MCHM/PPH in the Elk and Kanawha Rivers after the January 2014 Spill: Lessons Learned

Jennifer Weidhaas, Karen Buzby
Aubrey Harris, Paul Ziemkiewicz, Kung Wang
and Lance Lin

West Virginia University
April 1, 2015

WestVirginiaUniversity.
Department of Civil and Environmental Engineering

Spill Timeline

Jan 8-9 spill of 10,000 gal to Elk River

Jan 9 WVDEP informed WVAmW, “do not use order” issued

Jan 10 CDC says 1 ppm safe

Jan 13 ban lifted for 25,000 customers

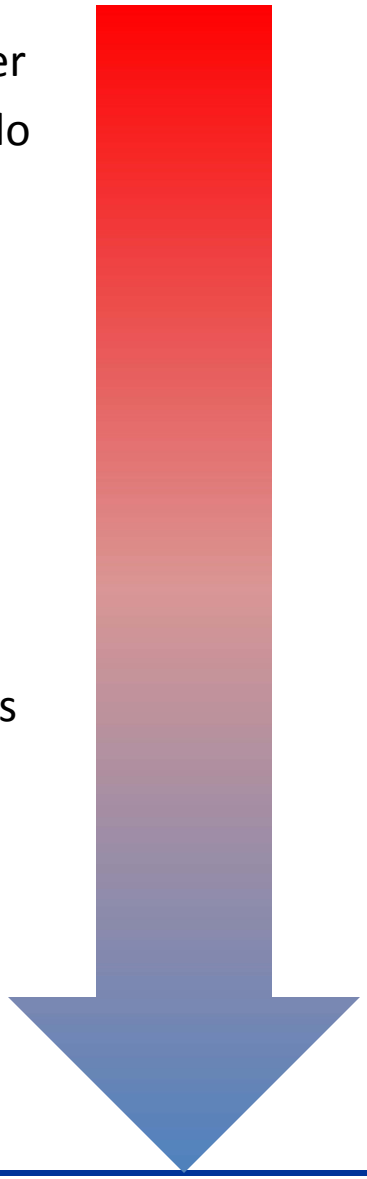
Jan 15 CDC recommends pregnant women not drink the water

Jan 17 Freedom Industries files for bankruptcy

Jan 18 ban lifted for remaining users

Jan 21 WVDEP informed of PPH release

Feb 11 6 ppb MCHM in schools



Jan 11 prepared proposal

Jan 13 called NSF

Jan 15 conducted round 1 sampling (CEE Department $10,000)

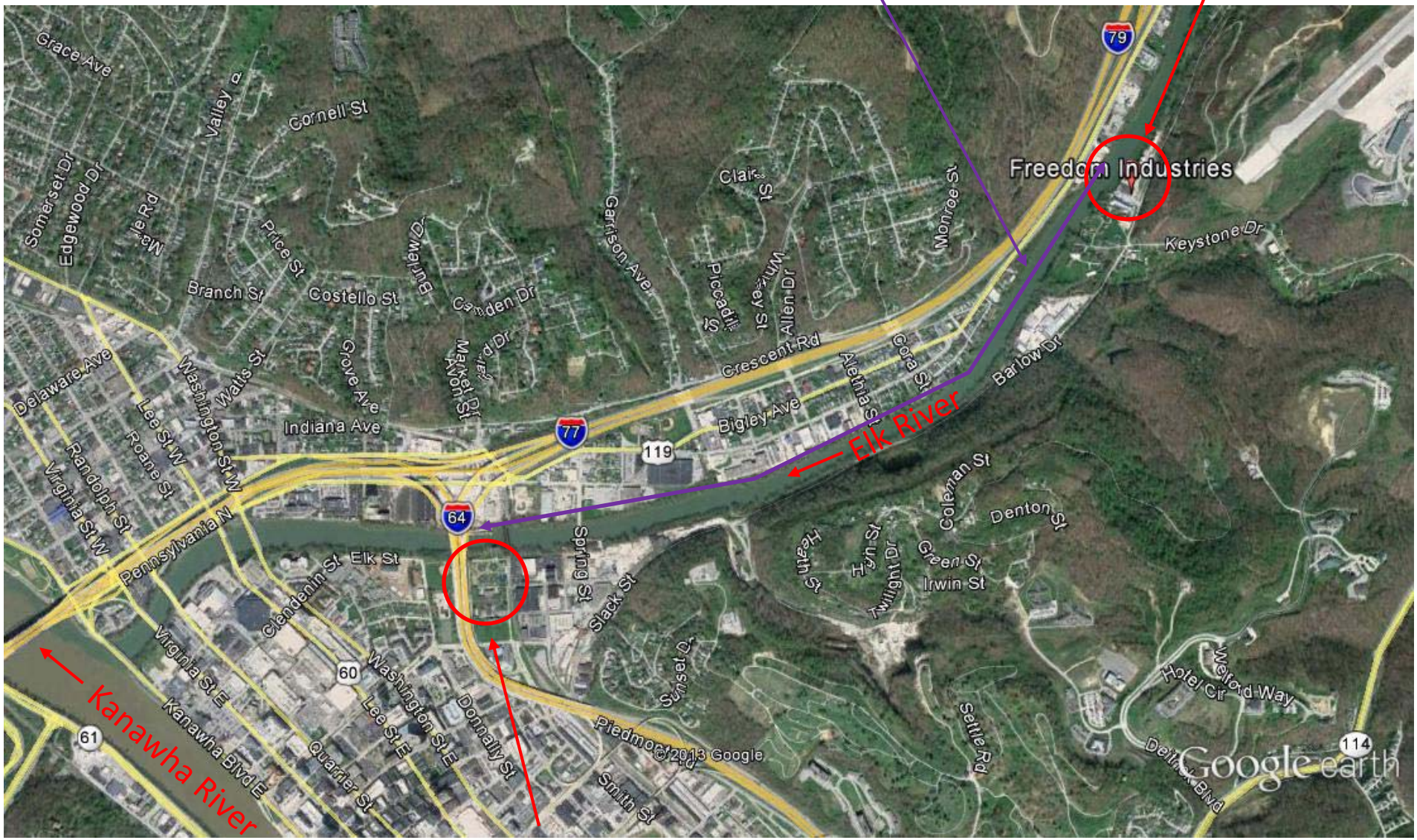
Jan 22 conducted round 2 sampling

Jan 30 conducted round 3 sampling

Laboratory studies

http://www.dhsem.wv.gov/Pages/WV-American-Water-Emergency.aspx

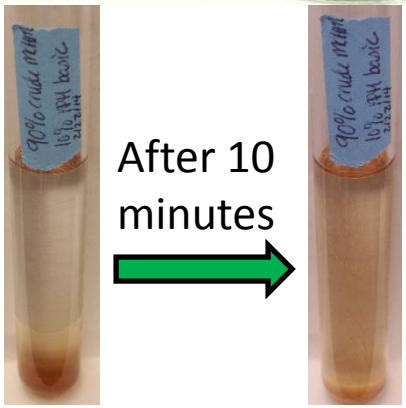
WestVirginiaUniversity.
Department of Civil and Environmental Engineering



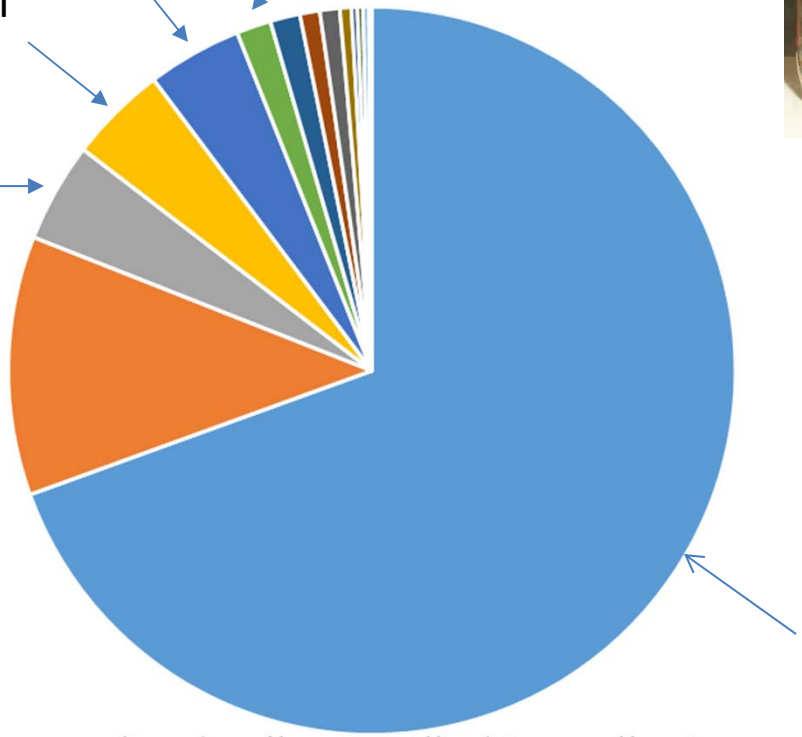
WestVirginiaUniversity.
Department of Civil and Environmental Engineering

