2000 mg/kg (only dose tested)	---	---	---	---	NO	>2000 mg/kg (only dose tested), irritant, necrosis	---	---	---	---	---
14-day dermal NOAEL (rat) systemic tox	---	---	---	---	---	---	---	2000 mg/kg		---	---	---	---	---
Repeated dose CHDM (rat 90d)	---	---	8000 mg/L	---	---	---	---				---	---	---	---
Skin irritation (rabbit)	Moderate to strong	strong	strong	---	---	---	---	---	---	Irritating at 0.5 mL of pure	---	---	---	---
Skin sensitization (guinea pig)	None	None	None	---	---	None	---	---	---	---	---	---	---	---
Rats for acute dermal toxicity,	---	---	---		---						---	---	---	"moderately toxic by the dermal route"
Guinea pigs for acute toxicity-dermal irritation,	---	---	---		---	---	---	---	---	---	---	---	---	"a strong skin irritant"
Guinea pigs for acute toxicity – skin sensitization, and	---	---	---		---	---	---	---	---	---	---	---	---	"a strong skin irritant"
Rabbits for acute toxicity-eye irritation.	---	---	---	---	---	---	---	---	---	---	---	---	---	"a moderate eye irritant"
Eyes	Irritation of eyes	---	---	---	---	---	---	---	---	---	---	---	---	---
Serious eye damage;eye irritation (rabbit)	---	---	Moderate	---	---	---	---	---	---	---	---	---	---	---
Dermal	Irritation	---	---	---	---	---	---	---	---	---	---	---		---
Fathead minnow														---
Acute toxicity (fathead minnow, 96 h) - LC50	---	---	57.4 mg/L	---	---	---	---	---	---	---	57.4 mg/L		---	---
Acute toxicity (fathead minnow, 96 h) - NOEC	---	---	25 mg/L	---	---	---	---	---	---	---	25 mg/L		---	---
EU label		---									Harmful to aquatic organisms		---	---
USEPA assessment		---									Moderate concern level		---	---
Daphnid														
Aquatic invertebrates (daphnid, 48 hr) - EC50	---	---	98.1 mg/L	---	---	---	---	---	---	---	---	98.1 mg/L	---	---
Aquatic invertebrates (daphnid, 48 hr) - NOEC	---	---	40 mg/L	---	---	---	---	---	---	---	---	50 mg/L	---	---
Aquatic invert EU label		---		---	---	---	---	---	---	---	---	Harmful to aquatic organisms	---	---
Aquatic invert USEPA assessment		---		---	---	---	---	---	---	---	---	Moderate concern level	---	---
Hematuria														
Hematuria		---	---	Effect	No effect (500 mg/kg)	---	---	---	---	---	---	---	Effect	---
Hematuria - male		---	---	---	---	---	---	---	---	---	---	---	No effect	---
Hematuria - female	---	---	---	---	---	---	---	---	---	---	---	---	Effect. 400 mg/kg, lower mean red blood cell, hemoglobin conc., and hematocrit	---
Blood dissorders	"May cause"													
Liver/Kidney													Effect	
Mutagenicity														
Mutagenicity/Genotoxicity Salmoella-E Coli (Ames)	negative	---	---	---	---		Negative						---	---
Stumbling		---	---	---	Yes (500 mg/kg)		---	---	---	---	---	---		
Inhalation														
Inhalation LC50	Not available	---	---	---	---	---	---	---	---	---	---	---	---	---
Inhalation	Vapor may be irritating	---	---	---	---	---	---	---	---	---	---	---	---	---

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APPENDIX C: SLIDES FROM APRIL 1, 2014 PUBLIC MEETING

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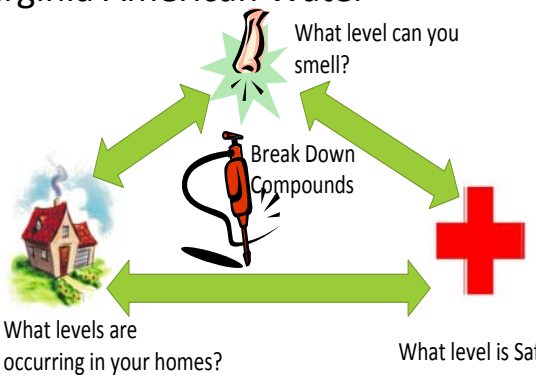
Preliminary Results of the Health Effects Expert Panel

Dr. Michael L. Dourson, Panel Chair
Toxicology Excellence for Risk Assessment (TERA)

April 1, 2014

The WVTAP Program Mission

- Provide independent scientific assessment of the spill of MCHM into the Elk River and its distribution throughout the 9 counties served by West Virginia American Water



Why Convene a Health Effects Expert Panel?

- To provide **independent expert review** of screening levels.
- **Essential part of science**
  - Evaluate by experts who are equivalent (that is "peers") of those who did the work.
  - Review to ensure that results are scientifically sound.
- **Complex issues** require participation by diverse types of scientists.

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Questions to Be Addressed by TAP Expert Panel

- **Review and discuss the available toxicology data** and the scientific support for the West Virginia 4-MCHM Screening Level established at 10 parts per billion (ppb).
- Initial starting value of 1 part per million (1,000 ppb) 4-MCHM established by the CDC and then **consider if the additional safety factor applied by the State of West Virginia was protective of public health**, based on available data.
- **Identify data gaps and make recommendations** for additional studies or analyses that could strengthen the screening level and reduce uncertainty.

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THE Charge Questions

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

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WV TAP Expert Panel

(affiliations listed for identification purposes only)

- **Dr. Michael Dourson**, Toxicology Excellence for Risk Assessment, Cincinnati, Ohio
- **Dr. Shai Ezra**, Mekorot, Israel National Water Company Ltd, Tel Aviv, Israel
- **Dr. Paul Rumsby**, National Centre for Environmental Toxicology at WRc plc, United Kingdom
- **Dr. Stephen Roberts**, University of Florida, Gainesville, Florida USA
- **Dr. James Jacobus**, Minnesota Department of Health, Saint Paul, Minnesota USA

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Panel's Thoughts on CDC Results

- CDC used traditional methods and reasonable assumptions to develop their screening levels.
- The panel chose to consider additional routes of exposure (inhalation and skin).
- The panel was not constrained to use any particular methods.
- The panel included international and US state experts.

Panel's Approach

- The Panel agreed with CDC on the choice of key toxicity data for MCHM, but not for PPH.
- The Panel agreed with CDC on the choice of uncertainty (safety) factors for MCHM, but had a different choice of factors for PPH.
- The Panel chose to consider additional routes of exposure (inhalation and skin).
- The Panel chose to calculate values based on the most highly exposed population (that is, formula-fed infants).

Exposure & Sensitive Groups

- The Panel considered the following exposures:
  - Direct ingestion of water, including formula-fed infants
  - Inhalation from showering and cooking
  - Skin exposure to water uses in the house
  - Incidental exposures, including brushing teeth, watering plants, etc.
- These exposures protect all populations, including:
  - Infants
  - Children
  - Pregnant Women

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Preliminary Conclusions

- The panel developed safe levels of exposure that are protective for all populations.
- These levels are averages for exposures up to 28 days:
  - 120 ppb for MCHM
  - 250 ppb for DiPPH
  - 850 ppb for PPH

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Research Needs

1. Determine MCHM potential to cause skin irritation.
2. Conduct toxicology studies for MCHM in pregnant animals.
3. Organize all available data on exposures and health effects (from immediately following the spill) to facilitate the estimation of initial conditions.
4. Pending results of #2 and #3, consider the need for long term health effects study.
5. Determine chemical fate and transport within the treatment plant and water distribution system.

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The Panel thanks you for the opportunity to help.

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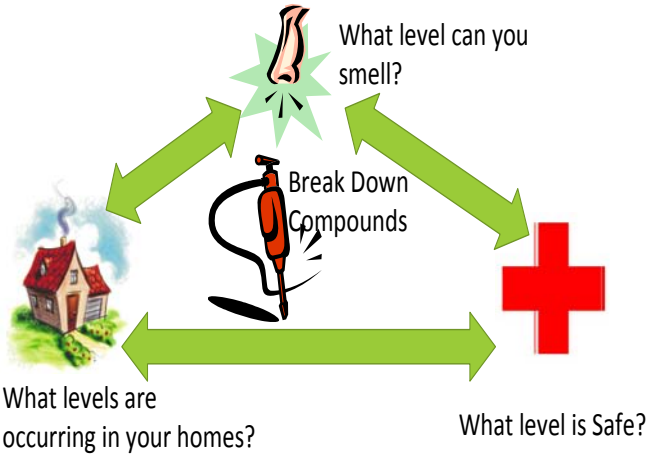
Summary



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Data Postings

- We posted in the last few days
  - Integrated relational database (Access) with all sample results and relevant quality control data
  - Over 1300 pages (12,000 data points) of raw chemical analysis reports
- We will be posting in the next few weeks
  - Odor threshold results for consumer panel
  - Health Effect Expert Panel final report
  - Statistical design for larger sampling program
  - Final report integrating all the results together along with recommendations for next steps and suggested long term research programs.

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Completing the WV Tap Program

- WV TAP anticipated ending in May 15
  - Final report summarizing all the results
  - Includes recommendations to State for short- and long-term activities

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Thank you!

The WV Tap Program

Extra slides

CDC	Panel
No Observed Effect Level (NOEL) = 100 mg/kg-day	No Observed Effect Level (NOEL) = 71 mg/kg-day
Uncertainty Factor = 10H, 10A, 10D	Uncertainty (Safety) Factor = 10H, 10A, 10D (provision for refined factor possible)
Ingestion of water only	Ingestion, inhalation and skin
Exposure to 1-year old child	Exposure to formula-fed infant
Screening level = 1000 ppb	Screening (safe) level = 120 ppb

10H = 10x for human variability; 10A = 10x for animal to human extrapolation; 10D = 10x for data base sufficiency

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CDC	Panel
No Observed Effect Level (NOEL) = 40 mg/kg-day	No Observed Effect Level (NOEL) = 146 mg/kg-day
Uncertainty Factor = 10H, 10A, 10D	Uncertainty (safety) Factor = 10H, 10A, 3D (provision for refined factor possible)
Ingestion of water only	Ingestion, inhalation and skin
Exposure to pregnant woman	Exposure to formula-fed infant (provision for pregnant woman available)
Screening level = 1200 ppb	Screening (safe) level = 850 ppb

10H = 10x for human variability; 10A = 10x for animal to human extrapolation; 10D = 10x for data base sufficiency

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CDC Not Determined	Panel
	No Observed Effect Level (NOEL) = 146 mg/kg-day
	Uncertainty (safety) Factor = 10H, 10A, 10D (provision for refined factor possible)
	Ingestion, inhalation and skin
	Exposure to bottle fed infant (provision for pregnant woman available)
	Screening (safe) level = 250 ppb

10H = 10x for human variability; 10A = 10x for animal to human extrapolation; 10D = 10x for data base sufficiency

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APPENDIX D: WV TAP PRESENTATION SLIDES

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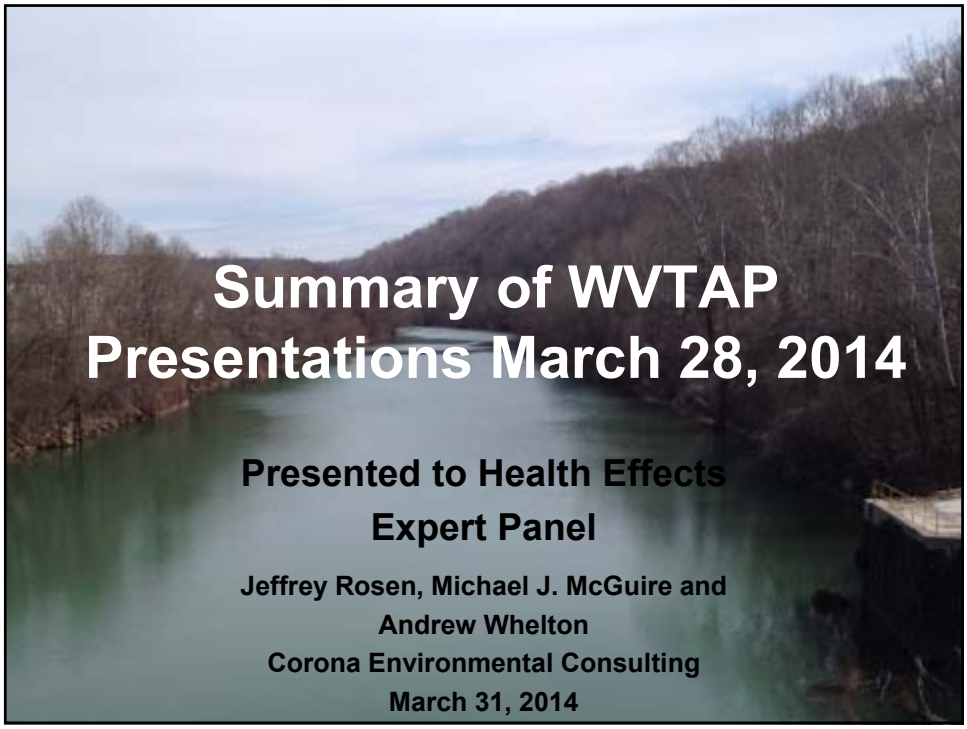
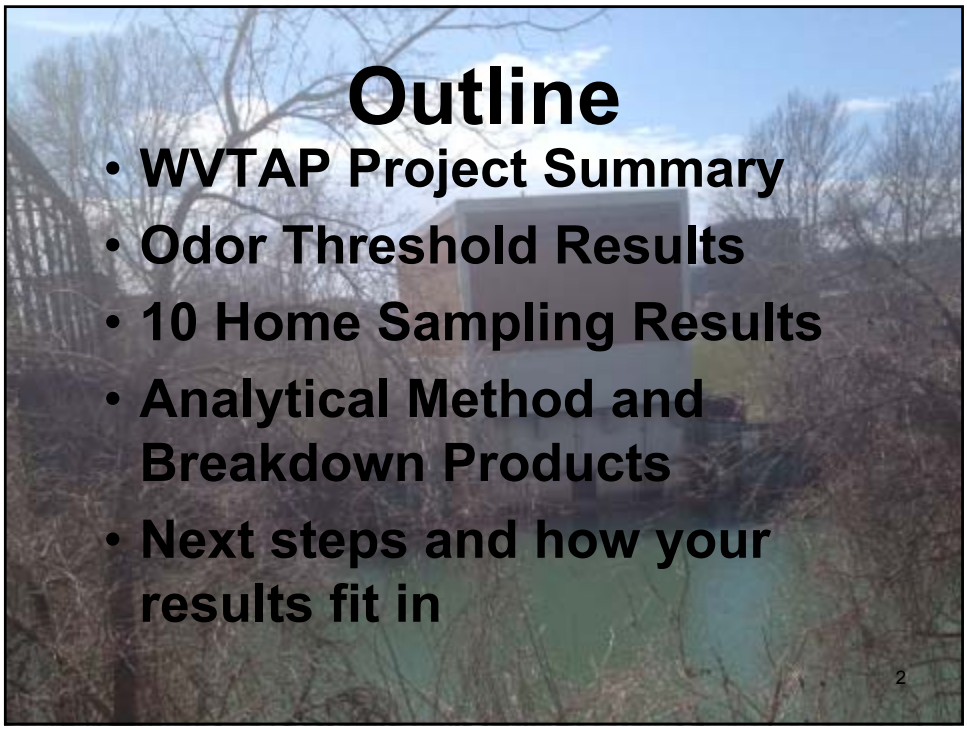
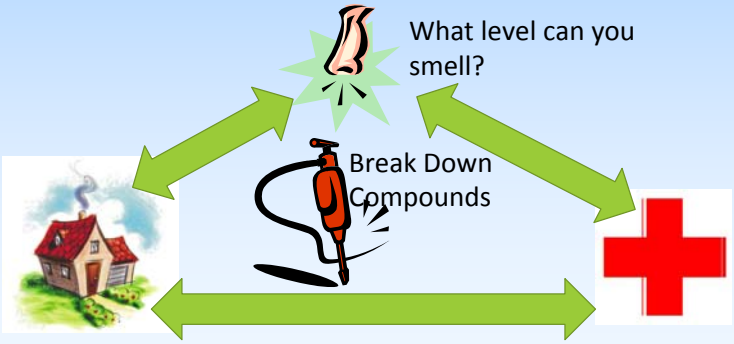
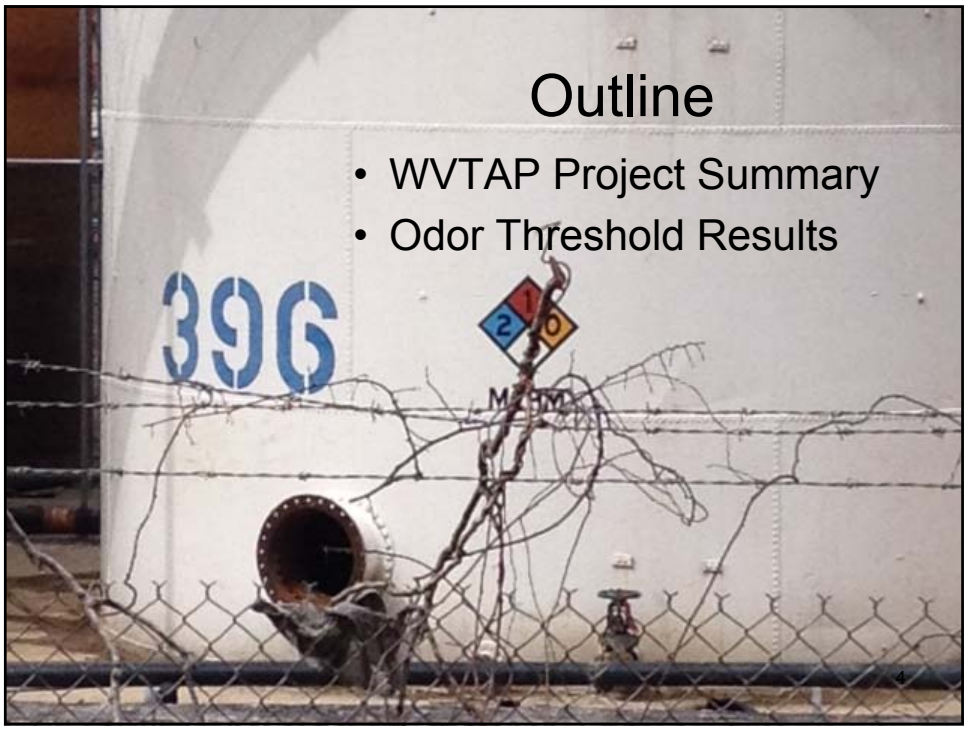

Summary of WVTAP Presentations March 28, 2014
Presented to Health Effects Expert Panel
Jeffrey Rosen, Michael J. McGuire and Andrew Whelton
Corona Environmental Consulting
March 31, 2014


Outline
• WVTAP Project Summary
• Odor Threshold Results
• 10 Home Sampling Results
• Analytical Method and Breakdown Products
• Next steps and how your results fit in
2

The WVTAP program mission

- Provide independent scientific assessment of the spill of MCHM into the Elk River and its distribution throughout the 9 counties served by West Virginia American Water





Objectives of Odor Threshold Task

- Develop a method to estimate odor thresholds for the licorice-smelling substance in water
- Convene a panel of odor experts to estimate concentrations of detection, recognition and objection/complaint for the licorice-smelling substance in water
- Understand how the Expert Panel results explain consumer observations in Charleston, WV

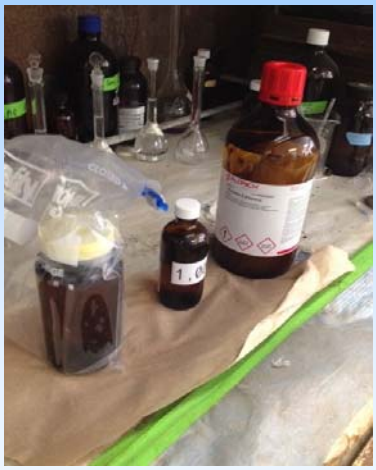
5

Odor Response Terminology

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 where 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

Crude MCHM Odor Characteristics

- Crude MCHM has a sharp, irritating licorice odor
- Pure MCHM smells like licorice but is not sharp or irritating
- The odor smelled by consumers in tap water was Crude MCHM
- Crude MCHM spiked into Arrowhead spring water



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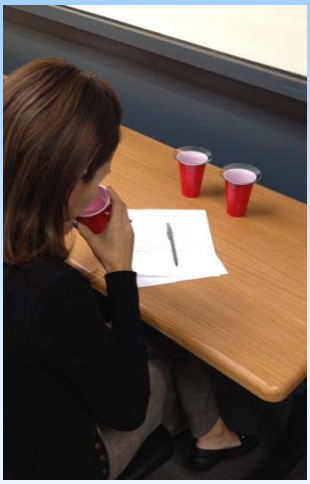
Odor Methodology

- Method ASTM E679-04 (2011)
- 8 concentrations were presented in sets of 3—2 blanks and 1 spiked with Crude MCHM
  - Choose the cup that had a different odor
  - Describe the odor
  - Determine degree of liking
  - Would panelist object/complain about odor?



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Odor Threshold Findings

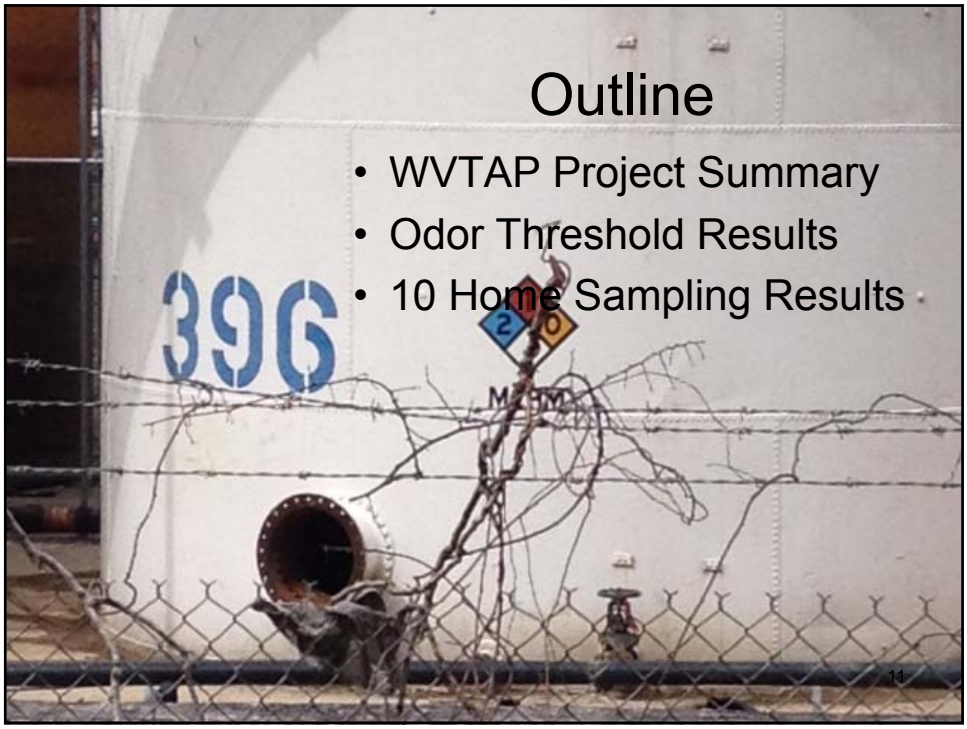
Odor Thresholds	Geometric Mean, ppb	Factor: Greater than OTC
Odor Threshold Concentration (OTC)	less than 0.15	---
Odor Recognition Concentration (ORC)	2.2	15
Odor Objection Concentration (OOC) Based on Degree of Liking	4.0	27
Odor Objection Concentration (OOC) Based on Objection/Complaint	4.0	27

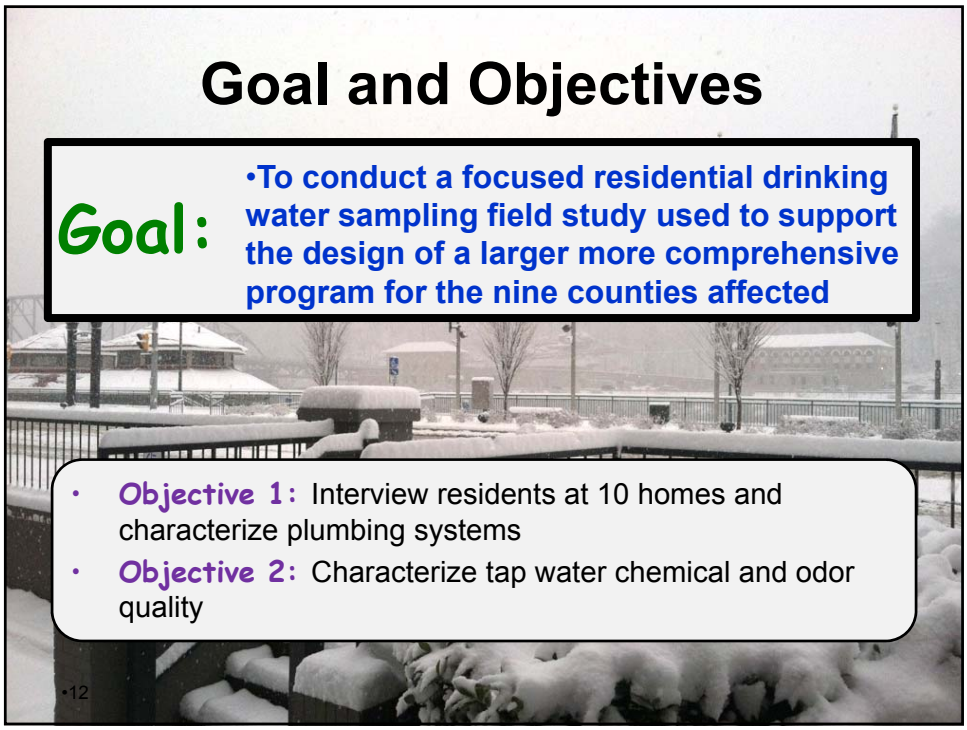
9

Odor Threshold Findings (cont.)

