Source water quality impacts on drinking water treatment plant performance and disinfection byproduct formation during a storm event

255th ACS National Meeting

Water Use Optimization: Water Quality, Reuse & Treatment

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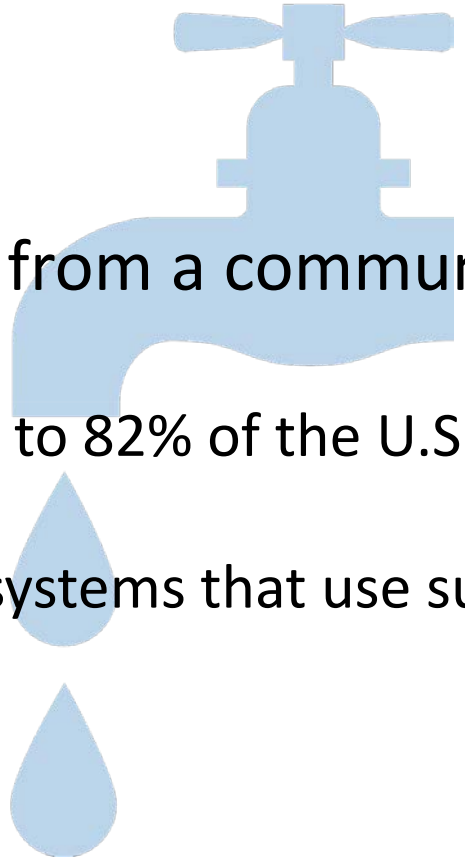
Drinking water treatment

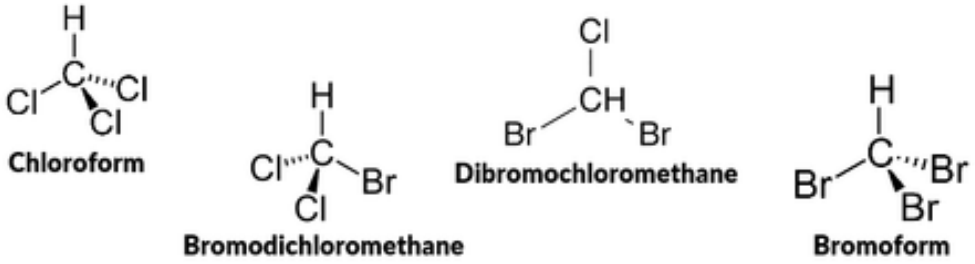


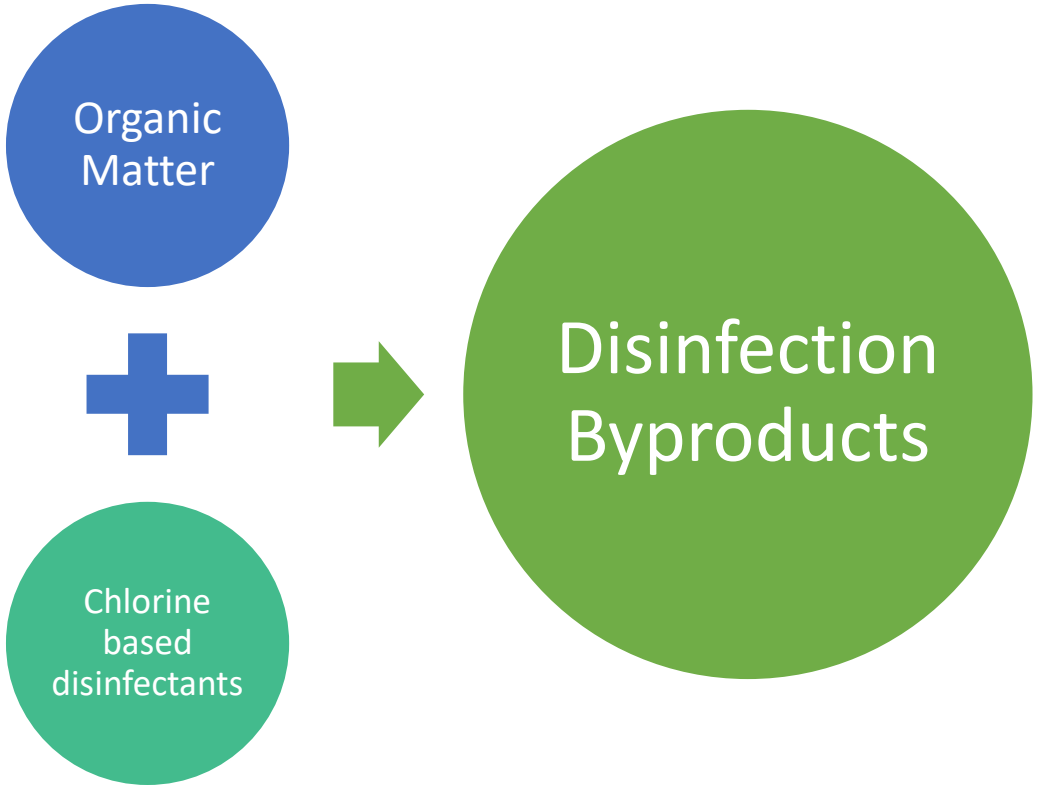
- Over 286 million Americans get their tap water from a community water system
  - 8% of U.S. community water systems provide water to 82% of the U.S. population through large municipal water systems
  - 68% are supplied year-round by community water systems that use surface water
- Increased source water variation
  - Higher organic matter content

Will current water treatment methods provide enough safe drinking water into the future?

