MCHM CHEMICAL PROPERTIES, TRANSPORT, AND FATE IN COAL PREPARATION PLANTS

Aaron Noble, PhD
Assistant Professor
Mining Engineering

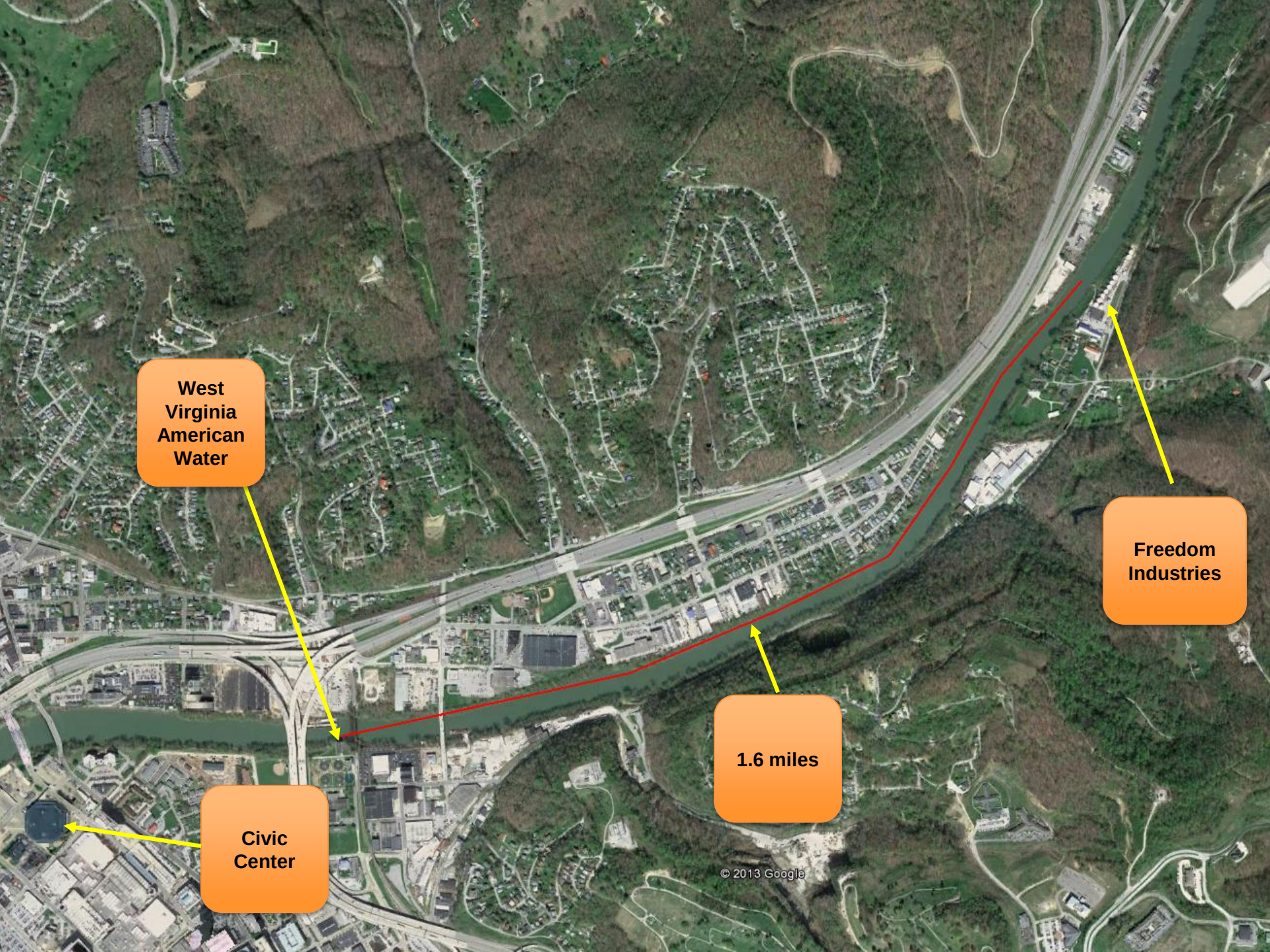
Tom He, PhD
Environmental Geochemist
West Virginia Water Research Institute

April 1, 2015

BACKGROUND

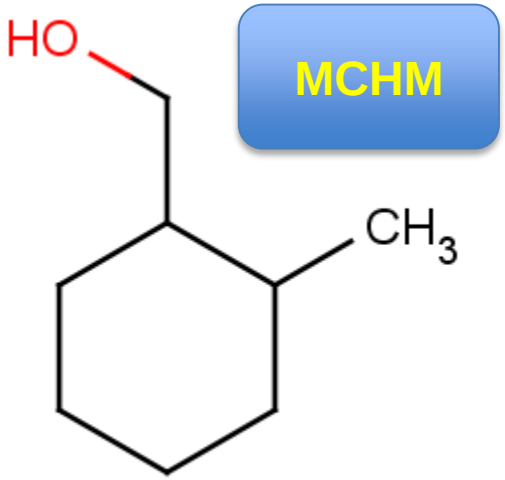
BACKGROUND

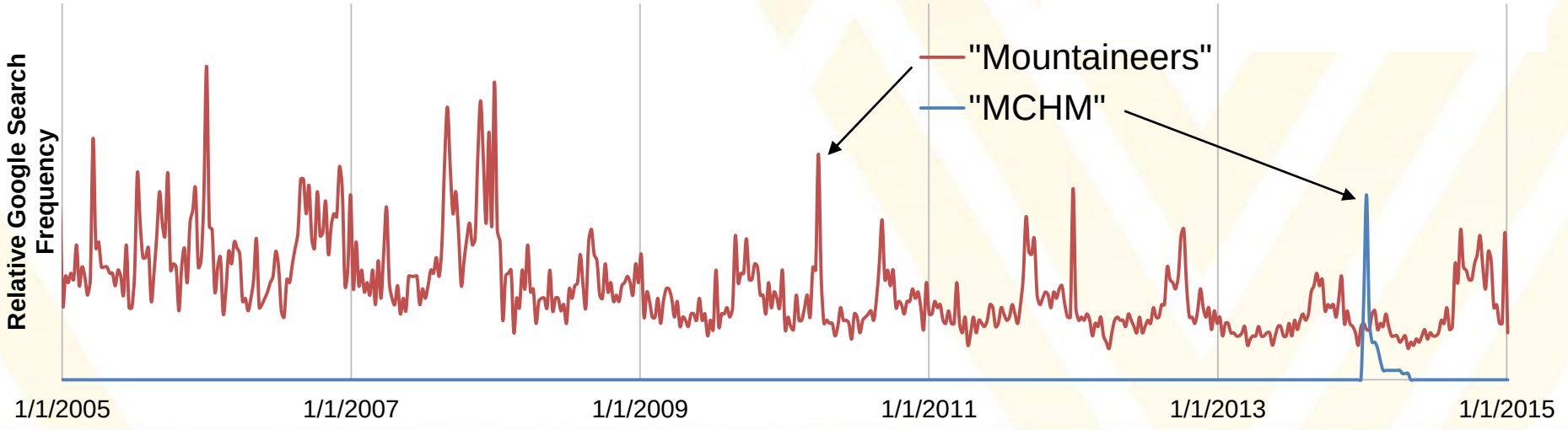
- January 9, 2014: Elk River Chemical Spill
- 10,000 gallons reportedly leaked into Elk River, Charleston
- WV American Water intake 1.6 miles downstream
- Contaminated water in system before WVAW can shut off intake
- ‘Do not use’ order issued to 300,000 customers
- In effect for about 10 days


West Virginia American Water
Freedom Industries
1.6 miles
Civic Center
© 2013 Google

4-METHYLCYCLOHEXANE METHANOL

- Chemical notably involved in the spill
- Was really important this time last year