Mixture constituents

Crude MCHM (88.5% of tank contents), PPH Stripped (7.3% of tank contents)
Assuming 10,000 gallons spilled



After 10 minutes



PPH, 154 gal

water

Di-PPh, 435 gal

methyl 4-methylcyclo hexanecarboxylate
443 gal

4-(methoxymethyl) cyclohexanemethanol
1151 gal

MCHM
6947 gal

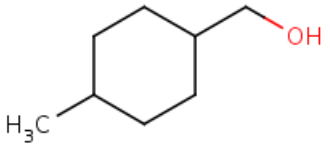
Normalized gallons spilled into Elk River

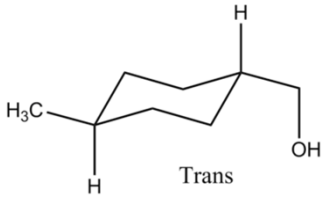
Eastman Chemical and DOW MSDS's, 2014

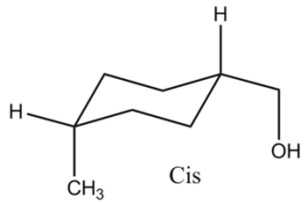
WestVirginiaUniversity.
Department of Civil and Environmental Engineering

What was in the tanks?

- **Crude MCHM (89% of tank contents)**
  - **4-methylcyclohexanemethanol** (68 to 89 % of crude)







SG = 0.9074

log K_{ow} = 2.35 (*cis* isomer, Dietrich et al, 2015)

log K_{ow} = 2.46 (*tran* isomer, Dietrich et al, 2015)

Water solubility = 2,250 mg/L at 23 °C (Dietrich et al., 2015)

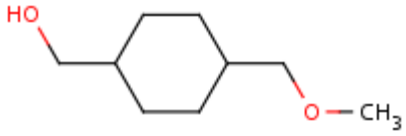
= 1,585 mg/L at 23 °C (He et al., 2015)

Odor threshold concentration = 0.06 ppb-v, *tran*-isomer

= 120 ppb-v, *cis*-isomer (Gallagher et al., 2014)

Henry's constant = ~6.4 * 10^{-6} atm·m^3/mol (EPA Suite v4.11)

  - **4-(methoxymethyl)cyclohexanemethanol** (4 to 22 % of crude)



Unknown properties

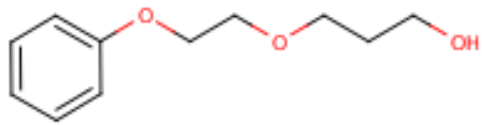
Eastman Chemical and DOW MSDS's, 2014

WestVirginiaUniversity.
Department of Civil and Environmental Engineering

What was in the tanks?

- **PPH stripped? PPH Basic? (7% of tank)**
  - **Dipropylene glycol phenyl ether** (<= 85% of PPH Basic)

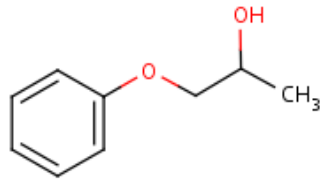
    Henry's constant = 4.7* 10^{-10} atm · m^3/mol



  - **Propylene glycol phenyl ether** (<= 20 % of PPH Basic)

    log K_{ow} = 1.52 (calc); water solubility = 1.1 g/L

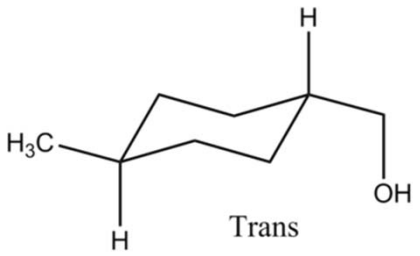
    Henry's constant = 4.4* 10^{-7} atm · m^3/mol



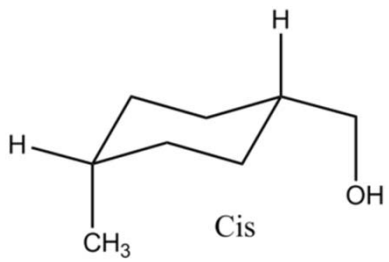
WestVirginiaUniversity.
Department of Civil and Environmental Engineering

NMR analysis of MCHM

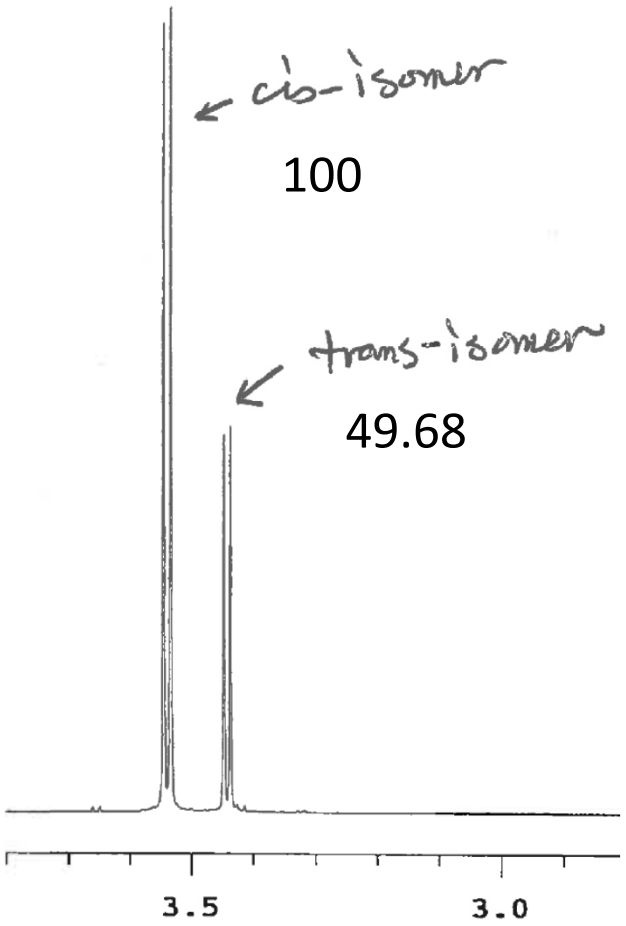
Kung Wang, Chemistry



Trans

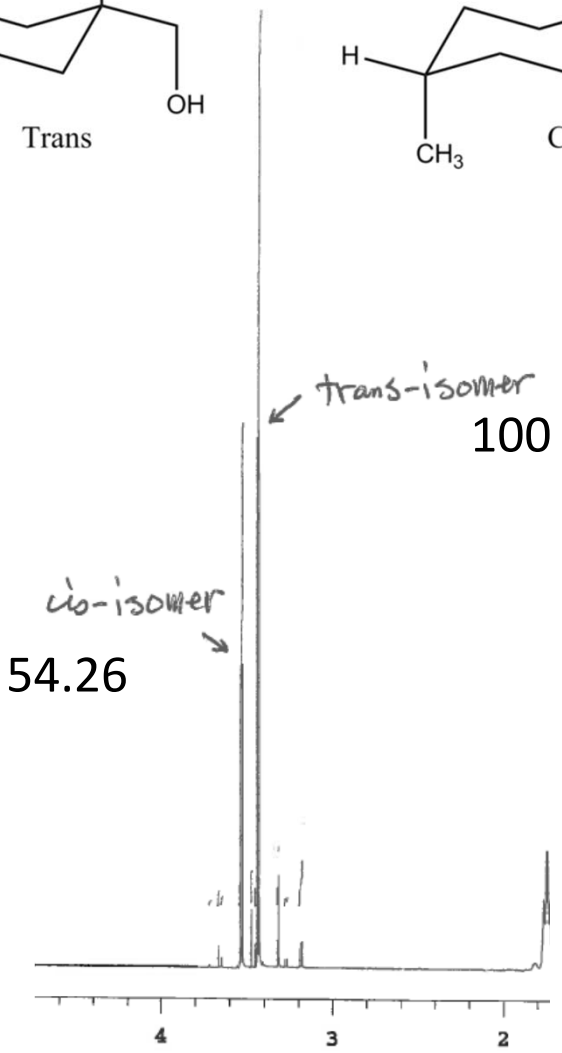


Cis



TCI America Analytical Standard

^{1}H-NMR spectrum (600 MHz)



