INTRODUCTION

Q

B

 \cap

Q

JEFFREY ROSEN & ANDREW WHELTON

SCHEDULE FOR TODAY'S SEMINAR

- 9:30 Introductions and content
- 9:40 Overall project progress
- 9:50 Odor threshold testing results McGuire
- 10:10 10 Home study results Whelton
- 10:30 Optimized MCHM analysis,

Tentatively identified compounds & implications – Eaton/Neslund

2

10:50 Break

 \bigcirc

- 11:05 Preliminary design for the larger home monitoring plan Rosen
- 11:25 Health Effects Expert panel Patterson/Whelton
- 11:35 Integrated summary Rosen
- 11:45 Next steps Whelton/Rosen

12:00 BREAK FOR LUNCH

1:15 -2:45 Public questions and answers

THE WV TAP TEAM

- Jeffrey Rosen, program manager/statistician, MS, 39 years experience as a scientist, statistician and information specialist, Corona Environmental Consulting
- Andrew Whelton, Ph.D., Environmental Engineering Professor, University of South Alabama
- Michael McGuire, Ph.D., A.P Black Award Winner, author <u>The Chlorine</u> <u>Revolution: Water Disinfection and the Fight to Save Lives</u>, Taste and odor expert, Michael J. McGuire, Inc.
- Andy Eaton, Ph.D., Eurofins, Chemist, Technical Director and Vice President, Eurofins Eaton Analytical Laboratory

3

 Charles Neslund, Eurofins, Chemist, Technical Director, Eurofins Lancaster Laboratory Environmental

ACKNOWLEDGEMENTS <u>MANY OTHER PEOPLE SUPPORTING THESE EFFORTS</u>

- Corona Team
 - Ayhan Ergul, Jennifer Clancy, Tim Clancy, Annemarie Naughton, Chad Seidel, Mel Suffet, Craig Adams
- At Eurofins
 - Duane Luckenbill, Rick Karam, many others.
- UCLA
 - Mel Suffet team including odor testing professionals and volunteers
- ALS Laboratory
 - Paul Painter, Rebecca Kiser

- Residents of the 10 homes
- West Virginia citizens and volunteers
- West Virginia Department of Health and Human Resources
 - MANY people
- Governor Tomblin's Office
 - MANY people
- West Virginia National Guard
- Whelton's students and other volunteers

THE WV TAP PROGRAM MISSION

6

 To provide independent scientific assessment regarding the spill of MCHM into the Elk River and its subsequent distribution throughout the 9 counties served by West Virginia American Water.
 Our focus is on:

1. Establishing the levels at which MCHM can be smelled

2. Develop a sampling plan to assess how much MCHM remains in the homes of the citizens of West Virginia

3. Evaluate possible breakdown products of crude MCHM

4. Evaluate the screening levels recommended to the people of West Virginia by the State officials.

5

OUR SCHEDULE

•We started our efforts on February 11th approximately one month after the spill

•We plan to complete our work by May 15th

6

PROGRESS

Q

- Today we will report out results of our research to date and we will also lay out a timetable for additional results. Specifically:
 - Odor Threshold Results: Expert and Consumer Panels
 - Ten Home Testing: Resident Interviews, Tap Water Chemical and Odor Characteristics
 - Ten Home Testing: Tentatively Identified Chemicals related to possible break down products
 - Initial plans for a large scale sampling program to better characterize the long term concentrations of MCHM and other compounds in the distribution system
 - Plans for the expert panel that will review the established screening levels

OVER THE NEXT FEW WEEKS WE WILL BE POSTING PRODUCTS REGULARLY

- Health Effects Expert Panel Preliminary results will be reported on Tuesday April 1st. Final Expert report the last week of April
- Final odor threshold results by the middle of April
- Report on the breakdown products and the Tentatively Identified Compounds

8

Final design for the full scale monitoring program

STAY TUNED ON LINE

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

- Literature review for components of Crude MCHM, PPH and DiPPH have been posted
- CDC response to WVTAP questions regarding screening levels
- Supporting document for this presentation
- Odor Threshold Technical Memo on Expert panel reviews

[°]ANTICIPATED POSTINGS

- We expect to post during the next month
 - 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
 - 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.

10

GROUND RULES FOR THIS PRESENTATION

- No questions during the presentations
- Break for Lunch

Ò

- Return to auditorium for questions and answers
- Line up at the microphones for questions
- STRICT 2 minutes for each question. If you go over I will firmly, but politely, cut you off. Our answers will not exceed 3 minutes.
- Short questions mean we will be able to answer more questions. PLEASE BE POLITE AND BRIEF.

11

Odor Threshold Testing Results

Presented at WV TAP Seminar and Public Meeting

Michael J. McGuire, PhD, PE Michael J. McGuire, Inc. March 28, 2014

Outline

- Introduction and Objectives
- Panel Methodology
- Results and Discussion
- Summary and Conclusions
- Recommendations

Objectives of This Work

- Develop a method to estimate odor thresholds for the licorice-smelling substance in water
- Develop a spiking method for the licoricesmelling substance in water for Expert Panel presentation
- Convene a panel of odor experts to estimate concentrations of detection, recognition and objection/complaint for the licorice-smelling substance in water

Objectives of This Work (cont.)

- Understand how the Expert Panel results explain consumer observations in Charleston, WV
- Make recommendations for additional work to supplement and confirm the Expert Panel findings

Odor Response Terminology

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

Outline

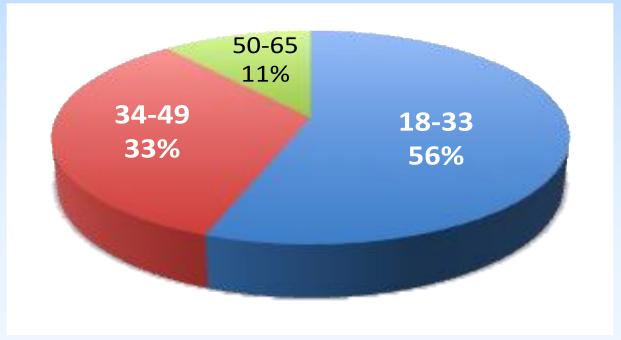
- Introduction and Objectives
- Panel Methodology

Panelist Selection Criteria

- Trained panelists
- Between the ages of 18 and 65
- Balance of women and men
- 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

Panel Demographics

- Gender split: 67% women and 33% men
- Age distribution reflects the fact that most panelists were students



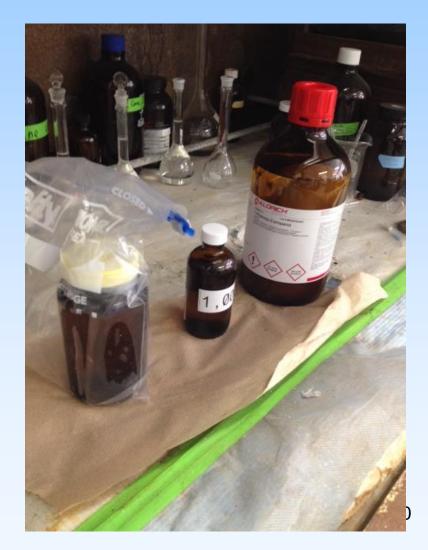
Panel Sessions

- Panels were held at Hazen and Sawyer Los Angeles offices and the specialized taste and odor room at the University of California, Los Angeles
- Total number of panelists = 9



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
- Therefore Crude MCHM
 was used in all of the
 odor studies



