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TECHNICAL MEMORANDUM

April 20, 2014

To: Jeffrey Rosen, Corona Environmental Consulting

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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 Bureau for Public Health 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

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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 not added in the treatment plant until after the licorice odor was detected. 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.

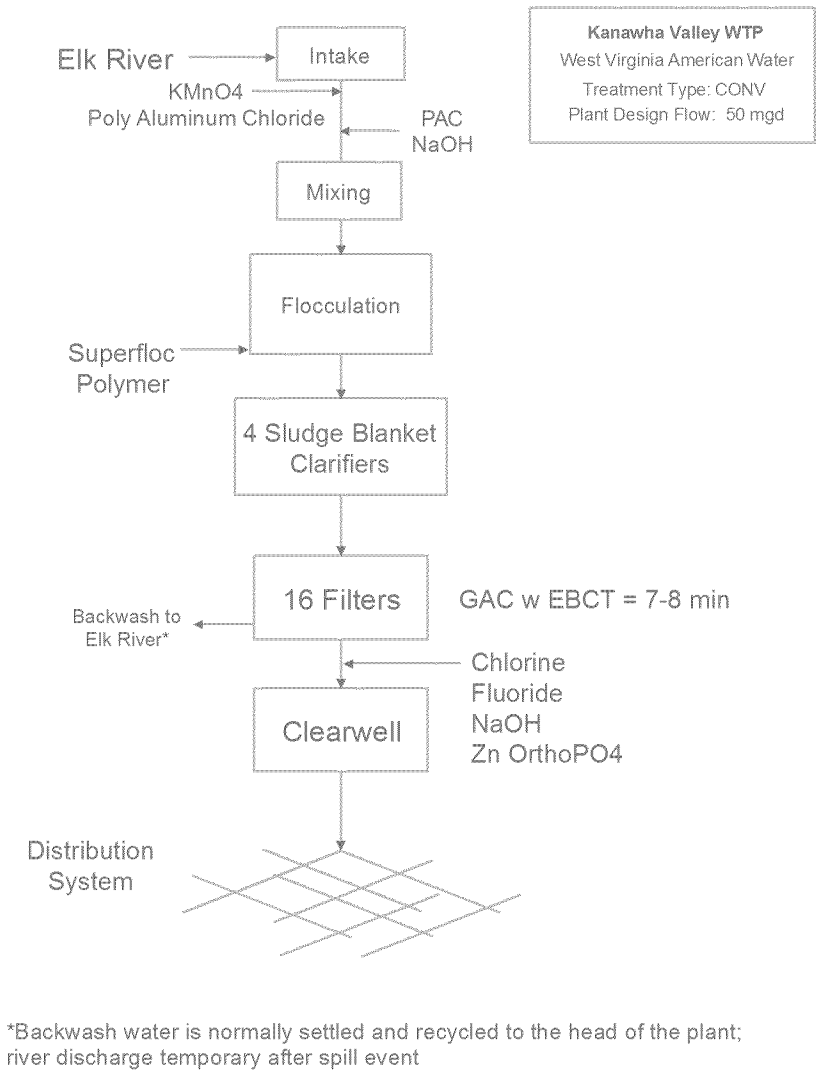

Figure 1. Schematic of KVWTP Treatment Processes

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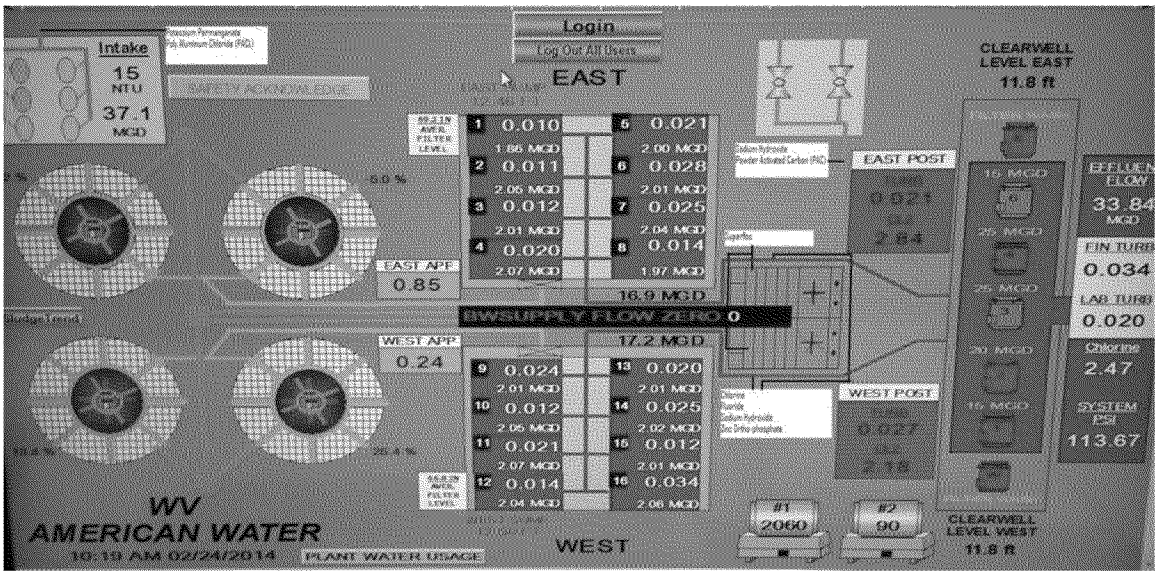