MCHM TOXICITY

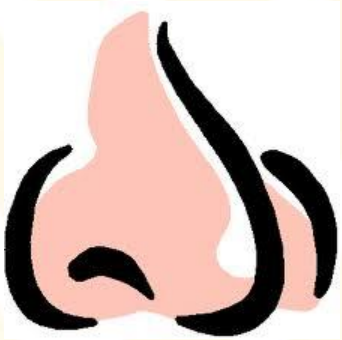
What we knew at the time:

- Not well characterized
- Acute oral dose-825 to 2,000 mg/kg body weight, test results from rats
- Irritant
  - Skin
  - Eyes
  - Lungs
- Information based on concentrated MCHM

MCHM TOXICITY

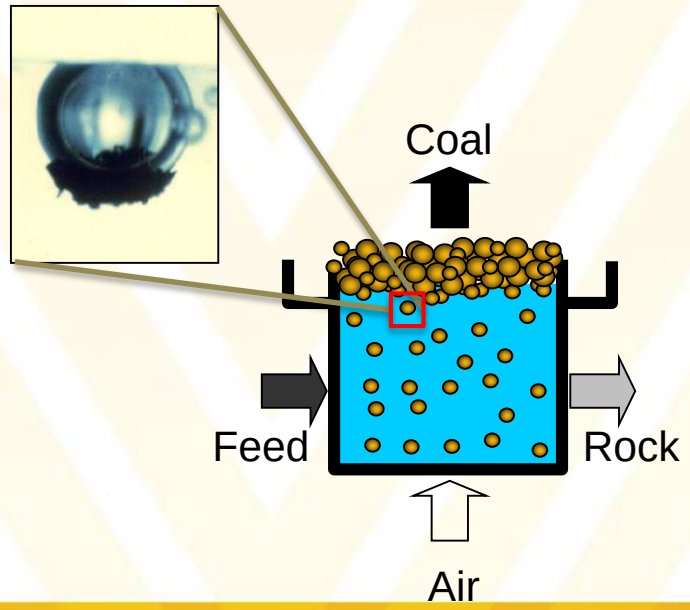
What we have learned since then:

- CDC Threshold = 1 mg/ L MCHM in drinking water.
- Aqueous Smelling Threshold
  - WVTAP = 0.15 µg/L
  - VT = 1.2 µg/L



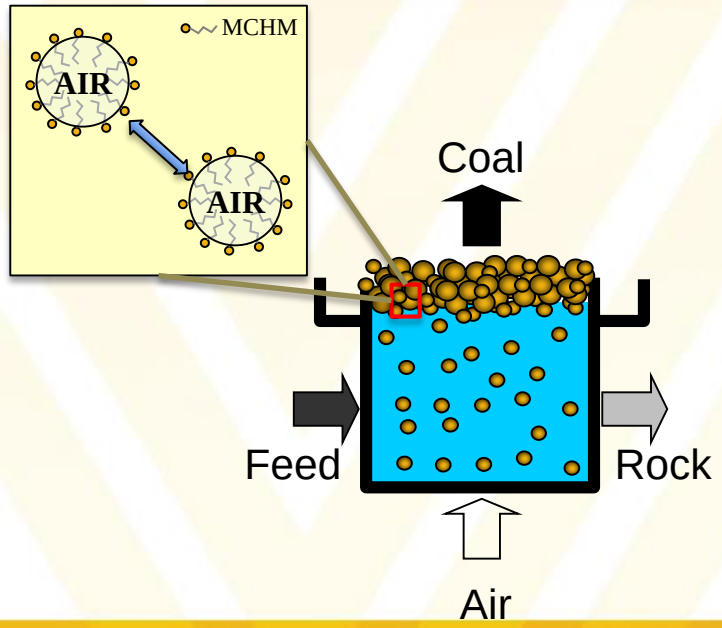
MCHM USES

- MCHM is a “frother” used in froth flotation
- Flotation is used to treat the finest fraction of coal (<150 microns)
- In flotation, coal attaches to air bubbles and floats forming a layer of froth.