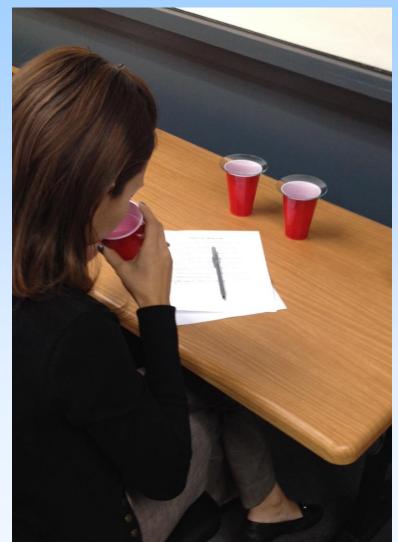
Samples Presented to Panelists

- Crude MCHM was sampled from the contents of Tank 396 that leaked into the Elk River
- Arrowhead spring water used for matrix and blanks
- Crude MCHM was spiked into Arrowhead water



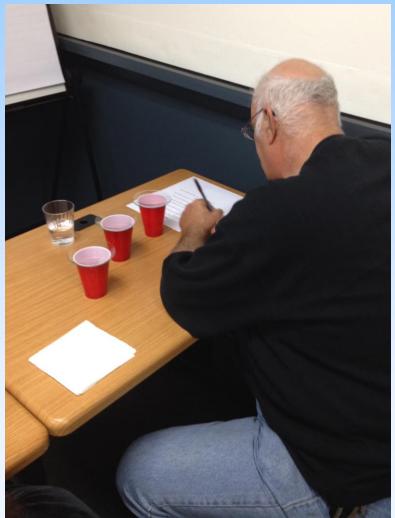
Odor Methodology

- Method ASTM E679-04 (2011)
- Eight concentrations were presented in sets of 3—two blanks and one spiked with Crude MCHM
- Panelists had to choose the cup that had a different odor



Odor Methodology (cont.)

- Next, panelists were asked to describe the odor characteristics of the water in the different cup
- Panelists were asked to express their degree of liking using a standard scale
- Panelists were asked if the odor in the different cup would cause them to object/complain to the water company



Outline

- Introduction and Objectives
- Panel Methodology
- Results and Discussion

Odor Threshold Concentration

			Best Estimate Threshold, ppb							
Panelists	Date Study Conducted	0.16	0.41	1.0	2.6	6.4	16	40	100	Value
02	2/21/14	+	+	T		+	+	+	+	0.10
03	2/21/14	+	+	+	+	+	Ŧ	+	+	0.10
04	2/21/14	+	+	+	+	+	+		+	0.10
07	2/24/14	+	+	Ŧ	Ŧ	+	+	+	+	0.10
08	2/24/14	+	+	+	+	+	+	+	+	0.10
09	2/24/14	+	+	0	+	+	+	+	+	1.6
10	2/24/14	0	+	+	+	+	+	+	+	0.26
11	2/24/14	+	+			+	+	+	+	0.10
12	2/24/14	+	+	+	+	+	+	+	+	0.10

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. The actual OTC for these panelists is less than 0.15 ppb

Geometric Mean, ppb = < 0.15

Odor Recognition Concentration

			Concentrations of Crude MCHM Presented to Panelists, ppb										Best Estimate Threshold, ppb	
	Panelists	Date Study Conducted	0.16	0.41	1.0	2.6	6.4	16	40	100	Refe	erence Odor	Value	
7	02	2/21/14	licorico	licorice,	-	licorice, solvent,	syrupy sweet, pineapple	syrupy sweet, pineapple	syrupy sweet, ripe fruit	syrupy sweet, ripe		rice, sweet,	0.10	
P	02	2/21/14	licorice	sweet	syrupy sweet anise	syrupy sweet anise	juice anise, lemony	juice anice, cough syru	lemony,	fruit lemony, bile, anise		woodsy ise, sweet, vanilla	0.10	
,	04	2/21/14						paints, gasoline exhaust	sweet chemical	sweet chemical	ha	very, sweet, and wipes chemical	25	
1	07	2/24/14	sweet, grassy (fades)	sweet, faint licorice, candy	faint sweet	faint sweet, licorice	sweet licorice	faint swee licorice sweet,	t faint sweet licorice sweet,	sweet licorice sweet,	swe	eet, licorice, candy	0.26	
ļ	08	2/24/14		sweet	sweet, licorice	sweet, licorice	sweet, licorice	licorice	licorice	licorice	swe	eet, licorice	0.64	
tro	ng so	olven	t <i>,</i>	licor	ice,	lic	orice,		lico	rice,				
	swe	et		SWE	eet	S\	weet		SW	eet		li	corice,	pine
Ţ	11	2/24/14					rerresning	glue, rubbery, licorice	glue, rubbery, licorice	sweet, licorice, glue		ncorice eet, licorice	10	
-	12	2/24/14					Bide, Tubbery	liconce	liconce	giue	344		10	

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.

S

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.
- I don't think 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.

Odor Objection Concentration— Degree of Liking

			Best Estimate Threshold, ppb							
Panelists	Date Study Conducted	0.16	0.41	1.0	2.6	6.4	16	40	100	Value
02	2/21/14	3	7	4	8	9	9	9	9	1.6
03	2/21/14	4	3	1	6	7	8	7	6	1.6
04	2/21/14	6	6	6	6	6	6	6	6	0.10
07	2/24/14	2	3	1	1	4	3	4	4	160
08	2/24/14	3	3	4	5	6	7	7	8	4.1
09	2/24/14	3	4	2	4	6	6	5	4	160
10	2/24/14	5	5	4	5	7	8	8	8	4.1
11	2/24/14	2	1	2	4	6	7	7	7	4.1
12	2/24/14	5	5	6	6	7	8	8	8	0.64

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 liking to a score of 6 or above which is noted by gray-shaded cells.

Geometric Mean, ppb = 4.0

Odor Objection Concentration— Complaint/Objection

			Concentrations of Crude MCHM Presented to Panelists, ppb									
Panelists	Date Study Conducted	0.16	0.41	1.0	2.6	6.4	16	40	100	Value		
02	2/21/14	Ν	Y	N	Y	Y	Y	Y	Y	1.6		
03	2/21/14	Ν	N	N	Y	Y	Y	Y	Y	1.6		
04	2/21/14	Y	Y	Y	Y	Y	Y	Y	Y	0.10		
07	2/24/14	Ν	N	N	N	N	N	N	N	160		
08	2/24/14	Ν	N	N	N	N	Y	Y	Y	10		
09	2/24/14	Ν	N	N	N	Y	Y	Y	N	160		
10	2/24/14	Y	Y	N	Y	Y	Y	Y	Y	1.6		
11	2/24/14	Ν	N	N	N	Y	Y	Y	Y	4.1		
12	2/24/14	Ν	N	Y	Y	Y	Y	Y	Y	0.64		

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

Outline

- Introduction and Objectives
- Panel Methodology
- Results and Discussion
- Summary and Conclusions

Summary and Conclusions

- 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.
- Spiked concentrations of Crude MCHM were measured by a sensitive analytical method and found to be within acceptable percent recoveries.

Summary and Conclusions (cont.)

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

Summary and Conclusions (cont.)

- 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.

Summary and Conclusions (cont.)

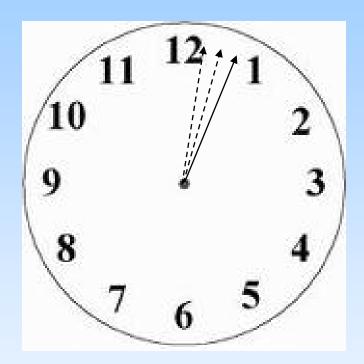
 The estimated thresholds determined in the Expert Panel study support consumer observations in Charleston, WV that people could recognize and object to the licorice odor caused by Crude MCHM in their drinking water even though the analytical reports were showing non-detect at a minimum reporting level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

Recommendations

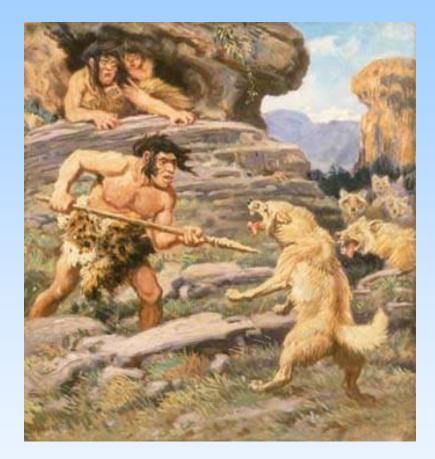
- Convene a large panel comprised of untrained consumers and determine the OTC, ORC and OOC concentrations
- Change the range of concentrations presented to the consumer panel to 0.027 to 60 ppb
- Conduct oxidation studies of Crude MCHM with chlorine and potassium permanganate and determine if the odor characteristic or intensity of the licorice odor is changed after oxidation.