Figure 2. SCADA Screen Capture Showing Treatment Processes

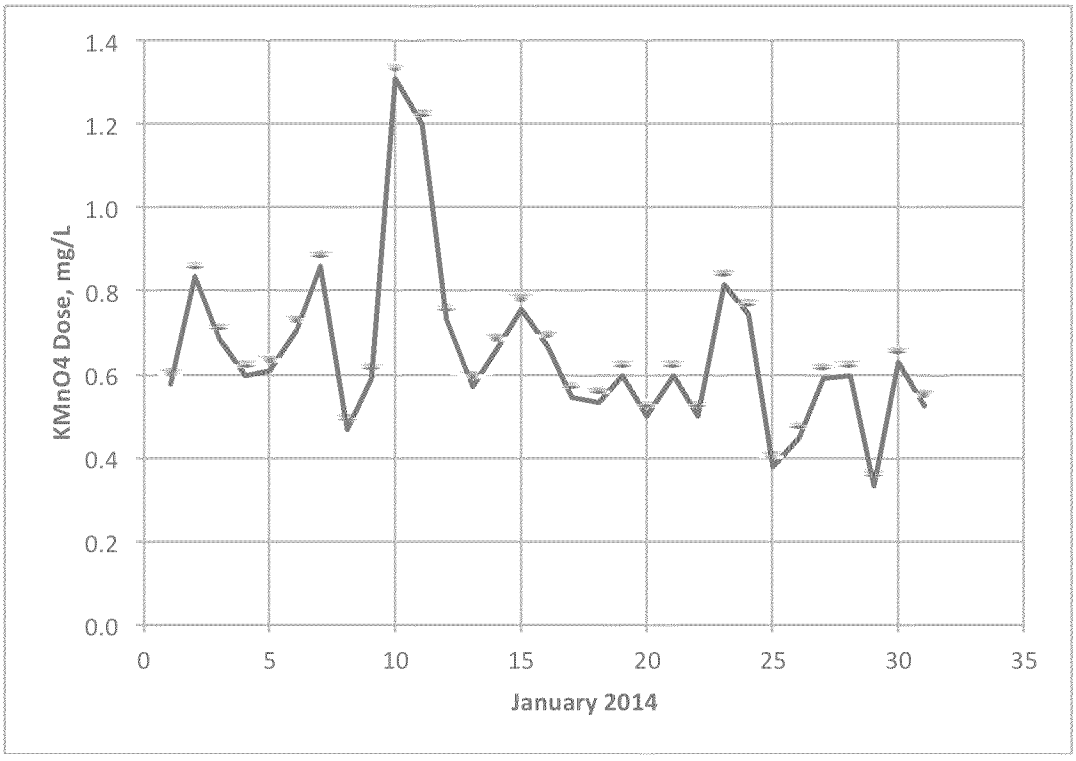

Figure 3. Potassium Permanganate Doses in the KVWTP During January 2014

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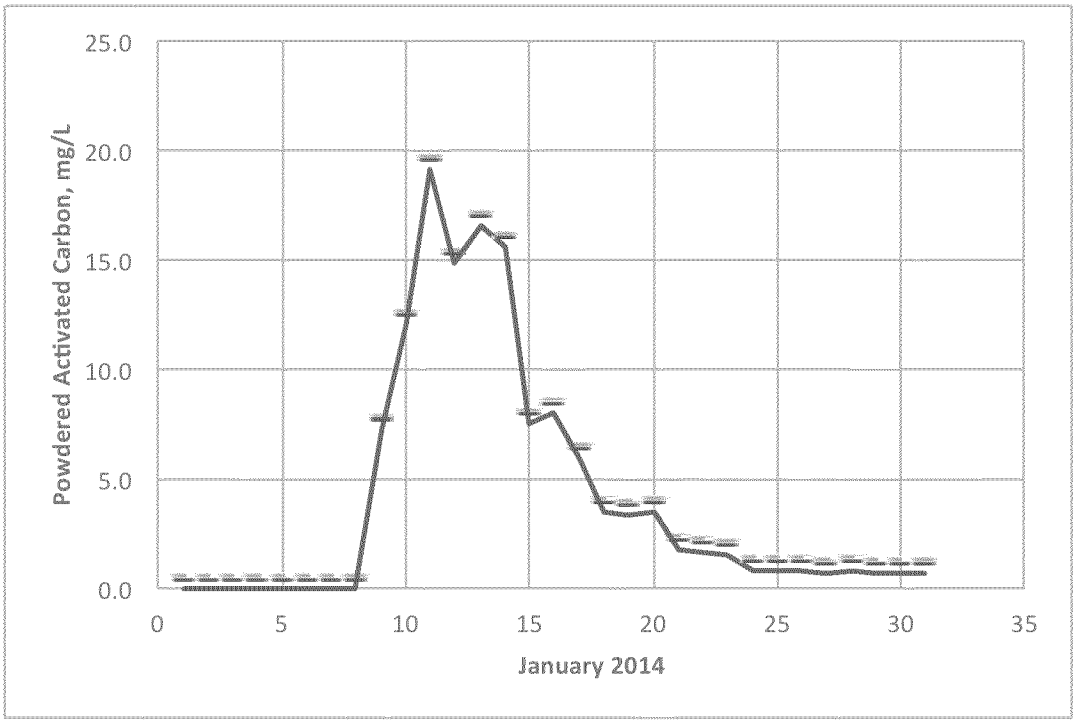

Figure 4. Powdered Activated Carbon Doses in the KVWTP During January 2014

