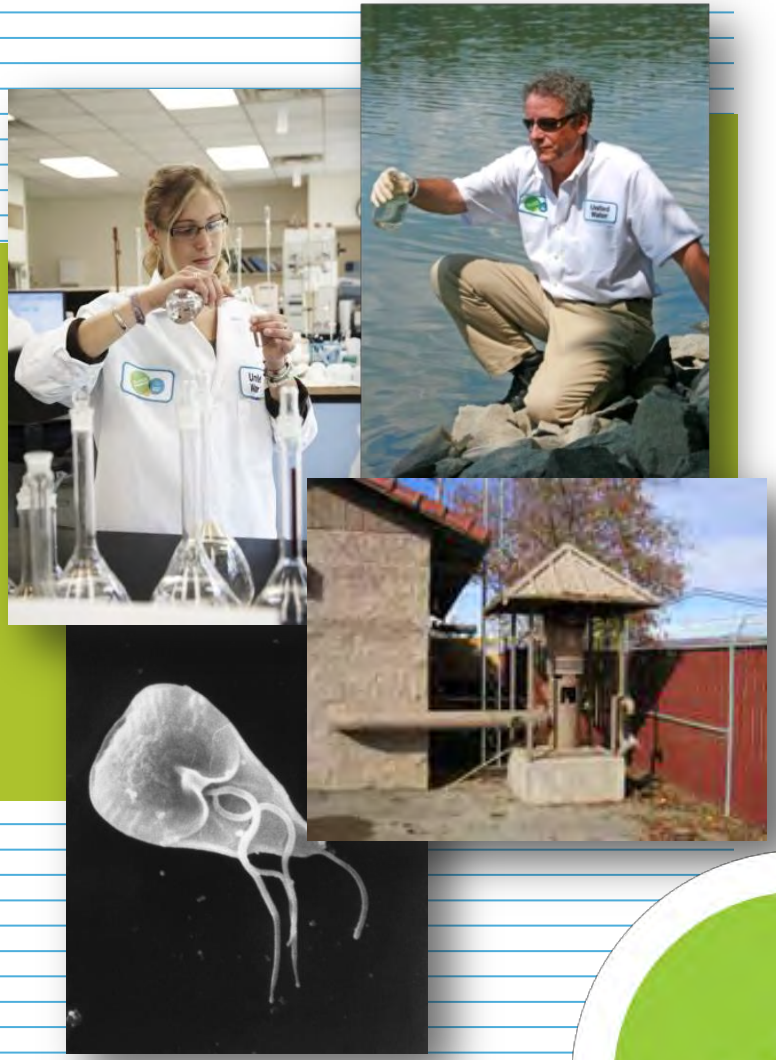

# *UTILIZING AN ON-LINE TTHM ANALYZER TO AID IN COMPLIANCE WITH DBP REGULATIONS*


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# Disinfection By-Product Formation

+


= DBPs

Naturally-Occurring Organic Matter (NOM)
**e.g.**
- **Humic Acids**
- **Fulvic Acids**

Chlorine Based Compounds for Microbiological Disinfection
**e.g.**
- **Chlorine**
- **Hypochlorite**
- **Chlorine Dioxide**

Disinfection By-Products*
**e.g.**
- **Trihalomethanes**
- **Haloacetic Acids**
- **Bromate**
- **Chlorite**

Disinfection By-Products*
- Several thousand are known
- More than 500 have been toxicologically reviewed
- Several classes and compounds are regulated in drinking water:
  - Trihalomethanes
  - Haloacetic Acids

# Evolution of DBP Regulations

## Evolution of DBPs (THMs) Regulations

US-EPA Stage 2 DBPR in force with levels of THMs to 80 µg /L

US-EPA Stage 1 DBPR proposed levels of 80 µg /L

2012

1994

**WHO published guideline values for THMs**

1984

U.S. EPA regulation to control THMs at 100 µg /L

1976

1976

NCI published results linking chloroform to cancer

1976

NOM Survey reported high THMs in US Chlorinated Drinking water

1975

NOR Survey reported high THMs in US Chlorinated Drinking water

1972

**Rook reported first THM – Chloroform in chlorinated drinking water**

1918

Over 1000 US cities were using chlorinated drinking water

1908

US First Chlorination, Jersey City, New Jersey, began chlorination of drinking water

1900

1850

Chlorine was widely used as a disinfectant of drinking water.

Snow used Chlorine to disinfect London's water supply during now-famous cholera epidemic

NORS-US National Organics Reconnaissance Survey

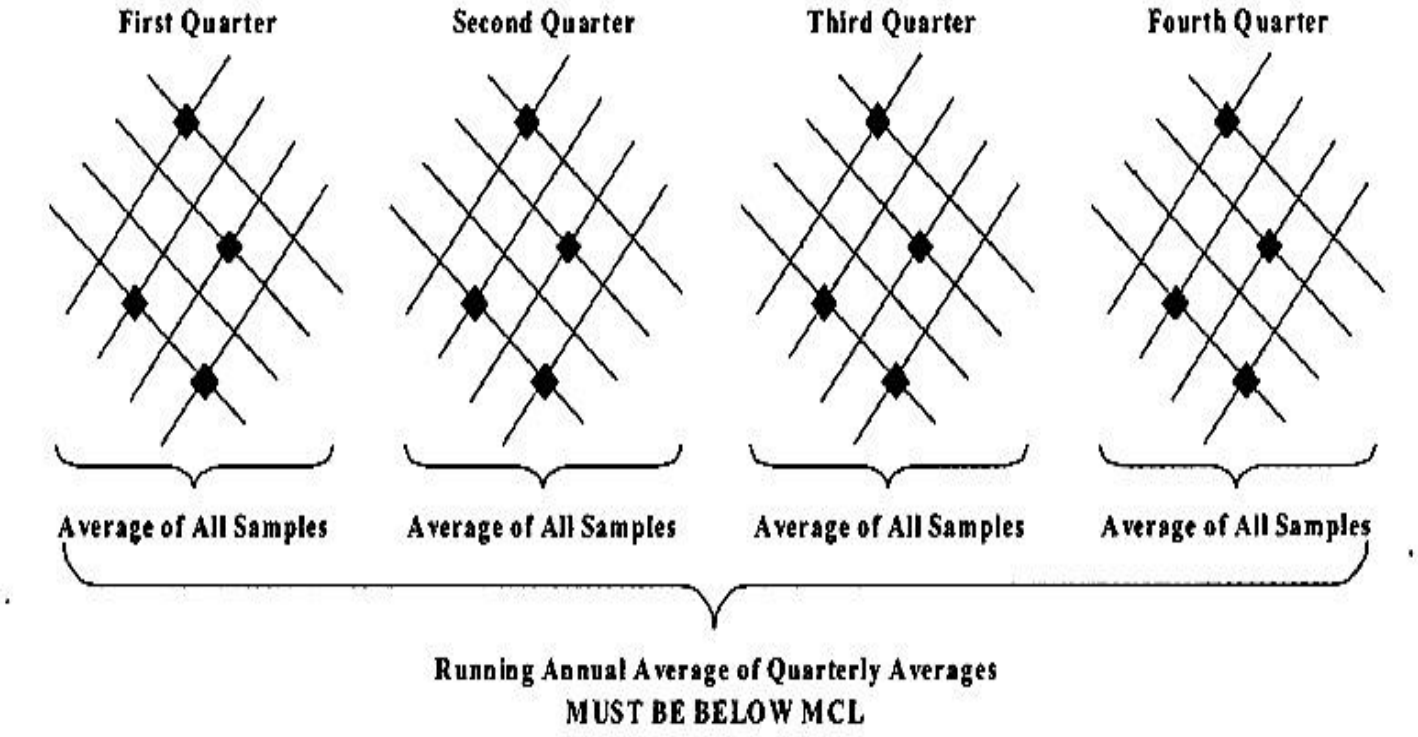
NOMS-US National Organic Monitoring Survey