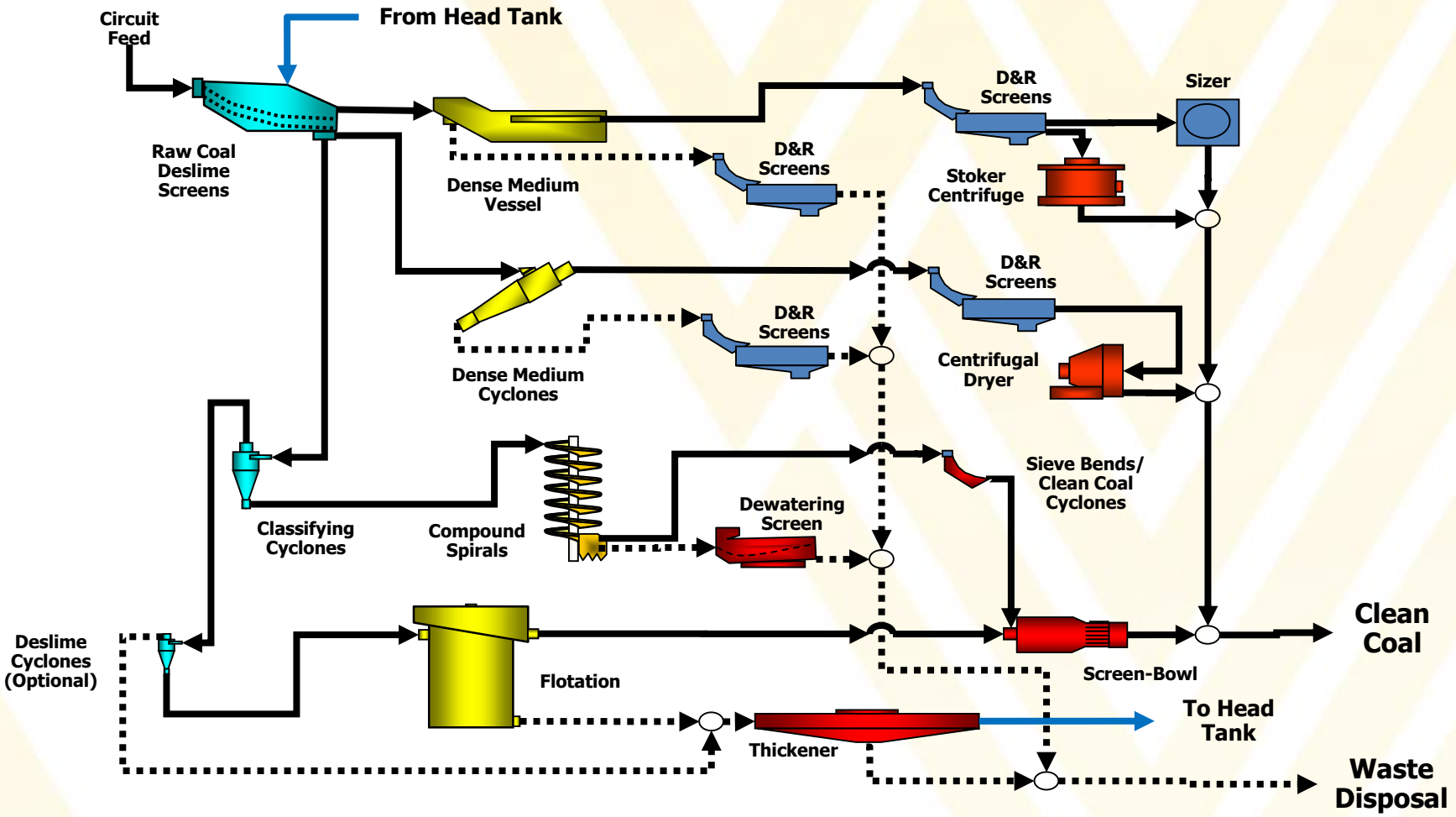


MCHM USES

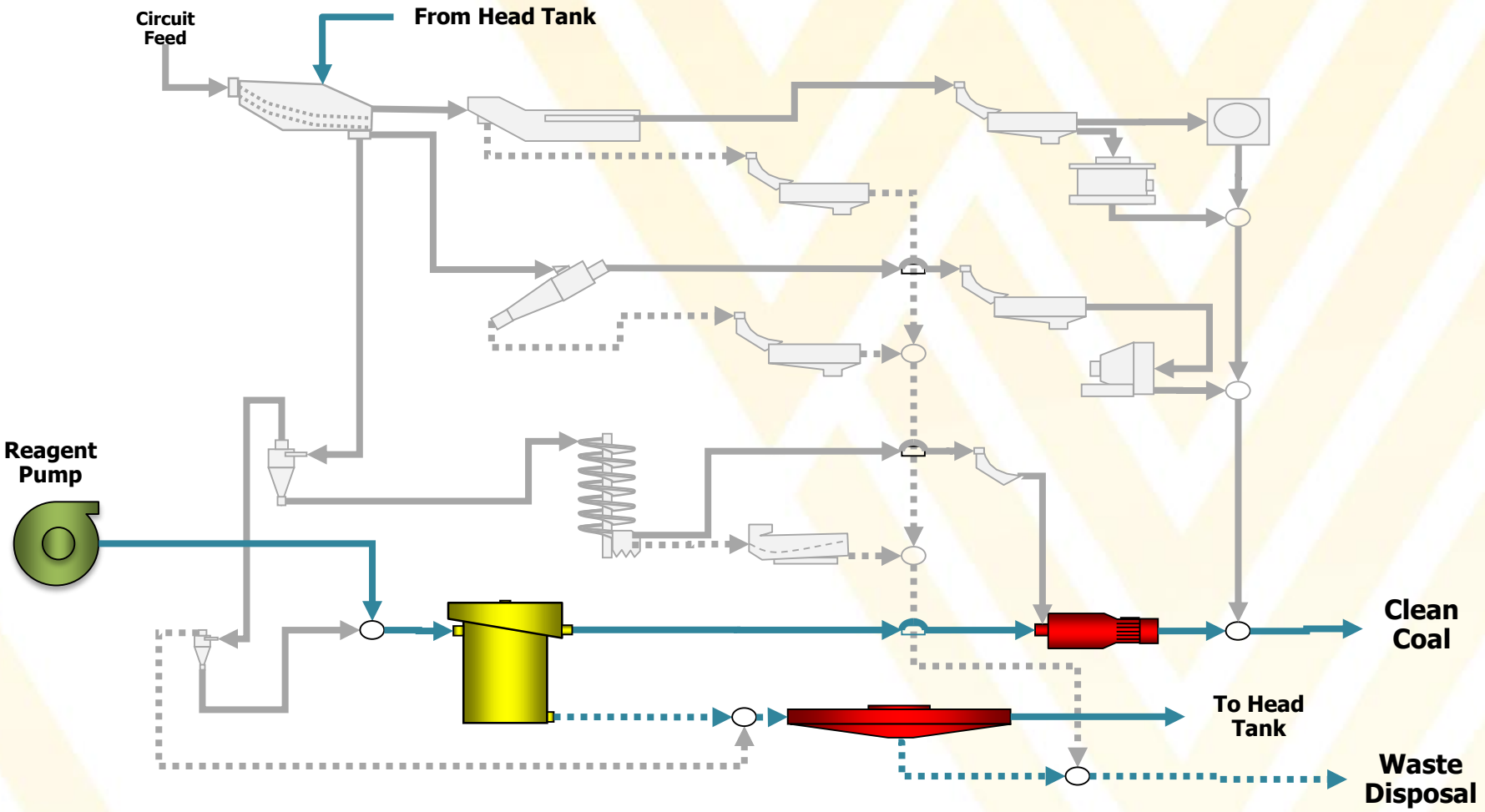
- Flotation requires:
  - *A lot* of small air bubbles to capture the coal.
  - A fairly *stable* froth that can cleanse the mixture.
- Bubble size is very important.
- MCHM regulates bubble size by preventing coalescence.



COAL PREPARATION PLANT



COAL PREPARATION PLANT



OUR QUESTION

- Spilling 10,000 gallons of anything into the river at one time is usually a bad thing…

- But what about the ~½ gallon of MCHM used daily by several active coal prep plants?

ESTIMATED MAXIMUM MCHM CONCENTRATION IN A VERY HIGH USE SETTING: MET COAL, HIGH FINES CONTENT

MCHM density	0.88	g/mL
MCHM use	7,500	gal/yr
	0.014	gpm
	54.01	ml/min
	47.53	g/min
	47,529	mg/min
Slurry liquid/solid	0.70	
Prep plant throughput	5,000	gpm
	18,925	L/min
MCHM concentration	3.59	mg/L

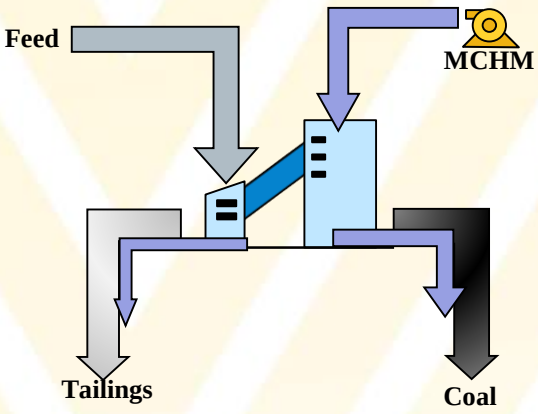
- Assumes:
  - No MCHM adheres to coal or tailings
  - No decomposition in the slurry impoundment

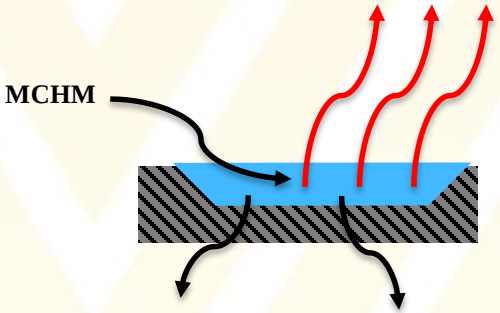
What about the "smell test?"

Source: Ziemkiewicz, WVCA Meeting, 2014

OUR QUESTIONS

- How does MCHM *partition* between the coal and tailings?
- Does significant MCHM *drain* from the tailings impoundment/ underground storage?
- What *other mechanisms* control MCHM concentration?





RESEARCH APPROACH

- Site Sampling
  - Goal: Directly measure MCHM in plant and discharges
- Laboratory Tests
  - Goal: Explain the plant data by examining the transport mechanisms

SITE SAMPLING

SITE SAMPLING

- Two sites selected for MCHM partitioning study:

Site A	Site B
Northern Appalachia	Central Appalachia
Conventional Flotation	Column Flotation
Slurry Feed: 9,600 gpm	Slurry Feed: 1,200 gpm
MCHM: 6 – 7 PPM	MCHM: 6 – 10 PPM
Underground Injection	Surface Impoundment
No Deslime	Deslime