- The estimated thresholds determined in the Expert Panel study support consumer observations in Charleston, WV that people could recognize and object to the licorice odor caused by Crude MCHM in their drinking water even though the analytical reports were showing non-detect at a minimum reporting level of 10 ppb.

10


Outline
• WVTAP Project Summary
• Odor Threshold Results
• 10 Home Sampling Results
396
11

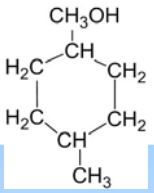

Goal and Objectives
Goal:
•To conduct a focused residential drinking water sampling field study used to support the design of a larger more comprehensive program for the nine counties affected
• Objective 1: Interview residents at 10 homes and characterize plumbing systems
• Objective 2: Characterize tap water chemical and odor quality
•12

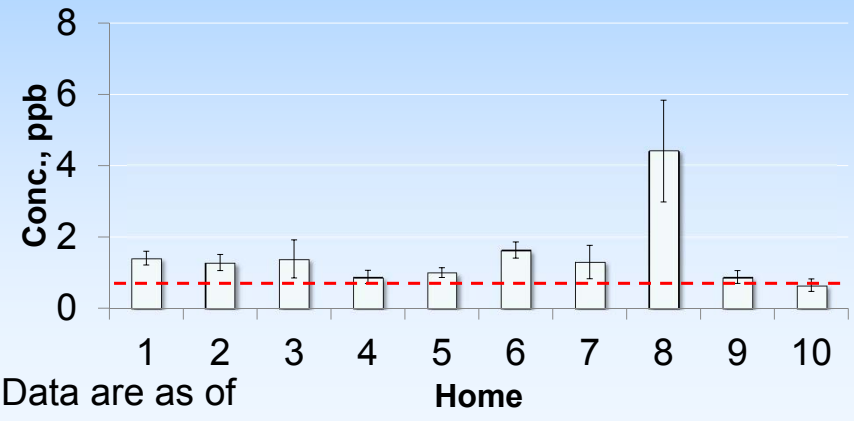
8 of 10 Households Reported Chemical Exposure Symptoms

As of Feb 18, 4 Households Had Sought Medical Assistance

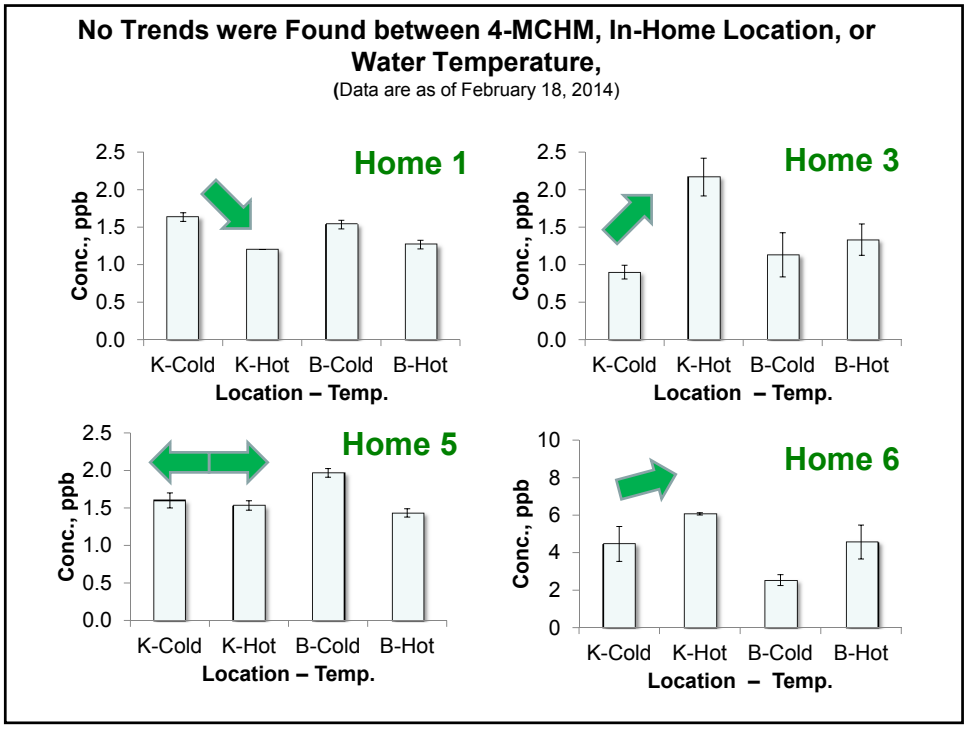
Symptom	No. Households	Ratings
Rash	4	3,4,5,5
Dizziness	4	3,3,3,5
Burning	4	3,3,3,4
Nausea	3	2,3,3
Numbness	2	2,3
Memory loss	2	4,4
Vomiting	1	2
Other: Headache	3	No rating
Other: Flu like symptoms	1	No rating
Other: Agitated	1	No rating
Other: Skin itch	1	No rating
Other: Eyes red	1	No rating

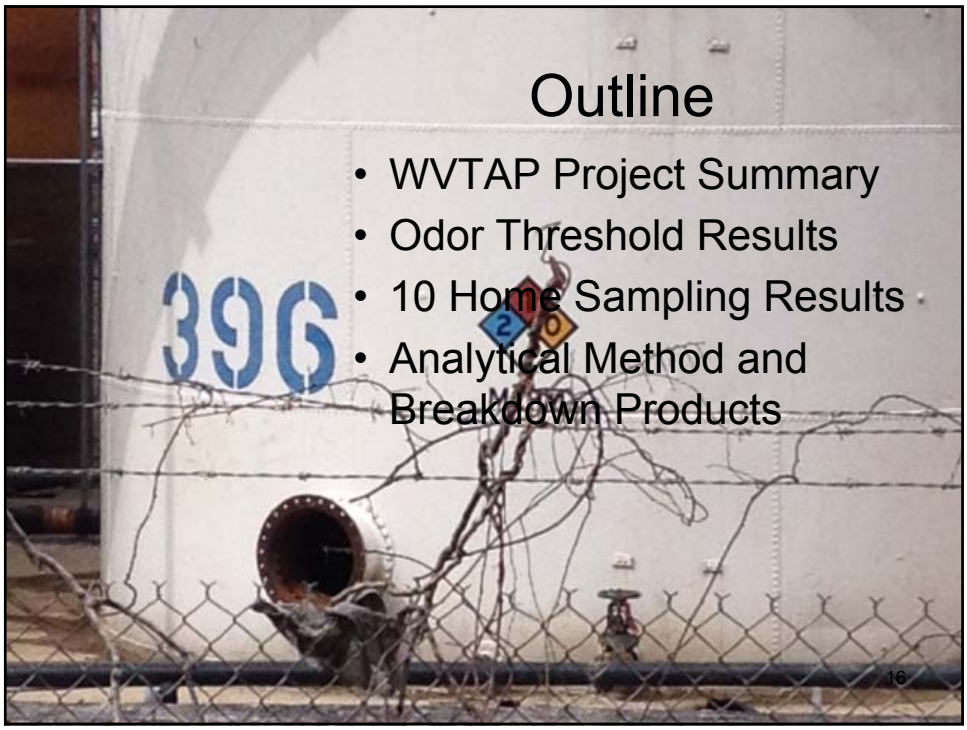
All Home Tap Waters Contained 4-MCHM
No Levels Exceeded 6.1 ppb
90% of the Samples ≤ 2.2 ppb





Data are as of February 18, 2014


No Trends were Found between 4-MCHM, In-Home Location, or Water Temperature,
(Data are as of February 18, 2014)
Home 1
Home 3
Home 5
Home 6
Conc., ppb
K-Cold
K-Hot
B-Cold
B-Hot
Location – Temp.


Outline
• WVTAP Project Summary
• Odor Threshold Results
• 10 Home Sampling Results
• Analytical Method and Breakdown Products
396
16

Eurofins 4-MCHM/PPH Analytical Method

Adapted EPA Methods 3510, for the extraction, and 8270D for the analysis. Method 8270D uses GC/MS.

Method 3510 uses methylene chloride to extract (remove) organic compounds from a water sample.

Method Detection Level = 0.5 ppb; Method Reporting Level = 1.0 ppb

These levels are the lowest of any laboratory in the U.S.

17

Breakdown Product Findings

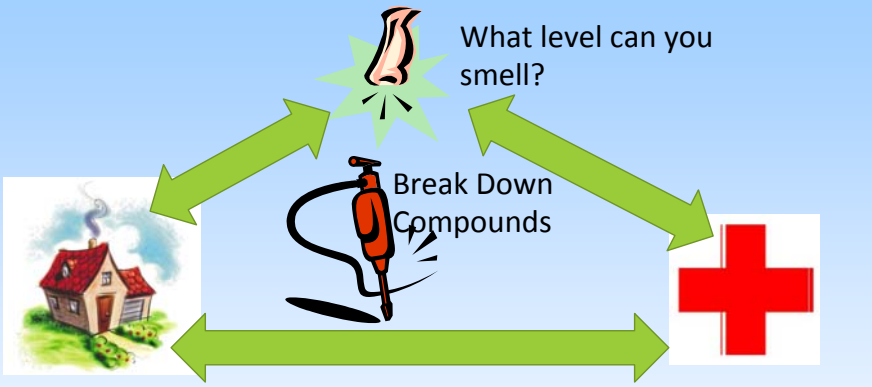
- No extraneous compounds found that could not be explained as analytical artifacts (as of 2/18/14)
- No PPH detected in any samples (as of 2/18/14)
- 4-MCHM appears to be the only compound of interest that we are currently detecting in the house samples (about 0.6 ppb) (as of 2/18/14)
- Low levels of 4-MCHM are still coming out of WVAW treatment plant (as of 3/22/2014)
- Focus on GAC as source of low level contamination

18

Next Steps

- Access database with all sample results and relevant quality control data has been posted
  - Over 1300 pages (12,000 data points) of raw chemical analysis reports
- Coming weeks
  - Finalization of health effects expert panel report
  - Finalization of report for 10 home study
  - Finalization of report for Consumer odor panel
  - Finalization of design for larger home study
- WV TAP anticipated ending on May 15
  - Final report summarizing all the results
  - Include recommendations to State for short- and long-term activities

The WVTAP program mission



Questions

21

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APPENDIX E: KANAWHA-CHARLESTON HEALTH DEPARTMENT SYNDROMIC SURVEILLANCE

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Methods Description from Dr. Gupta

Using active syndromic surveillance, we monitored in real-time the frequency of illnesses with a specified set of clinical features not identified with a specific diagnosis. The population for analysis was chosen among patients self-reporting illness symptoms related to MCHM water exposure with onset after January 9, 2014.

Sentinel providers were identified to complete a line list tool. Sentinel providers included physicians and mid-level providers (Nurse Practitioners, Physician Assistants, etc.) who had agreed to report all cases (patients) who presented with self- reported symptoms related to exposure to MCHM. Medical practices were specifically selected based on defined criteria which included: community centered (defined as practices more likely to see those patients presenting with symptoms they reported as related to MCHM exposure as opposed to random specialty practices such as hospitalist, cardiologist etc.); with multiple facility locations in Kanawha and Putnam counties such as large pediatric practices, primary care centers, school-based health centers, and Urgent Cares. The facilities had multiple providers covering a large geographical area and were representative of the two largest counties affected (Kanawha and Putnam).

A line list was developed to collect data on each patient which included:

Demographic data was collected in aggregate and limited to gender and age.

Descriptive epidemiology methods were used to define data collected which including time and place of occurrence (home, work, food facilities, other) and the self-reported symptoms of the persons affected.

The list included multisystem symptoms (respiratory, digestive, integumentary (skin), neurological)

Respiratory: cough, sore throat

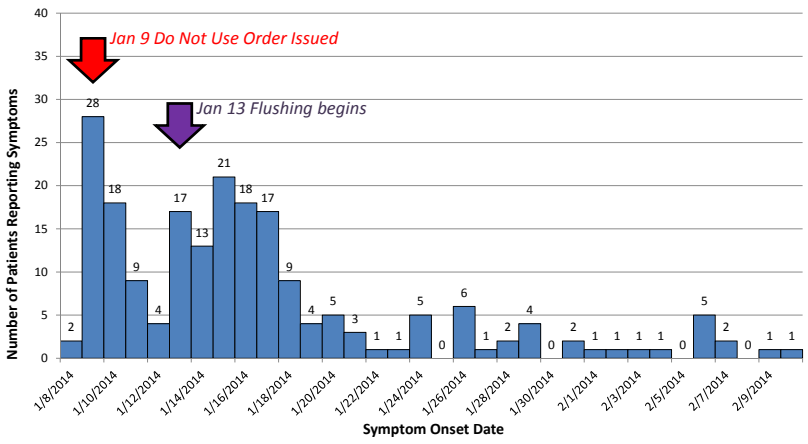
Digestive: nausea, vomiting, diarrhea

Skin: rash, skin irritation

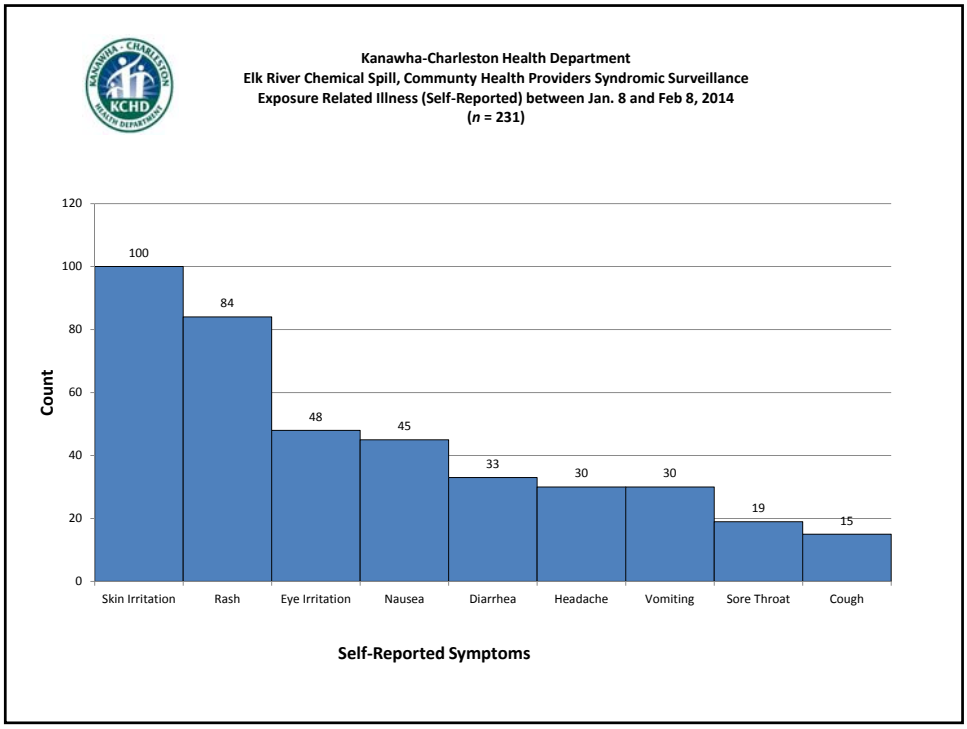
Neurological: Headache

As symptoms had not been defined we included a column: Other symptoms

Kanawha-Charleston Health Department
Elk River Chemical Spill, Community Health Providers Syndromic Surveillance



Data represent only 10 multi-provider practices; There are at least 1,300 providers in the area


Kanawha-Charleston Health Department
Elk River Chemical Spill, Community Health Providers Syndromic Surveillance
Exposure Related Illness (Self-Reported) between Jan. 8 and Feb 8, 2014
(n = 231)
Count
120
100
80
60
40
20
0
100
84
48
45
33
30
30
19
15
Skin Irritation
Rash
Eye Irritation
Nausea
Diarrhea
Headache
Vomiting
Sore Throat
Cough
Self-Reported Symptoms

Appendix F. The Crude MCHM Chemical Spill 10 Home Study: Resident Behaviors, Perceptions, and Residence Characteristics

WV TAP
WEST VIRGINIA TESTING ASSESSMENT PROJECT

The Crude MHCM Chemical Spill 10 Home Study: Resident Behaviors, Perceptions, and Residence Characteristics

Andrew J. Whelton[1], Jeffrey S. Rosen[2], Jennifer L. Clancy[2], Timothy P. Clancy[2], Ayhan Ergul[2]
1. University of South Alabama, 2. Corona Environmental Consulting, LLC

March 27, 2014

1.0 Introduction and Methods

As part of the West Virginia Testing Assessment Program (WV TAP) project Task 3, 10 households affected by the Crude MCHM chemical spilled were visited. The objective of Task 3 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. They include: Boone, Cabell, Clay, Kanawha, Lincoln, Logan, Putnam, and Roane counties.

An affected home in Jackson County was not visited because several of the Jackson County residents contacted declined participation and had switched to private well water since the drinking water contamination incident occurred. Further investigation revealed Jackson County had the fewest number of West Virginia American Water (WVAW) customers of the nine counties affected. A second home in Putnam County near the Jackson County line was visited in response.

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 this document. Another document will be released that describes tap water chemical and odor testing results.

Resident interviews were conducted using the questionnaire found in the Appendix. Project team members completed the questionnaire while speaking with the household representative. Not all residents responded to all questions. Results shown in this document explicitly describe how many households are represented for each question.

2.0 Interview Results

2.1 Demographics and Notification

The survey of the 10 homes revealed an average of 3.3 people (range from 2 to 7) in each house and the age range of the person responding to the survey was 23 to 65 years old. Children, people older than 70 years of age, or individuals who may be immunocompromised lived in two (2) of the 10 households. All of the households learned about the ‘Do Not Use’ Order on January 9, 2014, the date the order was issued.

Most of the household representatives first learned about the 'Do Not Use' Order through discussions with friends and family members (Table 1). The next most popular method was television broadcast. Radio, Facebook, and phone alerts were less frequently cited.

Table 1. Communication Method Households First Learned about the 'Do Not Use' Order

Mode of Communication	Number of Households Responding
Word of Mouth	4
TV	3
Radio	1
Facebook	1
Phone Alert	1
Word of Mouth	4

Representatives from all 10 households responded to this question.

2.2 Residential Property Service Line, Plumbing System, Water Treatment, and Storage Characteristics

Plumbing system components were inspected and results showed a wide range of materials installed in the 10 homes examined (Table 2). Several homes visited had undergone plumbing renovations between 1986 and 2013. Of the 10 homes visited, water service connections were reported to be copper pipe (5), plastic pipe (4) and a combination of plastic and copper pipe (1). None of the homes had water treatment systems after the tap water passed through the water meter (whole house filter systems). Inside the homes, approximately 60% contained a single type of water plumbing pipe such as copper or plastic, while 40% contained mixed material plumbing systems. Nine of 10 homes had electric hot water heaters and water heaters were typically nine (9) years old with an age range of 3 to 16 years. Two (2) homes had a refrigerator water filter installed. Residents of one (1) home stored tap water in a container in the refrigerator or on a shelf. Another household (1) used a point-of-use filter to treat their tap water before drinking.

Table 2. Type of Plumbing System Materials Installed in Each Home

Characteristic Identified	Number of Households Responding
Single type of plumbing pipe	6
Mixed plumbing pipe system	4
Contained some plastic pipe	8
Contained some copper pipe	6
Electric hot water heater	9
Gas hot water heater	1
Refrigerator water filter	2

Representatives from all 10 households responded to each question; plumbing systems that contained plastic pipe included cross-linked polyethylene (PEX), polybutylene (PB), and chlorinated polyvinylchloride (cPVC) pipe materials.

2.3 Tap Water Odor, Taste, and Color Reports

Resident behavior and perceptions were recorded by asking a series of before incident / after incident questions. A tap water odor was reported by residents in nine (9) of the 10 homes before, during, or following the January 9 "Do Not Use" Order (Table 3). Only three (3) persons reported an unusual tap water color in their homes (Table 4). One person tasted the contaminated tap water and said the water had a sweet taste. None of the other people in the homes drank the contaminated tap water once the "Do Not Use" Order was issued (Table 5).

Table 3. Date Households Detected the Odor in their Tap Water

Date	Number of Households Responding	Odor Level
Odor never detected	1	-
6-Jan	1	3
9-Jan ('Do Not Use' Order issued)	3	3,4,4
10-Jan	1	5
11-Jan	1	4
12-Jan	1	5
13-Jan	1	4
14-Jan	1	4

Representatives from all 10 households responded to this question; Odor ratings: 1 no odor, 2 slight, 3 moderate, 4 strong, 5 unbearable.

Table 4. Date Households Detected Unusual Color in their Tap Water

Date	Number of Households Responding	Color Rating	Comments
Color never detected	7	-	-
14-Jan	1	2	-
30-Jan	1	3	-
8-Feb	1	NR	Oily film on water in sink

Representatives from all 10 households responded to this question; Color ratings: 1 clear, 2 slight, 3 moderate, 4 dark, 5 very dark.

Table 5. Date Households Detected the Unusual Taste in their Tap Water

Date	Number of Households Responding	Taste Rating	Comments
Did not taste the water	9	-	-
Date not reported	1	Not reported	Sweet

Representatives from all 10 households responded to this question; Taste ratings: 1 no taste, 2 slight, 3 moderate, 4 strong, 5 unbearable.

2.4 Plumbing System Flushing and Reported Symptoms

On average, residents flushed their plumbing systems 14 days after the January 9 'Do Not Use' Order was issued following the guidance provided by West Virginia American Water (WVAW). Some residents flushed within 4 days of the incident while other residents waited 37 days. Most of the residents reported experiencing rashes or eye burning symptoms when they contacted the contaminated tap water while flushing (7 of 10, respondents, see Table 6). These symptoms were reported most frequently. Dizziness was the second most frequently reported symptom followed by nausea and headaches. As of the date of the survey, four (4) of the 10 persons had spoken with a doctor since the incident occurred about the medical implications of exposure. Of the 10 homes, outside individuals visited four of those homes during and following the incident, but none were exposed to tap water because those homes were restricting exposure to tap water because of the contamination incident.

Table 6. Symptoms Reported by Each Household Following Tap Water Exposure

Symptom	Number of Households Responding	Ratings
Rash	4	3,4,5,5
Dizziness	4	3,3,3,5
Burning	4	3,3,3,4
Nausea	3	2,3,3
Numbness	2	2,3
Memory loss	2	4,4
Vomiting	1	2
Other: Headache	3	No rating
Other: Flu-like symptoms	1	No rating
Other: Agitated	1	No rating
Other: Skin itch	1	No rating
Other: Eyes red	1	No rating

Representatives from all 10 households responded to each question; Ratings: 1 no effect; 2 slightly different, 3 moderately differently, 4 very different, 5 severely different.

2.5 Level of Tap Water Contact

Results demonstrated that residents had not resumed their pre-spill water use activities. While all persons used tap water for flushing toilets before and after the incident, one (1) person chose not to use tap water for laundry purposes. At the time of the survey, four (4) households were not using tap water for showering and nine (9) were not using it for brushing teeth; none were using it for drinking, cooking, or baby formula. One (1) household had resumed using hot tap water for mixing hog feed. Surveyed results demonstrate that residents have not resumed their pre-spill water use activities.

Table 7. Level of Contact with the Water before the Incident and as of the Survey Date

Tap Water Use	Total Responding	Number of Households Responding	
		Before	After
Drink	10	5	0
Shower	10	10	6
Laundry	10	10	9
Flush toilets	10	10	10
Brush teeth	9	8	1
Cook	7	7	0
Animals	6	3	1
Baby formula	1	1	0

Representatives from 1 to 10 households responded to each question.

2.6 Resident Attitudes Toward Organizations and Comments

To ascertain resident opinions about the incident and organizations involved, a series of questions were asked regarding what organization they felt was the most responsible for causing the incident and their attitudes towards various agencies. Half of the persons surveyed felt that a West Virginia State Government Agency was most responsible, while some named Freedom Industries and WVAW (Table 8). Some respondents felt two organizations were equally responsible but were asked to select one. In the five (5) instances when two agencies were named, four (4) of five (5) named WVAW as bearing some responsibility.