WHO-World Health Organization

NCI- US National Cancer Institute

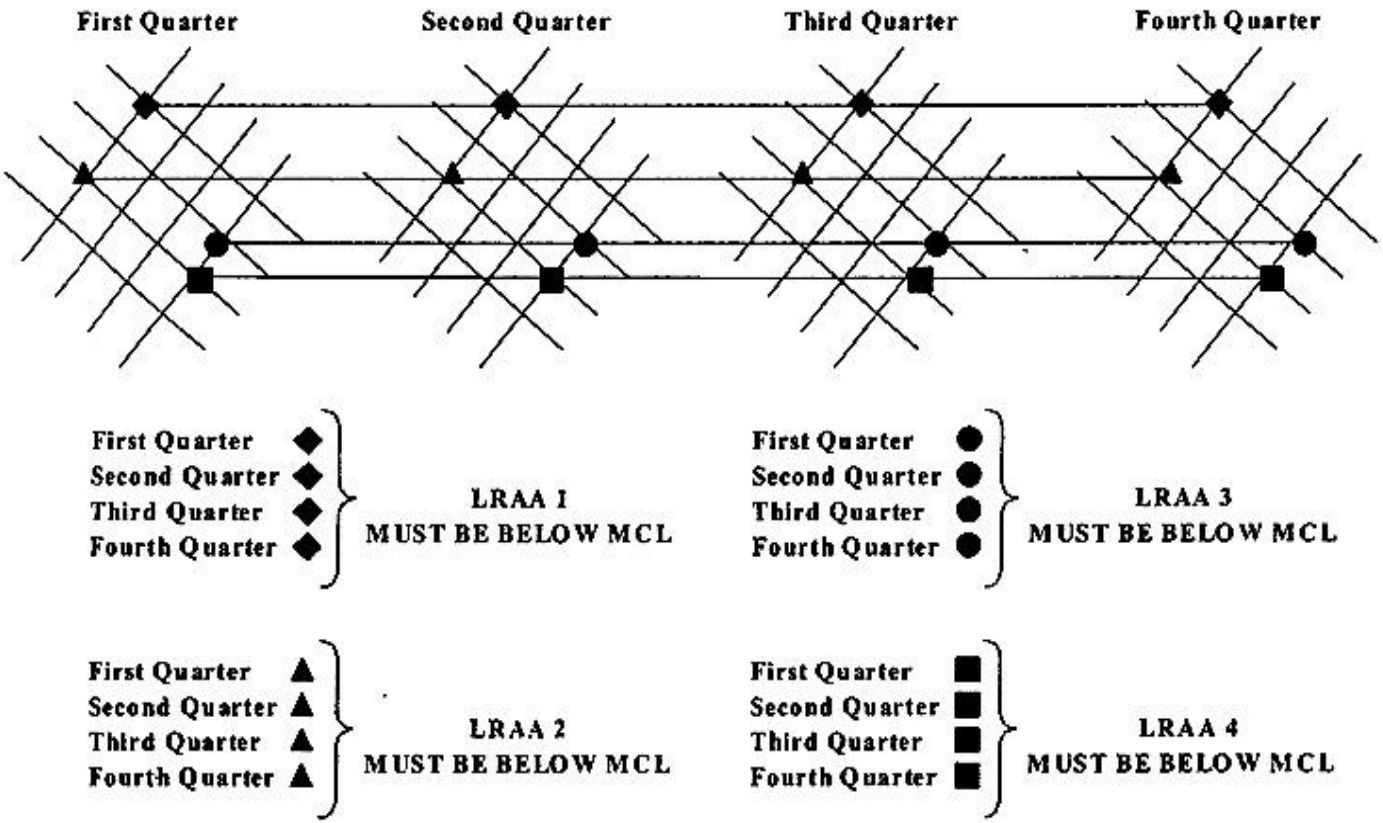
US-EPA-Environmental Protection Agency

# Stage 1 Disinfection By Product Rule




Source: EPA, 40 CFR Parts 9, 141, and 142 National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; Final Rule, p 411

# Stage 2 Disinfection By Product Rule




Source: EPA, 40 CFR Parts 9, 141, and 142 National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; Final Rule, p 411

# Stage 1 vs. Stage 2 Rule

- Stage 2 sample sites chosen from the highest results of Stage 1 and IDSE sampling.
- Stage 2 compliance based on running annual average per location rather than a system average.
- Specific distribution “hot spots” become compliance risks since compliance calculated as a running annual average per location.