Different

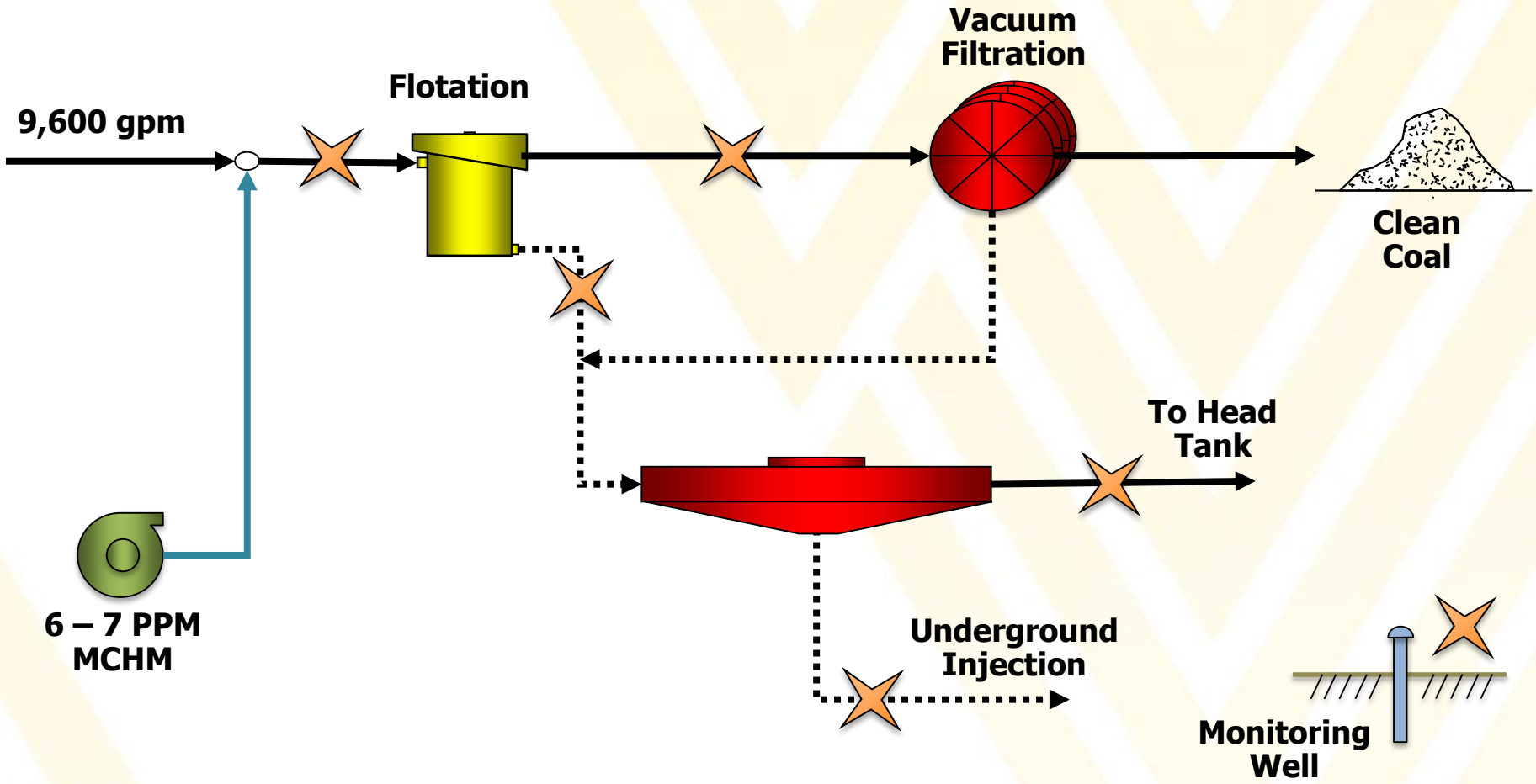
Similar

Different

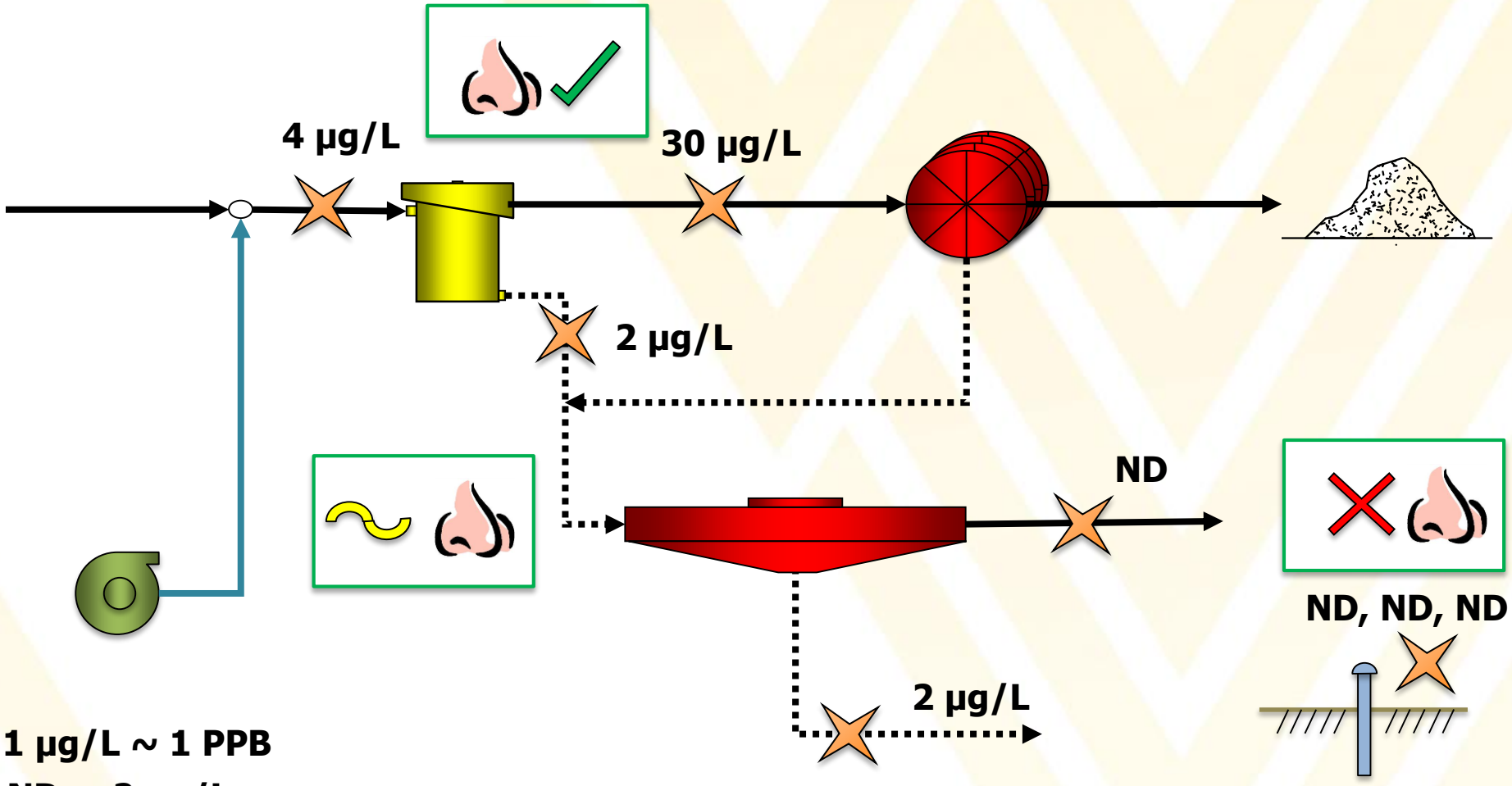
DATA COLLECTION

- Collected water/slurry/solid samples from various streams in plant:
  - Flotation Feed
  - Flotation Con
  - Flotation Tailings
  - Thickener Feed
  - Thickener UF
  - Thickener OF
  - Filter Effluent
  - Clean Coal
  - Etc.
- Collected water samples from environmental discharges
  - Impoundment Drain
  - Groundwater monitoring wells
- Analyzed water for MCHM (EPA Method SW8015C)
- Analyzed solids for size, ash, moisture.