Table 8. Organization Most Responsible for the Problems of the Incident

Organization	Number of Households Responding
West Virginia Government Agency	5
Freedom Industries	4
West Virginia American Water	1

Representatives from all 10 households responded to each question.

Discussions with homeowners generally revealed residents had reduced confidence in the US Centers for Disease Control and Prevention (CDC), US Environmental Protection Agency (EPA), and State Agencies. Confidence in WVAW was eroded as well. Interestingly, residents attributed more confidence to outside consultants than any other organization.

Table 9. Level of Confidence in Organizations before the Incident and as of the Survey Date

Organization Type	Name	Confidence Rating	
		Before	After
Federal Government	CDC	4.2 ± 1.5 (7)	2.3 ± 1.2 (9)
	EPA	3.5 ± 1.8 (8)	2.1 ± 1.3 (10)
	White House	3.0 ± 1.7 (6)	2.8 ± 2.0 (6)
Water Utility	West Virginia American Water	4.0 ± 1.4 (8)	1.6 ± 1.3 (10)
State Government	State Health Department	3.6 ± 1.5 (7)	1.8 ± 1.0 (9)
	County Health Department	3.5 ± 1.9 (4)	3.1 ± 2.0 (7)
	Governor's Office	2.9 ± 1.4 (9)	1.7 ± 0.9 (9)
	West Virginia DEP	2.6 ± 1.9 (9)	1.7 ± 1.3 (10)
Nongovernmental	Outside Consultants	4.3 ± 1.6 (6)	4.7 ± 0.8 (7)

Representatives from 6 to 10 households responded to each question; Ratings represent 5 = High confidence and 1 = Low confidence; Mean and standard deviation values shown for (n) persons responding.

In addition to the posed survey questions, the interviewer captured comments made by the residents about the spill and its aftermath. These comments are presented verbatim in most instances and summarized in Table 10.

Table 10. Comments by Residents

Home	Resident Comments
1	County was not in first official notification; resident called WVAW and was told incorrectly they were not in the affected area. Had to call for bottled water, feels County was forgotten. No confidence in Bureau of Public Health. Did not have confidence in the County Health Department in the beginning as they relied on WVAW and others in saying the water was safe, but then changed position and made independent comments, gained respect. State should have been checking chemical tanks all along. Wrote to the White House, 60 Minutes, Rachel Maddow and local weatherman; no response initially from anyone but Maddow then gave some coverage. Government handled the situation horribly and relied too much on WVAW and they knew the water wasn't safe. Government screwed up and said water was safe so no FEMA emergency money is available. No confidence in Obama administration, not mentioned in State of the Union address. Feels like this is the 1800s or Third World. West Virginia has been ignored.
2	Baby boy 8 months old went to the emergency room for throat rash as he was very hoarse. Water was brown when flushed on Jan 30.
3	City did not use emergency alarm system; felt City should have done so as that is what it is for. Female resident got nosebleed walking to work along the Elk River on the morning of January 9. Residents are long-term users of ceramic filter for all water ingested. Did taste some water at a restaurant on January 9 around 4:30 pm before 'Do Not Use' Order and thought it tasted off so they did not drink it, thought the Coke lines and water lines were mixed in the drink machine. Felt

Home	Resident Comments
	disoriented and left town for the weekend after the event occurred and shut off the water to the house. The smell from the water still comes and goes when running taps. High regard for Kanawha County Health Department. Feels State is responsible for spill as it is their role to regulate industry and keep people safe.
4	Resident flushed the house on January 18. Smelled sweet odor 3 to 4 days before January 9; headaches during flushing. Washed berries in tap water prior to January 9 and felt sick after eating them. Favorable opinion of Kanawha County Health Department.
5	Opinion of Kanawha County Health Department improved as the event progressed.
6	Smelled sweet odor in water 3 weeks prior to January 9; was licorice odor, now is lighter and sweet. After showering skin felt soft and silky like lotion that was not completely washed off. WVAW should have alarm system to detect when river water is contaminated; strong smell at first flush of taps each day. “No one in politics is doing anything”.
7	Homeowner worked with MCHM in 1980's and remembers the smell in the water as that same smell. Odor began on the third day, was unbearable. Did not shower or wash clothes for first two weeks after spill as clothes smelled of licorice. "Politics rules everything", would have preferred to receive call directly, not hear from news reports. Favorable opinion of Kanawha County Health Department.
8	District water agency that supplies WVAW was excellent, provided lots of information. Resident said that water is not piped from WVAW but there is a tank that is filled periodically from a truck. Thought they were spared as it took five days before smell occurred in their water.
9	Use tub hot water tap to mix hog feed in the morning; still have odor in water on first flush.
10	Felt faint after showering after flushing, lungs felt tight, wife had chemical burns after shower. They are at end of the system and had no odor until January 13, thought they had avoided the contamination.

3.0 FINDINGS

Interviews with representatives of the 10 households affected by the tap water contamination incident revealed several key findings:

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. Residents across the WVAW service area that were interviewed 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, and only one (1) had a treatment system after the tap. Two (2) homes had refrigerator water filters.

4. Residents in one (1) of the 10 homes never detected any odor in the water. The other nine (9) homes reported moderate to unbearable odor at some point on or after January 9.
5. Three (3) of the 10 homes noted some color change in their water which may have been as a result of flushing the system.
6. Nine (9) 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. All 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 (7) of the 10 reported rashes or burning eyes associated with flushing.
8. All homes used water for toilet flushing before and throughout the event. Four (4) homes were not using water for showering and nine (9) were not using tap water for teeth brushing at the time of the survey. None were using tap water for drinking, cooking, or making baby formula; only one (1) 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 (2) of 10 did not use tap water for brushing teeth and three (3) of 10 did not use tap water for cooking.
10. Half of the 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 (4) 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. Outside consultants were also identified as holding resident confidence.

APPENDIX

WV TAP
WEST VIRGINIA TESTING ASSESSMENT PROJECT

CONSENT FORM FOR PARTICIPATION IN WATER ANALYSIS

RELATED TO THE MCHM SPILL

Corona Environmental Consulting, LLC has been contracted by the State of West Virginia to undertake a study of homes in Charleston, WV to assess presence and levels of 4-Methylcyclohexanemethanol or MCHM that may be present in tap water in homes. This study includes sampling domestic water within the home and interviewing household members. Observation of obvious plumbing in the homes will be noted.

Corona scientists are working with Dr. Andrew Whelton from the U. of South Alabama who has been involved in the incident from the earliest stages. The goal of this sampling and testing is to determine if MCHM as well as other chemicals that may be present in the water and at what levels.

Corona Environmental has contracted with two independent certified drinking water laboratories to conduct these analyses. Corona Environmental will collect the samples and ship them to the contracted labs. Corona samplers will conduct a brief interview with homeowners and/or those living in the home to understand: the water usage pattern prior to the event, water quality changes if any noted by persons living in the homes, and a short survey on household plumbing. **Homeowner/resident names in this study will be kept confidential.** By signing this consent form the homeowner releases the State of West Virginia, the Contractor, and its agents from liability.

Address: _____

Signature of homeowner: _____

Signature of interviewer: _____

WV TAP
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West Virginia Drinking Water Survey Questionnaire

1. Name of person(s) interviewed:
2. Address:
3. Phone: email:
4. Number of people living in the household (ages, sex):

5. When did you find out about the drinking water being contaminated?

_____

6. Where did you hear about the incident first?
   a. TV b. Newspaper c. Radio d. Word of mouth
   e. Other:_____
7. Do household members regularly drink tap water? If no, do residents drink bottled water or use home water treatment devices (describe)?

Aesthetic

8. When did you first notice the water odor and describe the types? Has the odor(s) changed?

_____

   a. Rate the strength of the water odor from 1-5
   (1 no odor, 2 slight, 3 moderate, 4 strong, 5 unbearable)

DAY:_____ 1 2 3 4 5

DAY:_____ 1 2 3 4 5

DAY:_____ 1 2 3 4 5

DAY:_____ 1 2 3 4 5

9. Did you notice any coloration in your water? Has the color changed?

_____

   Rate the intensity of the color from 1-5 (1 clear, 2 slight, 3 moderate, 4 dark, 5 very dark)

DAY:_____ 1 2 3 4 5
DAY:_____ 1 2 3 4 5
DAY:_____ 1 2 3 4 5
DAY:_____ 1 2 3 4 5

If you noticed any changes in taste, when did first occur? Has the taste changed?

_____

Rate the strength of the taste from 1-5 (1 no taste, 2 slight, 3 moderate, 4 strong, 5 unbearable)

DAY:_____ 1 2 3 4 5
DAY:_____ 1 2 3 4 5
DAY:_____ 1 2 3 4 5
DAY:_____ 1 2 3 4 5

10. Do you have any children, people older than70 years of age, or individuals who may be immunocompromised in the household:_____

11. Describe your level of contact with the water before the incident? After the incident?
    a. Drinking: _____
    b. Showering/bathing: _____
    c. Washing clothes: _____
    d. Brushing teeth: _____
    e. Cooking: _____
    f. Watering animals: _____
    g. Making baby formula: _____
    h. Flushing toilets:_____

12. Have you felt differently after contacting the water?_____Yes/No_____
    (1 No affect; 2 slightly different, 3 moderately differently; 4 very different, 5 severely different)
    i. Nausea: 1 2 3 4 5
    j. Vomiting: 1 2 3 4 5
    k. Diarrhea: 1 2 3 4 5
    l. Dizziness: 1 2 3 4 5
    m. Rash: 1 2 3 4 5
    n. Numbness: 1 2 3 4 5
    o. Memory loss: 1 2 3 4 5
    p. Other: _____ 1 2 3 4 5

_____
_____

13. Number of people (sex, age) visiting the household during the event if known:
14. Length of visit(s) if known.
15. What did visitors experience, if anything from air or water exposure?
16. Who/what organization do you feel is most responsible for the problems this incident?
17. Have you talked with your/a medical doctor since the event occurred? Yes/No

Information on Premise Plumbing

18. What type of pipe is installed in your –DRINKING WATER– plumbing system?
    a. Copper
    b. PEX
    c. cPVC
    d. PVC
    e. Other:_____

19. When was your plumbing system installed or last renovated?
    _____

20. Have you flushed out your entire house, if so when? Date/
    Time_____

Observations of Interviewer

Entrance of piping/material from meter into the house:

Is water treated after it leaves the service meter?

Whole house filter: Pitcher filter:

Fridge filter: Stored in container in fridge or on shelf

Materials noted in premise plumbing by interviewer:

Hot water heater: Type (electric, gas) Operation (on demand, continuous, intermittent)

Piping material in and out of heater:

Age of heater (if known):

Kitchen faucet: Separate cold and hot or blended, aerator, treatment device (ask homeowner to remove)

Level of confidence in agency before and after incident: Rate 5 high -1 low
CDC
USEPA
STATE DEP
STATE HEALTH DEPT
COUNTY HEALTH DEPT
WV AW
GOVERNOR'S OFFICE
WHITE HOUSE
OUTSIDE CONSULTANTS

Appendix G. The Crude MCHM Chemical Spill 10 Home Study: Tap Water Chemical Analysis

WV TAP
WEST VIRGINIA TESTING ASSESSMENT PROJECT

The Crude MCHM Chemical Spill 10-Home Study: Tap Water Chemical Analysis

Andrew J. Whelton[1], Jeffrey S. Rosen[2], Jennifer Clancy[2], Timothy Clancy[2], Ayhan Ergul[2]
1. University of South Alabama, 2. Corona Environmental Consulting

May 5, 2014

1.0 Introduction

As part of the WV TAP project Task 3, ten households affected by the crude MCHM that was spilled into the Elk River and contaminated the Charleston, WV region's drinking water were surveyed and sampled. The objective of Task 3 was to assess concentration and variability of MCHM in homes in a focused study. Data resulting from the sampling effort will be used to support the design of a larger, more comprehensive sampling and assessment program for the nine counties affected. Households were surveyed and sampled in eight (Boone, Cabell, Clay, Kanawha, Lincoln, Logan, Putnam, and Roane) of the nine counties affected by the chemical spill and between February 11, 2014 to February 18, 2014.

No affected homes in Jackson County were visited because the Jackson County residents contacted declined participation and switched to private well water in response to the contamination incident. Jackson County had the lowest number of West Virginia American Water (WVAW) customers of the nine counties affected. A second home in Putnam County near the Jackson County line was visited in lieu of visiting a residence in Jackson County.

During each household visit, three tasks were completed:

1. Residents were interviewed by the WV TAP project team;
2. Basic chemical and physical properties (temperature, pH, turbidity, chlorine residual) were determined for tap water from kitchen faucets and bathroom fixtures; and
3. Water samples were collected for detailed analyses at commercial laboratories.

Results of the tap water chemical analyses are presented in this document. Results of the resident interviews are presented in a companion report. Together, these two documents describe results of the WV TAP 10 home study.

2.0 Methods

2.1 Field Water Sample Collection, Analysis, and Shipping

Three individuals conducted home sampling and surveying. Premise plumbing sampling was done for four tap conditions in the following order: (1) kitchen cold tap; (2) kitchen hot tap; (3) cold water from the most frequently used bathtub; and (4) hot water from the most frequently used bathtub. Onsite water quality measurements included water temperature, pH, turbidity, free and total chlorine, and odor. The physical measurements were taken at each tap before sample collection. The time was recorded at the beginning of sampling at each tap, and when each sample bottle for chemical analysis was collected.

Total and free chlorine were measured separately using the HACH® Pocket Colorimeter™ II, Chlorine (Free and Total). The *N*,*N*-diethyl-*p*-phenyldiamine (DPD) reagents used were as follows: for total chlorine measurements, DPD reagent A3035, expiration date, 08/2018; and for free chlorine DPD reagent A3238, expiration date 02/2018.

Water temperature and pH levels were measured using a Thermo Scientific Orion 5 Star™ portable meter. The pH meter was calibrated at the beginning of each day of sampling using Fisher pH standards at pH 4, 7, and 10. Turbidity measurements were made using a HACH® 2100Q™ portable turbidimeter. Water samples were tested immediately upon collection at the temperatures recorded. After the physical measurements were recorded, one sampler collected approximately 120 mL tap water in a 250 mL beaker and covered the sample. The sample was then shaken several times while covered and presented to one of the three samplers who smelled it and made a record of the odor. In many instances the individual asked for a second sample before recording results. Each of the three samplers recorded results independently of the others so as not to influence one another. At the conclusion of the physical measurements at each tap, sample collection for laboratory analysis began.

Nine samples were collected for each tap condition. One set of triplicate samples was sent to the commercial laboratory ALS for analysis, a second set of triplicate samples was sent to ALS for archiving and a third set of triplicate samples was sent to the commercial laboratory Eurofins for analysis. The commercial laboratories provided sample containers for all samples. ALS samples for 4-methylcyclohexanemethanol (MCHM) and propylene glycol phenyl ether (PPH) were collected in a single 1 L amber glass bottle with 1 mg sodium thiosulfate and samples for total organic carbon (TOC) analysis were collected in 125 mL or 250 mL plastic bottles with sulfuric acid preservative. Eurofins samples for MCHM/PPH were collected in 1 L amber glass bottles and TOC samples were collected in 125 mL glass bottles. Sampling and recording at each tap condition took 5 minutes to 7 minutes.

After the tap condition samples were collected, a set of matrix spike (MS) and field blank (FB) samples were collected for each analytical laboratory and for archiving. MS and FB samples were collected in the same manner as tap water samples. MS samples were prepared for kitchen cold tap and kitchen hot tap conditions. The FB was a clean sample bottle from each laboratory filled at the kitchen sink counter with laboratory-purchased deionized (DI) water that was free of the analytes of interest. Field blanks are used to assess whether contamination with the analyte of interest (MCHM or PPH) occurred during sampling.

As soon as sampling was completed the bottles were placed in coolers and transported to a local hotel for icing, repacking, and shipping to the designated laboratory. Three laboratories, ALS Environmental Laboratory (Charleston, WV), Eurofins Lancaster Laboratories (Lancaster, PA) and Eurofins Analytical Laboratories (Monrovia, CA) were selected for this project. Samples for ALS Environmental Laboratory were picked each morning by ALS staff at 7 am. Coolers for shipment to Eurofins Laboratories were sent by FedEx® overnight and received on the next business day after shipping. All samples were received within hold times at both Eurofins Laboratories. Upon sample receipt at Eurofins Laboratories, cooler temperatures sometimes slightly exceeded the recommended standard 4°C for most drinking water samples. In these cases half of the samples were hot tap water, which is not typical of drinking water samples.

2.2 Analysis Conducted by Commercial Laboratories

The three laboratories that analyzed samples for this study reported different method detection limits (MDL) and minimum reporting limits (MRL) for TOC, PPH and 4-MCHM (**Table 1**). The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (USCFR 1986). The MRL is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard for that analyte, and can be used only if acceptable quality control criteria for the analyte at this concentration are met. Put simply, the MDL indicates that the analyte is present at a concentration of greater than zero, and the MRL is the level at which the concentration of the analyte can be reported with confidence.

Table 1. Minimum Detection Limits and Minimum Reporting Limits for the Two Commercial Laboratories

Contaminant[2]	**ALS Environmental Laboratory Charleston, West Virginia**		**Eurofins Laboratories**[1] **Lancaster, Pennsylvania Monrovia, California**	
TOC, ppm	MDL = 0.07	MRL = 0.50	MDL = 0.04	MRL = 0.30
PPH, ppb	MDL = 3.7	MRL = 5.1	MDL = 0.5	MRL = 1.0
4-MCHM, ppb	MDL = 2.7	MRL = 5.0	MDL = 0.5	MRL = 1.0

1. Monrovia, California carried out TOC testing while Lancaster, Pennsylvania conducted 4-MCHM and PPH analysis
2. Parts per million (ppm); parts per billion (ppb)

2.2.1 ALS Environmental Laboratory. WV TAP samples were analyzed for TOC, MCHM, and PPH. TOC was determined via Standard Method 5310C. Samples exceeding the calibration range were diluted and reanalyzed. The instruments used for analysis were a 1010 Analyzer coupled with a 1051 Autosampler and a 1030W Analyzer coupled with a 1088 Autosampler, both manufactured by OI analytical. Before sample analysis, the instrument was calibrated using five calibration standards.

A method blank, a laboratory control sample (LCS) and a matrix spike/matrix spike duplicate (MS/MSD) pair were analyzed to serve as batch quality control. The method blank acceptance criterion was no detection of TOC above the reporting limit. The LCS (reagent water spiked at approximately the mid-point of the calibration curve) acceptance criterion was acceptable recovery within the laboratory control limits. Both method blank and LCS criteria needed to be met for the batch to be considered acceptable. The MS/MSD recoveries were also compared to laboratory control limits, and if outside of those, the parent sample would be qualified.

4-MCHM and PPH were examined according to standard US Environmental Protection Agency (US EPA) SW-846 methods for both preparation and analysis. The water samples, (approximately 1000 mL), were extracted using method 3510C with methylene chloride as the extraction solvent under an acidic pH. The extract was initially concentrated on a steam bath using a Kuderna Danish (KD) apparatus, and brought down to a final volume of 1.0 mL using nitrogen evaporation. The extract was then analyzed using method 8270C, which is a gas chromatograph/mass spectrometer (GC/MS) analysis technique. Prior to analysis the internal standards were added to each sample per the method requirements.

Before sample analysis, the GC/MS was tuned to meet the method Decafluorotriphenylphosphine (DFTPP) relative mass abundance criteria and calibrated using a six calibration standards. 4-MCHM was calibrated from 5 μg/mL to 500 μg/mL and PPH was calibrated from 2.5 μg/mL to 250 μg/mL. Instrument performance was verified prior to each 12-hour analytical sequence by the analysis of the DFTPP tune solution and continuing calibration standards, which were compared to the initial calibration curve. ALS instrumentation used for this project was an Agilent 5890/5973 GC/MS system.

With each preparation batch (not to exceed 20 field samples), a method blank, a LCS and a MS/MSD pair were extracted to serve as batch quality control. The method blank acceptance criterion was no detection of target analytes above the reporting limit. The LCS (reagent water spiked at approximately the mid-point of the calibration curve) acceptance criterion was acceptable recoveries within the laboratory control limits for both of the target compounds. Both method blank and LCS criteria needed to be met for the extraction batch to be considered acceptable. The MS/MSD recoveries were also compared to laboratory control limits, and if outside of those, the parent sample would be qualified. All field and quality control samples were spiked with the surrogate standards listed in EPA SW-846, Method 8270C to measure extraction efficiency. The surrogate recoveries were compared to laboratory control limits and, if within those limits, the results were considered acceptable and valid to be reported.

2.2.2 Eurofins Laboratories (Lancaster and Monrovia). 4-MCHM and PPH analyses were carried out by application of the following methods. A water sample was serially extracted with methylene chloride following EPA SW-846, Method 3510. The resulting extract was reduced in volume and an aliquot was injected into a GC/MS. The GC/MS analytical system was tuned and calibrated following the principles outlined in EPA SW-846, Method 8270D. This included tuning the system to DFTPP relative mass abundance criteria and calibration using a minimum of five calibration points from 1 ppb to 60 ppb. An internal standard based initial calibration was used. The analytical system was tuned and the calibration responses checked, relative to the initial calibration responses, every 12 hours.

Field samples were extracted in batches that were not to exceed 20 field samples. With every extraction batch, a method blank, a LCS and an MRL LCS were extracted to monitor the effectiveness of the extraction batch. A method blank was free of target compounds to be considered acceptable. The LCS (which was an aliquot of laboratory water spiked at approximately the mid-point of the calibration curve) and the MRL LCS (laboratory water spiked at or near the MRL) must have demonstrated acceptable recoveries of the target compounds for the extraction batch to be considered acceptable. Additionally, every field sample, method blank, LCS and MRL LCS were spiked with a surrogate standard that also went through the extraction process. If the surrogate standard recovery was acceptable then the inference was that any target compound present in the field sample was recovered. The work was performed on an Agilent 7890 GC with an Agilent 5975 MSD.

3.0 RESULTS AND DISCUSSION

3.1 Tap Water Analysis for Basic Parameters

On-site measurements of tap water quality are summarized in **Table 2.** Tap water temperature is important because temperature influences the contaminant volatility. Volatilized compounds can contribute to resident chemical exposure and off-odors. Cold tap water temperatures ranged from

6.9°C to 21.9°C and hot water temperature ranged from 31.6°C to 58.1°C. Water pH values were within the US EPA Secondary Maximum Contaminant Level (MCL) of 6.5 to 9.5. Nearly all the tap water pH levels found in homes however, exceeded the pH levels leaving WVAW (pH 7.1 to pH 7.3). No chlorine concentrations exceeded the US EPA Primary MCL of 4.0 ppm. As expected, both total and free chlorine concentrations were greater for cold water than hot water within homes. Tap water turbidity levels were in the expected range and varied from 0.05 NTU to 1.47 NTU.

Table 2. Range of Tap Water Quality Conditions Observed Across all Ten Homes

Parameter[1]	Kitchen Sink Faucet		Bathtub Faucet	
	Cold	Hot	Cold	Hot
Temperature, °C	6.9 to 21.9	31.6 to 47.7	7.0 to 14.6	33.6 to 58.1
Water pH, unitless	7.5 to 8.3	7.0 to 7.5	7.4 to 8.1	7.0 to 7.5
Total Chlorine, ppm	2.2 to 2.8	0.2 to 2.4	2.0 to 3.1	0.6 to 2.4
Free Chlorine, ppm	2.0 to 2.9	0.1 to 2.0	2.0 to 2.9	0.6 to 2.1
Turbidity, NTU	0.05 to 1.47	0.05 to 0.65	0.06 to 1.62	0.07 to 0.54

1. NTU = Nephelometric turbidity units; Total chlorine represents free chlorine and combined chlorine results; Results represent a single measurement conducted at each tap within each home

Tap water odors were detected in all 10 homes studied. The sampling team frequently noted licorice, sweet, and chlorine odors. Musty odors were reported less frequently. Licorice odors (considered to be a typical odor of MCHM) were only reported in three of the 10 homes studied. These odors were considered "sharp" and were similar to the licorice odor detected by one team member January 17-22, 2014 during a previous tap water sampling visit to Kanawha, Lincoln, and Putnam Counties. The intensity of the licorice odors observed during the present study were significantly less than those observed in January following discovery of the contaminated tap water. Sweet odors were reported in 7 of 10 homes visited.

Chlorine odors were detected in tap water from 9 of the 10 homes studied, and were reported less frequently for cold water than for hot water samples. This finding is likely due to the fact that hot water had less chlorine present than cold water (**Table 2**). Consumers have been shown to detect chlorine odors in tap water at 25°C when chlorine is present at 0.28 ppm [pH 5] and 0.36 ppm [pH 10] (Krasner and Barrett 1984). With the exception of a single water sample, all tap water contained chlorine above both odor threshold values. Though, for the single 0.1 ppm chlorine water sample, the sampling team detected a chlorine odor likely because its temperature was 41°C and volatilized readily from the tap water. A musty odor was reported in two of the ten homes studied, but only in hot water samples and not from both taps. In some cases, licorice, sweet, and musty odors were observed even when chlorine odors were also detected.