# United Water Hummelstown WTP

## 4 MGD

- ACH
- Chlorine
- KMnO4

## Membrane Filtration

- Post Caustic
- H2SO4

# DBP Formation and Variables

- ✓ **Disinfectant**
  - ▪ Type
  - ✓ Point of Application
  - ✓ Dose
  - ✓ Residual
- ❑ Contact Time/Water Age
- ✓ pH
- ❑ Bromide
- ❑ TOC
  - ➢ TOC Removal
- ❑ Temperature

# Changes to Reduce DBPs at Hummelstown

- **2010-2011**
- **Optimize Control of Permeate and Entry Point Chlorine**
  - Reduce Permeate Residual to 0.1-0.2 ppm
  - By Reducing Pre Cl2 dose
  - Reduce and Be Consistent with Post Cl2 dose/residuals
- **2011**
- **Implement H2SO4 feed (started July 28, 2011)**
  - Reduce Permeate pH to 6.8 - 7.2
  - Enhanced Coagulation vs Manganese Removal
  - TOC removal increased by 15% after pH decrease
  - THMs decreased by 20%; HAAs increased by 15%- limited data
  - THMs reduced through membrane, but EP THMs similar to past
  - THM formation reaction quick and not complete through membrane
- **2012**
- **Additional KMnO4 contact time**
  - Install additional contact pipe for 20 min contact time
  - Reduce THMs
- **2013**
- **Treatment Anomalies with high pre Cl2 demand from 2012 -2013**
- **Partner with PA DEP, SRBC, PA American to set up watershed study**

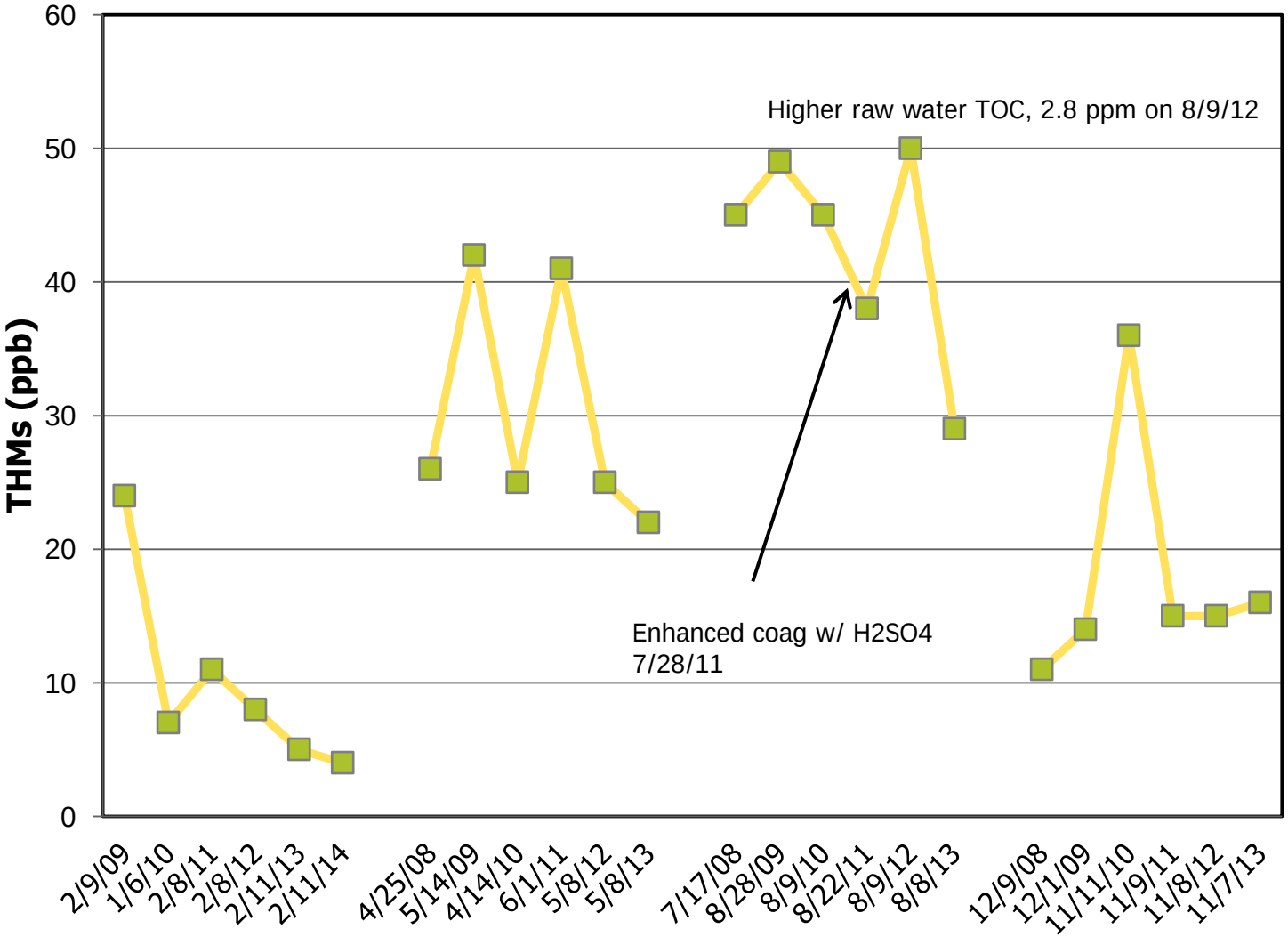
# Swatara Creek Treatment Anomalies Observed by Both United Water and PA American

- Aug 20 - Sept 8 2012
- Sept 19 - 22 2012
- Oct 3 - 5 2012
- Oct 19 - 23 2012
- Oct 29 – Nov 1 2012 (Hurricane Sandy)
- Nov 12 – 16 2012
- May 6 – 14 2013

# Impacts Observed at UW Hummelstown WTP

- Pre-Cl2 Demand increased from 130 % to **290** %
- Post Cl2 Demand increased from 144 % to 167 %
- Raw Water TOC increased from typical 1.5 - 2 ppm to **5** - **7** ppm
- Finished TOC increased from avg 1.1 - 1.7 ppm to **3 - 4.5** ppm
- Finished TTHMs increased by 3 – 3.5 times
- Finished HAA5s increased by 3 times
- For 5 events, TTHMs estimated by mathematical regression models increased from 19 ppb to 140 ppb
- For 5 events, HAA5s estimated by mathematical regression models increased from 13 ppb to 140 ppb
- For 1 event, Actual finished water **TTHMs** were 67 and 80 ppb at 2 different labs while the model estimated 90 ppb on Oct 30, 2012
- For 1 event, Actual finished water **HAA5s** were 149 and 112 ppb at 2 different labs while the model estimated 119 ppb on Oct 30, 2012