Thank You!

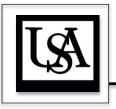
One part per trillion



3 seconds



100,000 BC (actually 95,129 years) 27



The 10 Home Study: Results and Implications

Andrew Whelton, Ph.D. Jeffrey Rosen Jennifer Clancy, Ph.D. Tim Clancy Ayhan Ergul



WEST VIRGINIA TESTING ASSESSMENT PROJECT



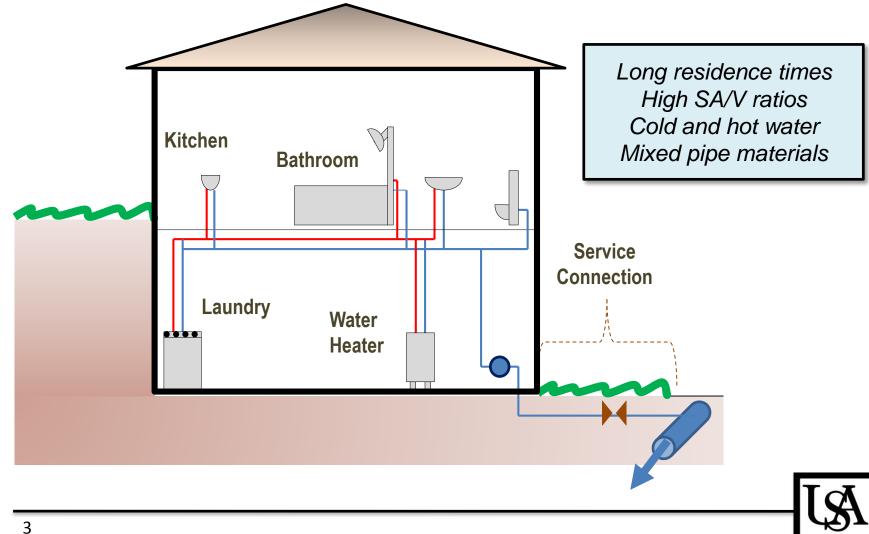
Follow us at @WVTAP.



Outline

Introduction Goal and Objectives Approach Results and Implications

The 10 Homes in WVAM's Water Distribution System had Complex Plumbing Systems



Project 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

Objective #1: Household Interviews



West Virginia Drinking Water Survey Questionnaire

Name of person(s) interviewed:

DAY:

Address:

2.

- Phone:
- Number of people living in the household (ages, sex):

email:

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

sthetic

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

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

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

1

2

	Rate the intensity o dark)	f the colo	r from 1	l-5 (1 cle	ar, 2 slig	ht, 3 mod	erate, 4 dark, 5 v	/ery
DAY:		1	2	3	4	5		
DAY:		1	2	3	4	5		
DAY:		1	2	3	4	5		
_			-	-	-	_		

5

D DAY: 1 2 3 5

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

G February 11 to 18, 2014

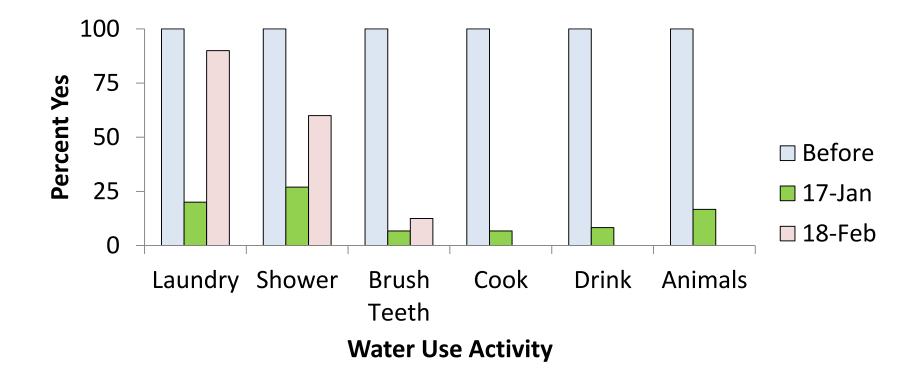
Visited 10 homes, 8 of 9 counties

Questions....

- Demographics
- Building plumbing pipe material and age
- Experiences before and after the Do Not Use Order
- Tap water aesthetics, health symptoms

0 - f 10	Symptom	No. Households	Ratings
<u>8 of 10</u> Households	Rash	4	3,4,5,5
Reported	Dizziness	4	3,3,3,5
Chemical	Burning	4	3,3,3,4
Exposure	Nausea	3	2,3,3
Symptoms	Numbness	2	2,3
	Memory loss	2	4,4
	Vomiting	1	2
As of Feb 18,	Other: Headache	3	No rating
<u>4 Households</u>	Other: Flu like symptoms	1	No rating
Had Sought	Other: Agitated	1	No rating
Medical Assistance	Other: Skin itch	1	No rating
	Other: Eyes red	1	No rating

Many Residents Still Did Not Cook with, Drink, or Shower in the Tap Water



Whelton Jan 17 Unfunded USA Data Included



Resident Comments

1: Cabell County was not in first official notification

3: Did taste some water at a restaurant on Jan 9 at 4:30 pm before 'Do Not Use' Order, <u>thought it tasted off.</u> Felt disoriented and left town for the weekend after the event occurred and shut off the water to the house.

4: Smelled sweet odor in water 3 weeks prior to Jan 9; was licorice odor, now is lighter and sweet. After showering skin felt soft and <u>silky like lotion that was not</u> <u>completely washed off</u>.

5: Did not shower or wash clothes for 2 weeks after spill, <u>clothes smelled of licorice</u>. 6: 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 5 days before smell occurred in their water.

7: Told *no information available about water safety for pets*.

8: 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.

Objective #2: Examine Tap Water Quality

Onsite testing: Water pH, free chlorine, total chlorine, turbidity, odor Commercial lab testing: TOC, PPH, 4-MCHM

Each Laboratory Had Different MDLs and MRLs for Each Compound

	AL	.S	Eurofins		
Compound	Environme	ental Labs	Labs		
	MDL	MRL	MDL	MRL	
TOC, ppm	0.07	0.50	0.04	0.30	
PPH, ppb	3.7	5.1	0.5	1.0	
4-MCHM, ppb	2.7	5.0	0.5	1.0	

TOC = Total organic carbon PPH = Propylene glycol phenyl ether 4-MCHM = 4-Methylcyclohexanemethanol Individual measurements sometimes did have different MDL/MRLs and were significant.