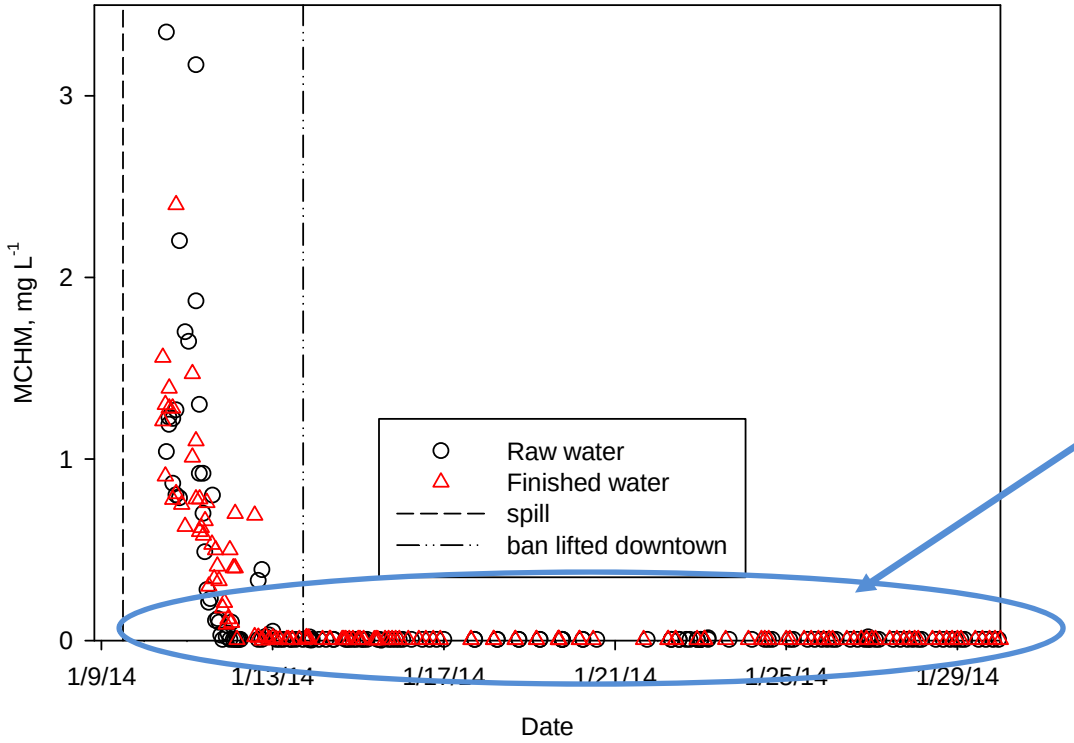
Eastman Chemical crude-MCHM

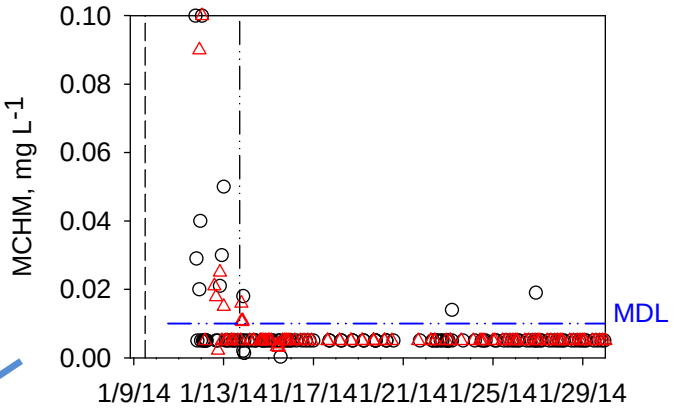
^{1}H-NMR spectrum (600 MHz)

ersity

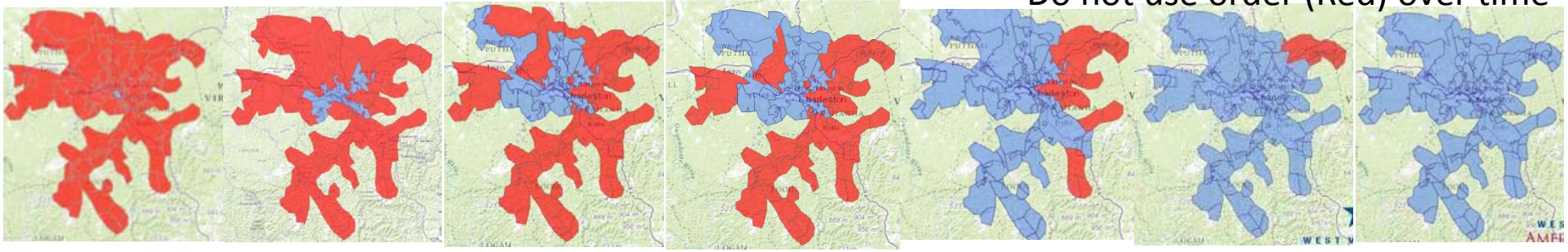
Department of Civil and Environmental Engineering

WVAmW: Influent and Effluent





Do not use order (Red) over time



Jan 13 AM | Jan 14 AM | Jan 14 PM | Jan 15 AM | Jan 16 PM | Jan 17 | Jan 18 PM

WestVirginiaUniversity.
Department of Civil and Environmental Engineering

HOW TO FLUSH YOUR PLUMBING SYSTEM

WEST VIRGINIA AMERICAN WATER

Following are step-by-step procedures customers can use to flush their plumbing system. To protect the health and safety of our communities, we recommend that you read carefully and follow the steps for flushing. Thank you for your cooperation. **NOTE: After flushing, your water filters need to be replaced. If you have any point of entry water treatment system such as a water softener or filter, please refer to "How to Flush Plumbing Appliances and Faucets."**

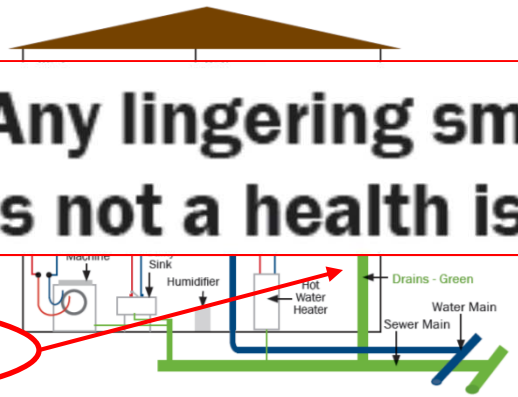
West Virginia American Water will be offering residential customers a credit of 1000 gallons, which is more than what will likely be required to flush the average residential home. The average residential customer uses approximately 3,300 gallons per month.

How to flush your plumbing system

Please complete these steps in the order set out below. Finish each step completely before moving on to the next step.

1. **Flush ALL hot water taps for 15 minutes**
   Begin the flushing procedure by opening the hot water taps in your bathroom(s). Open ALL hot water lavatory (sink) fixtures, hot water bath fixtures, and any other hot water fixtures, such as kitchens, wet bars, etc. **Run these hot water fixtures for at least 15 minutes. Shut water off after 15 minutes.** After you have flushed each hot water faucet for 15 minutes, your hot water heater will be safe for use.
2. **Flush ALL cold water taps for five minutes**
   Once the hot water tank and hot water piping have been flushed, open ALL of the cold water fixtures, flush each toilet at least one time. **Run these cold water fixtures for at least five minutes. Shut water off after five minutes.** This does include the water in your refrigerator water dispenser.
3. **Flush ALL remaining faucets and appliances**
   (Before starting step 3, please see **How to Flush Plumbing Appliances and Faucets** for more information.) Open any remaining fixtures such as hose bibs, external faucets or fixtures not used for drinking for at least five minutes to finish the plumbing system flushing. Take additional steps to remove water from other appliances. See **How to Flush Plumbing Appliances and Faucets** for more information. This includes:
   - Ice makers
   - Dishwashers
   - Washing machine
   - Humidifiers
   - Continuous Positive Airway Pres (CPAP)
   - Oral, medical or health care dev
   - Baby formula, food and drinks r with water during DO NOT USE
   - Water filters
   - Water softeners
   - Reverse osmosis units

Any lingering smell, which is expected, is not a health issue.



Any lingering smell, which is expected, is not a health issue.