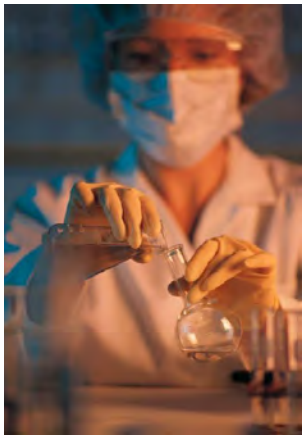
# Hummelstown EP DBPs per QTR 2008-2014




# Why monitor THMs online?

- THM100 enables Real-Time Monitoring of THMs in Drinking Water
- THMs can vary dramatically over time/days and during seasonal events
- Online THM monitoring and trending with online TOC, Turbidity, Chlorine and pH provides snapshot of overall WQ
- Allows for systems to optimize operational and chemical feed systems to minimize THMs
- Systems can test automatically at any location and also bring grab samples from around the plant or system to manually inject for analysis
- Regulatory Benefits
  - Enables Compliance Management – Proactive
  - Minimizes Public Health Hazards from exposure to contaminants
  - Minimizes Potential Regulatory Violations

# Standard Method for DBP Analysis



- System collects a water sample
- Physically delivers it to the lab
- A lab technician prepares the sample
- The sample is analyzed on a GC/MS instrument; costs?
- Results are reported to the water system **in 10-14 days**
- Water system logs data
- Operators make adjustment to the treatment process based on these results?
- How to get operators to use the data as an operational tool?

# AMS THM-100 – Another Option


- First commercial in-line instrument for TTHM and $CHCl_3$ monitoring with manual sampling capability
- Installed at multiple water utilities with excellent correlation to lab results
- Unattended 24/7 results in 1 hour which can immediately be used to modify the process
- Self calibrating – no need for skilled operator intervention at anytime
- 5-200 (in µg/L) range for TTHM and Chloroform
- 2’ (W) x1.3’ (D) x 5’ (H)
  100 lbs

# Organization of THM-100 System

W – 2.0’ (610mm), D - 1.33’ (406mm)
H – 5.0’ (1,524mm)
Weight – 100lbs (45.3kg)

Electronics Cabinet

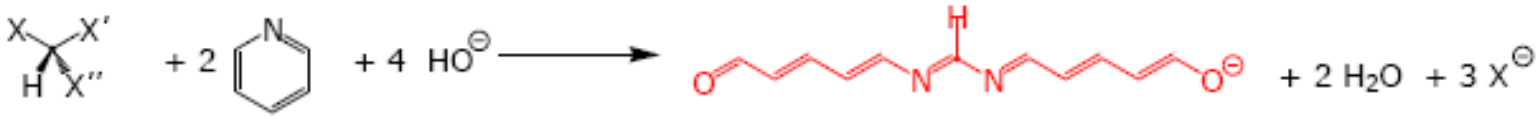
Process Cabinet

Chemical Reagents and Standards

# THM-100 Principal of Operation

| Analysis Steps | THM-100 Process Flow |
|---|---|
| ▪ Draw Finished Water Sample | Fill Reservoir (Purge Vessel) |
| ▪ Extract THMs | Purge Reservoir and Trap THMs |
| ▪ Concentrate THMs | Desorb Trap and Dissolve THMs into Reagents |
| ▪ React THMs with Reagents | Initiate the Fujiwara Reaction |
| ▪ Measure change in Absorbance | Spectrophotometric Detection at 540 nm |
| ▪ Determine Concentration of the dominant THM and TTHM | Quantitative Determination of dominant THM and TTHM Concentrations |
| ▪ Report total THM and Chloroform results | Make Results Available on the System and via 4-20 mA and the Ethernet |

- All four THMs are converted to the same product when treated with a pyridine derivative in an aqueous base:

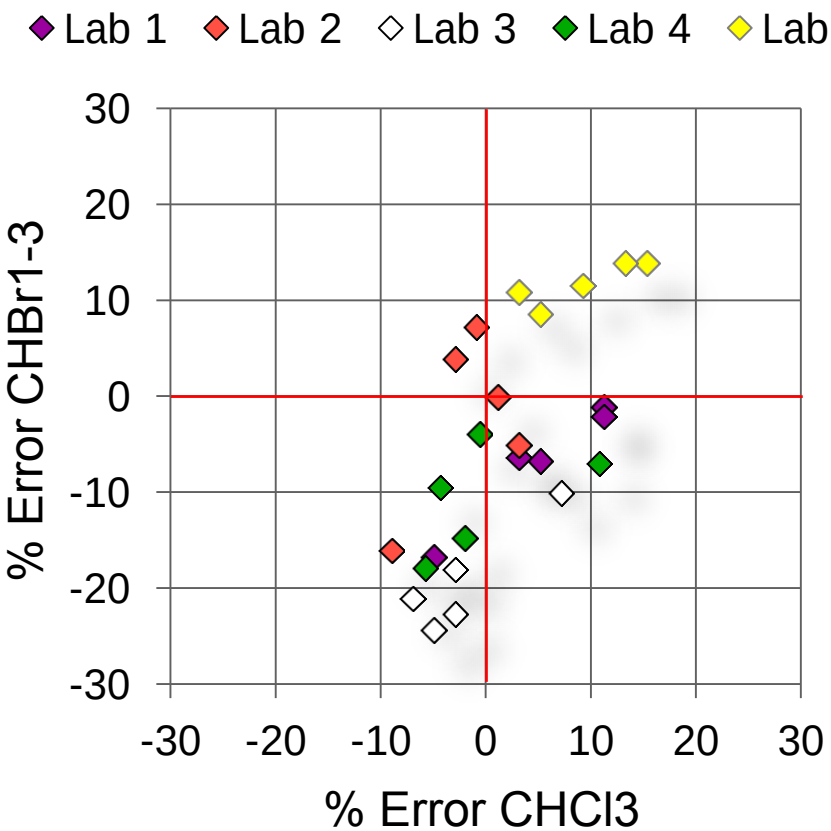


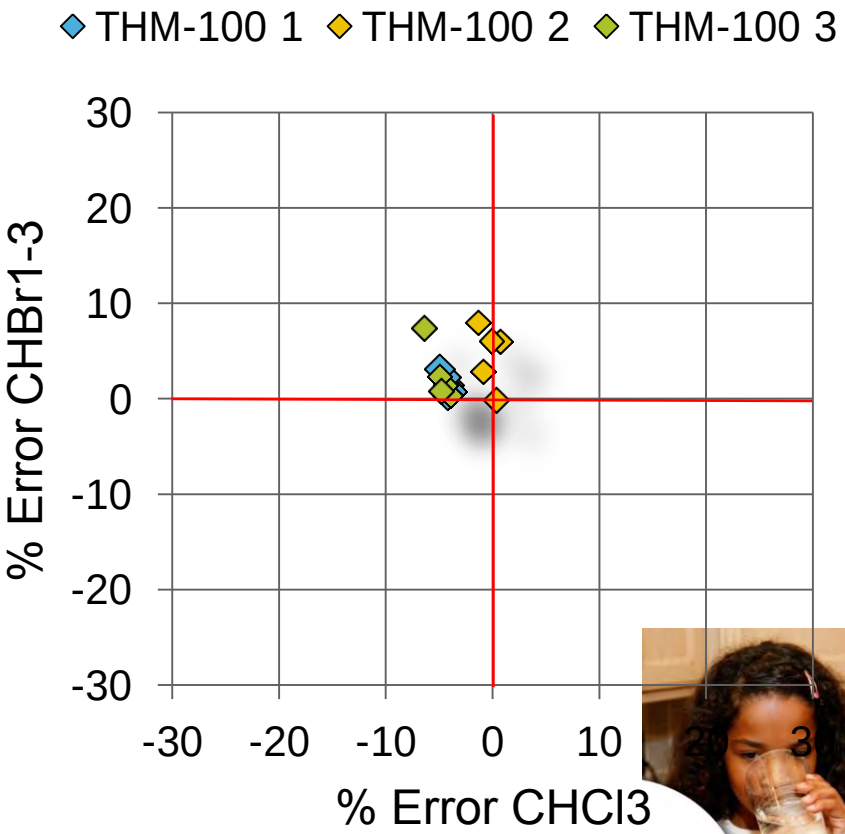

**X, X', X'' = Br, Cl**

**Fujiwara Product** $\lambda_{max} \sim 540$ nm

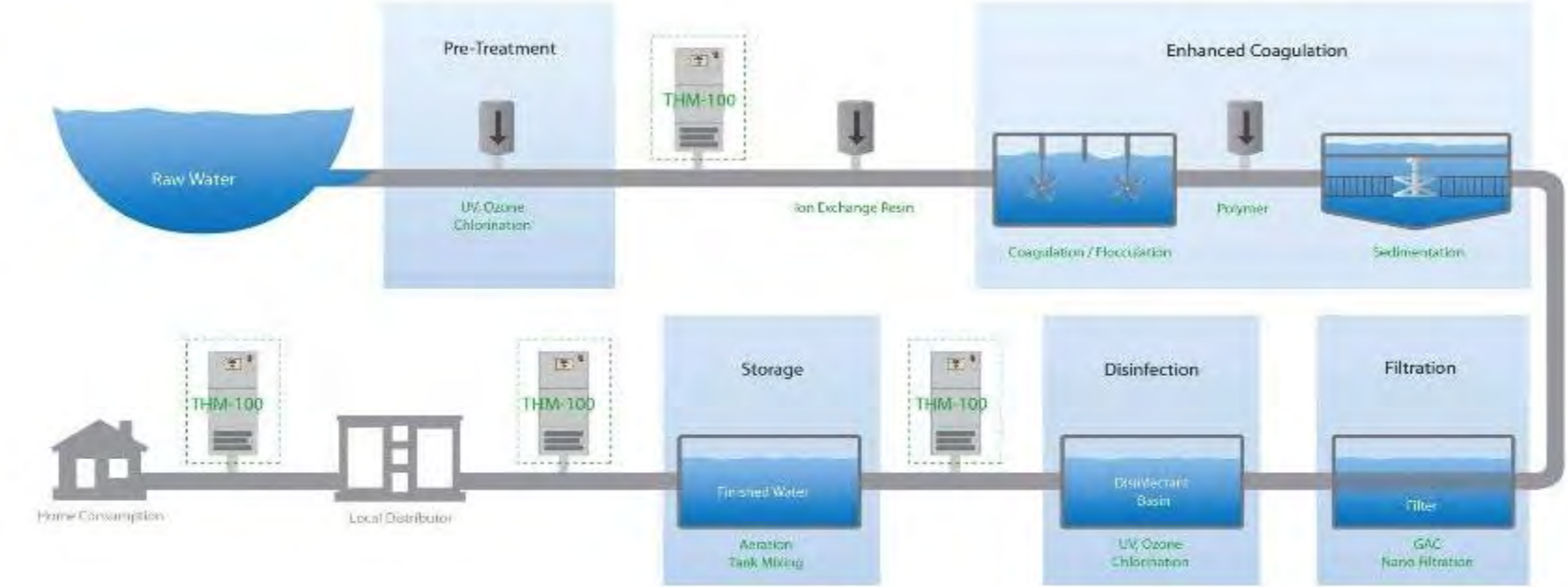
# Data Reliability: Labs *vs.* Online (Spiked Samples)

- 5 US-EPA Accredited Labs & 3 THM-100 Monitors
- Sample Water Spiked at TTHM 79.5 ug/L (60% $CHCl_3$)