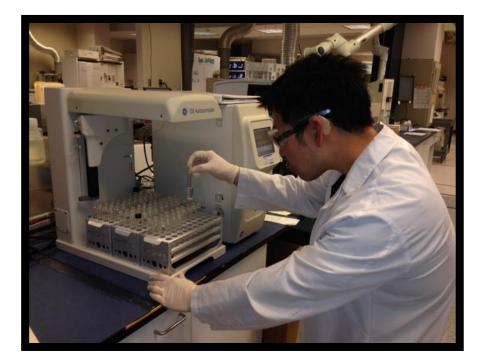
Water Sampling was <u>Not</u> Trivial

3 x 30 Water Samples Per Home

Laboratory Analytical Analyses: TOC, 4-MCHM, and PPH

Total Organic Carbon Analyzer (TOC)

Total mass of carbon in the water is quantified





Gas Chromatography – Mass Spectroscopy (GC-MS)

Chemicals are separated from one another and detected



As Expected, Water Quality Differences Were Detected Inside and Across the 10 Homes

Parameter	Cold	Hot	
Temp., °C	6.9 to 21.9	31.6 to 58.1	
рН	7.4 to 8.3	7.0 to 7.5	
Free Cl ₂ , mg/L	2.0 to 2.9	0.1 to 2.1	

Water Quality	·							
Regulated Substances (Measured on the Water Leaving the Treatment Facility Substan 2012 Annual								
Water Quality Report								
Beta/ph emitters Elk River Regional System PWS ID: WV3302016								
Chlorine Combine (pCi/L)						ERICAN	WATER hatural	
Fluoride (ppm)	2012	4	4	0.9	0.6 - 0.9	Yes	Water additive which promotes strong teeth	
$\begin{array}{c c} & & & & & & & & & & & & & & & & & & &$								
(TTHMs) (ppb) Total Organic Carbon (% Removal Range) ⁵	2012	NA	Π	1.01	1.0 - 1.02	Yes	Naturally decaying vegetation	
Turbidity (NTU) 6	2012	NA		0.25	0.02 - 0.25	Yes	Soil runoff	

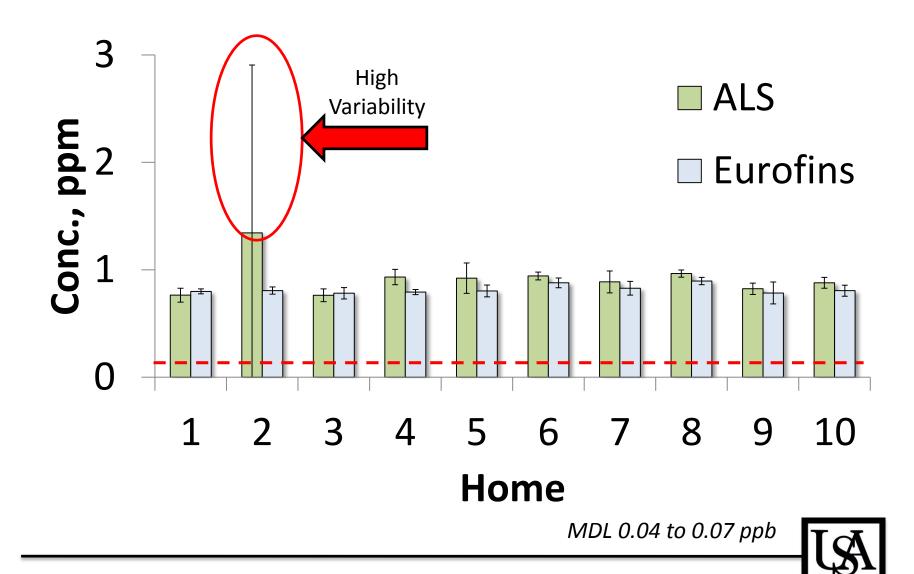


Different Odors were Detected and Not All Tap Water Samples Had Odor

Odor Type	No. Households Present	No. Water Samples Present		
Chlorine	9	26 of 40		
Sweet	7	15 of 40		
Licorice	3	6 of 40		
Musty	2	2 of 40		

Licorice odor intensity less than January 17-22 1+ odor, 14 of 40 samples

TOC Results Across All Homes Were *Not* **Unusual**



Notable Findings

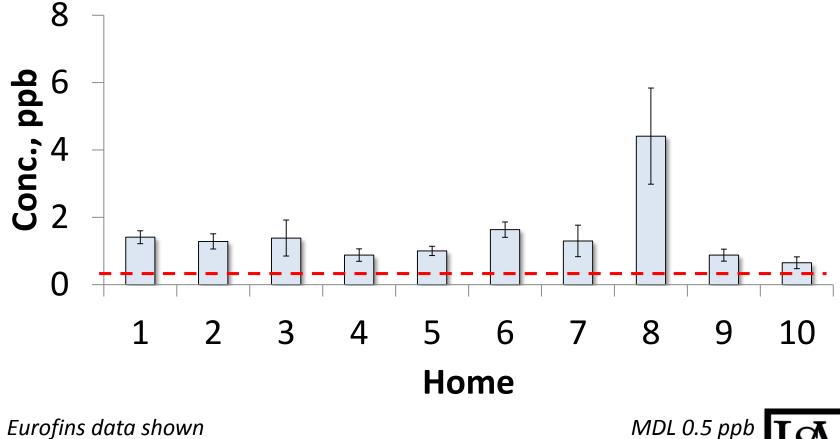
No PPH was Found 4-MCHM was Detected Laboratory MDLs Matter

Not detected by ALS Environmental Laboratory (MDL 2.7 ppb)

> Was detected by Eurofins Laboratory (MDL 0.5 ppb)



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



CH₃OH

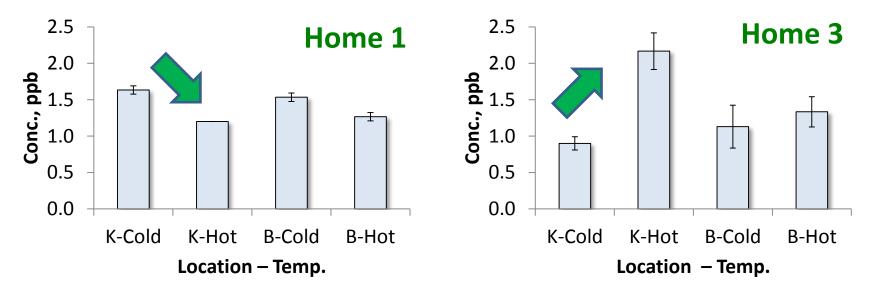
 CH_3

 CH_2

 H_2C

 H_2

No Trends were Found between 4-MCHM, In-Home Location, or Water Temperature



No Obvious Odor Trend Was Found When 4-MCHM was Present

	No. Water	Со	Concentration, ppb			
Odor Type	Samples Detected and Temp.	Low	High	Avg <u>+</u> Stdv		
Licorice	6	1.1	2.4	1.5 <u>+</u> 0.3		
No licorice	25	0.5	1.3	1.5 <u>+</u> 1.2		
Sweet	15	0.5	6.1	1.8 <u>+</u> 1.6		
No sweet	33	0.5	5.5	1.3 <u>+</u> 0.7		
Musty	2	0.8	1.2	1.1 <u>+</u> 0.1		
No musty	38	0.5	6.1	1.5 <u>+</u> 1.2		

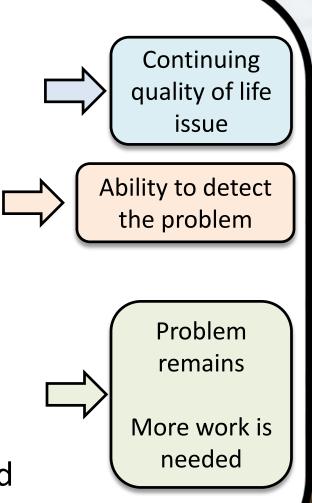
More science needed, What do these odors represent?