Estimate of odor threshold = 0.06 ppb-v

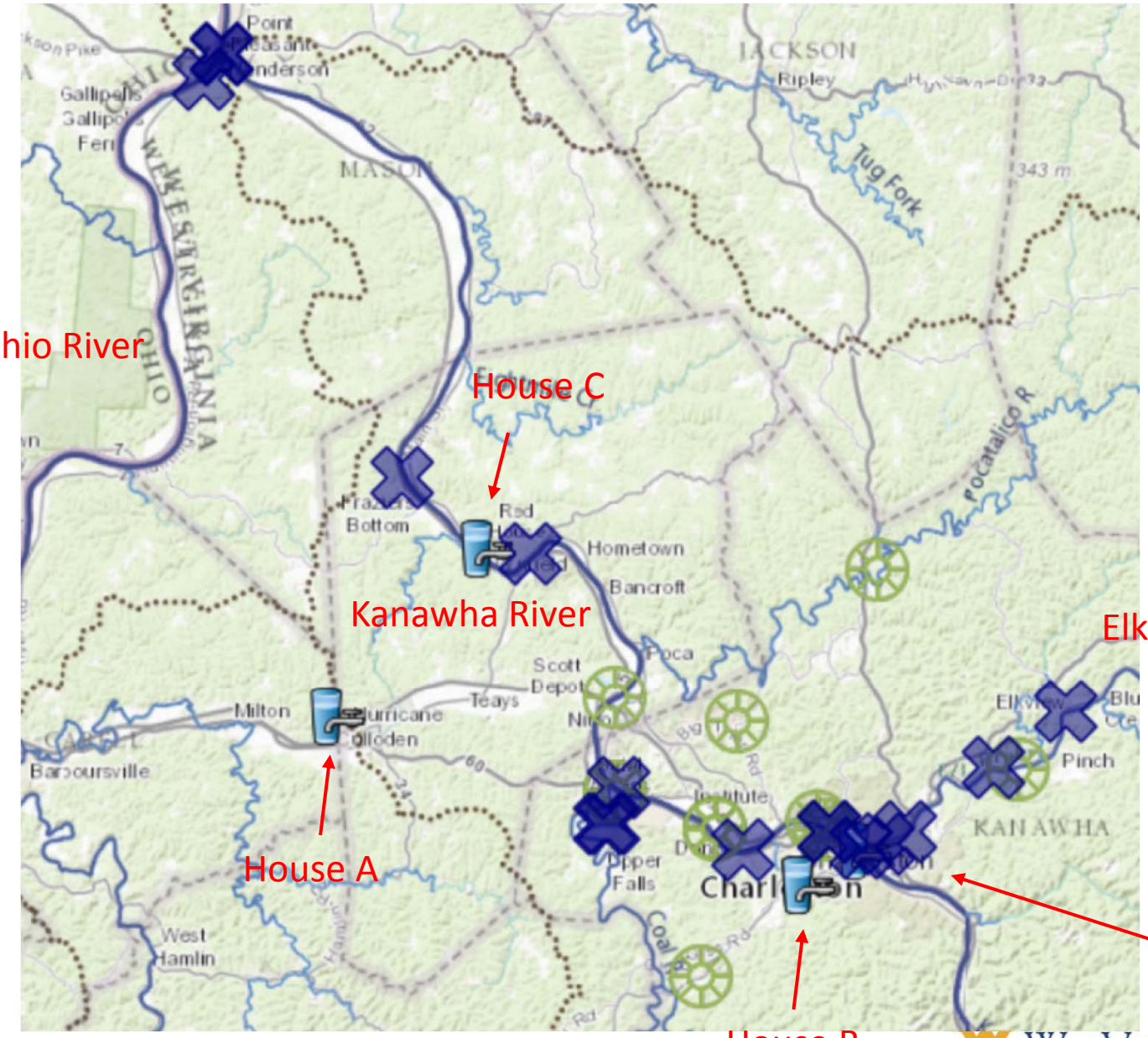
CDC "safe" limit in water = 1000 ppb

1. Open all hot water taps and run for 15 minutes

2. Open all cold water taps (inside) and run for 5 minutes, flush all toilets (once)

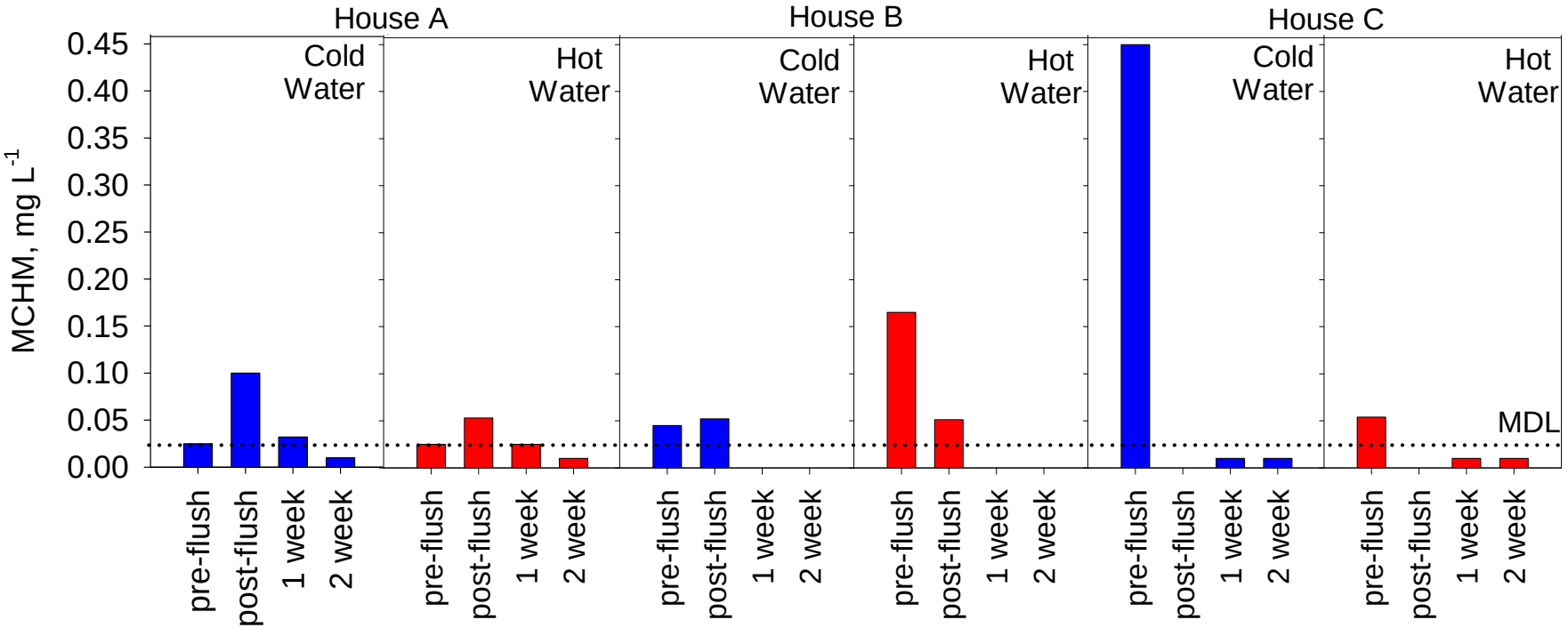
3. Flush all remain faucets and appliances