# Application of the THM-100



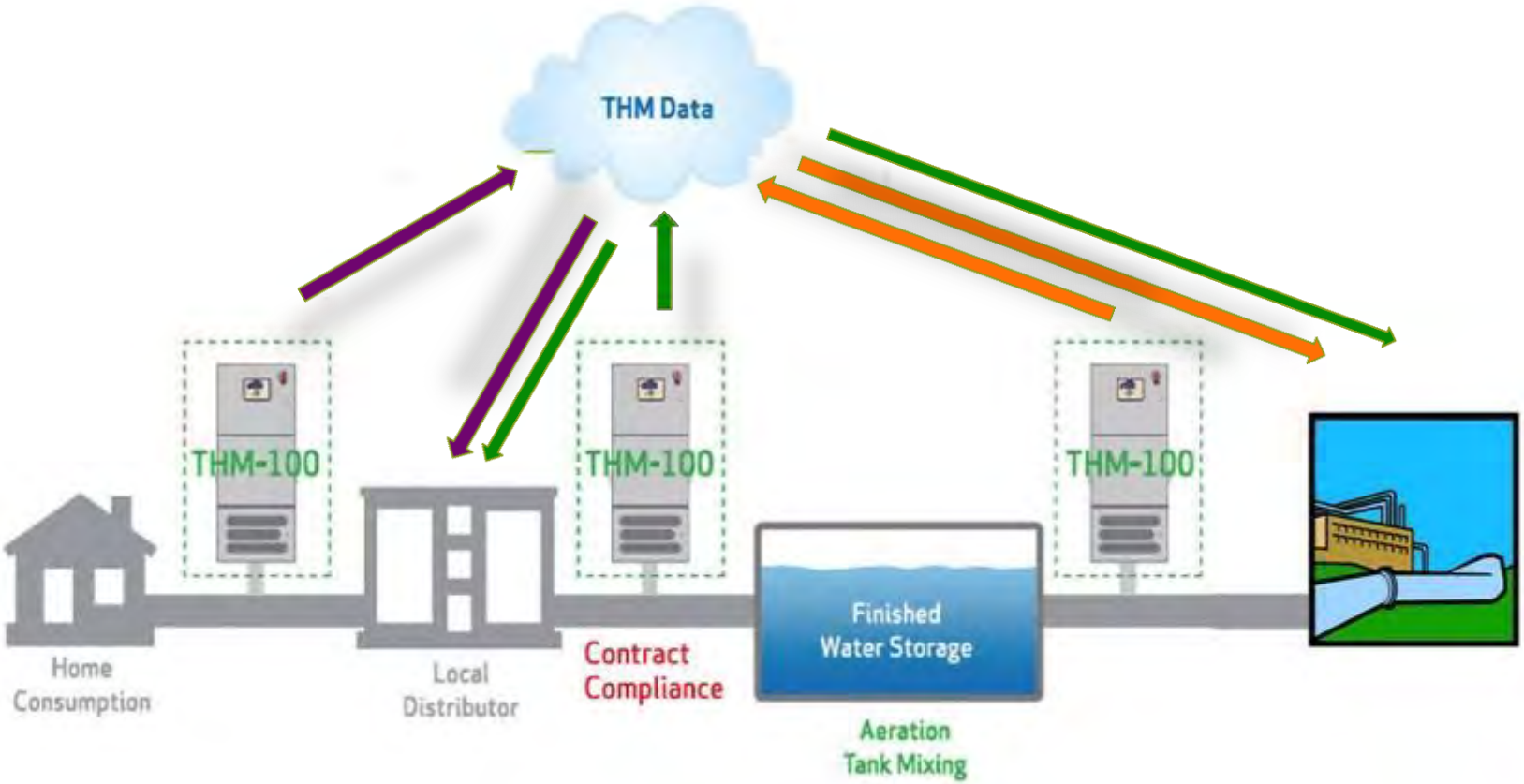

**1. Optimization of DBP Mitigation Technologies**

- Raw Water Blending
- Enhanced Coagulation
- Filtration – MIEX, GAC, Nano filtration
- Disinfectants – Chloramines, Chlorine Dioxide, UV, and Ozone
- Storage – Aeration, Tank mixing

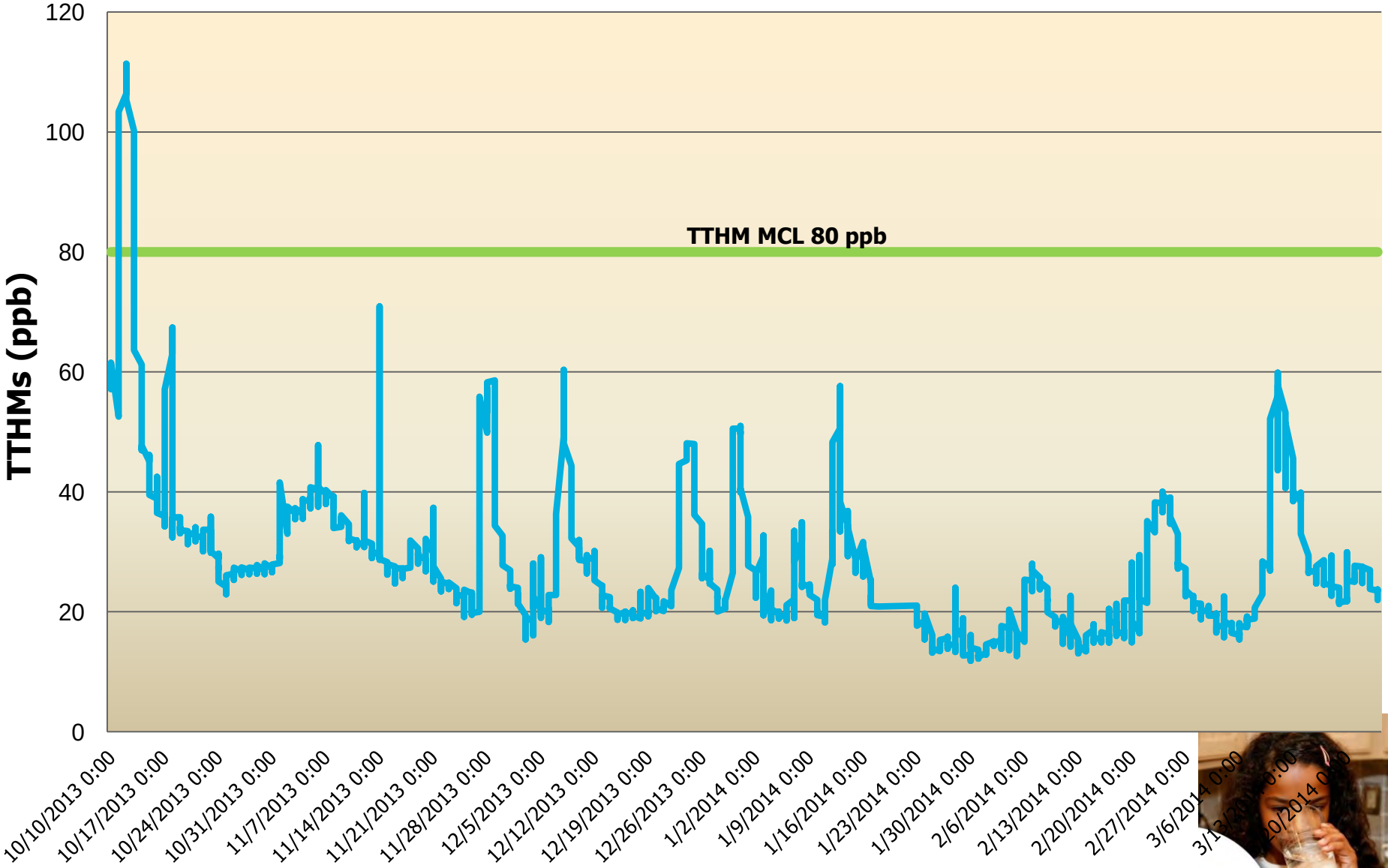
**2. Contract compliance and quality control in consecutive systems**