3.2 Organic Carbon Tap Water Levels

TOC concentrations were quantified for premise plumbing because TOC is a general indicator for organic contaminants present in drinking water and has been proposed by the US EPA and others as a metric for determining if drinking water contamination exists (Murray et al., 2010; Hall et al., 2007). There are no Federal or State drinking water regulatory standards for TOC tap water levels because TOC represents many compounds (not a single contaminant), and because the compounds contributing to the TOC may be benign.

TOC concentrations across and within all homes were relatively similar and were generally between 0.72 ppm and 0.92 ppm (**Figures 1 and 2**). A very high TOC concentration was observed for a single sample (6.3 ppm, house 2, kitchen tap cold water, ALS Environmental Laboratory) and was treated as an outlier. Concentrations observed in the water samples are typical of those in finished drinking waters and provide no information regarding the extent of contamination by MCHM or other potential contaminants. At the concentrations of interest, MCHM, PPH and other potential decay products of MCHM would make up a small portion of the overall organic carbon present in the tap water. Ninety percent of all TOC concentrations were less than 0.90 ppm. Standard deviation values (an indication of how much variation in TOC there is between samples collected in the same house) were relatively small, ranging from 0 ppm to 0.18 ppm.

3.2 PPH and 4-MCHM

No PPH was detected in any tap water sample by either commercial laboratory. No 4-MCHM was detected in any tap water sample by ALS Environmental Laboratory, but the Eurofins Lancaster Laboratory detected 4-MCHM in 105 of the 120 samples analyzed. The 105 detections can be attributed to Eurofins Lancaster Laboratory's lower MDL (**Table 1**).

4-MCHM was detected in all 10 homes, but all observed concentrations were substantially less than the 10 ppb State of West Virginia Screening Level (**Figure 3**). Ninety percent of samples had a 4-MCHM concentration equal to or less than 2.4 ppb. Home #8 had the greatest mean 4-MCHM concentration (4.4 $\pm$ 1.4 ppb), and the highest observed concentration (6.1 ppb). No consistent association was found between 4-MCHM concentrations and tap condition.

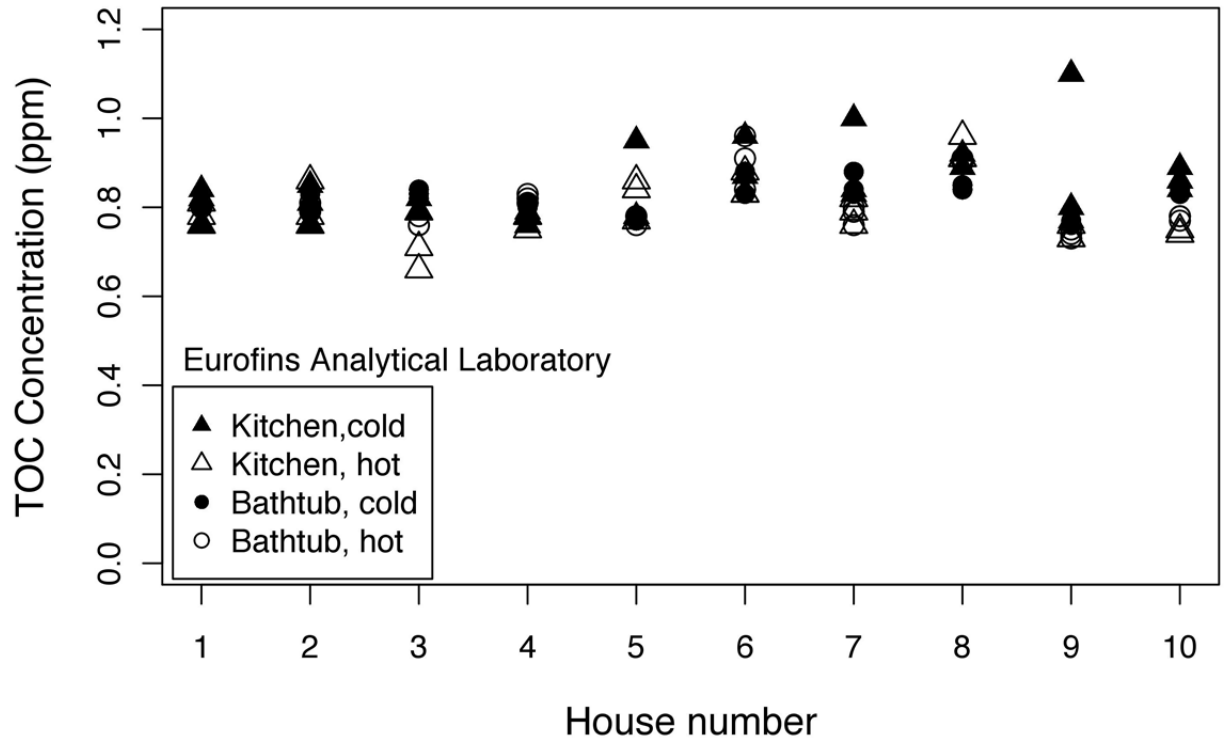

Figure 1. Mean TOC Concentration Across Homes as Reported by Eurofins Analytical Laboratory

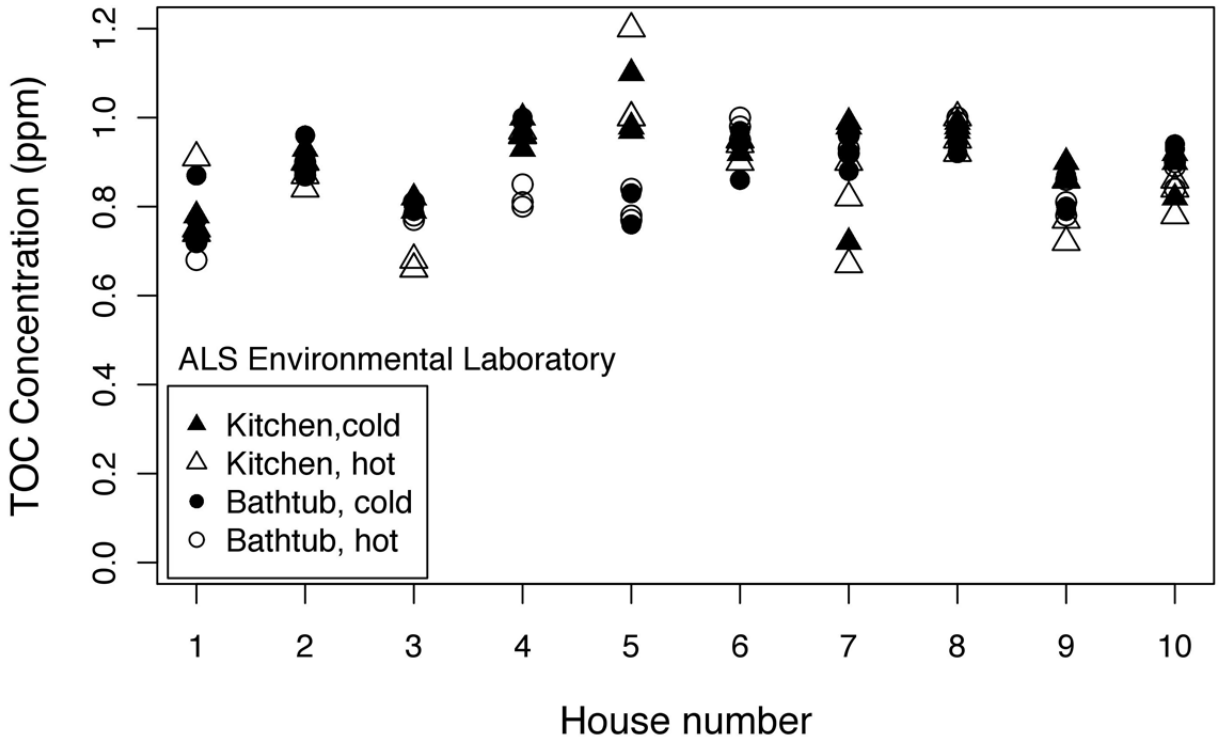

Figure 2. Mean TOC Concentration Across Homes as Reported by ALS Environmental Laboratory. A single apparent outlier (TOC = 6.3 mg/L for house 2) was omitted from the plot.

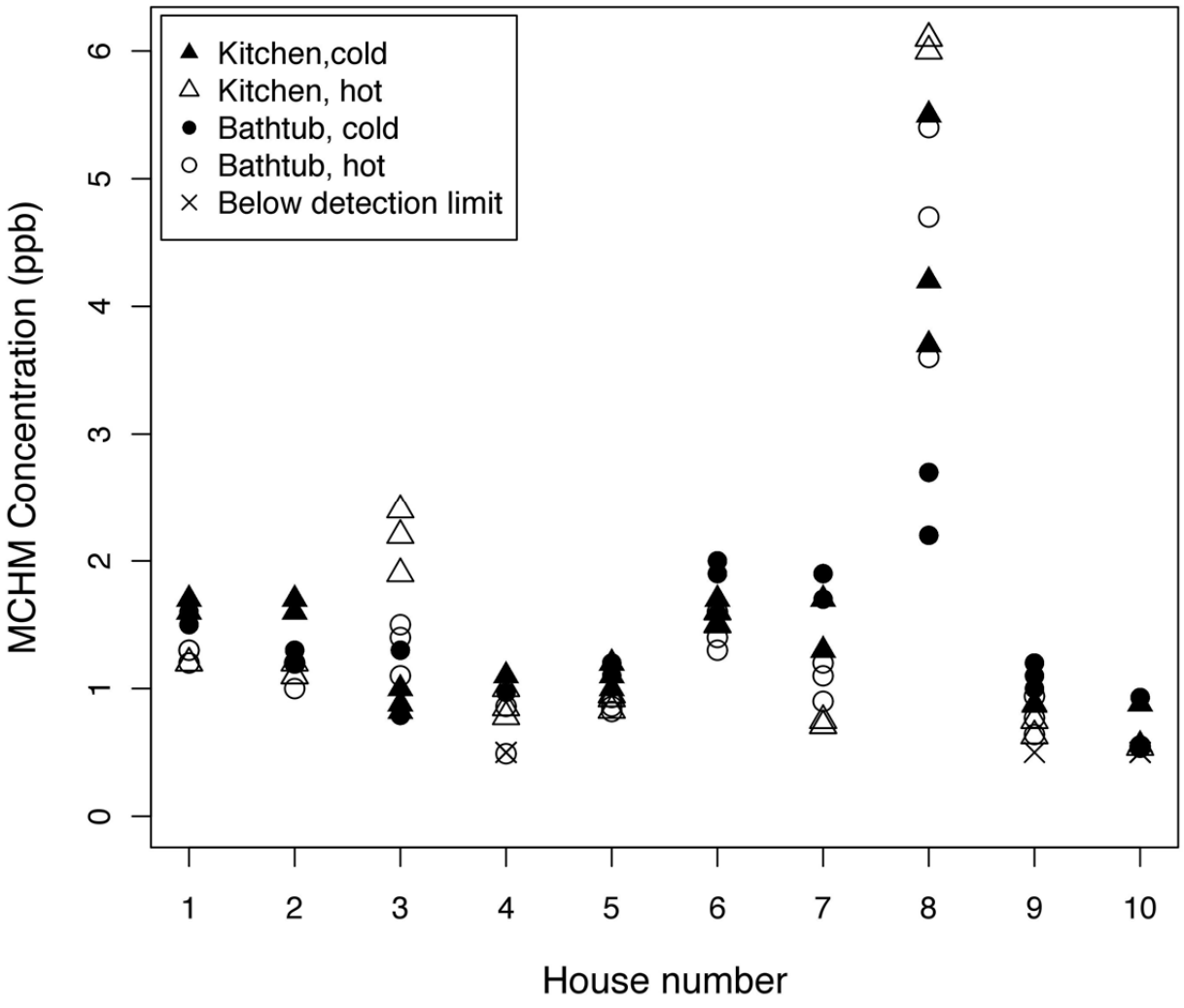

Figure 3. 4-MCHM Concentration by Home and Tap Condition. Only Eurofins Analytical Laboratory results shown because 4-MCHM was not detected in any samples analyzed by ALS Environmental Laboratory.

Table 3. Comparison of Tap Water Odor Descriptors, 4-MCHM and Free Chlorine Concentrations

Location and Water Temperature		4-MCHM, ppb	Free Cl_2, ppm	Licorice	Chlorine	Musty	Sweet
Home 1	Kitchen Cold	1.6	2.30	√	√	-	-
	Kitchen Hot	1.2	1.40	√	√	-	-
	Bath Cold	1.5	2.70	√	√	-	-
	Bath Hot*	1.3	1.80	-	-	-	-
Home 2	Kitchen Cold	1.6	2.60	√	√	-	-
	Kitchen Hot	1.1	2.20	-	√	-	-
	Bath Cold	1.2	2.60	-	√	-	-
	Bath Hot	1.1	2.20	-	-	√	-
Home 3	Kitchen Cold	0.9	2.60	-	√	-	-
	Kitchen Hot	2.2	0.20	√	√	-	-
	Bath Cold	1.1	3.00	-	Y	-	-
	Bath Hot*	1.3	1.10	√	-	-	-
Home 4	Kitchen Cold	1.1	2.70	-	√	-	√
	Kitchen Hot	0.9	2.40	-	√	√	-
	Bath Cold	1.0	3.10	-	√	-	-
	Bath Hot	0.7	2.40	-	-	-	-
Home 5	Kitchen Cold	1.1	2.40	-	√	-	√
	Kitchen Hot	0.9	1.80	-	-	-	-
	Bath Cold	1.1	2.80	-	√	-	√
	Bath Hot	0.9	2.00	-	√	-	-
Home 6	Kitchen Cold	1.6	2.70	-	-	-	√
	Kitchen Hot	1.5	1.60	-	-	-	√
	Bath Cold	2.0	2.40	-	-	-	√
	Bath Hot	1.4	1.90	-	-	-	-
Home 7	Kitchen Cold	1.6	2.20	-	√	-	-
	Kitchen Hot	0.7	0.50	-	√	-	√
	Bath Cold	1.8	2.40	-	√	-	-
	Bath Hot	1.1	0.60	-	-	-	-
Home 8	Kitchen Cold	4.5	2.60	-	√	-	-
	Kitchen Hot	6.1	1.90	-	√	-	√
	Bath Cold	2.5	2.70	-	√	-	√
	Bath Hot	4.6	2.00	-	√	-	√
Home 9	Kitchen Cold	0.9	2.80	-	√	-	-
	Kitchen Hot	0.7	1.90	-	√	-	√
	Bath Cold	1.1	3.10	-	√	-	-
	Bath Hot	0.8	2.20	-	-	-	√
Home 10	Kitchen Cold	0.7	2.20	-	√	-	√
	Kitchen Hot	0.5	1.50	-	-	-	√
	Bath Cold	0.7	2.00	-	√	-	-
	Bath Hot	0.5	1.80	-	-	-	√

Results for 4-MCHM data represent the mean of three discrete water samples collected from each location. Free chlorine data represent a single measurement at each location before water was collected for 4-MCHM analysis. Hyphen (-) indicates odor type was not detected by the tap water sampling team. Check mark (√) indicates an odor descriptor of "chemical" was reported by the tap water sampling team.

4.0 VALUE OF PARAMETERS MONITORED AND PATH FORWARD

4.1 Important Parameters

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.

4-MCHM analysis was valuable and should be included in additional studies. However, it is critically important that laboratories selected can detect and quantify low concentrations of MCHM (e.g., at the Eurofins MDL of 0.5 ppb). As time since the spill elapses, 4-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.

4.2 Needed Research

This study was designed as a focused residential drinking water sampling field study that supports the design of a larger, more comprehensive characterization for the nine counties affected. The study produced sufficient data for design of the larger study, but raised numerous questions regarding tap water chemical and odor quality at affected buildings. Those questions are presented below.

4.2.1 Expansive In-Home Tap Water Sampling Study

If an expanded in-home tap water survey were conducted, the following questions could inform the sampling plan:

1. How does water age affect 4-MCHM concentration?
2. What is the variability in 4-MCHM concentration between homes within the same pressure zone?
3. Does the residence time of the tap water in premise plumbing influence the 4-MCHM concentration?
4. Do certain plumbing materials (metals and plastics) affect 4-MCHM concentrations?
5. Are there additional chemicals (either break-down products of MCHM or unrelated compounds) present causing odor?

4.2.2 Continued Source. The purpose of this study was not to identify the source of the 4-MCHM, but to characterize 4-MCHM tap water concentrations across the 10 homes studied. The finding that 4-MCHM was present in tap water from all homes studied demonstrates that customers were still being exposed to 4-MCHM contaminated tap water more than 1 month after the incident began. The source of ongoing 4-MCHM loading to the distribution system must be determined so as to predict the assets affected and decontamination actions needed. 4-MCHM could reside in plumbing systems, the WVAW distribution system, or both.

During the initial days of the incident, officials issued a Do Not Use order. This order resulted in contaminated water stagnating in place, and the consequences of this stagnation period and

subsequent flushing of contaminated water through the infrastructure remain unknown. It is possible 4-MCHM adsorbed to or permeated into materials within the WVAW water distribution system and premise plumbing systems. Under this scenario, sequestered MCHM could gradually desorb into the drinking water over time and serve as an ongoing source of contamination.

Water distribution and premise plumbing systems are complex. They are comprised of both metal and plastic water transport components, storage tanks, and hot water heaters. Future studies could include a more detailed investigation into the fate and transport of 4-MCHM and minor components of crude MCHM in premise plumbing and drinking water infrastructure. A number of factors could contribute to detention of MCHM and gradual release from drinking water infrastructure. Corrosion scales on metal pipe surfaces increase the available surface area on which crude MCHM components or breakdown products could adsorb. Biofilms are also present in both drinking water distribution pipes and premise plumbing and could absorb contaminants. Corrosion scales and biofilms could present a greater problem in premise plumbing systems which have smaller diameter pipes than distribution systems pipes and higher surface area to water volume ratios. Prior studies indicate that certain plastics are penetrated more rapidly by organic chemicals than others. Biofilms, pipes, and hot water heaters are all potential in-home sources of crude MCHM components or any breakdown products that were formed.

4.2.3 Reevaluation of Decontamination Measures. The US EPA defines decontamination as "*the inactivation or reduction of contaminants by physical, chemical or other methods to meet a cleanup goal. Decontamination is a key component of the remediation phase in a contamination incident. During a water incident, once contamination and characterization are confirmed, decontamination is performed before returning a system to service*." In accordance with the decontamination cleanup goals established by the State of West Virginia, affected infrastructure and plumbing systems had been decontaminated to a level below the 10 ppb screening level. Despite attainment of this goal, the presence of 4-MCHM at resident taps was objectionable to residents and negatively impacted public perception about their drinking water and their water utility. Those factors should be considered in a reassessment of the clean-up goals for this spill.

5.0 CONCLUSION

The purpose of this work was to conduct a focused residential drinking water field study that included a resident survey and tap water testing. Ten homes affected by the Crude MCHM Elk River chemical spill were surveyed and sampled in eight of the nine counties affected (Boone, Cabell, Clay, Kanawha, Lincoln, Logan, Putnam, and Roane counties). Upon arrival, tap water was characterized for pH, free and total chlorine concentration, turbidity, and odor at the kitchen sink and bathroom tub faucets. Cold water quality was examined first followed by hot water analysis. Water samples were then collected and shipped to two commercial laboratories for determination of TOC, 4-MCHM, and PPH concentrations. MRL and MDLs for their respective methods differed for the two laboratories.

The only parameters that were tested that appear to contribute any useful information for spill characterization and response are MCHM concentration, odor, temperature, and chlorine concentration. The contaminant 4-MCHM was detected in all 10 homes by Eurofins Analytical 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 detect and quantify low concentrations of contaminants during a chemical contamination incident. The reason for this difference is likely due to 4-MCHM method MDL differences. Eurofins Analytical Laboratory's MDL and

MRL for 4-MHCM were nearly 0.5 ppb and 1.0 ppb while ALS Environmental Laboratory's MRL and MDL values were greater at 2.7 ppb and 5.0 ppb. Ninety percent of the 4-MCHM concentrations reported by Eurofins Analytical Laboratory were less than 2.4 ppb. Thus, ALS Environmental Laboratory's method could not detect the low levels of 4-MCHM present in tap water at a 4-MCHM concentration equal to or less than 2.4 ppb. Home #8 had the greatest average 4-MCHM concentration of 4.4 $\pm$ 1.4 ppb, and the maximum observed concentration of 6.1 ppb. No 4-MCHM concentration detected in any home exceeded the 10 ppb State of West Virginia screening level.

6.0 ACKNOWLEDGEMENT

Special thanks are extended to the residents who permitted the WV TAP team to enter their homes and test their tap water. These individuals, who will remain anonymous, have done a great service to thousands of West Virginians who were also affected by the spill. Appreciation is also extended to ALS Environmental Laboratory and Eurofins Laboratories for their participation.

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Appendix H. Sampling Plan Design

WV TAP
WEST VIRGINIA TESTING ASSESSMENT PROJECT

Sampling Plan Design

Sampling Plan Design

Jeffrey S. Rosen[1], Andrew J. Whelton[2], Jennifer L. Clancy[1] and Timothy A. Bartrand[1]

1 - Corona Environmental Consulting
2 - University of South Alabama

0.0 Executive Summary

Following the spill of approximately 10,000 gallons of crude 4-methylcyclohexanemethanol (MCHM[1]) into the Elk River on January 9th, 2014, there have been persistent calls from the area residents for in-home sampling to establish the concentrations of the constituent chemicals in people's residences. This paper explores the properties of a sampling program that can answer the main questions being asked by residents and government officials. Statistical sampling design principles are applied to estimate the amount of certainty that can be established based on different sampling strategies. The evaluation of sampling strategies is based on a pilot sampling program that was implemented by the West Virginia Testing Assessment Project (WV TAP).

Designing a sampling program requires a clear understanding of the questions that the sponsors want to answer. In this case there are many questions that 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 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?

Sampling plans were evaluated that would allow testing whether or not measured concentrations were statistically different from critical values established by the Centers for Disease Control and Prevention (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 that there were still detectable concentrations of MCHM in people's homes. The concentrations ranged from below detection levels of 0.5 parts per billion (ppb) up to 6.1 ppb. The standard deviation 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.

A list of possible critical values to be considered is presented in Table ES -1. These are values that have been considered as critical health effect levels or levels of concern throughout the MCHM spill event.

[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 MCHM makes up 68 - 89% of crude MCHM by weight. In this report crude MCHM denotes to the mixture spilled into the Elk River and MCHM denotes pure 4-MCHM

The values in the columns labelled as Differences in Measurements are the highest average value (4.9 ppb) and the highest individual measurement (6.1 ppb) recorded in the 10 home sampling program. In each of these columns is the difference between the critical value and the highest mean (4.9 ppb) and the highest individual measurement (6.1 ppb). One other difference, the difference between the current lowest detection level for MCHM and the Odor Threshold value which is the lowest concentration at which consumer panelists could consistently detect odors from crude MCHM, is evaluated.

Table ES-1 – List of critical values that might be evaluated relative to measured concentrations with the highest standard deviation observed in the 10 home sampling program (1.5ppb). The bottom row is a summary of the number of samples that would be needed to detect the difference between the Odor Threshold Concentration (0.55 ppb) and the lowest method detection limit (MDL) reported at the time this report was released (0.38 ppb). For this one row the standard deviation used is the lowest one observed (0.10 ppb).

		Difference from Measurements (ppb)			
Basis of Concern	**Level of Concern**	**4.9**	**6.1**	**0.38**	**Number of Samples Required**
CDC Screening Level	1 ppm	995.1	993.9		1
CDC Pregnancy Screening level[2]	50 ppb	45.1	43.9		1
WV TAP Health Effects Safe Level	120 ppb	115.1	113.9		1
Odor Recognition Concentration	7.4 ppb	2.5	1.3		17
Odor Objection Concentration	9.5 ppb	4.6	3.4		3
Odor Threshold Concentration	0.55			0.17	5

It is expected that once the GAC is completely replaced at the West Virginia American Water (WVAW) plant, the concentrations in the water delivered to the affected areas will be consistently lower than the concentrations measured in the 10 home sampling program. Therefore these sample sizes should be more than adequate to detect differences where they actually exist. The question that is asked will dictate the sampling design. 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 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 ensure that each of the regions

[2] Personal communication from Dr. V. Kapil, CDC, to the WV TAP team, 26 March 2014

sampled in the early days of the MCHM event can be declared safe and to develop some confidence on the part of the citizens of the affected area it is advised that 30 homes in each of the 24 regions be tested. 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 listed in Table ES-1. The confidence interval about any estimate of percent homes for the entire affected area would be in the range of ± 3% or better.