WestVirginiaUniversity.
Department of Civil and Environmental Engineering



WestVirginiaUniversity.
Department of Civil and Environmental Engineering

Residential sampling results



Water distribution system

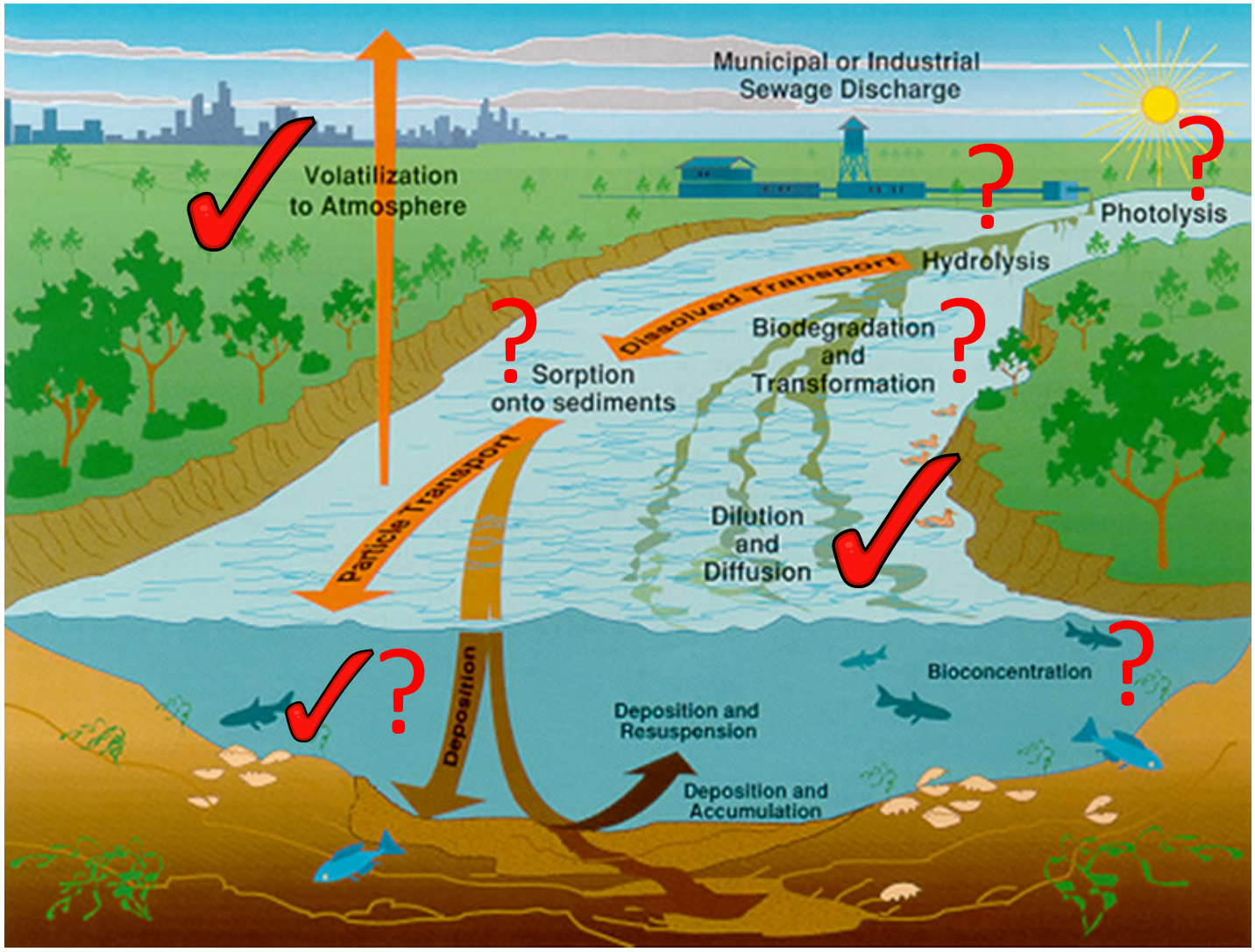
WestVirginiaUniversity.
Department of Civil and Environmental Engineering

Chemical Attenuation and Barriers in Current Water Supply Infrastructure

- Mixing and dilution in the river
- Other mass transfer processes resulting in losses of the chemicals from the river water
  - sorption, volatilization, degradation, hydrolysis, etc.
- Water treatment plant
  Vulnerability?
- Alternative water sources

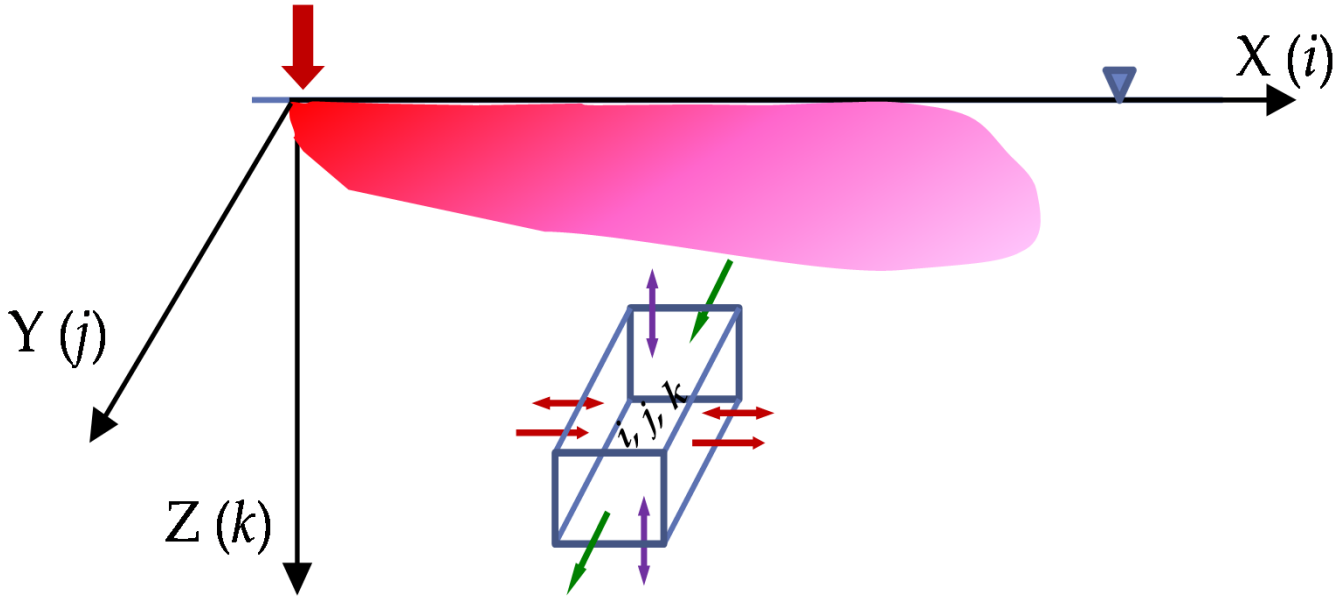
WestVirginiaUniversity.
Department of Civil and Environmental Engineering