**3. Compliance monitoring**

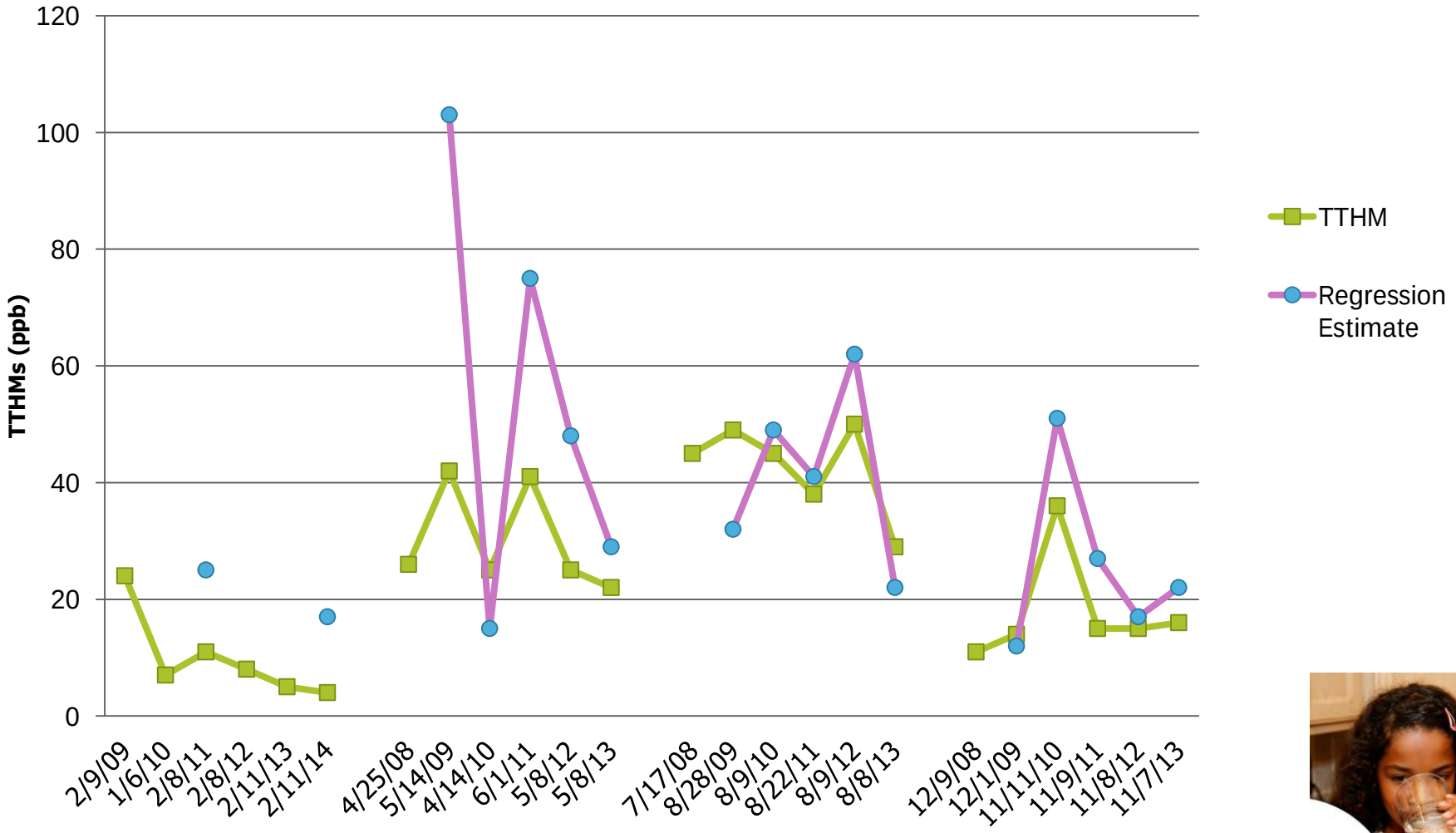
# Real-time TTHM Analysis for Local Water Quality Control and Consecutive System Monitoring



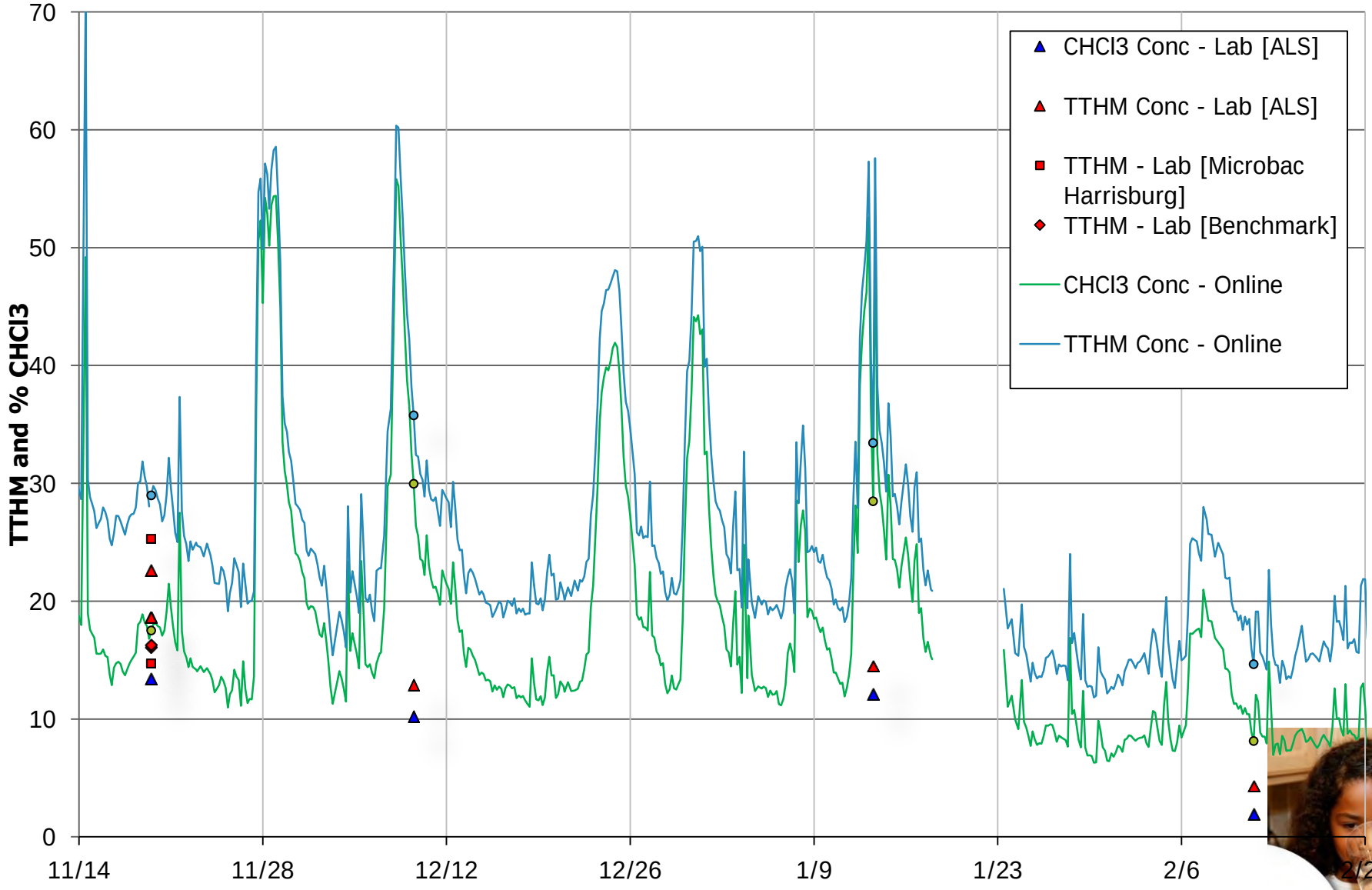
# UW Hummelstown WTP on-line TTHM (ppb)