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.

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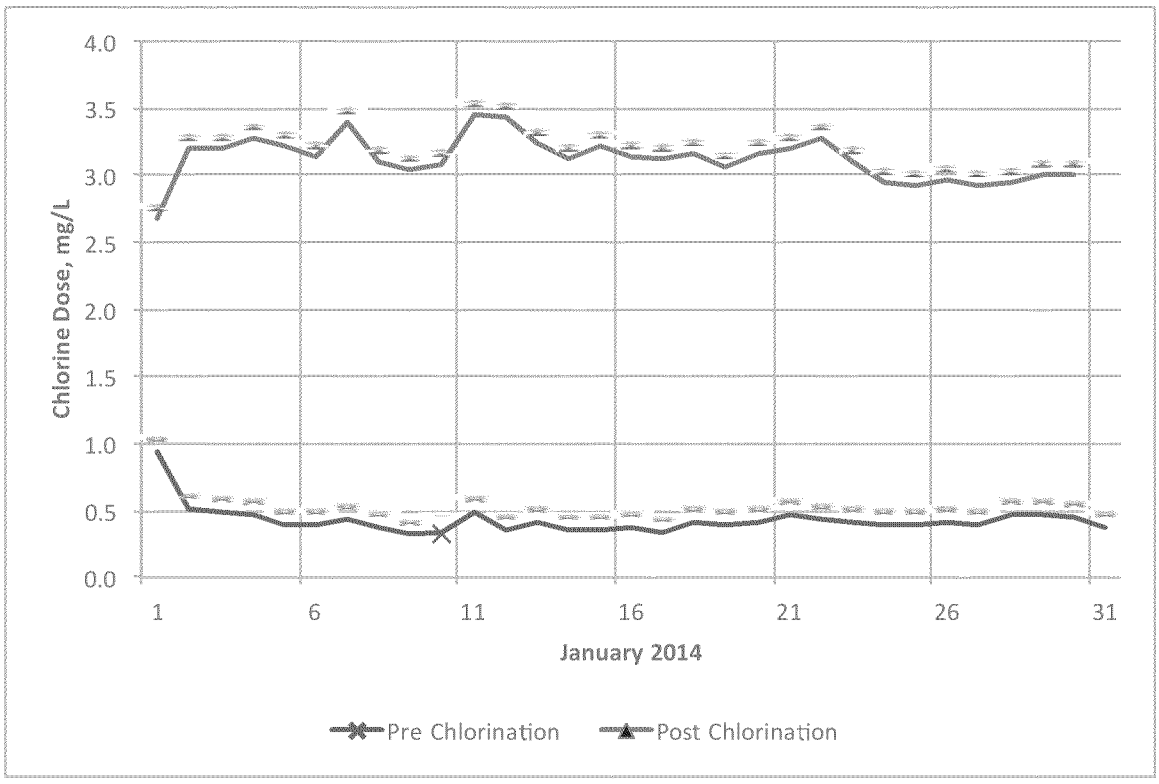

Figure 5. Free Chlorine Doses in the KVWTP During January 2014

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.