Conclusions

- <u>100%</u> no tap water cooking or drinking
- 40% no tap water showers

 ❑ MDLs were <u>very</u> important
 ❑ All home tap waters contained 4-MCHM less than 10 ppb
 – Max 6.1 ppb; 90% ≤ 2.2 ppb
 ❑ No relationship found between 4-MCHM level and in-home location or water temperature
 ❑ Odors types were not attributed to certain 4-MCHM levels



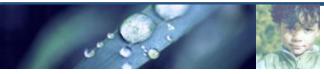
Perceptions About Tap Water Odor

1 no odor, 2 slight, 3 moderate, 4 strong, 5 unbearable

Date	No.	Odor
Dale	Households	Rating
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







EUROFINS

Charleston, WV

March 28, 2014

www.eurofins.com

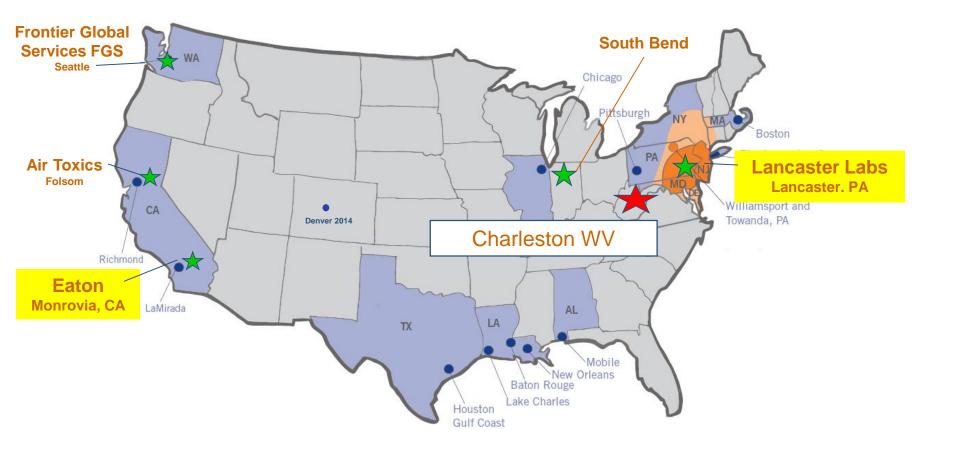
INTRODUCTIONS



- Andy Eaton, PhD, BCES Technical Director/Vice President Eurofins Eaton Analytical Inc.
 - Analytical Program Management
 - Total Organic Carbon Analysis
 - Quality Assurance
 - Data Interpretation
- Chuck Neslund Technical Director
 Eurofins Lancaster Laboratories Environmental
 - Methods Development
 - 4-MCHM +PPH Analysis
 - Tentatively identified Compounds Assessment and Interpretation

Eurofins Environment Testing US

🔅 eurofins



The Eurofins Team For This Project

🛟 eurofins

Eurofins Lancaster



- Largest full-service Testing lab in US
- Started in 1961
- 330,000 sq ft
- 900 staff chemists and support personnel
- Serves petrochemical companies, industrial companies, consultants and federal and state programs
- WV Certified for DW and WW/HW

Eurofins Eaton



- Largest Water Testing lab in US
- Started in 1969
- > 39,000 sq ft
- 130 staff chemists and support personnel
- Serves municipalities, consultants and beverage companies
- WV Certified for DW

How Small is a Part per Billion?

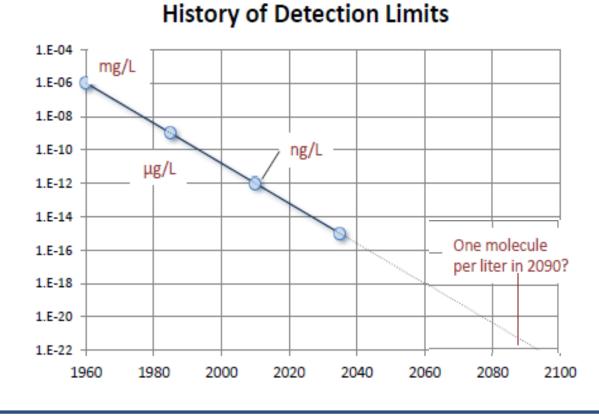


The population of China is 1.3 Billion people.

So 1 part per billion is like trying to find 1 specific person in all of China.

Detection Limits Keep Getting Better \$ eurofins

 The fastest-growing area of technoscience in water is analytical technology



Moore's Law: No. of transistors on A microchip doubles Every 2 years

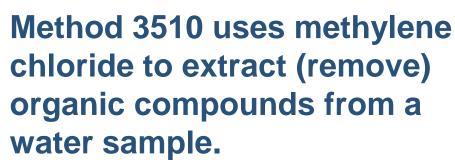
A new law Detection limits for trace organics drops 2-fold every 2.5 years.

MCHM detection law Detection limit drops 500-fold every month

Adapted from Trussell, Clarke Prize Lecture 2013 6

Optimizing the 4-MCHM/PPH Analytical Method

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



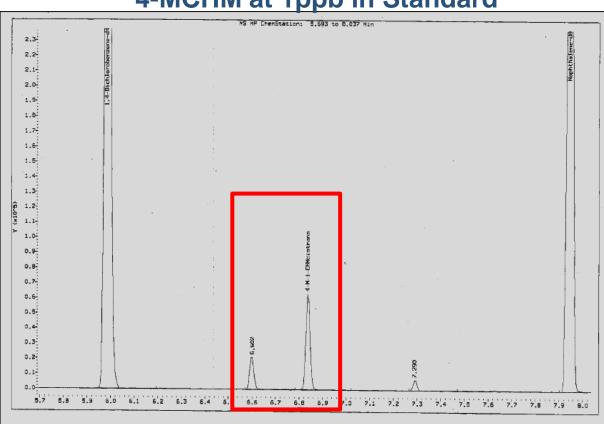




Optimizing the 4-MCHM/PPH Analytical Method



Worked to optimize the chromatography and the injection technique so that we could attain good sensitivity and good signal to noise ratio



4-MCHM at 1ppb in Standard

Limit of Quantitation (aka MRL) for 4-MCHM = 1 ppb

Minimum Detection Level (MDL) for 4-MCHM = 0.5 ppb

Statistically Derived Detection Level for 4-MCHM = <0.2 ppb



Types of Quality Control used for each batch

- Laboratory Control Standard (LCS) at 25 ppb (same range as expected samples)
- Matrix spike at a similar level
- Minimum reporting level (MRL) check spike at 2 ppb

Quality control for each sample

Surrogate compound added to each sample with retention time near 4-MCHM

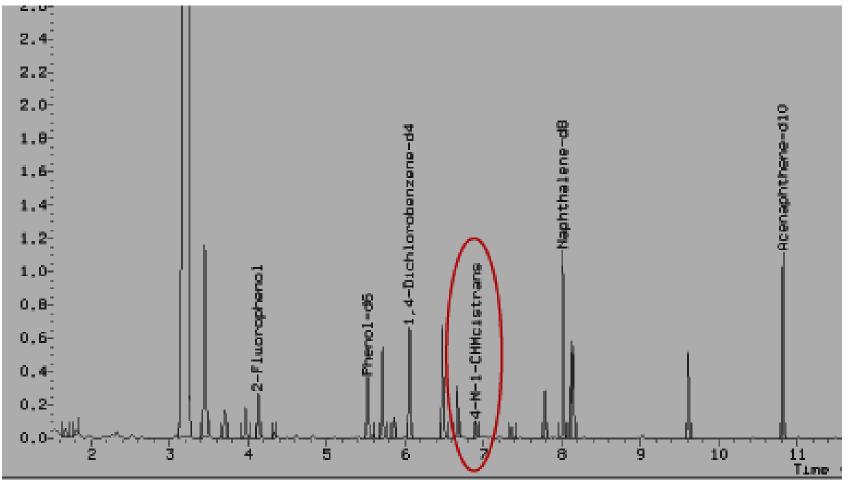
Calculated an MDL (which is a statistical calculation)

But then elevated that to represent a concentration where we knew we could demonstrate and ensure a positive response

Results of Optimization on House Survey Samples



House Sample with ~ 2 ppb 4-MCHM and other peaks





What is a "tentatively identified compound"?

What are the steps you need to go through to identify and quantify?