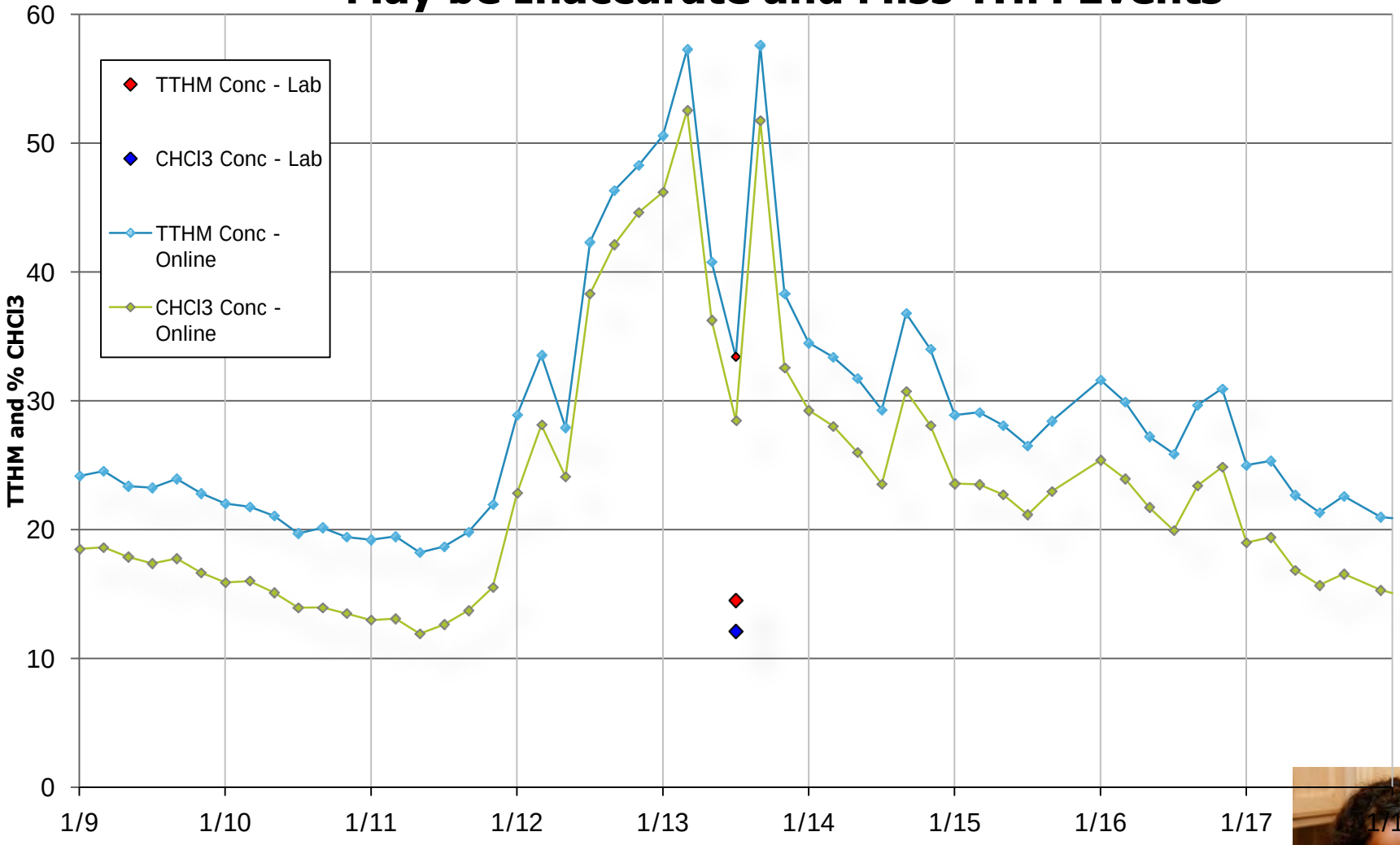

# Hummelstown EP TTHMs per Qtr vs Regression Estimates 2008-2014




# Hummelstown THM Measurements
# Online vs Three Analytical Labs




# Sporadic Grab-Samples and Lab Analyses May be Inaccurate and Miss THM Events




# United Water Take Aways

- **Not used during peak seasonal conditions- watershed study**
  - Partner with PA American, PA DEP and SRBC
- **No grab sample or "bottle injection" option**
- **No connection with online SCADA for trending**
- **Online TOC data not trended in SCADA**
- **TTHM Online Analyzer as an Operational Tool**
  - Provides real time changes to TTHM levels
  - Keep it simple
  - The Good, The Bad, The Ugly
  - Maintenance Free