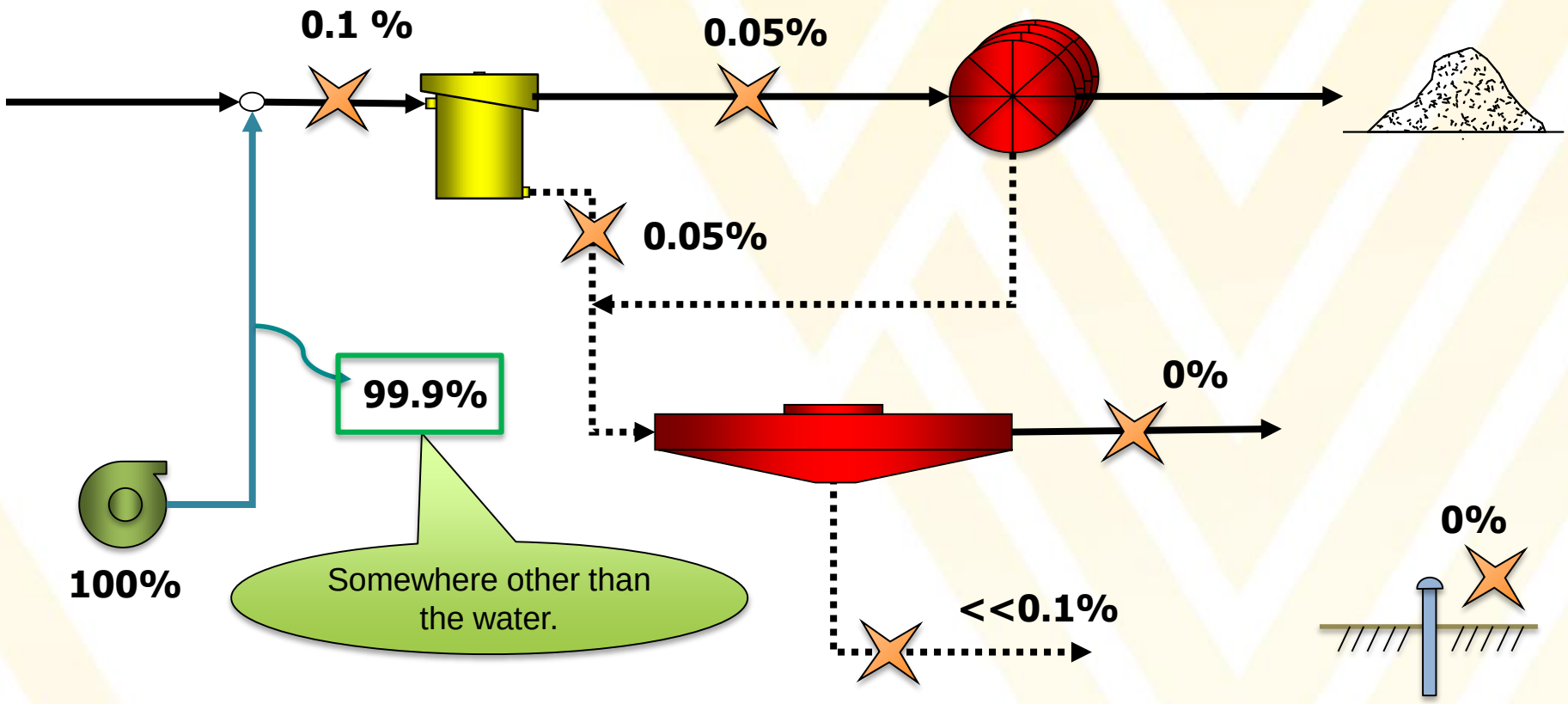
SITE A DATA: SAMPLING LOCATIONS



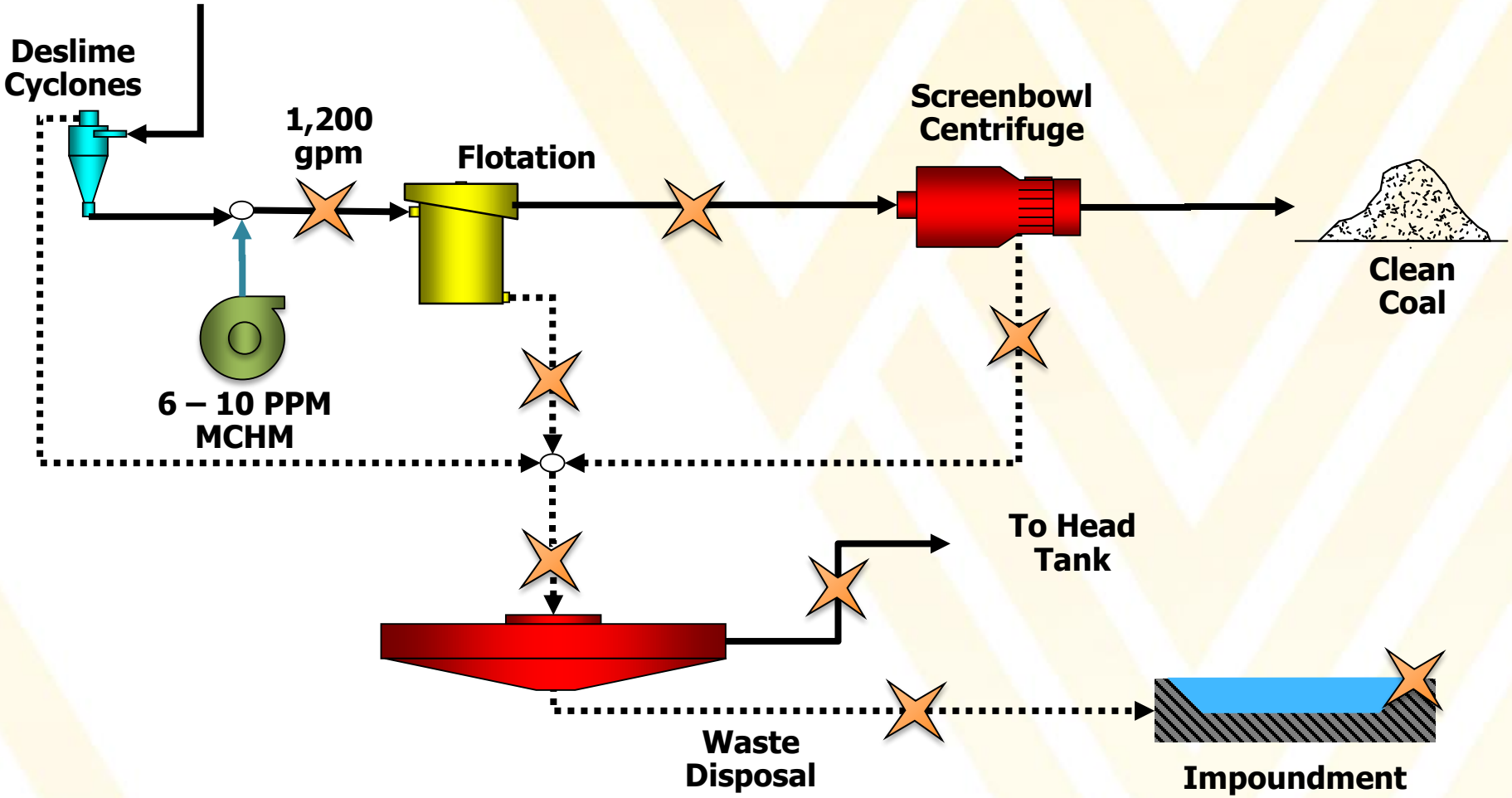
SITE A DATA: CONCENTRATIONS



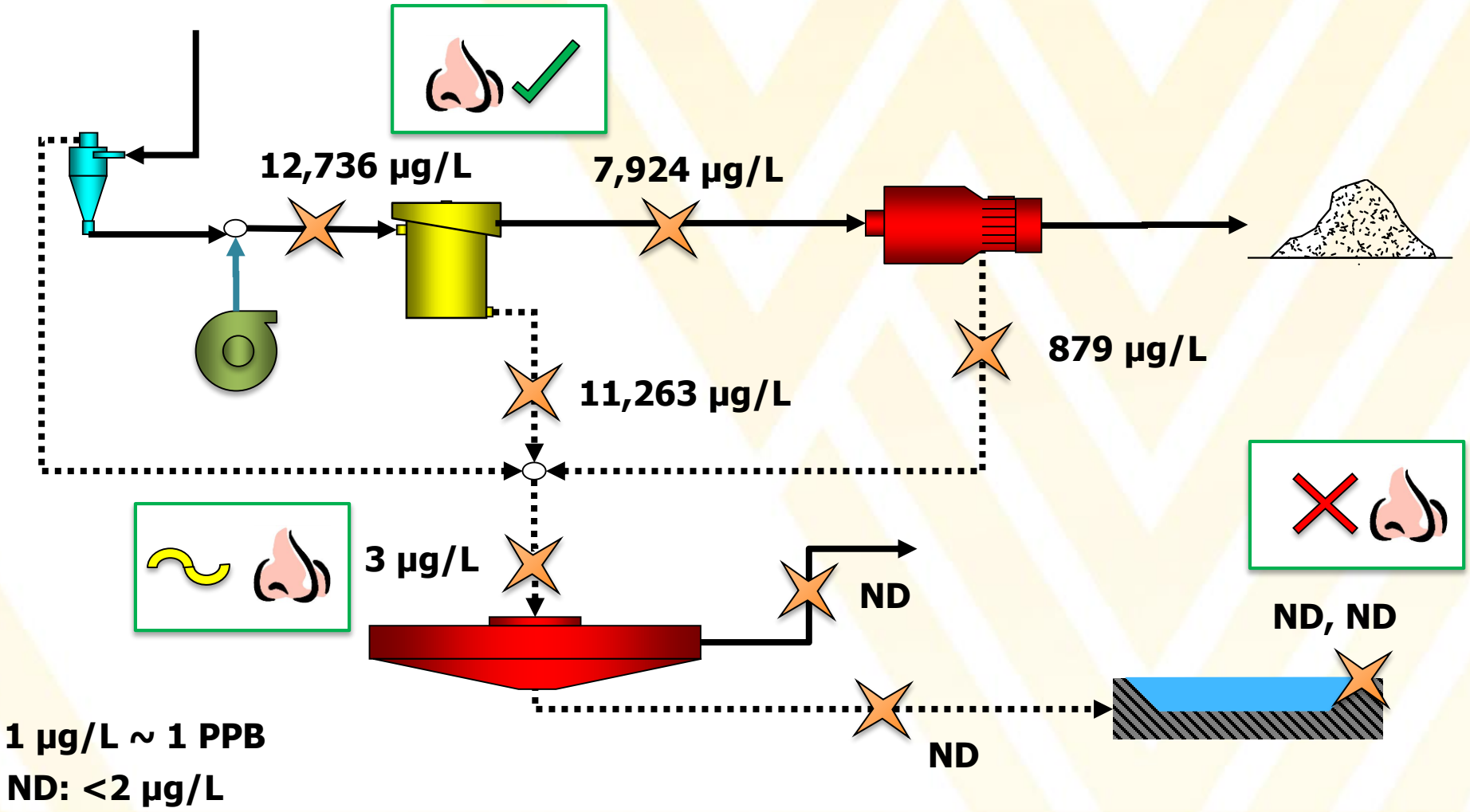
SITE A DATA: MASS DISTRIBUTION



SITE B DATA: SAMPLING LOCATIONS



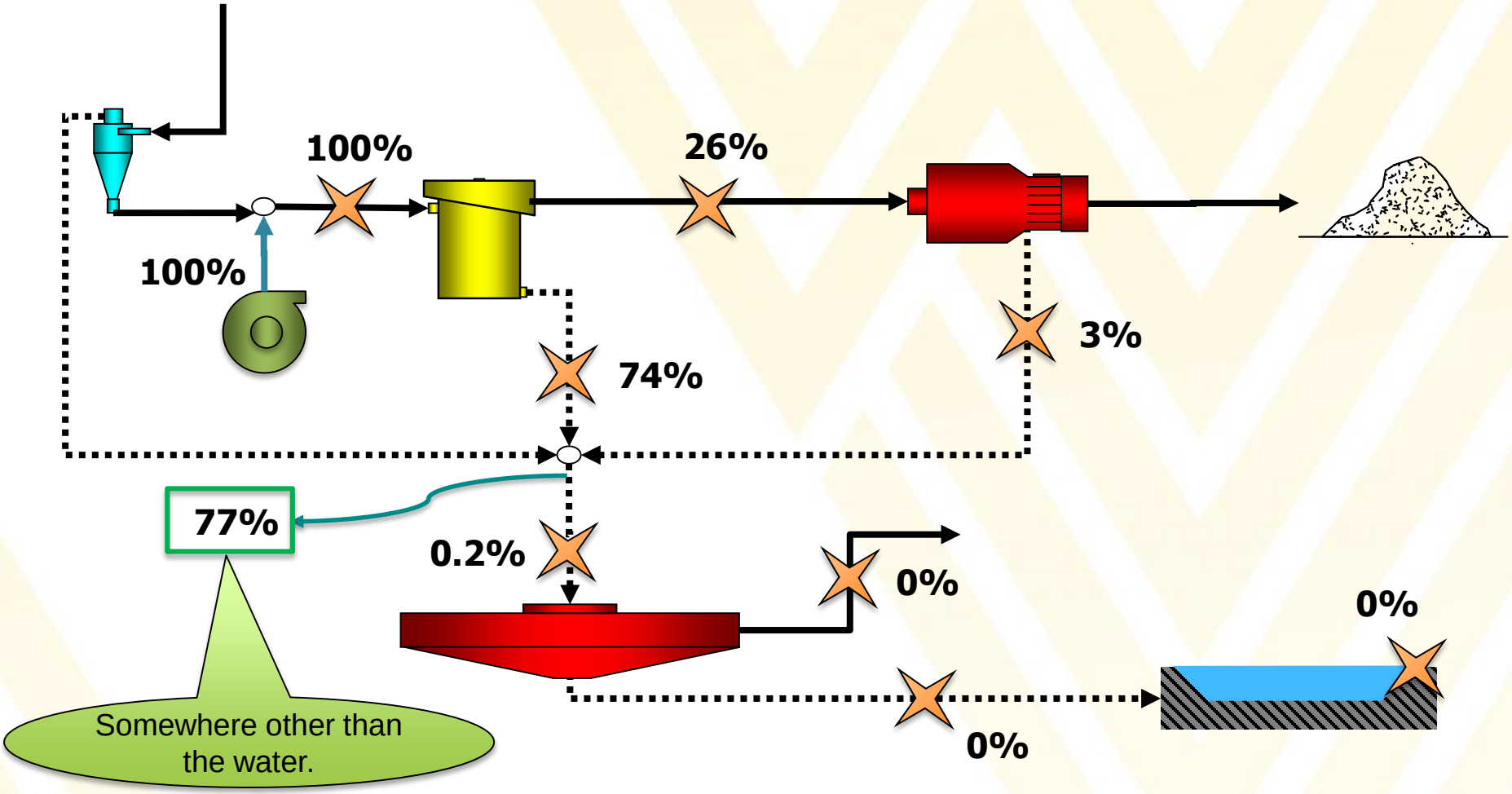
SITE B DATA: CONCENTRATIONS



1 µg/L ~ 1 PPB

ND: <2 µg/L

SITE B DATA: MASS DISTRIBUTION



PUTTING EVERYTHING TOGETHER…

SUMMARY

- In both cases, we observed a "mysterious" MCHM disappearance.
  - Was the plant operating at a lean dosage? ← No, we would have observed poor plant performance.
  - Did we randomly mishandle particular samples? ← No, downstream samples corroborate disappearance.
  - Did the lab systemically mishandle the samples? ← Can't be ruled out.
  - Is the MCHM sorbing or volatilizing? ← Hmm…