Fate of organic contaminants in rivers



WestVirginiaUniversity.
Department of Civil and
Environmental Engineering

3-D MCHM Fate and Transfer Modeling

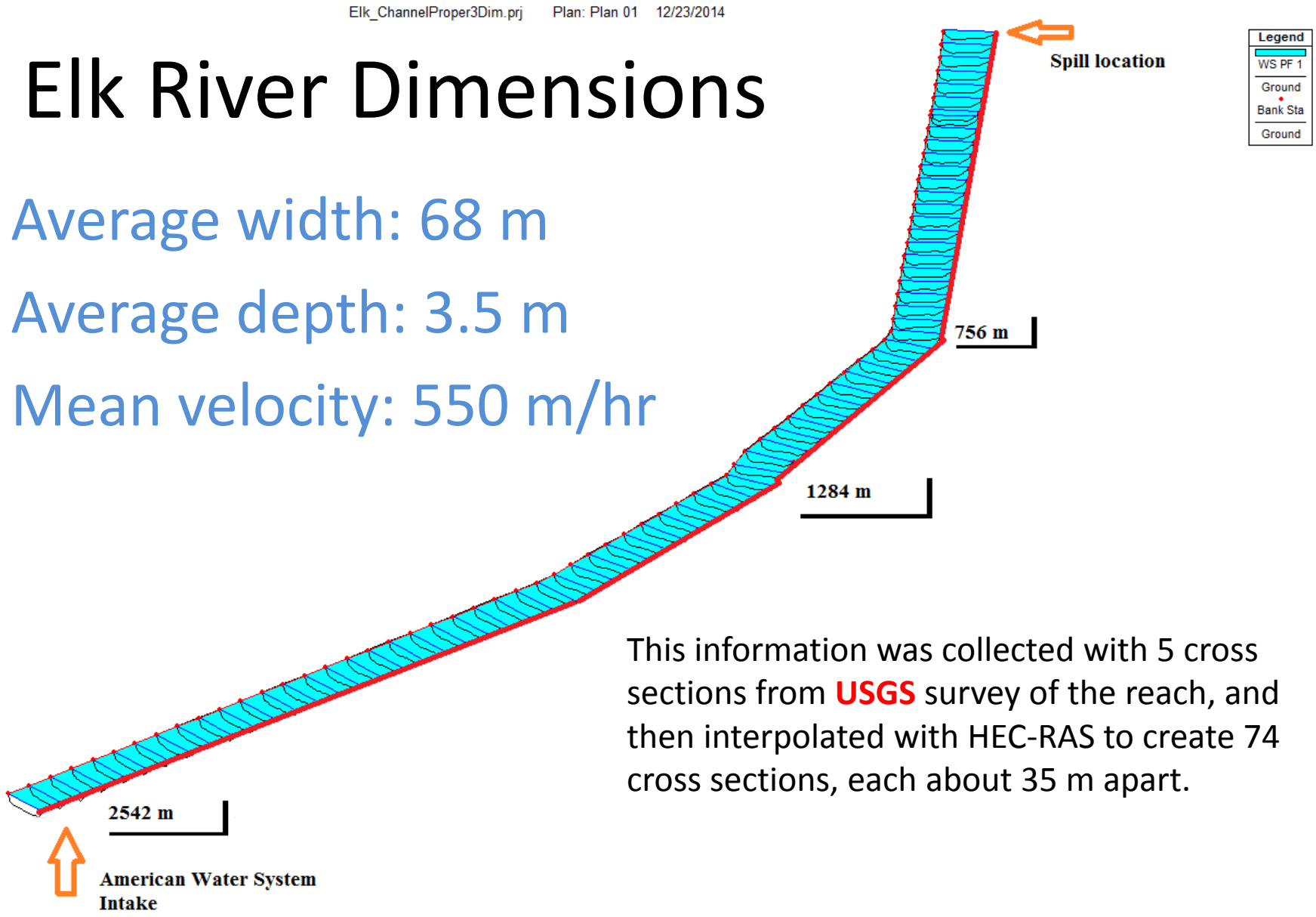


Elk River Dimensions

Average width: 68 m

Average depth: 3.5 m

Mean velocity: 550 m/hr



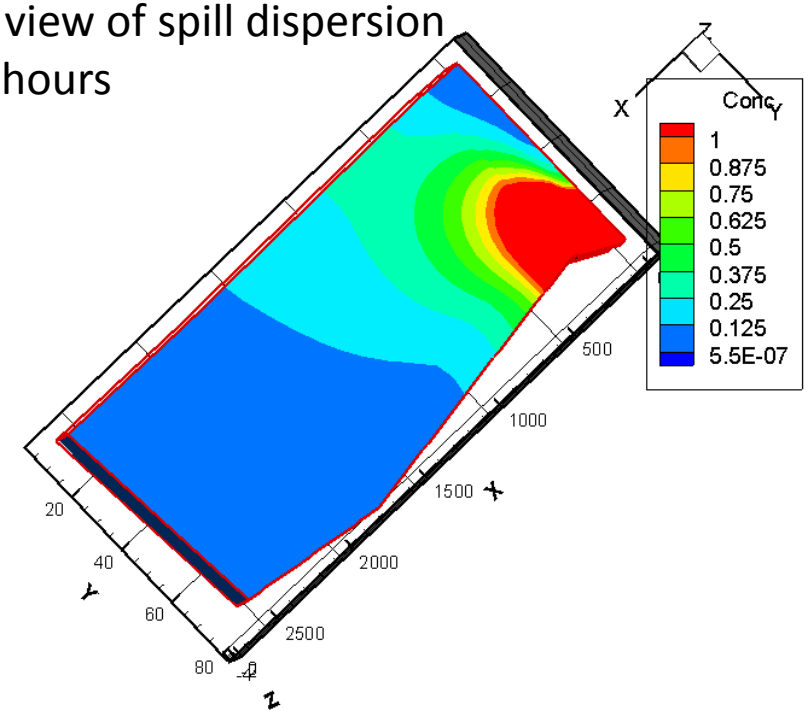
This information was collected with 5 cross sections from **USGS** survey of the reach, and then interpolated with HEC-RAS to create 74 cross sections, each about 35 m apart.

Spill Characteristics

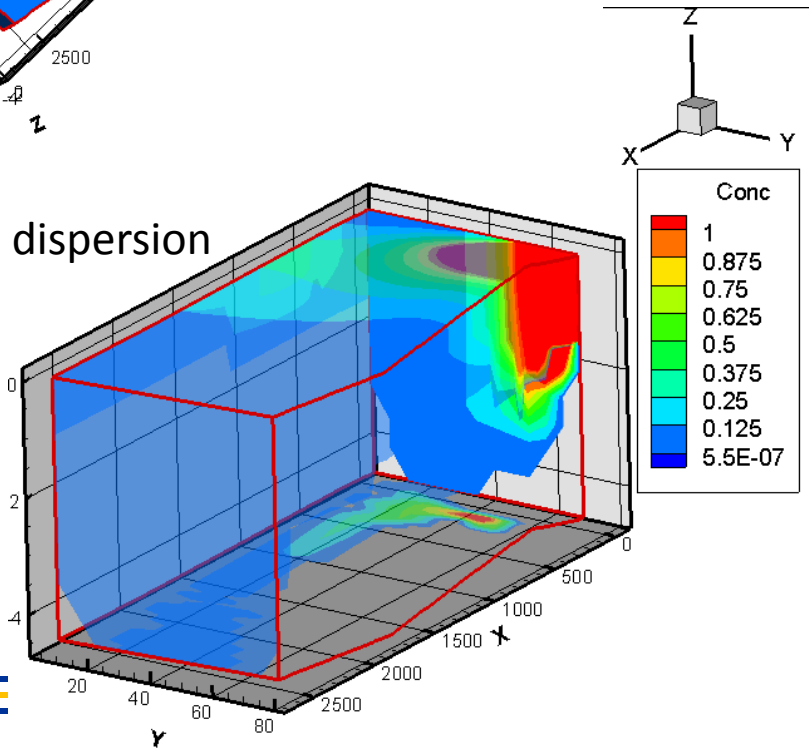
- MCHM was spilled for approximately 20 hours at a rate of (8 gpm); mass loading of 1,485 kg/hr.

- It travelled 2,600 m (1.61 miles) before being intercepted by the American Water System, a water intake for Charleston, WV

Areal view of spill dispersion at 10 hours



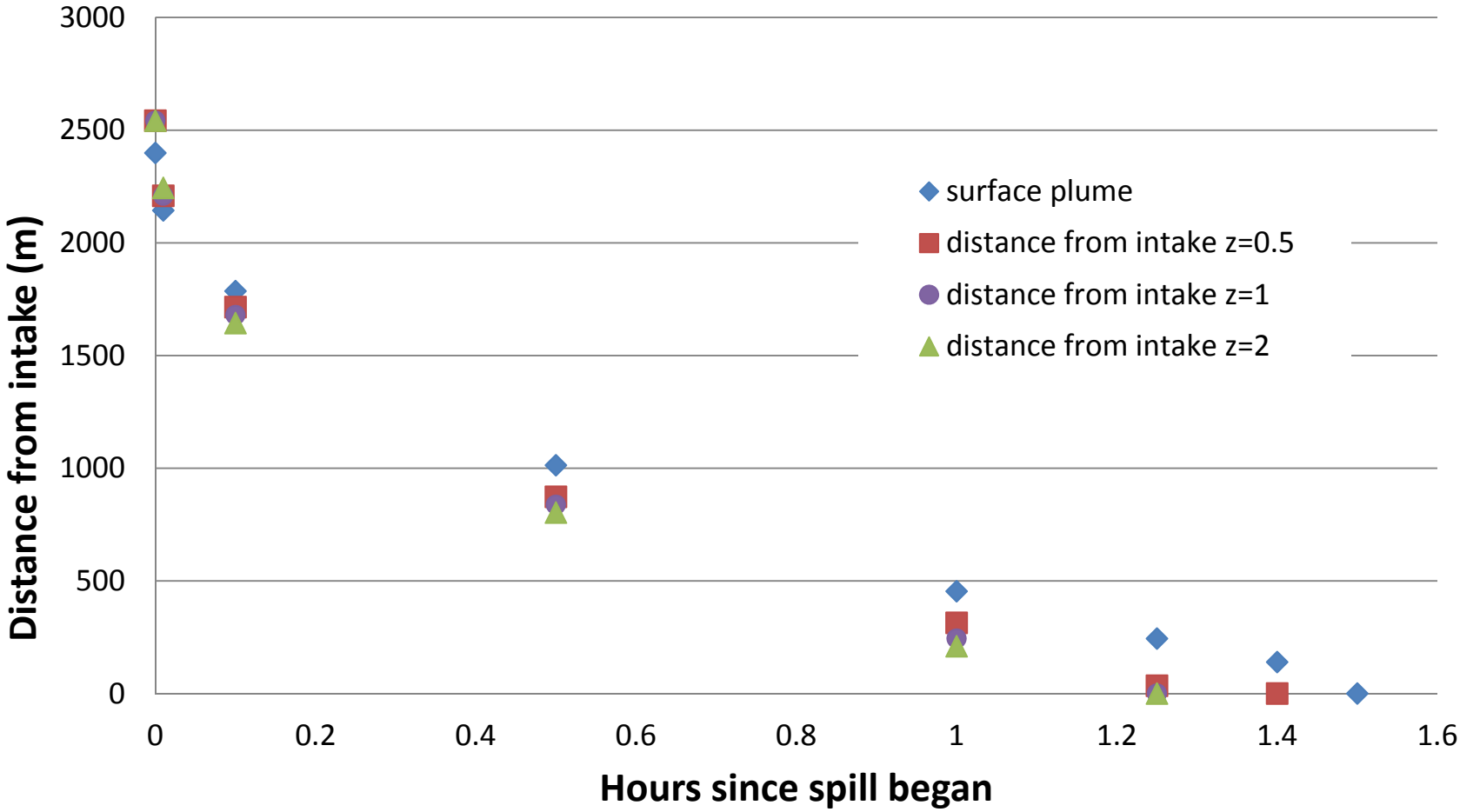
3-D view of spill dispersion at 10 hours



- Mixing characteristics: Within about 500 m the chemical becomes mixed across the lateral width and vertical depth.
- The implication is that even though the chemical is a lower-density, non-aqueous phase chemical, the surface water is not the only area impacted.