Retention time

Spectral library search

Manual review of the chromatogram to be sure all were identified

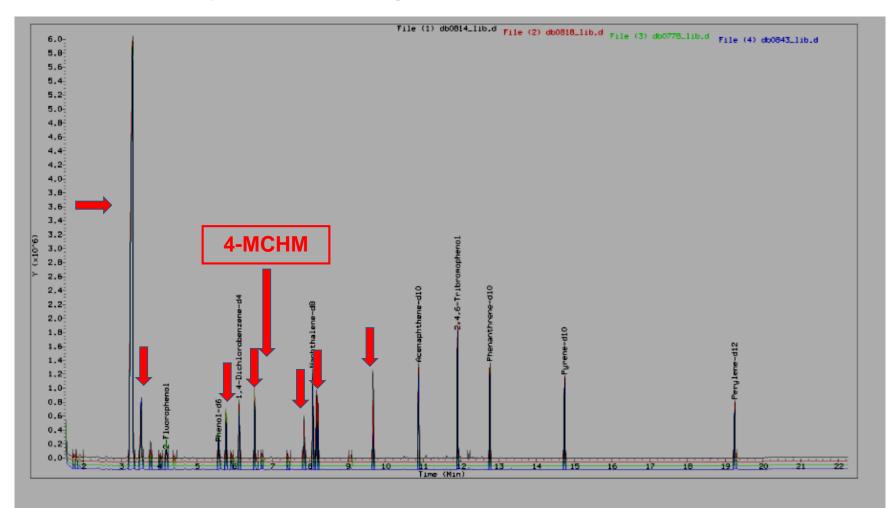
Manual review of the spectra – instrument library gives multiple possibilities

That only tells you what it **MIGHT** be

Take likely compound from library search and try to buy a standard

Extra Peaks Were Showing Up in <u>ALMOST</u> curofins All the House Samples

Overlay of Chromatograms from 4 different houses



Wanted to Confirm Possible Sources of Tentatively Identified Compounds

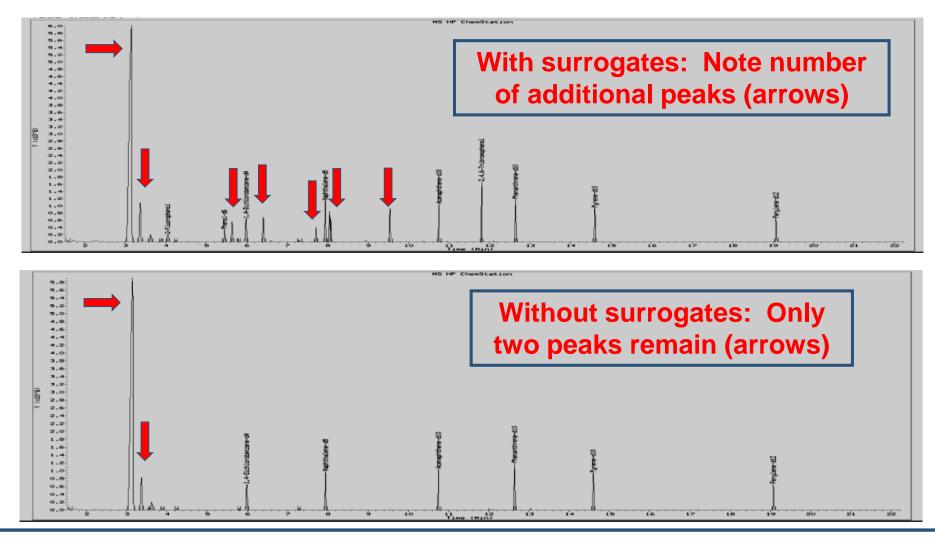
So we obtained multiple samples of:

Elk River above spill reason: no impact of MCHM WV American Influent reason: possible impact of MCHM still in river WV American Effluent reason: PLUS possible impact of chlorine House tap in Charleston reason: 4-MCHM and other peaks still present?

Part of the Story -Surrogates Cause Artifacts



House sample with and without surrogate standards added



Results:

- 4-MCHM in WV American Effluent and House sample at sub ppb levels and the major Tentatively Identified Compounds also in both samples.
- The WV American influent and the Elk River above spill samples did not show the Tentatively Identified Compounds or any 4-MCHM.
- The Tentatively Identified Compounds seemed to be related to chlorinated water.



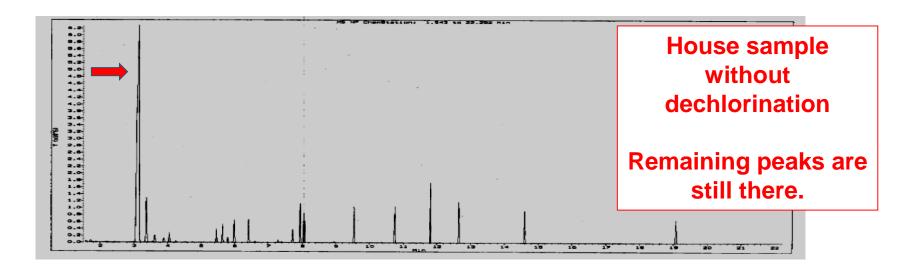
Took extra WV American (WVAW) Effluent sample. Dechlorinated with sodium sulfite

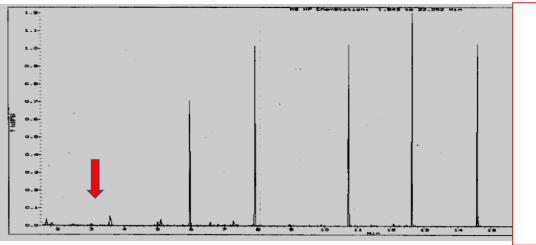
Processed with our optimized method

Results

WVAW dechlorinated effluent STILL had 0.6 ppb MCHM. Tentatively Identified Compound Peaks were gone.

Interpretation of Data – Tentatively Identified Compounds Are Artifacts





House sample dechlorinated with sulfite No more extra peaks Only peaks are internal standards and surrogates added by us

🔅 eurofins



- We found no extraneous compounds that we could not explain as analytical artifacts.
- 4-MCHM appears to be the only compound of interest that we are currently detecting in the house samples.
- As a result of this detective work we discovered the likelihood that low levels of 4-MCHM were still coming out of WVAW treatment plant.

DESIGNING THE LARGE SCALE SAMPLING PLAN

JEFFREY S. ROSEN

Ø

WV TAP PROJECT MANAGER

CORONA ENVIRONMENTAL CONSULTING



^bIN A PERFECT WORLD WE WOULD SAMPLE ALL HOMES

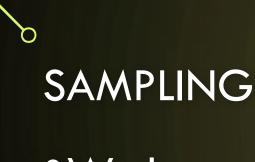
- West Virginia American estimates that there are 86,866 residential customers affected by the MCHM spill. Sampling every home would cost about \$635,000,000 to do the same sampling we did in the 10 homes presented if we continue pushing the detection limit down to level that are being observed
- It would take about 100 teams of 3 trained people each 86 weeks to complete the sampling.

Ó

CEC

 We can make estimates of the extent of the contamination doing many fewer samples

WV TAP



 \bigcirc

Q

SAMPLING FRAME

- •We have:
- 9 Counties

CEC

•21 Pressure zones

 As many as 6 different locations within the home that we might want to sample



^b RECAP OF PILOT SAMPLING STUDY

OVERVIEW

- Why? To collected data needed to design a full-scale sampling effort
- What?