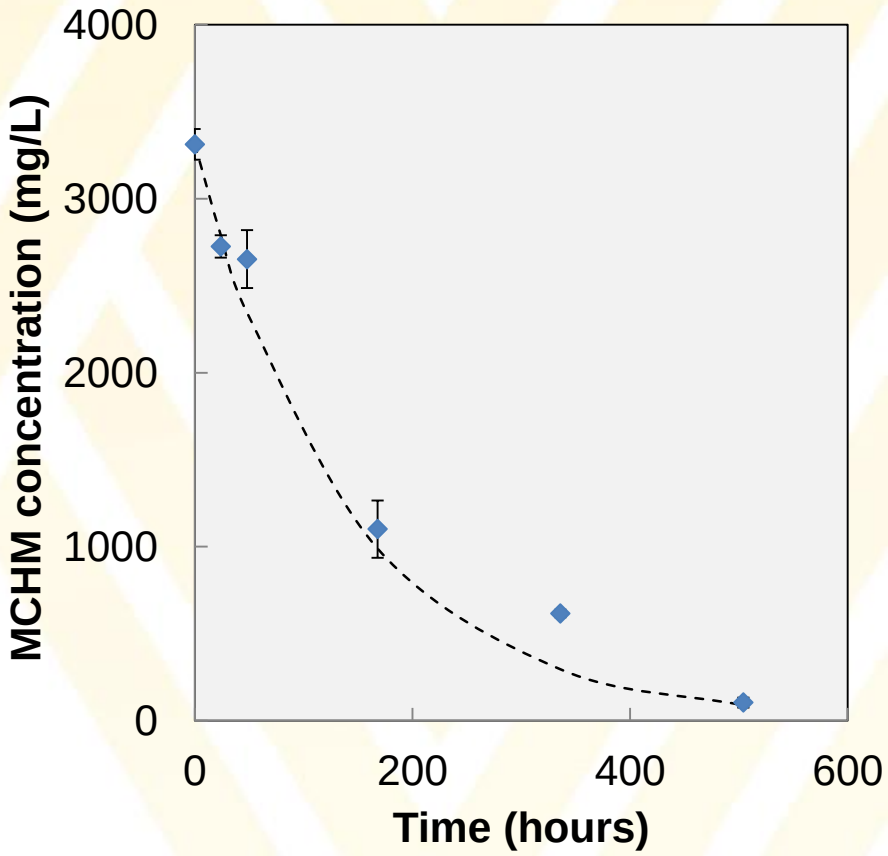
VOLATILIZATION?

- Frothers are known to quickly volatilize when exposed to agitation.

- Our laboratory data confirms that MCHM volatilizes rapidly, even without agitation

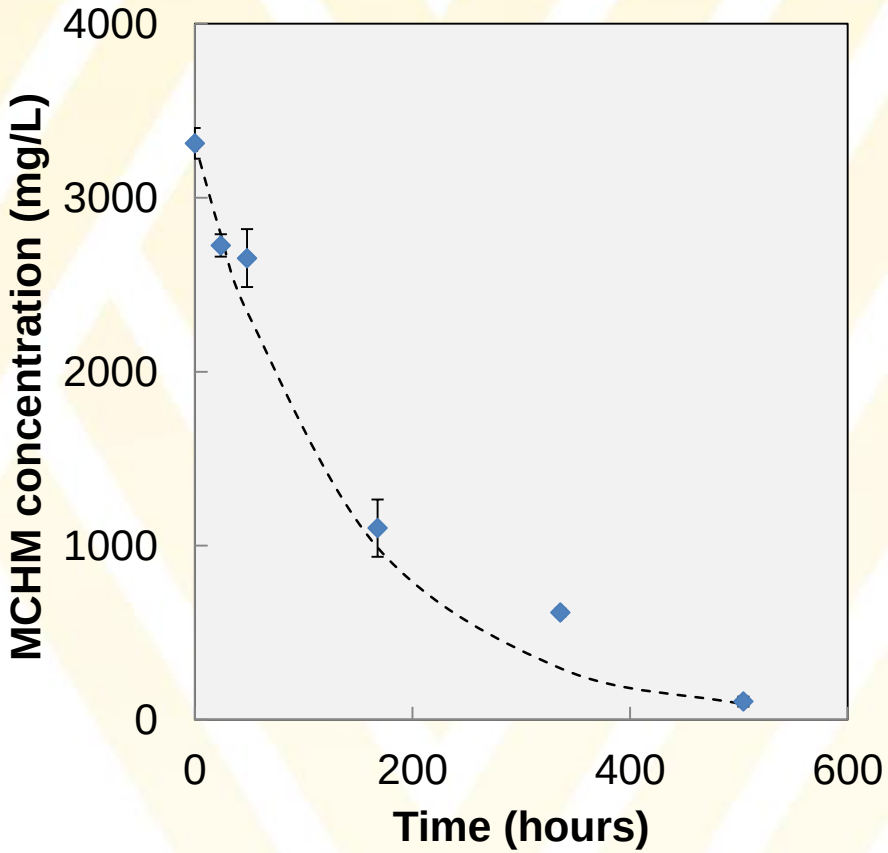
VOLATILIZATION

- MCHM volatilization measured under quiescent conditions
- Half-life = ~4 days
- Significant for long time-scales (impoundments)



VOLATILIZATION

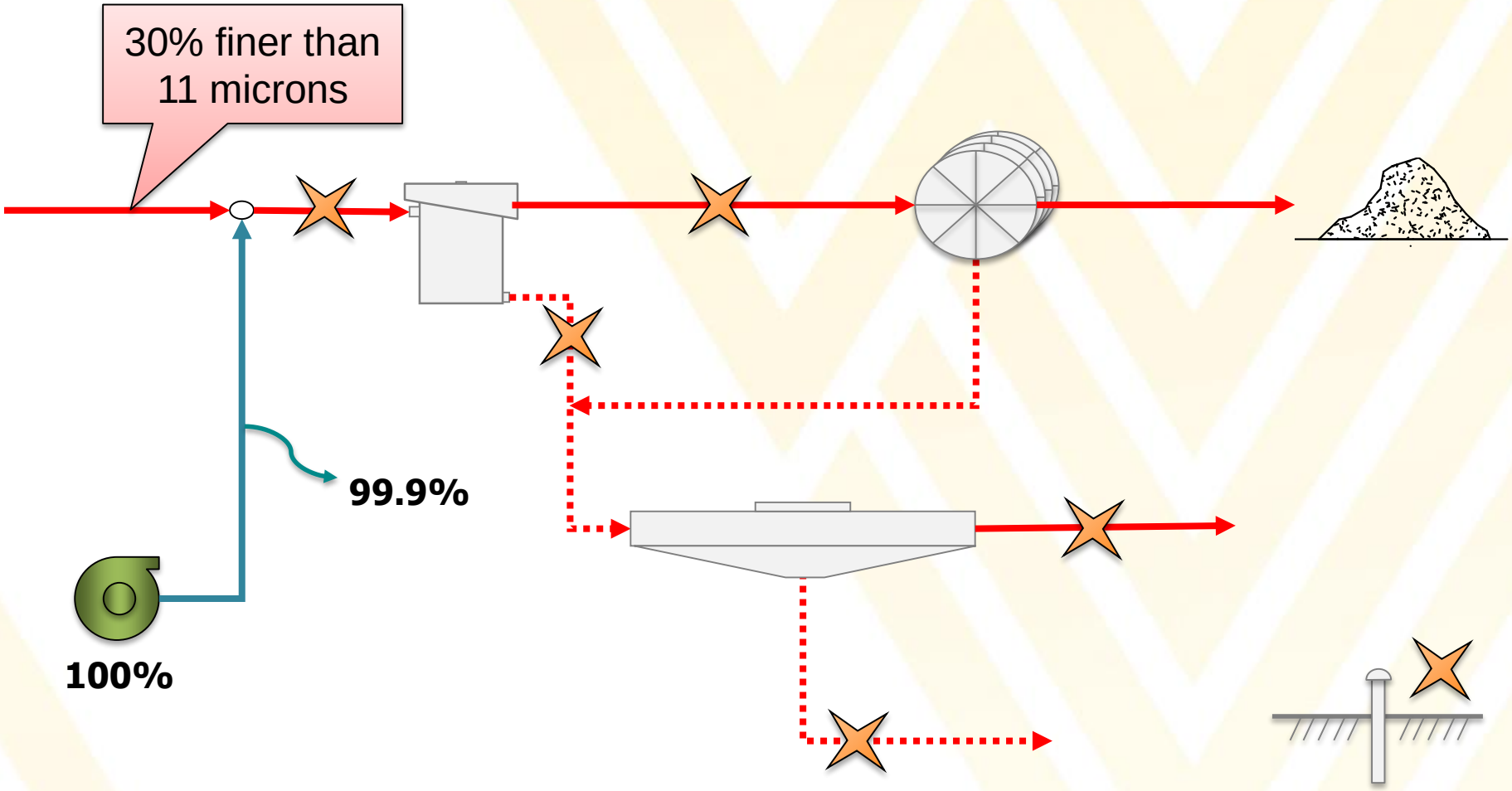
- Henry's law constant for MCHM ≈ 6.4 x 10^{-9} atm L mol^{-1}
  - Fragment constant estimation method (TOXNET)
- Predicted volatilization half-life = 51 days!
  - Model Lake Assumption