WestVirginiaUniversity.
Department of Civil and Environmental Engineering

Plume front (0.1 ppm) distance from intake



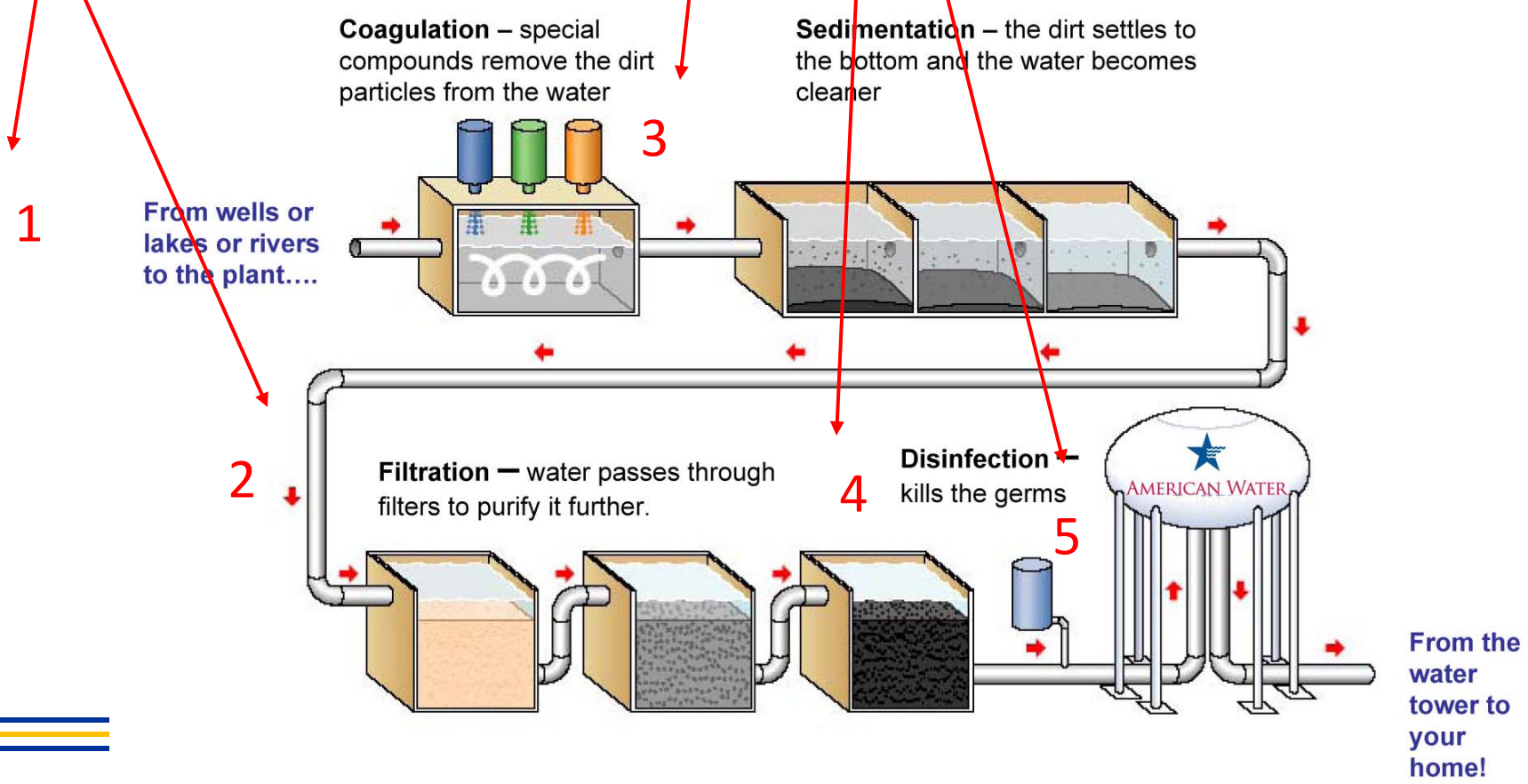
WestVirginiaUniversity.
Department of Civil and Environmental Engineering

WA American Water treatment plant unit processes

WestVirginiaUniversity.
Department of Civil and Environmental Engineering

Unit Processes & Lab Studies

1. River sediment sorption/desorption
2. Permanganate oxidation
3. Coagulation/flocculation with Alum
4. GAC adsorption
5. $HOCl^-$, OCl^- disinfection
6. Testing household filters

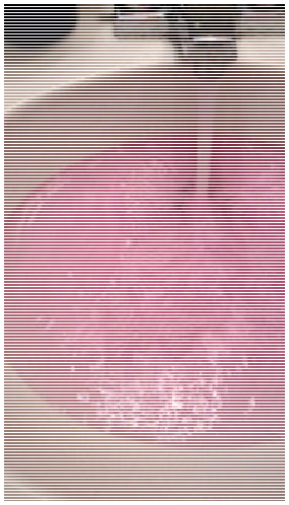


Permanganate oxidation

Experimental protocol

-Vary MCHM + PPH from 10 to 30 ppm
-De-ionized water
-Room temperature
-1 to 10 minute reaction
-0, 5, 10, 50 and 100 ppm $KMnO_4$

www.gunnook.com



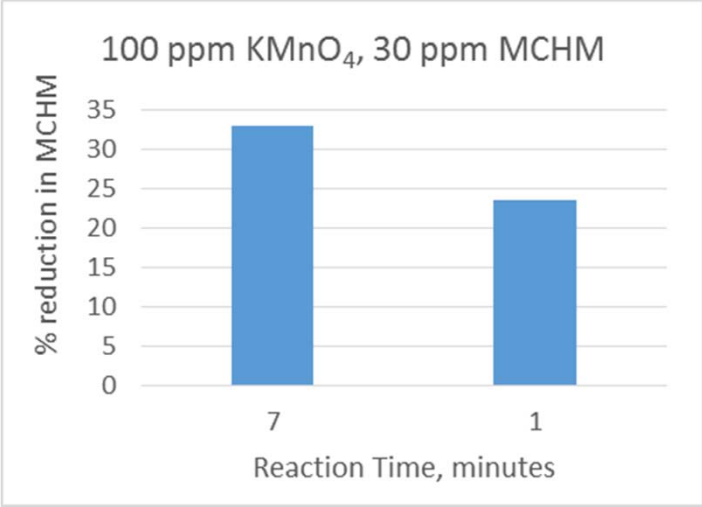
Pink water flows from tap in St. Michael