CEC

- 10 houses
- Four locations per house
- Three replicates samples per location
- Two commercial laboratories
- Three analytes

SOME KEY FINDINGS

- One lab Detected lower levels than the other – specifying the levels required by the labs is critical
- PPH was not present at an appreciable level in any of the samples
- MCHM, when present, was at concentrations below the screening level of 10 ppb



RECAPPING

 \bigcirc

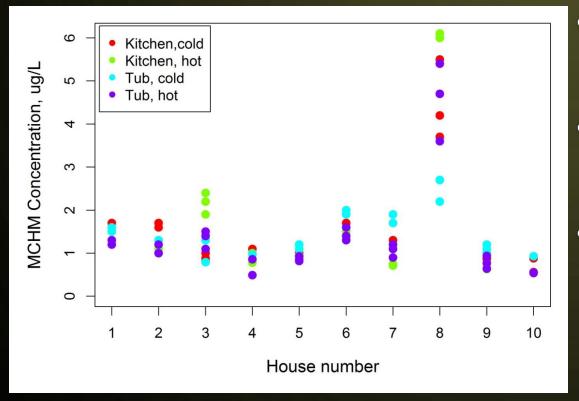
- 4 Locations sampled
 - 1 = cold kitchen,
 - 2 = hot kitchen,
 - 3 = cold tub,
 - 4 = hot tub

CEC

- All concentrations of MCHM are low
- There is variability (spread in the results and differences between locations) within each home but no clear patterns
- Some statistical differences between hot and cold water in kitchens versus bathrooms and in hot versus cold taps, but no clear pattern



^b PILOT STUDY MCHM CONCENTRATIONS



(

CEC

Q

- Below detection data excluded (10 out of 120 samples)
- Three samples per location for each of 10 houses
- In general, differences between
 houses are much greater than
 differences between locations within
 a given house



DIFFERENCES BETWEEN LOCATION WITHIN HOMES

- There are real statistically significant differences but no patterns
 - House is a bigger factor than sample location within the house
- Differences at most locations are very small
- We observed real variability in the homes

CEC

- Get the highest values in each home Cold Water Bathtub for many homes
- Best to take samples at multiple locations in the home to get an overall average concentration



STATISTICS IS ALL ABOUT THE QUESTIONS BEING ASKED

• We have many questions

CEC

- The two that we will focus on for designing the larger sampling plan are:
- 1. How confident can I be that the water in my home is less than the screening level?
- 2. What percentage of the homes are below any concentration level that we can pick (including a safety factor)?



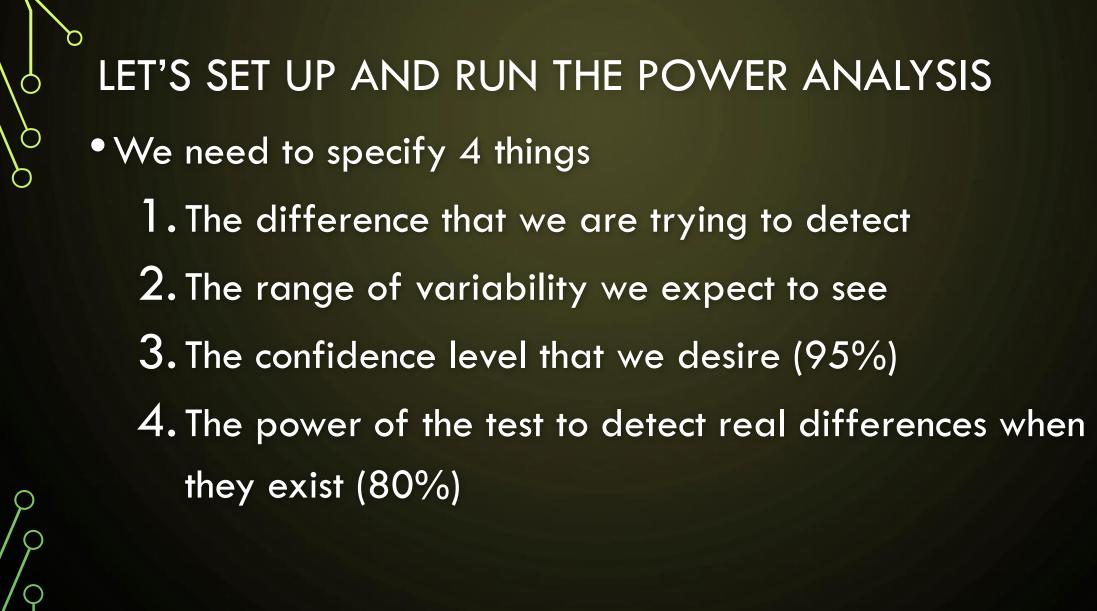
^bFOR QUESTION NUMBER ONE – IS THE CONCENTRATION IN MY HOUSE LESS THAN THE SCREENING LEVEL?

• How many samples should be taken in each home?

CEC

- The more sample taken, the more accurately you know the average MCHM concentration in a house, BUT, as you take more and more samples, the additional certainty you get with each sample decreases (diminishing returns)
- We will use power analysis to determine the number of samples necessary to have 95% confidence that the concentration of MCHM in a house is lower than the screening level
- Power analysis is an effective way to relate the sample size, the variability and the differences which are meaningful to the ability to detect real differences when they exist





Ċ

CEC

WEST VIRGINIA TESTING ASSESSMENT PROJECT

WHAT IS OUR LEVEL OF CONCERN?

- 10 ppb (will be re-evaluated next week by the Health Effects Expert Panel)
- We want to be able to say that an average observed in the home is less than 10 ppb with a 95% level of confidence.
- The highest mean that we observed in the 10 home sampling was 4.4 ppb.
- The highest concentration we observed was 6.1ppb

Ò

CEC

• The smallest difference that we will want to be able to detect is about 4 ppb



WHAT IS THE VARIABILITY THAT WE ARE SEEING IN THE HOMES

Highest standard deviation observed was 1.4 ppb.

- Next highest was 0.5 ppb.
- Lowest value 0.13 ppb

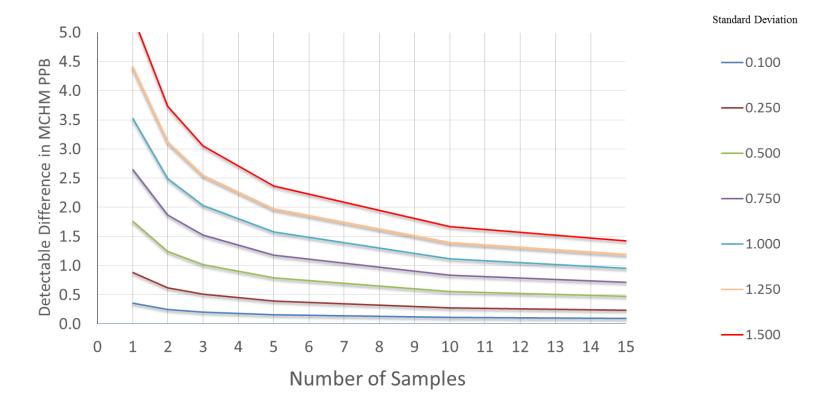
CEC

• Variability ranged from 0.13 – 1.4.



• THE POWER ANALYSIS

Detectable Differences in MCHM Concentration PPB





CEC

 \bigcirc

 \bigcirc

 \mathcal{O}

Q

 \bigcirc

Q

 \bigcirc

 TENTATIVE SUGGESTION SAMPLING PER HOME
 Minimum of 2 samples per home one each Kitchen Cold and Tub Cold

9

 \bigcirc

CEC

•Benefit 1 - An estimate of the house concentration overall

Benefit 2 - Continue to understand the variability within homes



HOW MANY HOMES IN EACH PRESSURE ZONE

- Variability (spread in MCHM concentrations) among homes in the study was also low
- The overall average concentration of MCHM in the homes was 1.48 ppb
- The standard error of the means was 0.339 ppb

CEC

- Estimating means and confidence intervals for each pressure zone can be done with low number of samples (20- 30 homes per pressure zone)
- If the question is what percent of the homes are below 10 ppb with a confidence interval for the entire affected area, then the sampling plan described works well



THE SECOND QUESTION

 \bigcirc

CEC

•What percentage of the homes are below the screening levels (including a safety factor)?