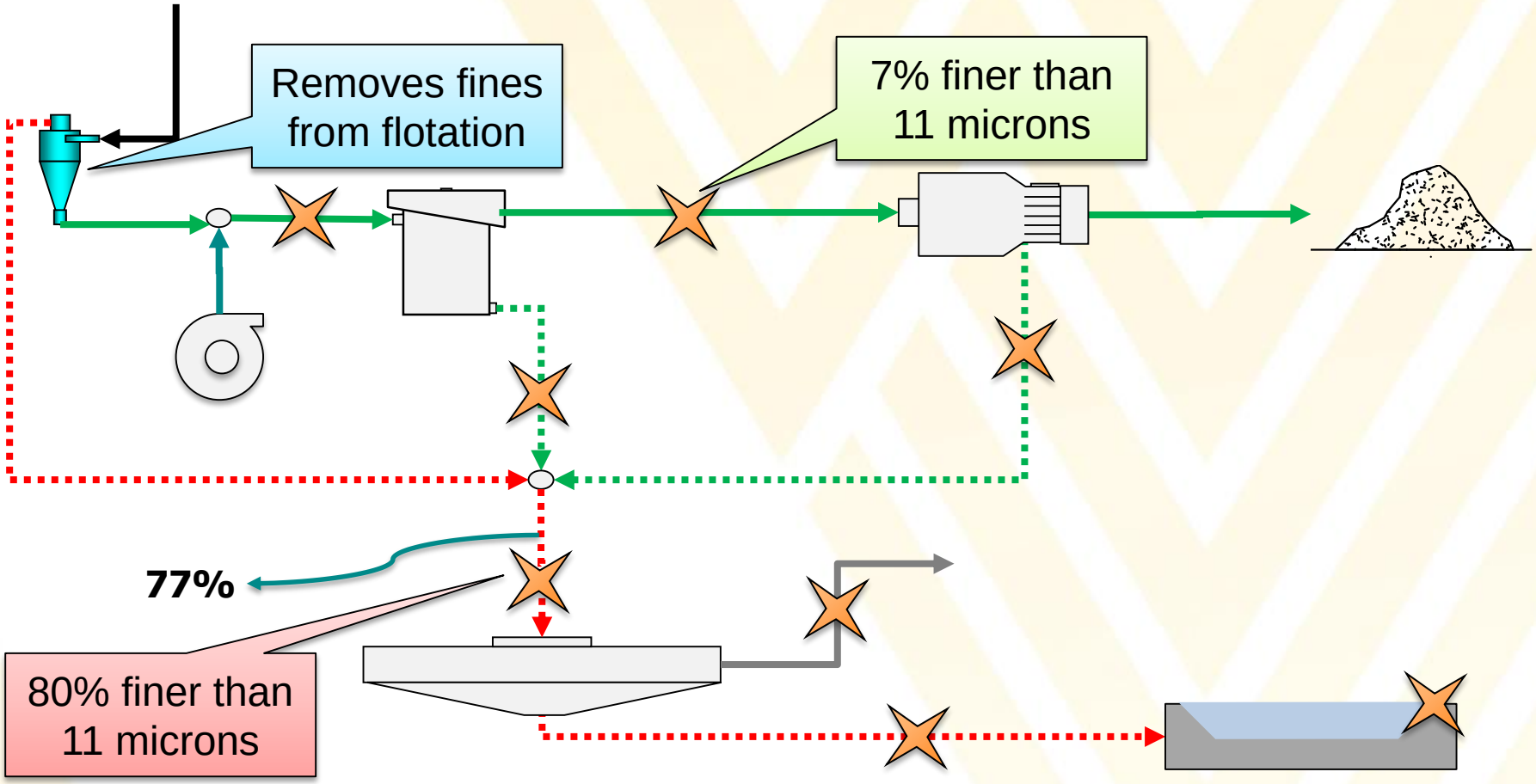
ADSORPTION TO FINES?

- In both cases, the mysterious disappearance accompanied the introduction of **fine coal particles**.

SITE A DATA: MASS DISTRIBUTION



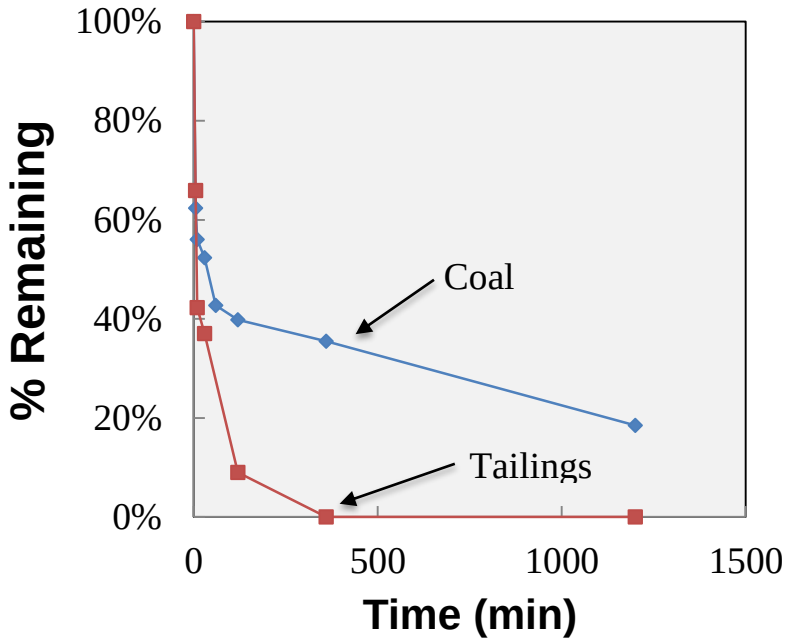
SITE B DATA: MASS DISTRIBUTION



ADSORPTION TO FINES?

- Lab data also confirms that MCHM sorbs quickly onto coal and tailings.

- ~50% removed within 5-10 minutes.



WHAT ABOUT DESORPTION?

- Repeated column leaching tests (x8) consistently showed no MCHM in the leachate, even under “spiked” conditions.

- Corroborates field testing that shows no MCHM in the environmental discharges.

CONCLUSIONS

- Empirical field data and laboratory testing show that MCHM is likely (and permanently) adsorbing onto the fine coal.
- Data shows that NO MCHM is present in environmental discharges.
- Peer reviewed publications have been submitted:
  - He, Y.T. Thomas, A. Noble, and P. Ziemkiewicz. "Investigation of MCHM transport mechanisms and fate: Implications for coal beneficiation." Chemosphere 127 (2015): 158-163.
  - Noble, A., Y.T. He, and P. Ziemkiewicz. “Partitioning Behavior of 4-Methyl Cyclohexane Methanol in Two Appalachian Coal Preparation Plants.” International Journal of Coal Preparation and Utilization (in review).

FOR MORE INFORMATION PLEASE CONTACT:

Aaron Noble, PhD

canoble@mail.wvu.edu

304-293-9959