1.0 Introduction

This document describes a pilot sampling effort and follow-on analyses that were conducted to support development of a large-scale sampling plan and to answer questions related to the response to the Elk River MCHM spill that occurred in January of 2014. Those questions include how many samples should be taken within a single residence to determine whether MCHM concentration is above a level of concern, where the samples should be collected in a residence, and how many samples should be collected to determine the proportion of houses in an area of interest that must be sampled to establish the proportion of houses with MCHM concentration above a level of concern. The answers that statistics provide to these questions must be weighed against practical considerations such as budget, logistical constraints and public perceptions.

The Elk River Chemical Spill: Kanawha Valley Water Treatment Plant, Distribution System and Customers

On January 9, 2014 the State of West Virginia discovered that a major spill of “crude MCHM” was occurring from a chemical storage tank into the Elk River. This liquid industrial product contained 4-methylcyclohexanemethanol (MCHM) along with several other compounds in lesser quantity. The spill occurred at a site approximately 1.5 miles upstream of the Kanawha Valley water treatment plant (KVWTP) which is operated by West Virginia American Water (WVAW). The initial determination that the water was contaminated was based on complaints by residents of a licorice odor in the air. The licorice odor would become the *de facto* indicator for the people of the Kanawha Valley that there was something wrong with their drinking water.

The Kanawha Valley WTP supplies water to approximately 300,000 residents through a complex system that has the following characteristics:

- A span of nine counties,
- 1,900 miles of water mains,
- 100 water storage tanks,
- 179 separate pressure zones.

The area affected by the spill includes:

- Single family residences,
- Multiple residence buildings,
- Schools,
- All types of businesses,
    - Manufacturing
    - Office buildings
    - Restaurants
- Public buildings,
- Hospitals, and
- Other medical care facilities.

Premise plumbing is the plumbing that is under the control of the building owner after it leaves the water main at the service meter and enters the building. The water provider does not have jurisdiction of the plumbing at this point. Premise plumbing systems differ widely between types of buildings and even between buildings of the same type due to materials, design, and operation. Differences include the plumbing system components (water heaters, washing machines, water treatment devices), plumbing system materials (pipe type, valve type and materials, seal materials, connector materials), service connection within the distribution system, and operation (e.g., presence of pipe segments in the premise that are seldom used). Premise plumbing system complexity and diversity results in a wide variety of water retention times in within buildings connected to the system.

The Elk River Chemical Spill Response

Once the State and water utility confirmed that the spill had occurred, rapid decisions were required regarding whether or not to shut down the raw water intake. Following the confirmation of the spill a decision was made to not shutdown the intake. Crude MCHM contaminated river water entered the treatment plant, underwent some treatment and was discharged from the plant into the distribution system with finished water. The Kanawha Valley WTP is a conventional treatment plant using GAC filtration with a relatively short empty bed contact time and a four-year regeneration cycle. The plant uses chlorine for both primary and secondary disinfection. Potassium permanganate is also applied at the facility for preoxidation, manganese oxidation, zebra mussel control and reduction of disinfection byproducts.

Crude MCHM is an industrial product used to remove coal dust from mined materials. It is used regularly in the coal mining and distribution industry. Because crude MCHM was never expected to be in drinking water sources, little was known about its health effects, treatability or odor characteristics before the Elk River spill. The West Virginia Department of Health and Human Resources (WVDHHR) requested help from the CDC in determining what concentrations of crude MCHM compounds were safe for human exposure. In the area affected, humans could be exposed to chemicals in water through oral ingestion, inhalation because of volatilization from contaminated water and through dermal exposure. After deliberations, the CDC established a screening level of 1 part per million in water (ppm) as a concentration below which water was safe for ingestion.

Within a short period after the spill was known, the WVDHHR and partner agencies conducted water sampling for MCHM:

- In the raw and finished water of the WTP,
- At multiple locations in the distribution system, and
- In public buildings including schools.

Sampling continued in these facilities for a number of weeks following the spill. Some independent sampling was done in personal residences but the sampling was not conducted by State, Federal, or WVAW officials, nor was it coordinated. Figure 1 shows the concentrations of MCHM in finished water, hydrants, and other locations such as schools and public buildings from samples coordinated by the WVDHHR from January 10 to February 5. The black symbols show MCHM concentration (in ppb which is equivalent to µg/Liter) for samples in which MCHM was detected and the grey symbols show the reported detection limit for samples in which no MCHM was detected. No systematic validation or interlaboratory comparison of analytical methods results was undertaken. It is important to note that many of these analyses were carried out using a variety of method detection levels that started out at 1000 ppb then dropped in incremental steps to a MDL at about 0.5 ppb for the work done on this project. Figure 1 indicates that for two weeks MCHM concentrations were frequently greater than 100 ppb, followed by decreasing MCHM concentration and an increasing proportion of non-detect observations.

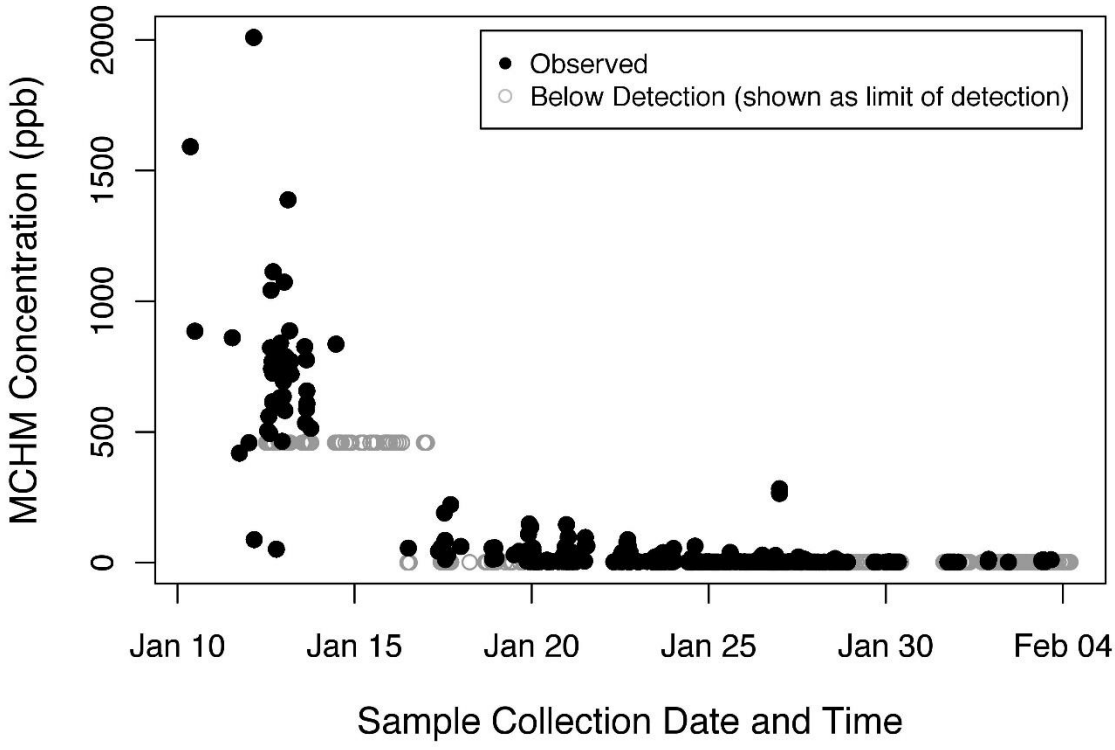

Figure 1. Time history of MCHM concentrations from samples drawn from the distribution system, school taps and faucets, and other public facilities. Note units on the y axis are equivalent to ppb.

After two weeks, most of the samples collected from the distribution system and in public buildings had MCHM concentrations below the detection level established by the laboratories (approximately 10 ppb). However, residents still reported smelling the licorice odor (and other odors described as medicinal, and sweet chemical) in their tap water, despite extensive flushing of the WVAW distribution system. The presence of sweet-licorice odors in their tap water along with analytical results that indicated that there were no detectable chemicals in their water resulted in distrust among the affected residents directed at WVAW, public health officials, the WV DEP and others. Many residents wondered if the concentrations in their homes were greater than the concentrations being measured in the distribution system and the public facilities. No in-home tap water testing had been carried out by the State at that time. Many residents called for an extensive residential sampling program to improve the understanding of their exposures to the contaminated water.

When the WVDHHR initiated the West Virginia Testing Assessment Project (WV TAP) one of the independent team's first tasks was to develop an in-home sampling plan that would address public concerns. The goal of this effort was to design a statistically defensible in-home water sampling plan for the residents affected by the Elk River spill. Specific objectives were to (1) describe important components of tap water testing, (2) quantify the variability in MCHM concentration within and among homes and its effect on in-home water sampling plan design, and (3) design a large-scale in-home sampling plan. To collect data for these purposes, the WV TAP team conducted a pilot sampling effort (called the 10 home study) in which extensive sampling of 10 homes was conducted. Among other objectives, the 10 home study was designed to develop an understanding of the variability of all components of the crude MCHM which might be measured within homes.

Objectives of this Study

The experience described above demonstrates the need for systematic, statistically designed sampling plans that produce actionable scientific data that can help restore customer confidence in their drinking water. To meet this need, the objectives of this study were to:

- Summarize available data,
- Estimate the number of samples that should be collected from an individual home to assess whether MCHM concentration in the home exceeds a level of concern, and
- Estimate the number of locations that must be sampled within a region of interest to establish the proportion of buildings with MCHM concentrations above a level of interest.

2.0 Factors that Determine In-Home Tap Water Sampling Design and Findings from the Ten-Home Study

The reason for an extensive sampling plan was to develop a good understanding of the concentrations of both the spilled industrial product, crude MCHM, its major and minor components and compounds which might be formed during water treatment or distribution or in the plumbing of affected homes. In an ideal world where funding, time and logistics are irrelevant, water samples would be collected at every residence in the affected area, at every tap in the building, and be analyzed for all components of crude MCHM along with testing that water for every possible breakdown compound. Table 1 is a

summary of the customers affected by the crude MCHM spill. Multiplication by 3 gives an estimate of the total population affected (93,866 * 3 = 281,598 people).

Table 1. Affected customers.

Affected Customers	Number (Estimates)
Total	93,866
Residential	86,866
Commercial	5,435
Industrial	58
Public	557

Sampling all of the residential customers one time would require sampling 86,866 separate residences, at a cost of more than 10 million dollars (depending on the details of sampling) and would require more than a year for completion of sampling and laboratory analyses. While collecting and analyzing tap water from all homes is not feasible, sampling a proportion of the residences is feasible and, if done properly, can effectively answer many of the questions. Sampling would result in estimates of the concentrations and the variability that is characteristic of the exposure. Ideally, this sampling should have been initiated as soon as possible following the spill.

In order to design an effective in-home tap water sampling plan it is important to understand the questions that the program will be designed to answer. In the case of the West Virginia spill, the following questions might be asked of a sampling program that would be implemented many months after the spill. Some questions relate to the extent of contaminants still remaining in the overall system (including premises) and other questions relate to the conditions in a particular home. For example:

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?
4. Are there significant differences between concentrations in hot and cold water?
5. Are there significant differences in the concentrations between different locations in the residences?

Along with consideration of the questions that are asked, the level of precision required from the resulting data and the level of concern (i.e., a concentration of MCHM) compared to those measurements must also be considered. Question 1 (above) is a characterization of the chemical concentration in people's residences on a specific day. It implies a level of certainty and this level of certainty depends on the number of samples collected, the number of homes sampled and the variability observed in the data, which also is impacted by the quality of the analytical methods.

Questions 2 and 3 are comparisons of concentrations observed in a sampling program to a screening level established by authorities. In order to compare the concentrations the screening level must be known. A number of concern levels have been articulated over the course of the response to the Elk River chemical spill. Those levels are summarized below.

A. The CDC screening level of 1 ppm (1000 ppb; the original level of concern).
B. A few days after the CDC's issued its original guidance of 1 ppm they issued a second level of concern for pregnant women at 50 ppb which at the time was the detection level of the participating laboratories. (http://www.dhsem.wv.gov/WVTAP/test-results/Documents/POSTED_WV%20TAP%20TOX%20APP%20M%20%28CDC%29.pdf).
C. The WV TAP health review expert panel indicated a 120 ppb screening level below which the experts were willing to say that the water was safe for all people for all intended uses, as long as this was for an exposure less than 28 days.
D. The results of the crude MCHM Odor Threshold study (conducted with a consumer panel as part of the WV TAP independent analysis) indicated that the odor threshold concentration is 0.55 ppb, the odor recognition concentration is 7.4 ppb and the odor objection concentration is in the range of 7.7 – 9.5 ppb.

Question 2 is a comparison of the observed concentrations of chemicals to a level of concern. For example, if the WV TAP safe level of 120 ppb is the level for evaluation then the number of samples (n) that would be required to conclude with 95% confidence (α) that the measured values are below the safe level (120 ppb) is dictated by how close the observed value ($\overline{X}$) is to the level of concern, C (in this example the level of concern = the safe level = 120 ppb). The difference, δ, to be detected is the difference between the level of concern and the observed values. Further, the greater the variability in the measurements, σ, the larger the sample sizes that are necessary to detect a given difference. For data that are normally distributed or that can be modeled based on a normal distribution, the relationship between δ, n and σ is given by Equation 1.

$$n = \frac{(Z_\alpha + Z_\beta)^2 \, \sigma^2}{\delta^2} \qquad (1)$$

In equation 1,

n is the number of samples per sample unit

$(z_\alpha + z_\beta)^2$ is a factor related to the level of significance and the power to detect real differences (α=0.90, β = 0.80)

σ is the standard deviation of the sampling unit and

δ is the difference that we wish to detect.

Similarly, the width of a confidence interval can be defined (Equation 2) for normally distributed data or data that can be modeled as normally distributed. When the variability of sampled data is not known and is based on fairly small sample sizes, the confidence interval is based on a student's t distribution instead of a normal distribution. The student's t distribution has longer tails than a normal distribution and accounts for uncertainty related to sample size.

$$\overline{x} \pm t_{(n-1,\alpha)} \, s/\sqrt{n} \qquad (2)$$

Where

$\bar{x}$ is the average concentration

$t_{(n-1,\alpha)}$ is a student t value with n-1 degrees of freedom for a particular confidence interval in this case (α = 0.9)

s is the standard deviation of the sample and

n is the number of samples included in the calculation of the average and the standard deviation.

To address question 3 above, it is necessary to determine the number of samples required to attain a particular level of confidence in the percentages estimated through a sampling program. If a number of buildings are sampled and the proportion of those buildings that are above any established critical level turns out to be some value $\hat{p}$, confidence levels around the proportion of buildings exceeding the level may be calculated using Equation 3.

$$\hat{p} \pm 1.96 * \sqrt{\hat{p}\hat{q}/n} \quad (3)$$

Where

$\hat{p}$ is the proportion in the sample above the critical level,
$\hat{q}$ is the proportion in the sample below the critical level, and
n the number of sampling units sampled.

3.0 Sampling Strategy to Assess Individual Homes

Review and Analysis of Data from the 10 Home Study Pertinent to Sample Design

As part of the WV TAP project, a focused in-home tap water sampling effort was conducted for 10 homes in the affected area. This effort was conducted to establish the variability of chemical concentrations within each home, among other objectives. That variability includes differences between concentrations for samples taken from the same tap and variation in concentration among samples collected at different taps within a residence. Households were visited in eight of the nine counties (Boone, Cabell, Clay, Kanawha, Lincoln, Logan, Putnam, and Roane) from February 11, 2014 to February 18, 2014. Detailed results of the 10 home study are presented in separate reports describing tap water quality (http://www.dhsem.wv.gov/WVTAP/test-results/Documents/POSTED%2010%20Home%20Study%20Chemical%20Analysis%20Report_FINAL.pdf) and the interview conducted with the residents of those residences (http://www.dhsem.wv.gov/WVTAP/test-results/Documents/POSTED%2010%20Home%20Study%20Interview%20Report_FINAL.pdf).

In the 10 home study, water samples were collected in both a kitchen and a bathroom for both cold water and hot water samples. Nine samples were collected for each category of sample (i.e., Kitchen Cold, Kitchen Hot, Bathroom Cold, and Bathroom Hot). Three samples from each category were sent to each of two different laboratories (Eurofins and ALS). Three samples were held as backups in case there were samples lost in shipment. Table 2 summarizes the samples collected for each home.

Table 2. Samples collected and analyzed for each home in the 10home study.

			Samples		
Location	Tap	Location Code	Total Analyzed	Analyzed by Eurofins	Analyzed by ALS
Kitchen	Cold	1	6	3	3
Kitchen	Hot	2	6	3	3
Bathroom	Cold	3	6	3	3
Bathroom	Hot	4	6	3	3

The 10 home sampling plan was designed to evaluate whether there were differences between the locations in the homes and whether there were differences between the concentrations of chemicals in hot and cold water.

Table 3 is a summary of the total number of samples analyzed in all 10 homes and the number of detections for MCHM and PPH. The only chemical that was expected to be found and that was observed was MCHM (no PPH was detected). The only detections of MCHM were in analyses done by the Eurofins laboratory. The differences in the detections is due primarily to the differences in the detection levels, method reporting level (MRL) and method detection level (MDL) that the laboratories were able to attain along with the reliability of those detection levels (Table 4). Since the only results with positive detections were for MCHM samples analyzed by Eurofins, further analyses were performed on these results and additional sampling, if undertaken, should only be for MCHM.

Table 3. Summary of the total number of samples analyzed for the 10 home study.

			Samples			Detections Eurofins		Detections ALS	
Location	Tap	Location Code	Total Analyzed	Analyzed by Eurofins	Analyzed by ALS	MCHM	PPH	MCHM	PPH
Kitchen	Cold	1	60	30	30	27	0	0	0
Kitchen	Hot	2	60	30	30	27	0	0	0
Bathroom	Cold	3	60	30	30	28	0	0	0
Bathroom	Hot	4	60	30	30	28	0	0	0

Table 4. Summary of the method detection and reporting limits for the two laboratories involved in the analyses.

	Eurofins		ALS	
Analyte	**Method Detection Level (MDL)**	**Method Reporting Level (MRL)**	**Method Detection Level (MDL)**	**Method Reporting Level (MRL)**
MCHM	0.5	0.94	2.7	5.0
PPH	0.5	0.94	3.6	5.0

Of the 120 analyses of MCHM performed by Eurofins, 10 were below the laboratory's MDLs. The non-detect samples provide useful information (i.e., that the concentration of MCHM is lower than in samples in which it was detected) and this information should be included in the assessment of MCHM concentrations and variability and in development of a sampling plan. In order for these analyses to be included in statistical analysis and design procedures, values need to be assigned to the below detection level (BDL) values. Many approaches may be used to assign values to these BDL responses (Helsel 2005). All approaches, however, have limitations.

Several simple, but standard approaches to characterizing non-detect observations were compared to determine how sensitive results are to the choice of approach and which approach is appropriate. Four approaches were evaluated for these data. First, BDL values were omitted from analyses. Second, BDL values were assigned the value 0. Third, the BDL values were assigned half the detection limit. Fourth, BDL values were assigned the detection limit. With these assignments summary statistics for the entire data set were generated. Table 5 shows the impact of the four approaches (all of which introduce biases) on overall mean and standard deviation for the full data set and Table 6 shows the impact of the four approaches on mean and standard deviation for each house. The results of this analysis suggest that the approach for handling non-detect data does not have a very large effect on the summary statistics. Only three of the 10 homes tested had BDL observations for MCHM as measured by Eurofins. Houses 4, 9 and 10 had 4, 1 and 5 measurements BDL, respectively.

Table 5. Summary statistics over all locations for four approaches to account for a below detection observations.

Statistic	**Result**	**BDL = Zero**	**BDL = Half MDL**	**BDL = MDL**
Minimum	0.49	0.00	0.24	0.47
Mean	1.55	1.42	1.44	1.46
Standard Deviation	1.168	1.197	1.175	1.157
Maximum	6.10	6.10	6.10	6.10

Table 6. Demonstration of the impact of approaches for assigning values to below detection level (BDL) measurements of MCHM in the 10 home pilot testing study. Cells for which the BDL count value is not 0 denote homes for which there were BDL observations.

House Number	N Rows	BDL count	drop BDL		BDL 1/2 MDL		BDL = MDL	
			Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
1	12	0	1.408	0.193	1.408	0.193	1.408	0.193
2	12	0	1.283	0.225	1.283	0.225	1.283	0.225
3	12	0	1.383	0.535	1.383	0.535	1.383	0.535
4	12	4	0.878	0.186	0.665	0.347	0.745	0.246
5	12	0	1.001	0.136	1.001	0.136	1.001	0.136
6	12	0	1.633	0.227	1.633	0.227	1.633	0.227
7	12	0	1.298	0.468	1.298	0.468	1.298	0.468
8	12	0	4.408	1.428	4.408	1.428	4.408	1.428
9	12	1	0.877	0.178	0.824	0.251	0.844	0.205
10	12	5	0.649	0.176	0.478	0.248	0.577	0.157

Since the method used to quantify the BDL values does not have a big effect on the means and standard deviations, any of the approaches described can be used. To make the mean and standard deviations conservative (i.e., biased toward overestimation) BDL values were assigned to the MDL in further analyses. Summary results with BDL replaced by the full detection limit are presented in Table 7 and Figure 2. These results are used to estimate the number of samples required to accurately characterize the concentration of MCHM in homes in the affected area.

Table 7. Summary statistics for MCHM concentration by home in ppb. All non-detect concentrations replaced with the method detection level.

House Number	Minimum	25th %ile	Average	Median	Standard Deviation	75th %ile	Maximum
1	1.20	1.20	1.41	1.40	0.193	1.60	1.70
2	1.00	1.13	1.28	1.20	0.225	1.53	1.70
3	0.79	0.91	1.38	1.30	0.535	1.80	2.40
4	0.48	0.48	0.75	0.82	0.246	0.97	1.10
5	0.82	0.88	1.00	0.98	0.136	1.10	1.20
6	1.30	1.50	1.63	1.60	0.227	1.85	2.00
7	0.71	0.79	1.30	1.25	0.468	1.70	1.90
8	2.20	2.93	4.41	4.45	1.428	5.88	6.10
9	0.48	0.67	0.84	0.87	0.205	0.99	1.20
10	0.47	0.48	0.58	0.54	0.157	0.56	0.93

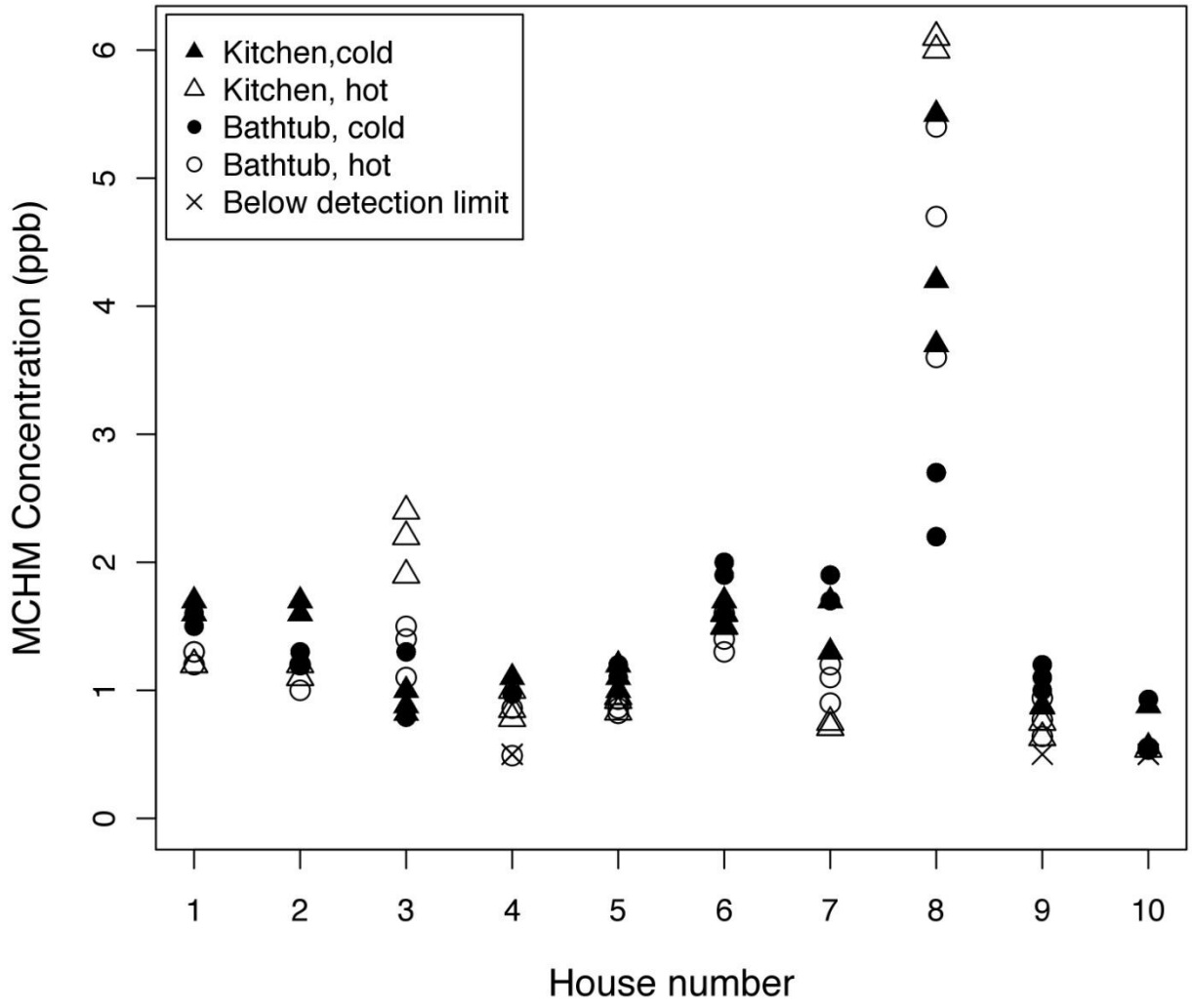

Figure 2. MCHM concentration (ppb) by house. Non-detect observations are shown as the detection limit.