CONFIDENCE INTERVALS AROUND PERCENTAGES

 \mathcal{O}

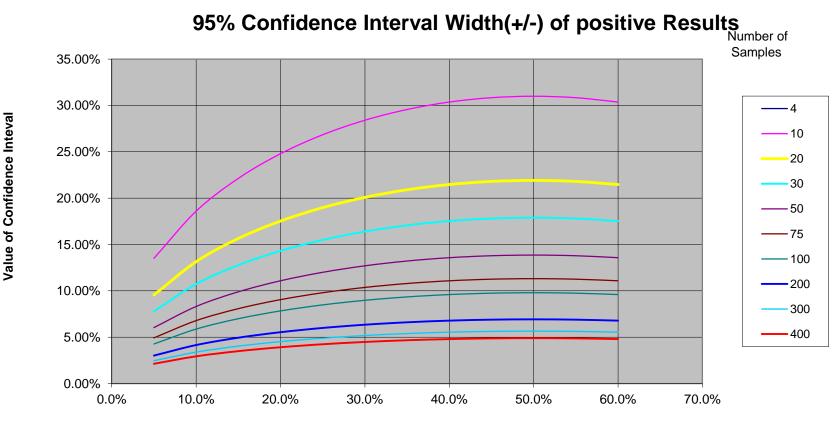
CEC

 \bigcirc

 \bigcirc

O

Q



Observed Percent Positive



LIMITED CONFIDENCE IN PERCENTAGE FOR EACH PRESSURE ZONE

- With only 30 homes per pressure zone our results might be for example
 - Within pressure zone 3, $10\% \pm 15\%$ of the homes are above a concentration of 2 ppb
- However, with 600 homes sampled our results could be that 10% ± 2% of the homes in the entire affected area are above any particular level

CEC



ANOTHER CONSIDERATION

 \bigcirc

 \bigcirc

CEC

- Our analysis thus far only accounts for single family or small number of residences per building. It does not consider multi-resident building like apartment buildings.
- Including multi resident buildings would require a different sampling plan for which we have not collected data yet.
- We are currently only planning to sample for MCHM. If we decide to sample for other chemicals the costs will increase, and the complexity of the logistics will increase
- Final plan will be influenced by the results of the Health Effects Expert Panel Review



^o SUMMARY OF A PRELIMINARY SAMPLING PLAN

- Sample 20 30 homes per pressure zone
- Take at least 2 samples per home
- Test for only MCHM concentration

Ċ

- Provide estimate the home concentrations per Pressure
 Zone
- Provide good estimate the percent of homes below any value (down to the method reporting limit) over the entire affected area.
 20 WV TA

THANK YOU FOR YOUR ATTENTION

Ó

Bo

CEC

WE WILL ANSWER QUESTIONS AFTER LUNCH BREAK.



Health Effects Expert Panel

Andrew Whelton

Why Convene a Health Effects Expert Panel?

• To provide <u>independent expert review</u> 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.
- <u>Complex issues</u> require participation by diverse types of scientists.

Expert Panel Organized by TERA http://www.tera.org



- Internationally recognized, independent, non-profit corporation
- Mission
 - 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's Independent Peer Review Process – Key Principles

• Scientific Robustness

- Diversity of expertise
- Comprehensive coverage of issues by panels

• Selection of appropriate expertise

- Training and experience in key scientific disciplines
- Diversity of backgrounds and perspectives
- Multiple experts to thoroughly discuss key issues

Transparency

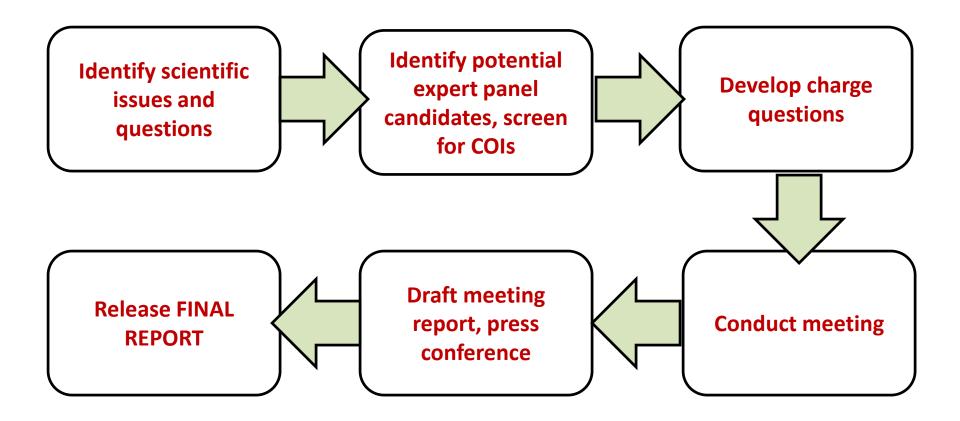
- Share information
- Comprehensive report on process, discussions, conclusions

Independence

- Screen candidates for conflict of interest
- Monitor discussions to recognize biases

Meek, M.E., J. Patterson, J. Strawson, and R. Liteplo. 2007. Engaging Expert Peers in the Development of Risk Assessments. Risk Anal. 27(6):1609-1621.

TERA's Peer Review Process



Expert Panel Selection

Types of scientific expertise

- Toxicology
- Derivation of screening levels
- Human health risk assessment
- Water contaminants and systems

• Diversity of perspectives and experiences

- University
- State government
- Research
- Non-profit

• Screened for Conflict of Interest

 Relationships with interested parties that may cause an expert to lack of objectivity

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

Questions to Be Addressed by TAP Expert Panel

- <u>Review and discuss the available toxicology data</u> 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 <u>consider if the</u> <u>additional safety factor applied by the State of West</u> <u>Virginia was protective of public health</u>, based on available data.
- Identify data gaps and make recommendations for additional studies or analyses that could strengthen the screening level and reduce uncertainty.

Review Materials

Professor Dr. Craig Adams, University of Utah

 Available at TAP Website
 http://www.dhsem.wv.gov/wvtap/Pages/defa

<u>ult.aspx</u>)

- Initial Literature Review
 - Studies and data that were available
- CDC response to WV TAP March 2014
 - Clarification on the MCHM and PPH screening levels

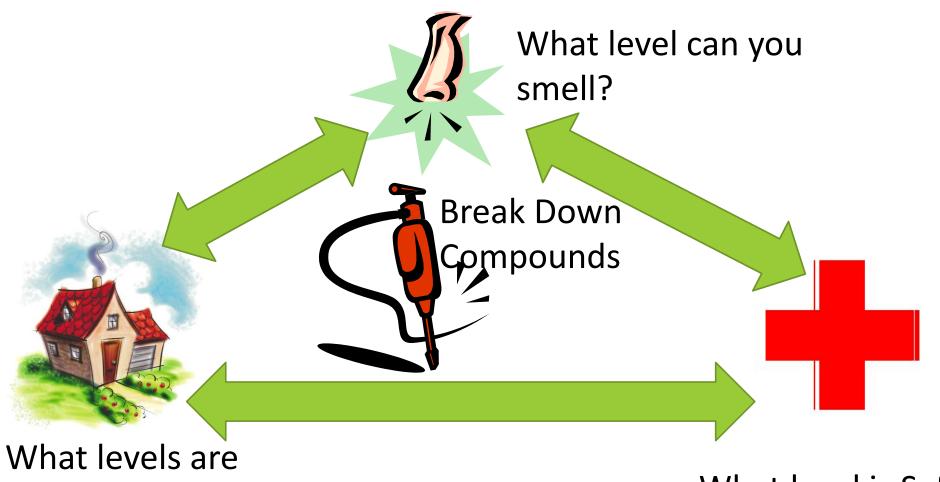
THE Charge Questions

- 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.

Summary

THE WV TAP TEAM

Our Goals



occurring in your homes?

What level is Safe?

Next Steps

Today

≻Break

≻Public Q&A

- Rules for the questions and answers
- Line up at the microphones for questions
- STRICT 2 minutes for each question. If you go over I will firmly, but politely, cut you off. Our answers will not exceed 3 minutes.
- Short questions mean we will be able to answer more questions.
- PLEASE BE POLITE AND BRIEF

Next steps in the next few weeks

Coming days

- Data will be posted, check the website and twitter!
- Health effects press conference/meeting April 1 1000am

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 in May 15

- Final report summarizing all the results
- Includes recommendations to State for short- and long-term activities

Thank you!

THE WV TAP PROGRAM