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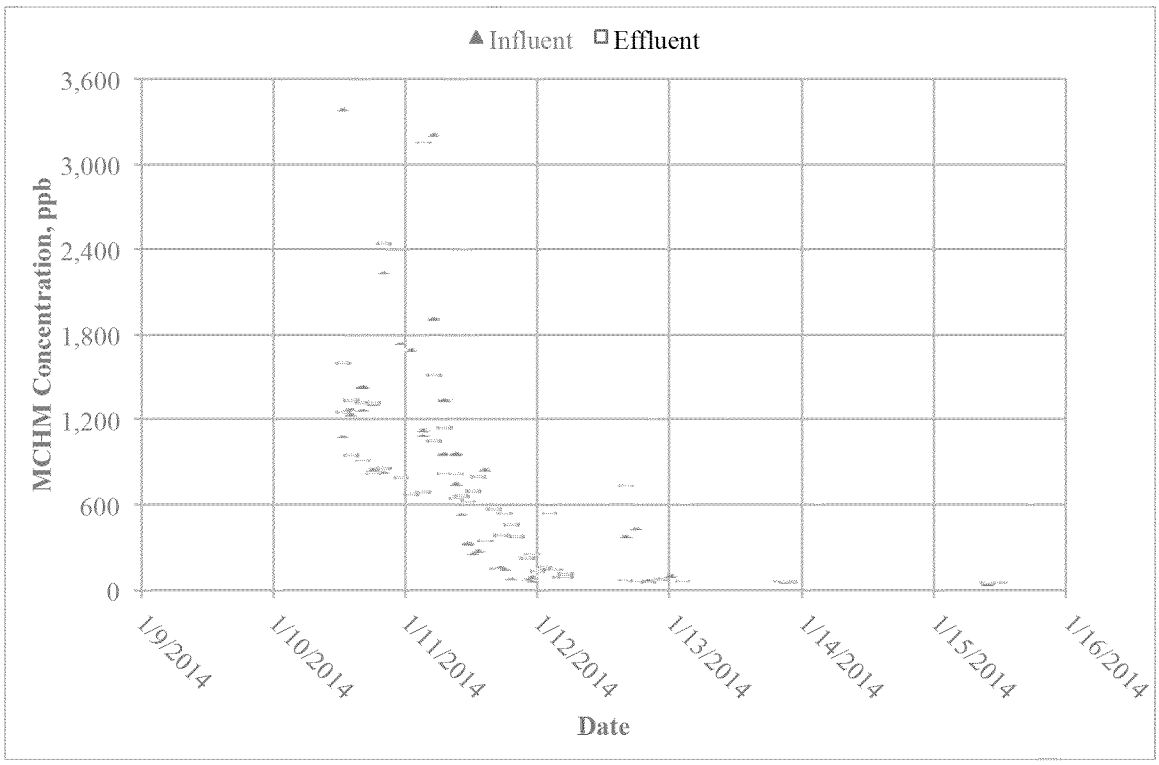

Figure 6. MCHM Concentrations in the KVWTP Influent and Effluent (Data Source: West Virginia Division of Homeland Security and Emergency Management)[4]

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.[5] 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.

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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	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

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.

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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 day	Same dechlor dose w Na2SO3
5	KMnO4 1.3 mg/L	10	1.3 KMnO4	3 hours	Remove KMnO4 w Na2SO3; filter 0.45 um
6	Filter Blank	0	0	3 hours	Same dose to reduce KMnO4 w Na2SO3; filter 0.45 um
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 um
9	Filtration Treatment	10	0	0	Filter through 0.45 um

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.

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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.[6] 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.[7] 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

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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

Sample No.	Description	MCHM Isomer Concentration, ppb			Ratio of Cis to Trans
		Trans 4 MCHM	CIS 4 MCHM	Total 4 MCHM	
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

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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	Flavor 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

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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.[8] 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.[9]

SUMMARY AND CONCLUSIONS

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

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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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