The mean and standard deviation estimates (using replacement of BDL data with the full detection limit) for each house were used in Equation 2 to produce 95th percentile confidence interval estimates for the mean concentration of MCHM in each house and for each tap condition. Results are presented in Table 8. Data subsets were also assigned to a non-parametric group based on Wilcoxon Rank tests in an attempt to discern similarities between houses or tap conditions. Non-parametric groups with the same letter within each home are not different from one another. For example, for house number 1 the Kitchen Cold and the Bathtub Cold samples are not statistically different from one another (both listed as non-parametric group A1) while the Kitchen Hot and the Kitchen Cold (both listed as non-parametric group B1) are also not different from one another.

Table 8. Summary results for MCHM in ppb by home and location. Columns marked CI (Confidence Interval) Low and CI High are the boundaries of a 95% confidence interval calculated according to equation 2. The column marked non-parametric group shows which results within a home are significantly different from one another. The rows with the same letter and number are not different from one another.

House Number	Location	Sample Size	Average	Standard Deviation	CI Low	CI High	Non Parametric Group
1	Kitchen Cold	3	1.63	0.058	1.4899	1.7768	A1
	Kitchen Hot	3	1.20	0.000	1.2000	1.2000	B1
	Bathtub Cold	3	1.53	0.058	1.3899	1.6768	A1
	Bathtub Hot	3	1.27	0.058	1.1232	1.4101	B1
2	Kitchen Cold	3	1.63	0.058	1.4899	1.7768	A2
	Kitchen Hot	3	1.13	0.058	0.9899	1.2768	B2
	Bathtub Cold	3	1.23	0.058	1.0899	1.3768	B2
	Bathtub Hot	3	1.13	0.115	0.8465	1.4202	B2
3	Kitchen Cold	3	0.90	0.092	0.6723	1.1277	B3
	Kitchen Hot	3	2.17	0.252	1.5415	2.7918	A3
	Bathtub Cold	3	1.13	0.294	0.3985	1.8615	B3
	Bathtub Hot	3	1.33	0.208	0.8162	1.8504	B3
4	Kitchen Cold	3	0.69	0.358	-0.2025	1.5759	A4
	Kitchen Hot	3	0.88	0.112	0.5975	1.1559	A4
	Bathtub Cold	3	0.81	0.283	0.1039	1.5094	A4
	Bathtub Hot	3	0.61	0.217	0.0720	1.1480	A4
5	Kitchen Cold	3	1.10	0.100	0.8516	1.3484	A5
	Kitchen Hot	3	0.90	0.062	0.7449	1.0551	B5
	Bathtub Cold	3	1.13	0.058	0.9899	1.2768	A5
	Bathtub Hot	3	0.87	0.056	0.7317	1.0083	B5
6	Kitchen Cold	3	1.60	0.100	1.3516	1.8484	B6
	Kitchen Hot	3	1.53	0.058	1.3899	1.6768	B6
	Bathtub Cold	3	1.97	0.058	1.8232	2.1101	A6
	Bathtub Hot	3	1.43	0.153	1.0539	1.8128	B6
7	Kitchen Cold	3	1.57	0.231	0.9930	2.1404	A7
	Kitchen Hot	3	0.72	0.023	0.6660	0.7807	B7
	Bathtub Cold	3	1.83	0.115	1.5465	2.1202	A7
	Bathtub Hot	3	1.07	0.153	0.6872	1.4461	B7
8	Kitchen Cold	3	4.47	0.929	2.1585	6.7748	A8
	Kitchen Hot	3	6.07	0.058	5.9232	6.2101	A8
	Bathtub Cold	3	2.53	0.289	1.8162	3.2504	B8
	Bathtub Hot	3	4.57	0.907	2.3126	6.8207	A8
9	Kitchen Cold	3	0.87	0.006	0.8590	0.8877	A9
	Kitchen Hot	3	0.62	0.135	0.2840	0.9560	B9
	Bathtub Cold	3	1.10	0.100	0.8516	1.3484	A9
	Bathtub Hot	3	0.78	0.150	0.4096	1.1571	B9
10	Kitchen Cold	3	0.64	0.212	0.1142	1.1658	A10
	Kitchen Hot	3	0.50	0.035	0.4139	0.5861	A10
	Bathtub Cold	3	0.65	0.248	0.0310	1.2624	A10
	Bathtub Hot	3	0.52	0.044	0.4117	0.6283	A10

Initial inspection of Table 7, Table 8 and Figure 2 suggests the following.

1. The concentrations of MCHM observed in the 10 homes studied are all lower than all the levels of concern listed above, except the odor threshold concentration.
2. While most of the measured values are below 2 ppb, there are measurements above 2 ppb in home 3 and in home 8. Home 8 appears to be an outlier for this data set.
3. There is no clear pattern between concentrations in either the bathroom versus the kitchen or between hot and cold water.

These initial observations are confirmed below applying standard statistical tests. In order to determine which tests should be used and whether or not Equation 1 can be used, an evaluation of the normality of the data was performed both on untransformed and on log transformed data. The data sets are small but there consistently was no indication that the data are normally distributed or that a simple transformation like a log transformation would make the data normal. Therefore, any comparisons done were made using non parametric procedures. All comparisons were made using Wilcoxon Rank Test (also known as the Kruskal- Wallis Rank Sums) (calculated by JMP version 11). The differences between the locations within the homes are presented in Table 8. There are no consistent differences in these results. In fact for most of the analyses completed, the results do not vary in meaningful ways. However, the results do demonstrate that there are real differences between locations in some of the homes and therefore it would be useful to sample from more than one location in a home. The variability of the results within homes ranges from a low of 0.2 up to a high of 1.5. This range includes all the estimates of variability observed in the data, irrespective of how the data are grouped.

The power analysis equation presented in Equation 1 depends on an assumption of normality. While the data gathered from the 10 home sampling are not normally distributed, they are not widely divergent of normality. The function of the equation is to develop a relationship between the sample size, the variability in the data and the differences that the experimenters want to detect for a certain level of certainty and level of power. Since the data do not vary from normality in a meaningful way the power analyses will be applied and the results will be considered with additional variability and with some added samples to account for the failure to meet the assumption that the data are normally distributed.

Power Analysis to Estimate the Number of Samples per Home

To perform the power analysis four values need to be selected or estimated. First, a difference needs to be defined which will be the object of the sampling. In this case the difference can be between the highest concentrations (or mean concentrations) observed in the 10 home pilot study. The greatest MCHM concentration observed was 6.1 ppb and the greatest mean was 4.41 ppb, both observed at house number 8. The differences that an in-home tap water monitoring program might want to detect are the differences between these values and the critical values listed above and summarized in Table 9. For example, a sampling program might be designed to answer the question: “Is the average MCHM concentration in a specific home greater than the CDC pregnancy screening level?” In this case the number of samples could be chosen such that a difference of 6.1 ppb between the in-home concentration and the screening level (50.0 – 6.1 = 43.9 ppb) would be confidently detected.

Table 9. **– List of critical values that might be evaluated relative to measured concentrations with the highest standard deviation observed in the 10 home sampling program (1.5ppb). The bottom row is a summary of the number of samples that would be needed to detect the difference between the Odor Threshold Concentration (0.55 ppb) and the lowest method detection limit (MDL) reported at the time this report was released (0.38 ppb). For this one row the standard deviation used is the lowest one observed (0.10 ppb).**

		Difference from Measurements (ppb)		
Basis of concern	Level of Concern	4.9	6.1	0.38
CDC Screening Level	1 ppm	995.1	993.9	
CDC Pregnancy Screening level	50 ppb	45.1	43.9	
WV TAP Health Effects Safe Level	120 ppb	115.1	113.9	
Odor Recognition Concentration	7.4 ppb	2.5	1.3	
Odor Objection Concentration	9.5 ppb	4.6	3.4	
Odor Threshold Concentration	0.55			0.17

The second parameter needed for the power analysis is a range of values for the expected standard deviation (σ). Regardless of how the data are grouped and analyzed, the variability in MCHM concentrations (as expressed by the standard deviation) ranges from a low of about 0.1 ppb to a high value of 1.5 ppb. This standard deviation is characteristic of the range of values that were detected in the 10 home sampling study. It is likely that any sampling done after the release of this plan will be in this range or lower. Therefore, the power analysis is conducted over this entire range of variabilities.

The third parameter required is the confidence level desired (α). In this case a confidence of 90% has been selected. In many scientific studies the confidence is set at 0.95. Given the many uncertainties that will be inherent in any sampling plan done for the vast area affected by MCHM, the authors feel that a 95% confidence level would not be a reasonable expectation and therefore a 90% confidence level is used in all calculations in this report.

The final parameter required in the power analysis is the desired probability of finding a difference when there is a real difference. This value is the power of the test (β). For the analyses in this report the value of β is set at 0.80, which means that in about 20% of the tests there may be a real difference that will not be detected. This selection for the power of the analyses adds additional conservatism to the analyses and means that when a difference is detected it will likely be real.

If the question that is being addressed is whether the concentrations observed at a home are different than any of the screening levels, then applying Equation 1 using the range of variability observed in the 10 home sampling program results in the family of curves shown in Figure 3. Referring to Table 9 and Figure 3, the only values of interest that would require more than a single sample are the differences between the maximum measurements, maximum mean, odor recognition and odor objection levels. At the highest estimate of variability observed, to be able to detect differences of 1.3 ppb (the difference between the highest observed value and the odor objection level) requires 17 samples per home. If the monitoring program focuses on the question: "Is the concentration in a home below the odor recognition level?", three samples would be required based on the highest variability (1.5) and the highest measurement (6.1 ppb) observed in the 10 home sampling. Detecting differences between any of the values or means observed and the safe level established by the WV TAP program (120 ppb) would require only one sample. However, estimating the within-home variability requires a minimum of two samples in each home. Even for evaluation of whether the mean MCHM concentration in a given home is different from 120 ppb, at least two samples per home are required. In all cases the hypothesis that would be tested statistically is that the measured concentration is greater than the established critical value.

The persistence of odors being experienced by residents months after the spill and after multiple flushes of the system raises another possible question. Specifically, are the concentrations of MCHM in residences below the odor threshold concentration? Since Eurofins is able to detect to an MDL of 0.38 ppb and the odor threshold concentration as established by the consumer panel is 0.55 ppb, there is a comparison that can be made between an average concentration measured in homes. The difference that is being estimated is 0.55 - 0.38 ppb = 0 .17 ppb. Referring to Figure 3 (and the underlying equation) even at very low estimates of the standard deviation ($\sigma = 0.1$) 12 samples per home would allow a comparison between concentrations observed and the odor threshold value. However, testing of values below the MRL has additional challenges since there are additional uncertainties that cannot be easily quantified for values between the MRL and MDL.

In all cases the hypothesis that would be tested statistically is that the measured concentration is greater than the critical value of interest. Since the actual value can be either higher of lower than the critical value being test all tests would be based on two tailed tests.

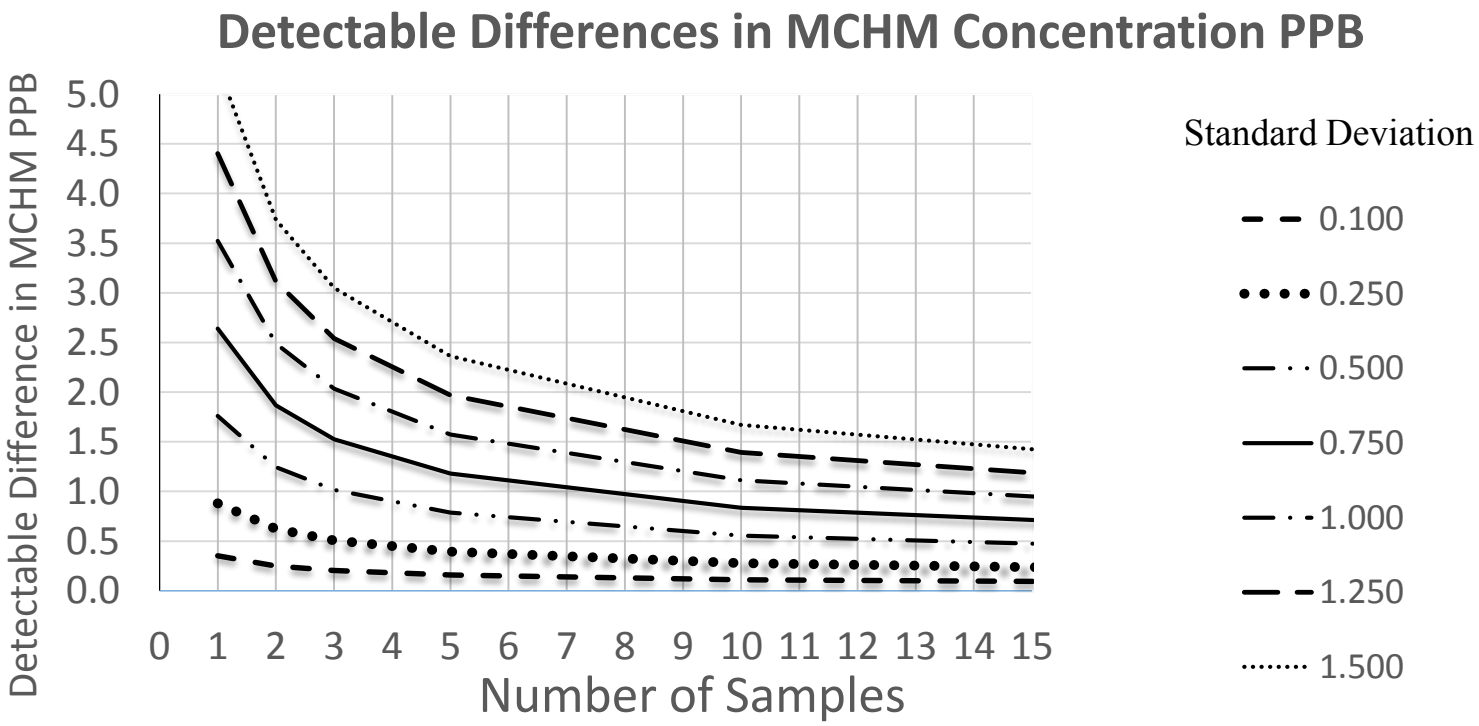

Figure 3. Results of the power analysis assuming a two-sided confidence interval with α (significance) = 0.1 and β (power) = 0.80.

Number of Samples to Assess the Proportion of Buildings in a Region with Concentration Above a Level of Concern

Developing a sampling plan to determine the proportion (percent) of homes in a given region that are above a certain threshold requires a decision regarding how much uncertainty is acceptable (see Equation 3). Figure 4 shows the value that will be added to and subtracted from the percent determined in sampling based on the sample size. For example, if the percent homes in the entire affected area above a threshold of 10 ppb were to be reported as 10% with a sample size of 400 then the resulting confidence interval would be 10% ± 2.4 % (solid line for 400 samples intersects 10% from the x axis at about 2.4% from the y axis).

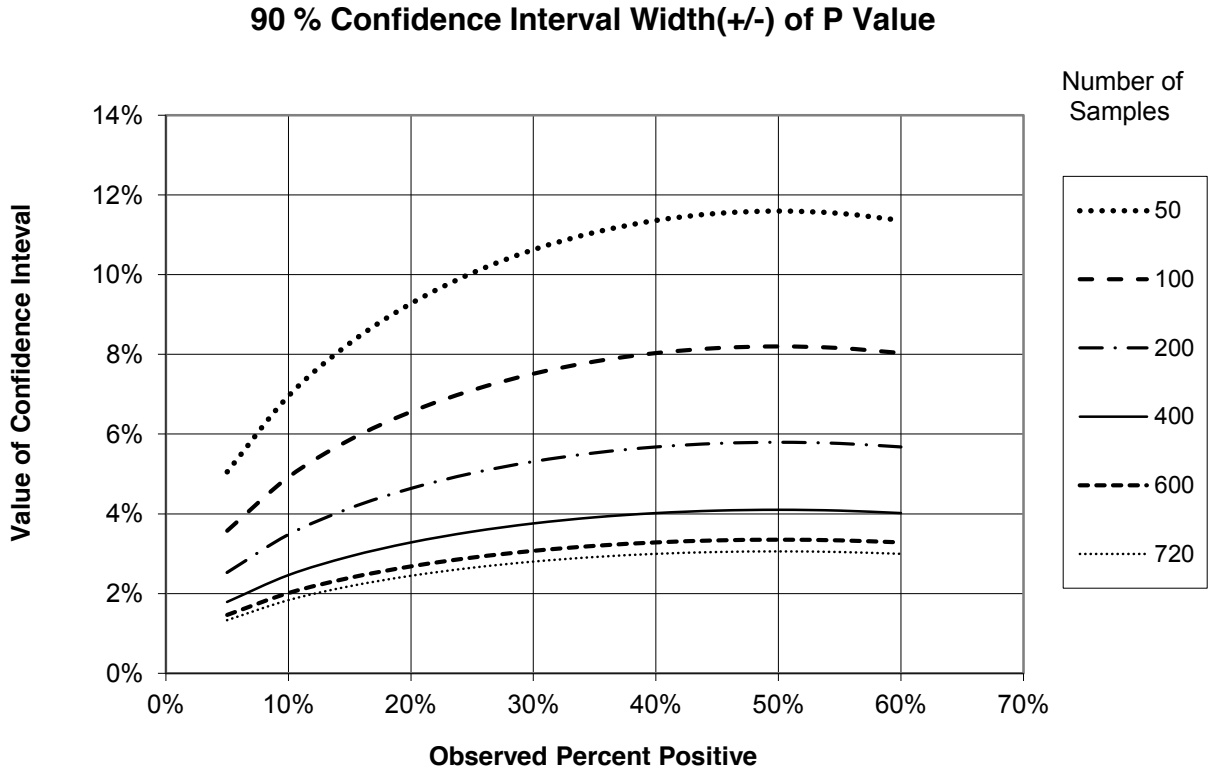

Figure 4. The width of the 90% confidence interval (value added to and subtracted from) the observed percent homes above a particular value. An illustrative example is provided in the text.

4.0 Large-Scale Sampling Plan

When the 10 home study was conducted, other sampling efforts conducted by the State had already indicated that the many MCHM concentrations at key locations within the distribution system were lower than the levels of concern discussed above. However, the 10 home study revealed that there were still significant concentrations of MCHM in all homes tested in eight counties and that there was some significant variability in both the concentrations and the variability between homes. The 10 home

study was conducted in February 2014, approximately one month after the spill. This report is being completed in May 2014, four months after the spill. In the intervening months the concentrations in the WVAW distribution system will have continued to decrease due to flushing and turn-over of the water in the distribution system and in people's homes. Additionally, in March 2014 the WV TAP team suspected that there was low level of MCHM (< 1 ppb) leaching from within the WVAW treatment plant. WV TAP alerted WVAW of the possibility. WVAW immediately implemented a sampling plan that demonstrated that MCHM was desorbing off of the Granular Activated Carbon (GAC) filters. At the time this report was prepared, GAC was being removed from WVAW filters and was being replaced with fresh material. When the replacement of the GAC is completed, MCHM concentrations in the water distribution system and premise plumbing systems should decrease further as a remaining source of MCHM will have been removed. If the combination of flushing of the system and the removal of GAC as a persistent low level source causes continued decreases in MCHM concentration throughout the water system, then few samples, if any, will have concentrations near those observed in the 10 home study. It is possible that most, if not all, samples collected hereafter will be below the detection levels of 0.3 ppb, the MDL of the Eurofins laboratory.

However, it cannot be ruled out that there are reservoirs in the distribution system and in people's homes that could result in concentrations similar to those observed in house 8. If there is a desire to determine once and for all what MCHM levels are in affected homes and if, in fact, they are near zero, then an in-home tap water sampling program such as the one described in this report should be considered. 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. Without the larger scale tap water sampling program, chemical levels in the affected area will remain unknown.

When the spill occurred, the distribution system was divided into 24 regions (see Figure 5) to expedite the water sampling and infrastructure flushing. It is proposed that these 24 regions also be used to organize and facilitate the proposed in-home tap water sampling approach; 30 homes per region should be sampled with three samples collected per home. Since the only contaminant that was detected in the 10 home study was MCHM, this is the only contaminant that is recommended for testing. This approach would address the questions outlined above and allow for robust answers to the 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 Odor Threshold Concentration (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 interval that would allow for meaningful comparisons of the mean concentrations of all the 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 clean-up 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 from Equation 3 and visualized on Figure 4. 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.

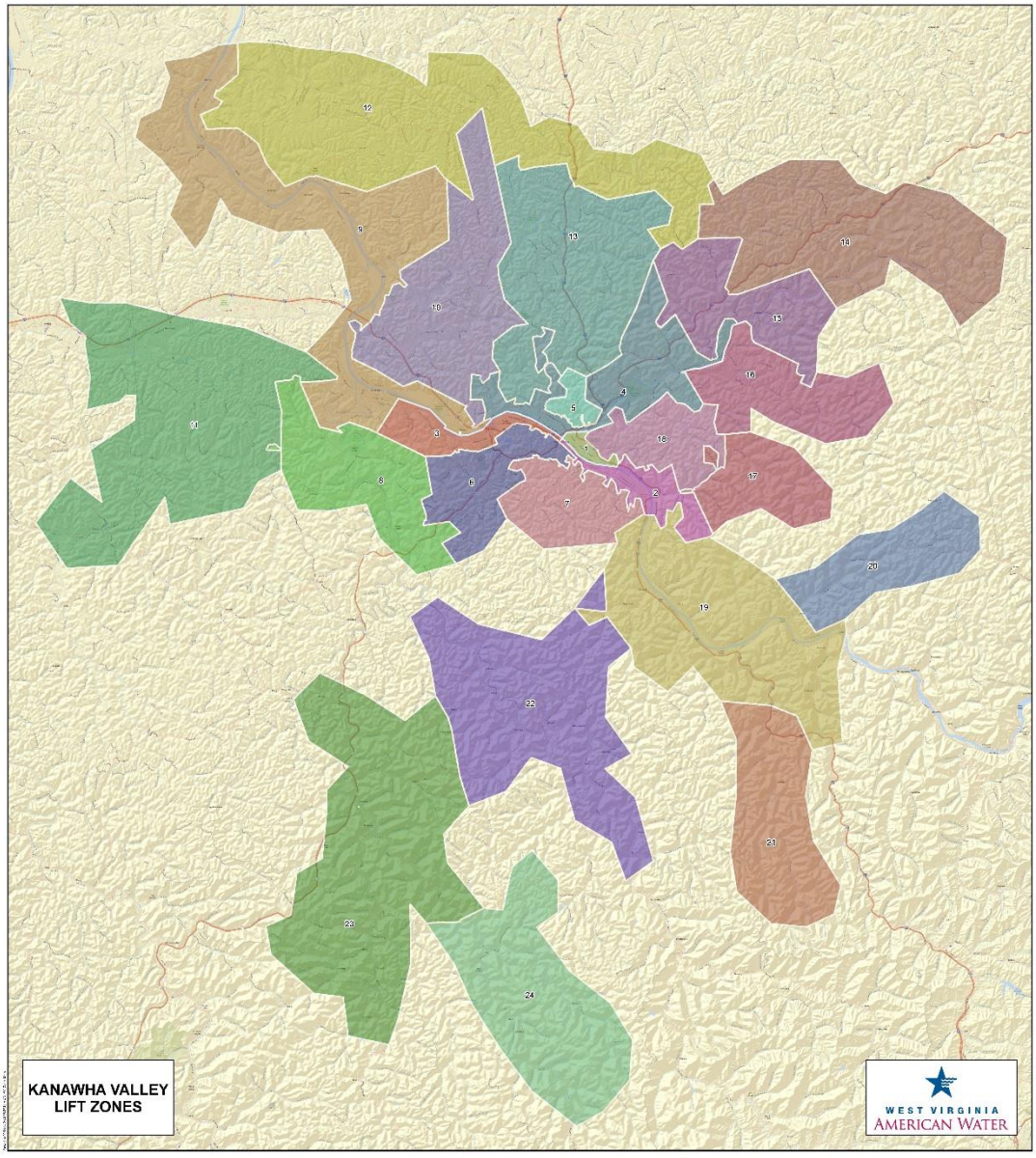

Figure 5. The 24 regions used to expedite sampling performed by the West Virginia National Guard.