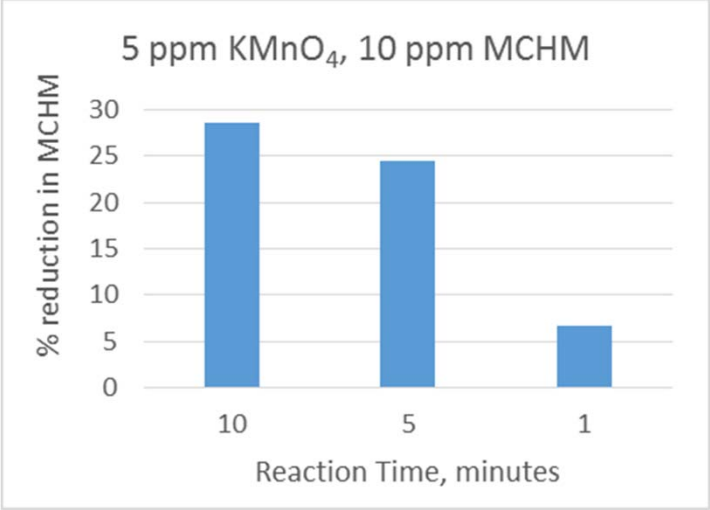
Recommend 376

Posted: May 07, 2012 1:58 PM EST
Updated: May 07, 2012 11:03 PM EST

by Bill Keller - bio | email

http://www.myfoxtwincities.com

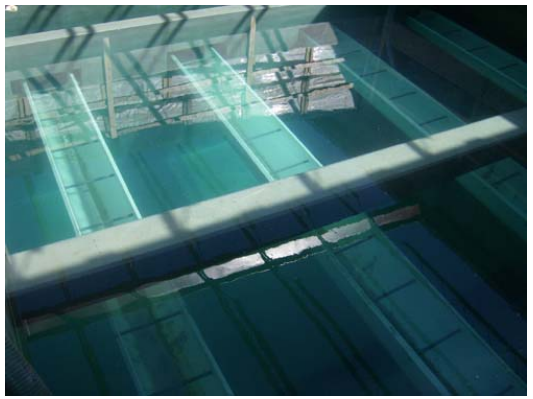




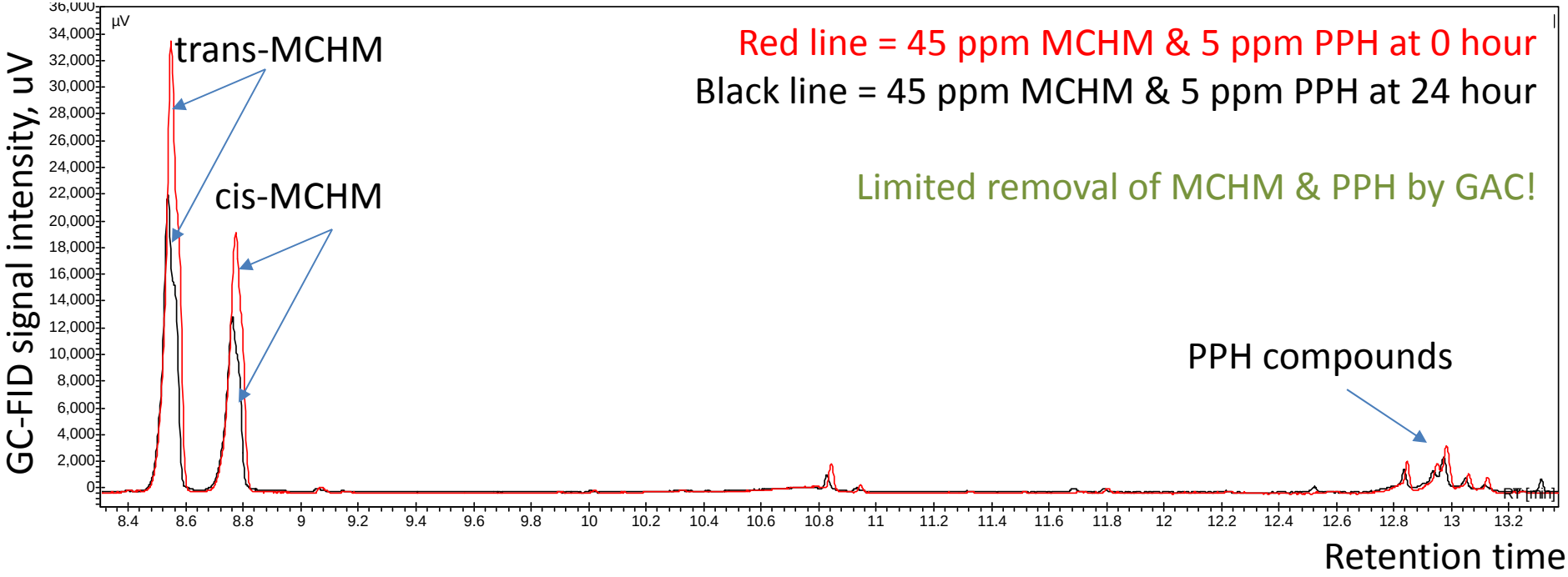
Conclusion: Permanganate oxidation would not have degraded the MCHM to any great extent in the treatment plant

WestVirginiaUniversity.
Department of Civil and Environmental Engineering

Granular Activated Carbon Sorption?



Sand filters with GAC commonly used to polish drinking water before distribution



WestVirginiaUniversity.
Department of Civil and Environmental Engineering

Biodegradation of MCHM

- Water flushed to wastewater treatment plant
  - Was the MCHM removed before it went back to the river?

- Was MCHM degraded in the Elk and Kanawha River?

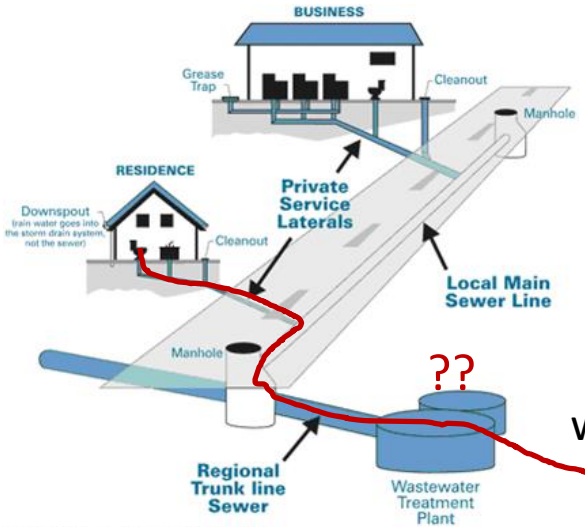


Diagram of a sanitary sewer system

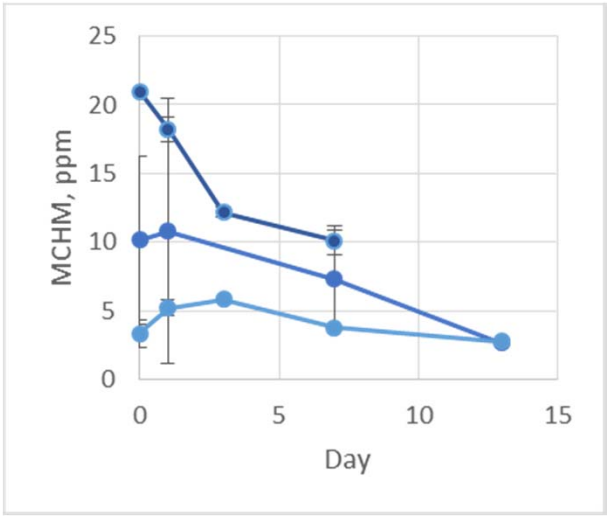
Treated wastewater

WestVirginiaUniversity.
Department of Civil and Environmental Engineering

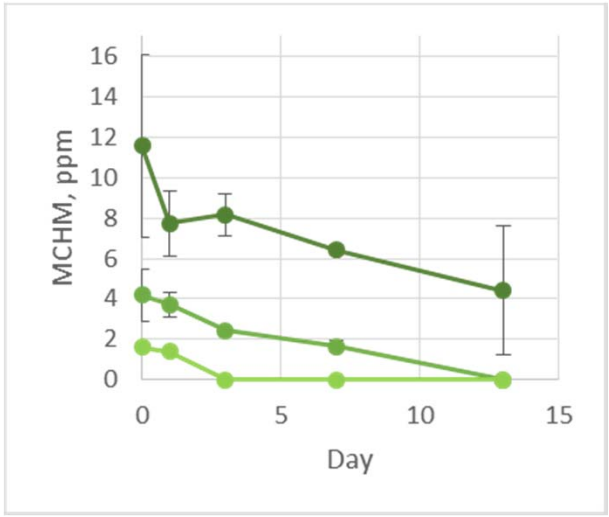
Biodegradation study

Experimental protocol
-50, 10 and 1 ppm MCHM + PPH
-Mon River water
-25-27 degrees Celsius
-12 days of degradation
-GC-FID analysis

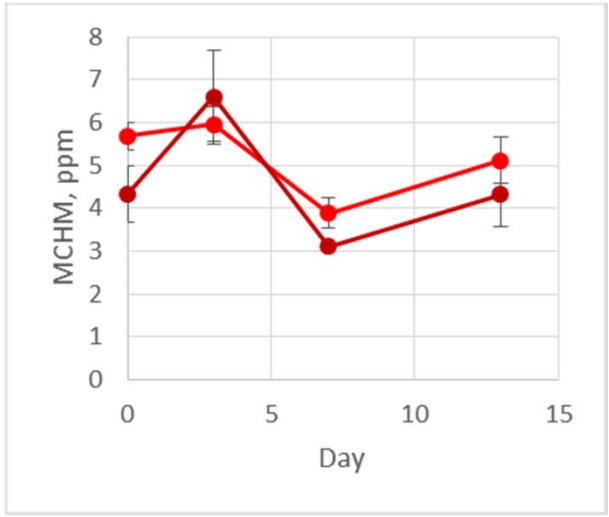
Media & Activated Sludge



River water & sediments



Controls (no biological activity)



Conclusions: 1) Anaerobic and aerobic biodegradation likely occurs
2) MCHM would have degraded biologically in Kanawha and Ohio

WestVirginiaUniversity.
Department of Civil and Environmental Engineering

Related Work by Others

- WV WRI – MCHM fate in coal beneficiation
- Virginia Tech—Chemical properties and fate parameters
- University of Southern Alabama—sorption to water pipe materials and desorption
- Ohio State University—social & behavioral responses for improving science communication
- USGS-NWQL—river sampling
- USGS-Shepherdstown—toxicity testing
- WVU-Biology—toxicity testing

Acknowledgements

- Bill Cooper, NSF Program Officer
  - CBET-1422803
- WVU CEE Department
- WV Water Research Institute

WestVirginiaUniversity.
Department of Civil and Environmental Engineering