Logistics

Implementation of this sampling plan will entail some complex logistics. First, a sampling plan of this type should be based on a random sample of homes. Since this sampling requires entry into private residences the plan cannot be completely randomized. A possible solution would be to develop a volunteer program to enable residents to volunteer to have their homes sampled. The volunteers would be grouped into the regions and random samples of 50 homes would be selected and prioritized. Fifty

homes would be chosen to ensure that 30 homes within the set could be sampled. As with any sampling program, unforeseen difficulties are likely and an additional 20% of homes could be sampled to ensure a sufficient number of samples is collected and analyzed to allow answers to the questions with the certainty and power required. Second, the logistics of the 10 home sampling, which is a fraction of the effort that will be required for this project, demonstrated the difficulties in preparations, sample collection, sample shipment, sample tracking, data capture, data management, data analysis, results integration and reporting. A sampling project of this magnitude will require a significant logistical effort.

5.0 Recommendations

As noted in this and other reports from the WV TAP team, within a short time after the MCHM spill the MCHM concentrations to which people were exposed were, in general, far below the WV TAP health effects safe level and concentrations in the distribution system have likely decreased since then. Yet, as of the writing of this report, members of the public still report detecting odors in tap water that were not perceived before the spill. These persistent odors have contributed significantly to the continued distrust of authorities. This concern along with a general need to understand the science of MCHM fate and transport in distribution systems and premise plumbing may be sufficient motivation for a follow-on sampling effort.

Sampling that could improve our understanding of MCHM fate and transport in fully or partially-treated drinking water could include carefully designed:

- Sampling of the GAC filter effluent after replacement of the activated carbon,
- Sampling portions of the distribution system with different characteristics (e.g., different water ages), and
- Sampling homes with different premise plumbing configurations and materials.

Sampling that could improve confidence in WVAW and other authorities among consumers could entail a large-scale sampling effort aimed at establishing the proportion of buildings in different regions that have average MCHM concentrations above a level of concern. Two levels of concern that could be used are the WV TAP health effects safe level (120 ppb) and the odor objection threshold (9.5 ppb) established by consumer panel in the odor testing component of the WV TAP. The latter level is considerably more stringent than the former and would require significantly greater sample sizes. However, it may be more closely related to customer perception and a more appropriate target concentration if a major goal of the sampling program is to improve consumer confidence in the use of tap water that is currently being supplied to the affected area.

Sampling homes with different premise plumbing type would be very difficult because we do not know the plumbing type (materials and configuration) in each home are before sampling is conducted. Further, in many buildings, the premise plumbing types are mixed and inaccessible for inspection. While a sampling program with this kind of design would potentially be helpful in understanding differences in concentrations and odors, initial indications from the 10 home sampling program were inconclusive regarding the importance of plumbing materials and configuration and the logistical challenges of developing good statistical design would difficult to overcome.

Sampling to evaluate whether the concentrations measured in homes are below the Odor Threshold Concentrations (OTC) will be difficult to interpret because the OTC is so close to the current MDL. Reported values below the MRL (which is currently 0.8 ppb) have additional uncertainty which is difficult to quantify and therefore the power analysis is limited in it predictability.

Any sampling effort that is undertaken needs to carefully consider the logistics and quality control components of a defensible sampling program. This includes the details of:

- How the samples should be collected including the types of sample bottles and reagents included (like dechlorinating agent),
- Where and when the samples should be collected including if and how long the sample taps should be run before samples are collected,
- What requirements should be established for chain of custody tracking,
- What blanks and spikes should be included in the sampling program,
- Methods for sample shipments,
- Holding times for samples,
- Analytical methods,
- Required method and reporting limits,
- What surrogates should be used, and
- How the results will be reported, managed and analyzed.

The 10 home sampling did not address sampling and quantification of MCHM concentrations in apartment buildings or other larger structures. Sampling these structures would require a much more complicated sampling design. Neither resources nor time was available to attempt this more complicated sampling. In order to do this sampling, multiple units within the building would need to be sampled on multiple floors. Multiple locations in each unit would still be required. While this was not attempted as part of WV TAP it could be implemented but it would require extensive resources and planning.

6.0 References

Eastman Chemical Company, 2011. Safety Data Sheet; Crude MCHM. SDSUS / EN / 05, Version: 2.0, Revision date: 08/18/2011.

Helsel, Dennis R. 2005. Nondetects and Data Analysis: Statistics for Censored Environmental Data. Wiley and Sons, Inc. 250pp.

Appendix I. WV TAP Literature Review

WV TAP
WEST VIRGINIA TESTING ASSESSMENT PROJECT
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West Virginia Testing Assessment Project (WV TAP)

Literature Review

Health Effects for Chemicals in 2014 West Virginia Chemical Release: Crude MCHM Compounds, PPH and DiPPH

C. Adams[1], A. Whelton[2], J. Rosen[3]

[1] *Professor, Utah State University*
[2] *Assistant Professor, University of South Alabama*
[3] *President, Corona Environmental Consulting*

March 17, 2014
(ver. 1.5)

DISCLAIMER

Neither the authors nor the WV TAP assume responsibility for use of the information contained herein. Readers are advised to refer to the original documents cited and to develop their own conclusions.

REPORT CONTENTS AND ORGANIZATION

GLOSSARY OF TERMS

ACToR	USEPA's Aggregated Computational Toxicology Resource
BOD	Biochemical oxygen demand (sometimes (incorrectly) "biological" oxygen demand)
BW	Body weight
CAS	Chemical Abstract Service
CAS number	Unique identifier for a chemical (Warning: Chemicals are sometimes mislabeled in the literature with respect to CAS number, the CAS number may be incorrectly assigned to a structure)
CDC	Centers for Disease Control and Prevention
CHDM	1,4-Cyclohexanedimethanol (CAS 105-08-8) (common usage)
CO_2	Carbon dioxide
COD	Chemical oxygen demand
Crude MCHM	Mixture of chemicals containing MCHM as the major component
DiPPH	Dipropylene glycol phenyl ether (CAS 51730-94-0) (common usage)
DMCHDC	1,4-Dimethyl cyclohexanedicarbonate (CAS 94-60-0) (this study)
DW Advisory Level	Drinking Water Advisory Level
EC50	Effective concentration for 50% response
LC_{50}	Lethal concentration for 50% mortality
LD_{50} Lethal dose	Lethal dose for 50% mortality
LOAEL	Lowest-observed-adverse-effect level
MCHM	Pure 4-methyl-1-cyclohexanemethanol (CAS 34885-03-5) (common usage). (Note: "MCHM" will indicated the pure MCHM compound, while "Crude MCHM" is the mixture of MCHM and other compounds described elsewhere.)
MeOH	Methanol (CAS 67-56-1) (common usage)
MMCHC	Methyl 4-methylcyclohexane-1-carboxylate (CAS 51181-40-9) (this study)
MMCHM	4-(Methoxymethyl) cyclohexane methanol (CAS 98955-27-2) (this study)
MSDS	Material Safety Data Sheet
NLM	US National Library of Medicine
NOAEL	No-observed-adverse-effect level
NOEC	No Observed Effect Concentration
NOEL	No Observed Effect Level
OECD	Organization for Economic Development
PPH	Propylene glycol phenyl ether (CAS 770-35-4)

Q&A	Question and answer
SIDS	Screening Information Data Set
Screening Level	Directly equated by CDC to DW Advisory (CDC, 2014c)
TOXNET	Toxicology Data Network (US National Library of Medicine (NLM))
UF	Uncertainty factor
USEPA	United States Environmental Protection Agency
WV	West Virginia

NOTE ON HYPERLINKS

To facilitate ease of tracking references for the reader of this document, hyperlinks were established at the point of reference throughout the document. As a disclaimer, it must be stated that the material referenced was based on the content of the hyperlinked webpage on Mar 1 to 3, 2014, and that the link may have changed or disappeared after that date.

1.0 BACKGROUND

On January 9, 2014, a chemical storage tank owned by Freedom Industries, Inc. leaked approximately 10,000 gallons of a mixture of Crude MCHM and Stripped PPH into the Elk River, West Virginia. The spilled liquid was transported downriver and was withdrawn into the West Virginia American Water treatment plant intake. This water treatment plant serves approximately 300,000 people located in nine counties in southwestern West Virginia. Contaminated water passed through the water treatment facility and was pumped into the water distribution system. Reports of licorice odors at homeowner taps and hospital admittances were signs that the population had contacted the contaminated tap water. The cause of the chemical spill appears to have been related to the failure of both the storage tank containing the chemical mixture and the failure of a containment wall (Eastman 2014a). The February 27, 2014 Eastman document replaced the original February 7, 2014 document.

Today, the exact chemical composition of the spilled liquid and what reached the drinking water taps of affected residents remains somewhat undefined. Initial reports disclosed the leak of Crude MCHM, which contains a mixture of six different organic compounds. Later reports by Freedom Industries disclosed the tank that leaked also contained PPH Glycol Ether (PPH). The statement by Freedom Industries stated that the tank contained 88.5% Crude MCHM, 7.3% PPH (CAS 770-35-4) and 4.2% water. A further report stated that in fact the tank also contained a third mixture, DiPPH as well. The exact composition however has not been chemically confirmed. The apparent source of the PPH was in a mixture called PPH Stripped (Freedom, 2013). DOW Chemical states that they do not produce nor sell Stripped PPH, did not sell PPH directly to Freedom Industries, and suggested contact with Freedom Industries directly to determine their supplier (DOW, 2014).

1.1 Advisory Level Terminology

Various exposure routes are possible for drinking water contaminants including ingestion, inhalation (e.g., during a shower), dermal uptake (e.g., during bathing), and other routes. Estimates of the relative contribution of these routes has not been documented in the literature for the study compounds.

Furthermore, tap water temperatures and air ventilation conditions within buildings are important factors to consider when examining chemical exposure potential. According to water quality monitoring results obtained by a January, 2014, in a study by Whelton and colleagues (2014), and again more recently by the WVTAP team, residential tap water temperatures in the study area of West Virginia ranged from 4 °C to 60 °C. Discussions with the West Virginia Army National Guard also revealed that industrial dishwashers at schools can reach temperatures of 140 °C to 160 °C (Whelton, 2014). Water temperature may play a key role in inhalation exposure because chemicals tend to become more volatile from water at higher temperatures (due to increasing Henry's Law constant). Temperature may play other important roles, as well, including faster reactions with oxidants (e.g., chlorine and permanganate) in the drinking water. Another factor related to chemical exposure potential is the effectiveness of air ventilation systems in houses in bathrooms and kitchens. For example, within homes visited in West Virginia by Whelton's team (2014), and the more recent WVTAP team, air ventilation varied significantly. During these investigations, some bathroom vent fans were found inoperable and some bathroom windows could not be opened because of mechanical problems. These non-ideal conditions influence the air exchange rate and, hence, potentially the concentration of any volatilized chemicals (Whelton, 2014). Consideration in detail of

various exposure routes including drinking water ingestion, inhalation and dermal exposure is a relevant topic to be considered by the expert toxicology panel which will convene in late March or early April, 2014.

Various terms are used to describe the significance of chemical concentrations in drinking water. For regulatory purposes, maximum contaminant levels (MCL) are used by the USEPA, specifically (USEPA 2012): ""The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to the MCLG as feasible using the best available analytical and treatment technologies and taking cost into consideration. MCLs are enforceable standards." Maximum Contaminant Level Goal (MCLG) is related is a non-enforceable health benchmark goal "…at which no known or anticipated adverse effect on the health of persons is expected to occur and which allows an adequate margin of safety." There are numerous chemicals that have established drinking water MCLs. None of the known chemical ingredients of Crude MCHM or Stripped PPH however have MCLs.

During the Freedom Industries chemical spill response, the Centers for Disease Control and Prevention (CDC) (CDC, 2014a) and West Virginia Governor Tomblin (Tomblin, 2014a) used the term "screening level". The term "screening level" is non-standard terminology for drinking water. For example, the term "screening level" is not used in the Drinking Water Advisory Communication Toolbox (CDC, 2013) put out jointly by the CDC, Department of Health and Human Services (DHHS), the United States Environmental Protection Agency (USEPA), and the American Water Works Association (AWWA). Nor is the term "screening level" used in the Drinking Water Standards and Health Advisories literature (e.g., USEPA, 2012).

According to the CDC document on the 2014 West Virginia Chemical Release (CDC, 2014c), the "screening level" is calculated using the same procedure as a health advisory (HA) level, and, specifically, the drinking water (DW) advisory level. For example, the CDC states (CDC, 2014c) "calculation to establish a short-term *screening level* of 1 part per million (ppm) for the MCHM spill in the Elk River" was: DW *Advisory Level* ≤ (NOEL × BW) / (UF × Intake)" and that the DW Advisory Level is 1 mg/L. In this literature review, we use the terms "screening level" and advisory levels to be consistent with the literature regarding the 2014 West Virginia chemical spill event.

A Health Advisory (HA) is "An estimate of acceptable drinking water levels for a chemical based on health effects information" (USEPA, 2012; Donohue and Lipscomb, 2002). An HA is not legally enforceable from a Federal perspective, but serves as a guideline for state and local officials. A One-Day HA is developed to provide protective (non-carcinogenic) guidance for a child assumed to weigh 10-kg and drinking 1 L/day water over a one-day exposure (USEPA, 2012). A Ten-Day HA is developed to protect a 10-kg child drinking 1 L/day over a ten-day period (USEPA, 2012). A Lifetime HA is the concentration of a chemical that is not expected to cause adverse health effects over a lifetime of exposure for a 70-kg adult drinking 2 L/day (USEPA, 2012).

Two further terms of interest include the Drinking Water Equivalent Level (DWEL), which is defined as (USEPA, 2012) as "…a drinking water lifetime exposure level, assuming 100% exposure from that medium, at which adverse, noncarcinogenic health effects would not be expected to occur." Finally, a reference dose (RfD) is defined as (USEPA, 2012) "…An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime."

1.2 Chemical Products in Spill

Several chemical products were in the spill into the Elk River. Information on these chemicals are summarized briefly in this section, and in more detail below.

1.2.1 Crude MCHM - The Crude MCHM is a mixture containing 4-methyl-1-cyclohexanemethanol (MCHM; CAS 34885-03-5); 4-(methoxymethyl) cyclohexane methanol (MMCHM; CAS 98955-27-2); methyl 4-methylcyclohexane-1-carboxylate (MMCHC; CAS 51181-40-9); 1,4-dimethyl cyclohexanedicarbonate (DMCHDC; CAS 94-60-0); 1,4-cyclohexanedimethanol (CHDM; CAS 105-08-8); and methanol (MeOH; CAS 67-56-1). According to the Material Safety Data Sheet (MSDS) for Crude MCHM (Eastman MSDS for Crude MCHM, 2005; Eastman MSDS for Crude MCHM, 2011), MCHM (CAS 34885-03-5) is the primary component at 68-89% (w/w), MMCHM (CAS 98955-27-2) is second most concentrated at 4-22% (w/w), MMCHC is at 5% (w/w) and the other constituents are at 1-2% (w/w) each. Crude MCHM is used in coal processing. Crude MCHM is used for a variety of applications including as a coal and ore flotation chemical (Eastman, 2014a).

1.2.2 DOW PPH Basic – It is reported (though not yet citable) that the source of the Freedom Industries' PPH was DOW PPH Basic (DOW MSDS PPH Basic, 2011) and also described somewhat in the DiPPH Product Data Sheet (DOW DiPPH, 2009). The MSDS for DOW Basic (DOW MSDS PPH Basic, 2009) contains ≤85% DiPPH (CAS 51730-94-0), ≤30% PPH (CAS 770-35-4), ≤ 10% propoxylated impurities, ≤5% 2-hydroxy-alpha-methyl-benzeneethanol (CAS 33206-31-4), ≤5% 2-hydroxy-beta-methyl-benzeneethanol (CAS 134342-25-9), ≤5% polypropylene glycol phenyl ether (CAS 28212-40-0), and ≤5% sodium hydroxide (CAS 1310-73-2). According to the DiPPH product datasheet (DOW DiPPH, 2009), DOW basic contains >40% dipropylene glycol phenyl ether (DiPPH) (CAS 51730-94-0), which, thus brackets the DiPPH concentration between 40% and 85%, with the remainder being PPH and other compounds. The exact composition of the PPH/DiPPH mixture will likely need to come from Freedom Industries.

Another common source of PPH is the DOWANOL PPH Glycol Ether product from DOW (DOW PPH, 2008; DOW PPH 2013; DOW PPH, 2012; DOW PPH, 2014). The DOWANOL PPH Glycol Ether mixture contains >99.5% pure PPH (CAS 770-35-4) (DOW PPH 2012a). While DOW PPH Basic was the likely source for the PPH (and DiPPH) in the spill, the citation for DOWANOL PPH Glycol Ether is provided for informational purposes.

Another common source of DiPPH is the DOWANOL DiPPH Gylcol Ether product from DOW (DOW DiPPH, 2009; DOW DiPPH, 2012). The DOWANOL DiPPH Gylcol Ether mixture contains >60% pure DiPPH (CAS 51730-94-0), <25% pure PPH (CAS 770-35-4), and polypropylene glycol phenyl ether (CAS 28212-40-0) (DOW DiPPH, 2009). Again, while DOW PPH Basic was the likely source for the DiPPH (and PPH) in the spill, the citation for DOWANOL DiPPH Glycol Ether is provided for informational purposes.

2.0 PURPOSE

The purpose of this literature review is to present a summary of toxicity information on the chemicals that were spilled into the Elk River in West Virginia in January 2014 from the Freedom Industries facility. While every effort has been made for accuracy and completeness, the information contained herein should be independently verified, and may contain inaccuracies. The authors and the WV TAP assume no responsibility for use of the information.

3.0 HEALTH DATA ON INDIVIDUAL CONSTITUENTS AND MIXTURES BASED ON EASTMAN TOXICOLOGY STUDIES

3.1 Drinking Water Advisory Based on Crude MCHM and Pure MCHM (CAS 34885-03-5) Studies

The Centers for Disease Control and Prevention (CDC) have suggested a screening level of 1 mg/L (ppm) for MCHM (CAS 34885-03-5), and state (CDC, 2014a):

> "A level of 1 ppm or below is not likely to be associated with any adverse health effects." (CDC, 2014a). The CDC release also suggests that pregnant women may consider additional caution.

The CDC calculated this screening level of 1 mg/L (ppm) using traditional drinking water toxicological assumptions for body weights, quantities of water consumed and uncertainty factors (USEPA, 2012; Donohue and Lipscomb, 2002). The CDC apparently intends this "screening" level to be equivalent to an "advisory" level, as they are clearly equated in the following (CDC, 2014c). Specifically, the "calculation to establish a short-term screening level of 1 part per million (ppm) for the MCHM spill in the Elk River" (CDC, 2014c) was:

$$\text{DW Advisory Level} \leq (\text{NOEL} \times \text{BW}) / (\text{UF} \times \text{Intake})$$

where:

- DW Advisory Level is the drinking water advisory level (mg/L or ppm)
- NOEL = No Observed Effect Level in the experimental species = 100 mg/kg/day
- BW = body weight of a child = 10 kg
- UF = uncertainty factors (unitless)
  - for differences between humans and animals (10x)
  - to account for more sensitive humans (10x)
  - to account for weaknesses in the toxicological database (10x)
- Intake = estimated quantity of water consumed daily by a 10 kg child (1 L/d)

Thus,

$$\text{DW Advisory Level} \leq (\text{NOEL} \times \text{BW}) / (\text{UF} \times \text{Intake}) = [(100\ \text{mg/kg/d}) \times (10\ \text{kg})] / [(10{\times}10{\times}10) \times (1\ \text{L/d})]$$

$$\text{DW Advisory Level} \leq 1\ \text{mg/L (ppm)}$$

The assumptions for BW, UF and Intake are common especially for short-term health advisories (USEPA, 2012).

Very limited toxicological data has been reported for MCHM Crude or pure MCHM (CAS 34885-03-5). The No Observed Effect Level (NOEL) used by the CDC in calculation of their DW Advisory Level was based on studies conducted for the manufacturer, Eastman Chemical in the 1997 and 1998. Eastman released the results of these studies after the Freedom Industries spill in January 2014.

Eastman reports that they perform "regulatory and toxicity review" of all their chemical products (Eastman, 2014a). They report that uses for Crude MCHM has been ongoing since the 1970s. Eastman reports that in 1990, "as part of its ongoing review process, Eastman…conducted toxicology studies on pure MCHM (CAS 34885-03-5)." They state that in 1997, they conducted further toxicological tests of Crude MCHM prior to its release for a coal cleaning application. These studies are listed at Eastman (2014b).

The CDC (CDC, 2014a) relied primarily on two of the Eastman toxicology studies to develop the DW Advisory Level: the 1998 first acute oral study on Crude MCHM (Eastman TX-97-306); and the 28-day oral feeding study on pure MCHM (CAS 34885-03-5) (Eastman TX-89-296).

While the CDC established a recommended screening level of 1 mg/L, the State of West Virginia established "a more stringent testing threshold of 10 parts per billion" (or 10 µg/L) for MCHM (CAS 34885-03-5) (Tomblin, 2014a).

On February 24, 2014, the West Virginia Department of Education issued a press release that stated: "The West Virginia National Guard is revisiting more than 100 schools in Kanawha, Boone, Clay, Cabell, Lincoln and Putnam counties. The results returned so far are indicating a non-detect level at the 2 ppb standard. Non-detect means that there are no traces of MCHM at the 2ppb screening level. After testing thousands of lab samples, chemists are now able to confidently test at 2ppb." (Tomblin, 2014b).

3.1.1 The first acute oral study on Crude MCHM (Feb. 1998; Eastman TX-97-306) was titled "Acute Oral Toxicity Study in the Rat". The tests were performed at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY. The purpose of this study was to estimate the LD_{50} for Crude MCHM in both male and female Sprague-Dawley rats ([SAS:VAF(SD)] obtained from SASCO, Inc.) with a single oral dose .

The rats were dosed with 500 mg/kg, 1,000 mg/kg and 2,000 mg/kg of Crude MCHM and observed for 14 days (Eastman TX-97-306). Each group of male or female rats for each of the three dosing levels consisted of from 501 to 540 rats. The results showed that Crude MCHM was a gastric irritant with edema (i.e., accumulation of fluid) in the glandular gastric mucous membrane. Red discoloration of the urine (hematuria) in some test subjects was noted. A combined LD_{50} for males and females was determined to be 825 mg/kg corresponding to a "slightly toxic" designation in the report (Eastman TX-97-306). Individual LD_{50} values were 933 mg/kg and 707 mg/kg for male and female rats, respectively. This two-week study was one of two Eastman studies evaluated by the CDC to develop the DW Advisory Level (or screening level) of 1 mg/L for MCHM (CAS 34885-03-5) (CDC, 2014a).

A release by Dyer (May 23, 2000) points out some problems, however, with the SAS:VAF(SD) rats from, SASCO, Inc., used in this study and, states specifically (Dyer, 2000):

> "CRUDE MCHM – Toxicology Assessment (972790): Hematuria was seen in acute oral and dermal toxicity studies of Crude MCHM conducted in August 1997. However, these studies were conducted with the SAS:VAF(SD) rat from SASCO, Inc. (Stone Ridge (Kingston), NY), which was used for a short period of time at the Eastman Kodak Company Health and Environment Laboratories. The Laboratories had a number of problems with this strain of rat and returned to using their former animal supplier, Charles River Laboratories. Because of the hematuria finding in the acute studies, a repeated skin application was conducted in CD(SD)BR/VAP Plus rats from Charles River Laboratories in April 1998 with doses of 2,000 mg/kg/day applied 6 hours/day for 13 consecutive days. Full hematology, urinalysis, clinical chemistry, grow pathology, and histopathology examination were included. Other than skin irritation at the site of application, no toxic effects were observed in this detailed examination. An acute oral study was conducted in female CD(SD)IG BR rates from Charles River Laboratories in November 1999: a single dose of 500 mg/kg did not produce any hematuria. Therefore, the finding in the SASCO rat is considered to be of limited value in risk assessment. [The same sample (97-0216) was used for all studies.]"

3.1.2 The 28-day oral feeding study on pure MCHM (CAS 34885-03-5) report (April 3, 1990; Eastman TX-89-296) was titled: "Four-Week Oral Toxicity Study of 4-Methylcyclohexane Methanol in the Rat." Tests were conducted at the Toxicological Sciences Laboratory, Health and Environmental Laboratories,

Eastman Kodak Co., in Rochester, NY. Regarding statistical procedures, the report states that mean values were calculated for clinical chemistry, hematology, organ weights, feed consumption and body weight. Further, the report states that the mean data (except feed consumption) were evaluated using Barlett's test (with $p \leq 0.01$, or 99% confidence), one-way analysis of variance (ANOVA) (with $p \leq 0.05$, or 95% confidence), and Duncan's multiple range test (with $p \leq 0.01$, or 99% confidence). Neither the statistical analysis nor control sample data, was presented in the report however.

In the first phase of the study, two male and two female rats were dosed with from 200 mg/kg/day to 800 mg/kg/day of pure MCHM (CAS 34885-03-5) in corn oil for five days via gavage (i.e., a tube through nose or mouth to the stomach). Results of the five-day experiments showed narcosis (i.e., state of stupor or unconsciousness) in one male and two female rats, and ataxia (i.e., lack of muscle control) in the other female rat at the highest dose level (800 mg/kg/day) (Eastman TX-89-296).

This five-day test was followed by a four-week study with dosing of five male and five female rats of from 0 mg/kg/day to 400 mg/kg/day of pure MCHM (CAS 34885-03-5) five days per week. The report summarizes its results as: "In summary, administration of 400 mg/kg/day of the test article for four weeks was associated with erythropoietic, kidney, and liver effects. None of the effects were indicative of more than minor toxicity, and all were most likely reversible. The no-observed effect level for this substance toxicity study was 100 mg/kg/day." This four-week study was one of two Eastman studies evaluated by the CDC to develop the DW Advisory Level of 1 mg/L for MCHM (CAS 34885-03-5) (CDC, 2014a).

The CDC stated about the Eastman studies and this 28-day oral feeding test in particular (CDC, 2014b):

> "Together, these studies provide a much-improved (but still incomplete) understanding of MCHM's toxicology profile. In particular, one of the studies, the 4-week rat study (study 5 above), provides a NOEL in rats. This NOEL, established by the authors of the study, is 100 mg/kg/day. The 4-week NOEL represents a more scientifically sound study and point of departure for establishing a short-term health advisory for MCHM."

3.2 Other Pure MCHM (CAS 34885-03-5) Study

The acute toxicity battery (containing 5 study reports) on pure MCHM (CAS 34885-03-5) (Jan. 26, 1990; Eastman TX-90-5) was conducted in 1990 and was titled: "Acute Toxicity of 4-Methylcyclohexane Methanol." The study was conducted at the same Eastman Kodak Co. laboratory as the other Eastman 1990 study. The acute toxicity battery study included tests with rats for acute oral toxicity, rats for acute dermal toxicity, guinea pigs for acute toxicity-dermal irritation, guinea pigs for acute toxicity – skin sensitization, and rabbits for acute toxicity-eye irritation. The details of the study may be found with the study report available on-line (Eastman TX-90-5). For the acute oral toxicity in rats testing, LD_{50} values of 1,768 mg/kg and 884 mg/kg were determined for male and female rats, respectively. Remarks from the rat studies included that MCHM (CAS 34885-03-5) was "slightly toxic by the oral route" and was "moderately toxic by the dermal route." For the guinea pig studies, remarks included that the MCHM (CAS 34885-03-5) was "a strong skin irritant." Remarks for the rabbit study included that MCHM (CAS 34885-03-5) was "a moderate eye irritant."

3.3 Crude MCHM Studies

The studies conducted by Eastman in 1997, 1998 and 1999 included a wide range of tests, specifically (Eastman, 2014b)

- Acute Minnow Study
- Acute *Daphnia* Study
- Ready Biodegradation Study
- Chemical Oxygen Demand
- Biological Oxygen Demand
- Skin Sensitization
- Ames Assay
- 14-Day Dermal Study
- First Acute Oral Study
- Second Acute Oral Study
- Acute Dermal Toxicity Study
- Skin Irritation Study

3.3.1 The acute minnow study on Crude MCHM (Feb. 10, 1998; Eastman ES-98-004) was titled "An Acute Aquatic Effects Test with the Fathead Minnow-*Pimephales promelas*." The tests were performed at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY. The test was a 96-hr, static, aquatic effects test with exposures ranging from 6.25 mg/L to 100 mg/L. The study concluded that the 96-hr LD_{50} as 57.4 mg/L and the 96-hr no-observed-effect concentration (NOEC) was 25 mg/L. The study concluded the 96-hr LD_{50} corresponded to a European Union label as "harmful to aquatic organisms" and to a "moderate concern level" by the USEPA assessment criteria (Eastman, ES-98-004).

3.3.2 The Acute *Daphnia* study on Crude MCHM (Feb. 9, 1998; Eastman ES-98-005) was titled "An acute aquatic effects test with the Daphnid – *Daphnia magna*". The tests were performed at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY. The test was a 48-hr, static, aquatic effects test. The study concluded that the 48-hr EC_{50} for Crude MCHM with *Daphnia magna* was 98.1 mg/L, and the 48-hr NOEC was 50.0 mg/L. The study concluded that 48-hr EC_{50} corresponded to a European Union label as "harmful to aquatic organisms" and to a "moderate concern level" by the USEPA assessment criteria (Eastman, ES-98-004).

3.3.3 The Ready Biodegradation study on Crude MCHM (Dec. 3, 1997; Eastman ES-97-112) was titled "Determination of Ready Biodegradability (Biotic Degradation) using the CO_2 evolution test (modified Sturm)." The tests were performed at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY. The 28-day biodegradability test results were that Crude MCHM "could not be classified as readily biodegradable" (Eastman ES-97-112).

3.3.4 The Chemical Oxygen Demand study on Crude MCHM (Oct. 2, 1997; Eastman COD-00775) was titled "Chemical Oxygen Demand Determination". The tests were performed at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY. The results showed a chemical oxygen demand (COD) of 2.54 g COD per g of Crude MCHM (Eastman COD-00775).

3.3.5 The Biological Oxygen Demand Study on Crude MCHM (Sept. 30, 1997; Eastman BOD-00774) was titled "Biochemical Oxygen Demand Determination". The tests were performed at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY. The results showed an average five-day biochemical oxygen demand (BOD_5) of 0.070 g BOD_5 per g Crude MCHM (Eastman BOD-00774). A 20-day

BOD test was also run resulting in a BOD_{20} of 1.3 g BOD_5 per g Crude MCHM (though inhibitory effects were noted except at the most dilute concentrations) (Eastman BOD-00774). The BOD_5/COD ratio was calculated as 0.028 indicating very low biodegradability.

3.3.6 The Skin Sensitization Study on Crude MCHM (Dec. 12, 1997; Eastman TX-97-271) was titled "Skin Sensitization Study (Footpad Method) in the Guinea Pig." Tests were performed at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY and did not cause serious lesions over a 48-hour observation period. No sensitization response was found for Crude MCHM. The researchers further noted that no toxic effects or systemic clinical signs were detected. Details of the study are presented in Eastman TX-97-271.

3.3.7 The Ames Assay on Crude MCHM (Sept. 12, 1997; Eastman TX-97-241) was titled "In the *Salmonella-Escherichia Coli*/Mammalian-Microsome Reverse Mutation Assay with a Confirmatory Assay." Tests were performed at the Covance Laboratories in Vienna, VA. The assay tests for mutagenic activity using *Salmonella Typhimurium* strains and one *E. coli* strains. The conclusions of the test were that the Crude MCHM did not cause a positive increase in the number of revertants per plate…either in the presence or absence of microsomal enzymes…", that is, that Crude MCHM was not mutagenic in the assay (Eastman TX-97-241). Eastman claims that 90% of carcinogens are identified by the Ames test (Eastman, 2014a; CDC, 2014b).

3.3.8 The 14-Day Dermal Study on Crude MCHM (Jan. 6, 1999; Eastman TX-98-129) was titled "A Two-Week Dermal Toxicity Study in the Rat." Testing was carried-out at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY. The test examined the effect of repeated application of Crude MCHM to the skin of both male and female rats over a two-week period. A NOEL was not determined in the test. However, a no-observed-adverse-effect level (NOAEL) of 2,000 mg/kg was determined for systemic toxicity (that is, toxicity associated with absorption of a toxicant) (Eastman TX-98-129).

3.3.9 The Second Acute Oral Study on Crude MCHM (Dec. 1, 1999; Eastman TX-99-188) was titled "Acute Oral Toxicity Study in the Rat." The tests were performed at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY. The purpose of the test was to determine acute toxicity of Crude MCHM in female Sprague-Dawley rats with a single Crude MCHM oral dose. The test was specifically interested in whether hematuria (i.e., blood in the urine) would be exhibited. Results showed that a single dose of 500 mg/kg did not result in either death or hematuria (i.e., blood in urine) of the five rats exposed. While the rats appeared clinically normal after both prior to 1 hr and also after 24 hr (for two weeks), at 4 hr reduced activity in all test rats and stumbling in 40% of test rats was noted (Eastman TX-99-188).

3.3.10 The Acute Dermal Toxicity Study on Crude MCHM (Feb. 24, 1998; Eastman TX-97-308) was titled "Acute Dermal Toxicity in the Rat." Testing was conducted at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY. The purpose of the dermal toxicity study was to assess a dermal LD_{50} for Crude MCHM in both male and female Sprague-Dawley rats observed over a two-week period based on a single topical dose of 2,000 mg/kg. The study demonstrated that Crude MCHM was a dermal irritant resulting in focal necrosis (i.e., occurrence of small foci of necrosis) and eschar (i.e., slough or scab) formation at the application site. An LD_{50} of >2,000 mg/kg was determined for Crude MCHM corresponding to "slightly toxic" (Eastman TX-97-308).

(Note: As discussed for the "Acute Oral Toxicity Study in the Rat" study above, a release by Dyer (May 23, 2000) points out some problems with the SAS:VAF(SD) rat used in this study (Dyer, 2000).)

3.3.11 The Acute Dermal Irritation Study in the Rabbit on Crude MCHM (Nov. 10, 1997; Eastman TX-97-256) was titled "Acute Dermal Irritation Study in the Rabbit." The tests were performed at Eastman Kodak's Health and Environmental Laboratories in Rochester, NY. The potential for Crude MCHM to irritate mammalian skin was examined during this study using three albino rabbits (Hra: (NZW)SPF) (Eastman TX-97-256) dosed with 0.5 mL of Crude MCHM. Test results revealed that Crude MCHM was "irritating to skin" (Eastman TX-97-256).

3.4 4-(MethoxyMethyl) Cyclohexane Methanol (MMCHM (CAS 98955-27-2))

MMCHM (CAS 98955-27-2) occurs at 4-22% in Crude MCHM. While the toxicity of pure MMCHM (CAS 98955-27-2) was not reported by Eastman, they noted that because MMCHM (CAS 98955-27-2) and MCHM are structurally similar, they would be expected to have similar toxicity (Eastman, 2014a).

4.0 HEALTH DATA ON INDIVIDUAL CONSTITUENTS AND MIXTURES FROM TOXNET SOURCES

4.1 MCHM (CAS 34885-03-5)

TOXNET relied on the Eastman toxicology studies cited above for toxicity and health effects information for MCHM (CAS 34885-03-5) (TOXNET – MCHM, 02/25/14).

4.2 4-(MethoxyMethyl) Cyclohexane Methanol (MMCHM (CAS 98955-27-2))

No pure MMCHM (CAS 98955-27-2) toxicity data were found.

4.3 Methyl 4-MethylCyclohexane-1-carboxylate (MMCHC (CAS 51181-40-9))

No pure MMCHC (CAS 51181-40-9) toxicity data were found.

4.4 1,4-Dimethyl CycloHexaneDicarbonate (DMCHDC (CAS 94-60-0))

DMCHDC (CAS 94-60-0) is a Crude MCHM constituent (Eastman, 2011). The MSDS for DMCHDC (CAS 94-60-0) (Sigma 2013) states that there is no data available for oral LD_{50}, inhalation LD_{50}, dermal LD_{50}, skin corrosion/irritation, serious eye damage/eye irritation, respiratory or skin sensitisation, germ cell mutation, reproductive toxicity, teratogenicity, nor other measures.

For DMCHDC (CAS 94-60-0), TOXNET states that "a specific review of the clinical effects and treatment of individuals exposed to this agent HAS NOT YET BEEN PREPARED." TOXNET goes on to state general evaluation information regarding irritation, hypersensitivity and other effects (TOXNET-dimethyl hexahydroterephalate (CAS 94-60-0).

4.5 1,4-CycloHexaneDimethanol (CHDM (CAS 105-08-8))

Similarly, CHDM (CAS 105-08-8) is a Crude MCHM constituent (Eastman, 2011). The MSDS for CHDM (CAS CAS 105-08-8) (Sigma 2012) states an oral LD_{50} for rats of 3,200 mg/kg. The MSDS also states that there is no data available for inhalation LD_{50}, dermal LD_{50}, skin corrosion/irritation, serious eye damage/eye irritation, respiratory or skin sensitisation, germ cell mutation, reproductive toxicity, teratogenicity, nor other measures.

For CHDM (CAS 105-08-8), TOXNET states that "a specific review of the clinical effects and treatment of individuals exposed to this agent HAS NOT YET BEEN PREPARED." TOXNET goes on to state general

evaluation information regarding irritation, hypersensitivity and other effects (TOXNET-1,4-cyclohexanedimethanol (CAS 105-08-8)).

5.0 TOXICOLOGY DATA AVAILABLE ON EPA ACToR

The USEPA has developed a system called Aggregated Computational Toxicology Resource (ACToR) to house publicly available toxicity information. The database includes data from ToxRefDB, ToxCastDB, ExpoCastDB, and DSSTox (USEPA, 2014).

5.1 4-Methyl-1-CyclohexaneMethanol (MCHM; CAS 34885-03-5)

No toxicology data were listed (http://actor.epa.gov/actor/GenericChemical?casrn=34885-03-5).

5.2 4-(MethoxyMethyl) Cyclohexane Methanol (MMCHM; CAS 98955-27-2)

No toxicology data was listed (http://actor.epa.gov/actor/GenericChemical?casrn=98955-27-2).

5.3 Methyl 4-MethylCyclohexane-1-Carboxylate (MMCHC; CAS 51181-40-9)

No toxicology data was listed (http://actor.epa.gov/actor/GenericChemical?casrn=51181-40-9).

5.4 1,4-Dimethyl CyclohexaneDicarbonate (DMCHDC; CAS 94-60-0)

The EPA ACToR database documented a large number of studies for this minor constituent (1%) of Crude MCHM. The studies were conducted at various laboratories including Eastman. The studies generally note low or slight toxicity for CHDM (CAS 105-08-8) (check this). The reader is referred to the EPA ACToR document for details of the many studies (http://actor.epa.gov/actor/GenericChemicalPdfServlet?casrn=94-60-0).

5.5 1,4-CycloHexaneDimethanol (CHDM; CAS 105-08-8)

The EPA ACToR database documented a large number of studies for this minor constituent (1-2%) of Crude MCHM. The studies were conducted at various laboratories including Eastman. The studies generally note low or slight toxicity for DMCHDC (CAS 94-60-0) (check this). The reader is referred to the EPA ACToR document for details of the many studies (http://actor.epa.gov/actor/GenericChemicalPdfServlet?casrn=105-08-8).

5.6 Methanol (MeOH; CAS 67-56-1)

A large amount of toxicology data is available for methanol (http://actor.epa.gov/actor/GenericChemical?casrn=67-56-1).

5.7 PPH (770-35-4)

No toxicology data were listed for PPH.

5.8 DiPPH (CAS 51730-94-0)

No toxicology data were listed for DiPPH.

5.9 Polypropylene glycol phenyl ether (CAS 28212-40-0)

No toxicology data were listed for polypropylene glycol phenyl ether.

6.0 FREEDOM INDUSTRIES "PPH STRIPPED"

6.1 Release of Information

Days following the Crude MCHM tank chemical spill, Freedom Industries disclosed that in addition to Crude MCHM, a second liquid product was also present in the tank that leaked called "PPH Stripped" (Freedom Industries, October 15, 2013). The MSDS for PPH Stripped listed its composition as "polyglycol ethers" at 100% with the CAS number shown as "proprietary" (and "being withheld as a "trade secret" in accordance with 29 CFR 1910.1200(i)."). It was later disclosed that the polyglycol ethers were a mixture of polypropylene glycol phenyl ether (PPH (CAS 770-35-4)) and dipropylene glycol phenyl ether (at 7.3% by weight in the total mixture in the tank) (CDC 2014a). The PPH (CAS 770-35-4) in PPH Stripped may have been originally purchased as DOWANOL PPH Glycol Ether (DOW PPH (2008)) and processed before being combined with Crude MCHM. The MSDS for DOWANOL PPH Glycol Ether (DOW PPH, 2013) states the product contains >99.5% PPH (CAS 770-35-4).

DOW states that they sell DiPPH (CAS 51730-94-0) in "several commercial products…including DOW DiPPH Technical and DOW PPH Basic" containing 75% and 40%, respectively, DiPPH (DOW DiPPH, 2009). DOW states that other constituents include PPH (CAS 770-35-4) and "other reaction products" (DOW DiPPH, 2009). Thus, it is not fully clear what, if any, other ethers (in addition to PPH (CAS 770-35-4) and DiPPH (CAS 51730-94-0)) were present in the liquid mixture that leaked into the Elk River, which is dependent on the source or products containing PPH (CAS 770-35-4) and DiPPH (CAS 51730-94-0) that were used by Freedom Industries. For example, if the DiPPH (CAS 51730-94-0) in the Freedom Industries tank (and spill) were purchased as DOW dipropylene glycol phenyl, it appears to also contain a third ether, polypropylene glycol phenyl ether (CAS 28212-40-0) ether (DOW DiPPH, 2012).

The CDC notes that limited toxicological data are available for PPH (CAS 770-35-4) and DiPPH (CAS 51730-94-0). The MSDS for both compounds are prepared by the manufacturer (DOW Chemical) and provided some relevant information. For example, the acute oral LD_{50} (rat) is reported by Freedom Industries (October 2013) to be >2,000 mg/kg (for the PPH (CAS 770-35-4)) (CDC, 2014a). Similarly, the dermal LD_{50} (rat) is reported to be greater than 2,000 mg/kg (for the Stripped PPH) (Freedom Industries, 2013). The document also states that PPH (CAS 770-35-4) is not reported to be a carcinogen. The source of studies for the reported Freedom Industries data is not provided.

The data appear to show that both PPH (CAS 770-35-4) and DiPPH (CAS 51730-94-0) are less toxic than Crude MCHM (CDC, 2014a). Specifically, the acute oral LD_{50} (rat) for PPH (CAS 770-35-4) is greater than 2,000 mg/kg (Freedom Industries, 2013) versus 825 mg/kg for Crude MCHM (Feb. 1998; Eastman TX-97-306).

6.2 PPH (CAS 770-35-4)

The MSDS PPH (DOW PPH, 2013) states that the toxicity is low if ingested and that animal toxicity studies "were predominantly negative". The MSDS states that PPH (CAS 770-35-4) has caused birth defects in laboratory animals only at levels that were toxic to the mother (DOW PPH, 2013). The LD_{50} for PPH (CAS 770-35-4) is reported at 2,000 mg/kg. It is also stated that PPH (CAS 770-35-4) can cause severe eye injury and irritation, and skin irritation. The MSDS states no chronic toxicity or carcinogenicity data were found. The MSDS states that birth defects only occurred at doses toxic to the mother, and that PPH (CAS 770-35-4) did not interfere with reproduction in reproductive animal studies. The MSDS for PPH (CAS 770-35-4) reported an LC_{50} for fathead minnows of 280 mg/L in a 96-hour static test. For *Daphnia magna* (water

flea), a LC_{50} of 370 mg/L for a 96-hr static test was determined. Biodegradation tests for PPH (CAS 770-35-4) showed 28% biodegradation in 28 days.

6.2.1 CDC Drinking Water Advisory for PPH - The CDC calculated its PPH drinking water screening level of 1.2 mg/L (ppm) (CAS 770-35-4) in a manner similar (but slightly different) to that reported for MCHM above. Specifically, the drinking water advisory level (DW Advisory Level) was calculated as (CDC, 2014d):

DW Advisory Level ≤ (NOAEL × BW) / (UF × Intake)

where:

- DW Advisory Level is the drinking water advisory level (mg/L or ppm)
- NOAEL = No Observed Effect Level in the experimental species = 40 mg/kg/day
- BW = body weight of a pregnant mother = 75 kg
- UF = uncertainty factors (unitless)
    - for differences between humans and animals (10x)
    - to account for more sensitive humans (10x)
    - to account for in the toxicity database data (10x)
- Intake = estimated quantity of water consumed daily by a 75 kg pregnant mother (2.5 L/d)

Thus,

DW Advisory Level ≤ (NOEL × BW) / (UF × Intake) = [(40 mg/kg/d) × (75 kg)] / [(10×10×10) × (2.5 L/d)]

DW Advisory Level ≤ 1.2 mg/L (ppm)

The assumptions for BW, UF and Intake are reasonable and common assumptions of the especially for short-term health advisories USEPA (USEPA, 2012).

6.2.2 OECD SIDS data for PPH (CAS 770-35-4) - The Organization for Economic Cooperation and Development/Screening Information Data Set (OECD SIDS) report titled "Propylene Glycol Phenyl Ether" provides the results of many detailed toxicological studies on PPH (CAS 770-35-4) as well as two related compounds (CAS 4169-04-4; CAS 41593-38-8) including (but not limited to) (OECD/SIDS, 2006):

- Acute Oral Toxicity in rats,
- Acute inhalation toxicity in rats,
- Acute dermal toxicity in rabbits,
- Eye irritation in rabbits,
- Sensitization in guinea pigs,
- Repeated dose toxicity in rabbits,
- Genetic toxicity "In Vitro" in *Salmonella typhimurium*,
- Genetic toxicity "In Vivo" in mice,
- Toxicity to fertility in rats, and
- Developmental toxicity and teratogenicity in rabbits.

No relevant human exposure information was included. A brief summary of these studies according to this Organization for Economic Cooperation and Development/Screening Information Data Set (report (OECD/SIDS, 2006), is that PPH (CAS 770-35-4) is absorbed, metabolized and eliminated via urine and feces rapidly after oral exposure (OECD/SIDS, 2006; Saghir et al., 2003). PPH (CAS 770-35-4) has low oral and inhalation toxicities with a 2,000 mg/kg oral LD_{50} in rats, and a 5,400 mg/m^3 4-hr inhalation LD_{50} in rats (OECD/SIDS, 2006). The document noted that PPH (CAS 770-35-4) was a severe eye irritant, but not a

dermal irritant in rabbits. In the OECD document, a study was cited that concludes PPH (CAS 770-35-4) only caused effects at the highest exposure concentration of 478 mg/kg/d (OECD/SIDS, 2006).

The NOAEL for drinking water based on a rat study (OECD/SIDS, 2006) was set to 1,000 mg/L (or 113 mg/kg/d) while the LOAEL was set to 5,000 mg/L (or 478 mg/kg/d) based on changes in body weight (OECD/SIDS, 2006). In another study, dermal exposure in rabbits was used to establish a NOAEL of 1,000 mg/kg/d.

In a two-generation study, no adverse effects were found with respect to fertility, reproductive performance, or reproductive tissue (OECD/SIDS, 2006). Specifically, a NOAEL and a LOAEL for maternal toxicity of 180 mg/kg/d and 540 mg/kg/d were established, respectively (OECD/SIDS, 2006).

It was further determined that PPH (CAS 770-35-4) was negative with respect to the Ames *Salmonella* assay (for mutagenicity) (OECD/SIDS, 2006; Bootman and May, 1985; BASF AG, 1996) and negative in an *in vitro* chromosome aberration study with lymphocytes (OECD/SIDS, 2006; Bootman, 1986).

Details of these studies may be found in OECD SIDS (2006) report.

6.2.3 Other Toxicity Data for PPH - A paper by Greenman (1984), infers that the sub-lethal concentration for the study bacterium was 0.1% w/v, whereas 0.2% caused complete inhibition of the bacterium. The BIBRA working group (1992) states that PPH (CAS 770-35-4) was "of low acute oral toxicity in rats, and was only a minimal irritant for dermal exposure in rats, but was an irritant for the eyes of rabbits (cited in TOXNET as BIBRA working group, 1992).

A SIDS Initial Assessment Report for SIAM 18 (2004) reports toxicology data for a mixture of PPH isomers (CAS 770-35-4 (major isomer), CAS 4169-04-4 (minor isomer), and CAS 41593-38-8 (commercial mixed isomer product) (BIBRA, 2014).

6.2.4 DiPPH (CAS 51730-94-0) - The MSDS for DOWANOL DiPPH Glycol Ether is for a mixture of approximately 60% DiPPH, 25% PPH (CAS 770-35-4), and 15% polypropylene glycol phenyl ether. The MSDS states that neither ingestion nor dermal LD_{50} values for the mixture have been determined, but for pure DiPPH (CAS 51730-94-0) the values were both >2000 mg/kg (the same reported values as for PPH (CAS 770-35-4)). Similar to PPH (CAS 770-35-4), DiPPH (CAS 51730-94-0) is an eye and skin irritant. The MSDS states that no chronic toxicity nor carcinogenicity data are available. Developmental, reproductive and genetic toxicity were reported identically to PPH (CAS 770-35-4).

The MSDS reported pure DiPPH (CAS 51730-94-0) was "practically non-toxic" to aquatic organisms on an acute basis. The LC_{50} for rainbow trout was 204 mg/L in a 96-hr static test. The aquatic invertebrate acute toxicity had the EC_{50} for *Daphnia magna* of 336 mg/L in a 48-hr static test.

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