Disinfection byproduct (DBP) formation

- Increased organic matter can contribute to carcinogenic DBP formation
- Trihalomethanes
  - Chloroform, bromoform, bromodichloromethane, and dibromochloromethane
  - Total trihalomethanes (TTHM) limit is 80 ppb in treated water.





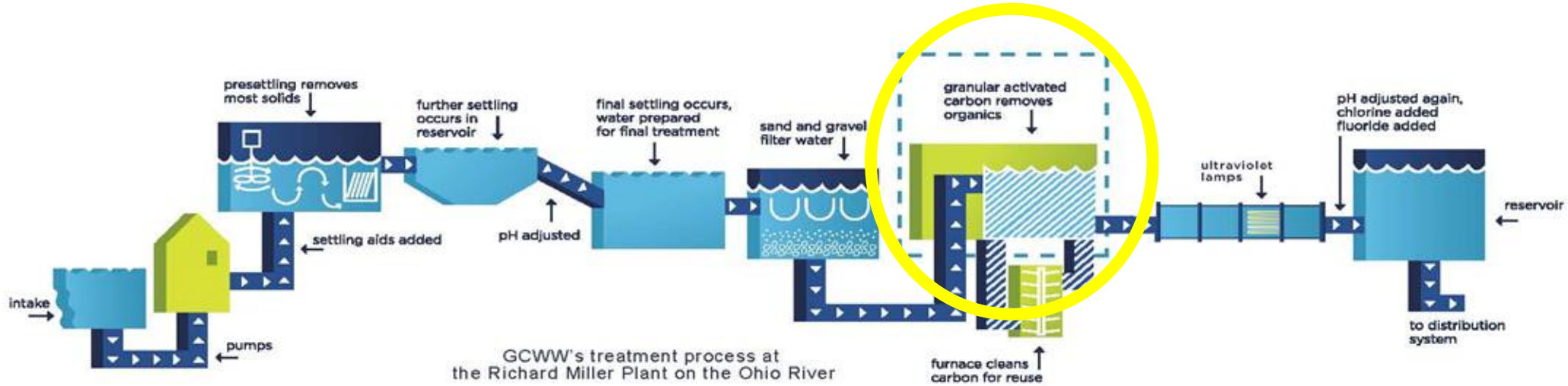
Research Questions

Which drinking water unit treatment processes safeguard against propagation of DBP precursor concentrations as source water quality changes?

How does the reactivity of DBP precursors change along the drinking water treatment train?

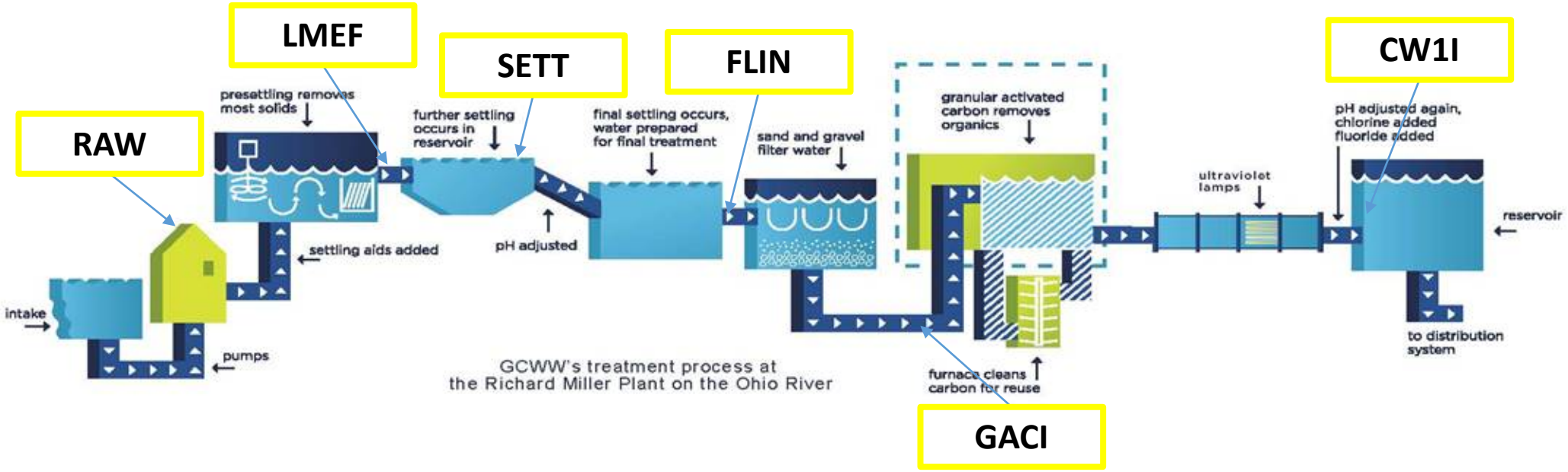
How can these observations be used to make recommendations for water treatment plant operation in the face of source water quality uncertainty?

Miller treatment plant, Cincinnati, OH



- GAC treatment unit
- Ohio River source water

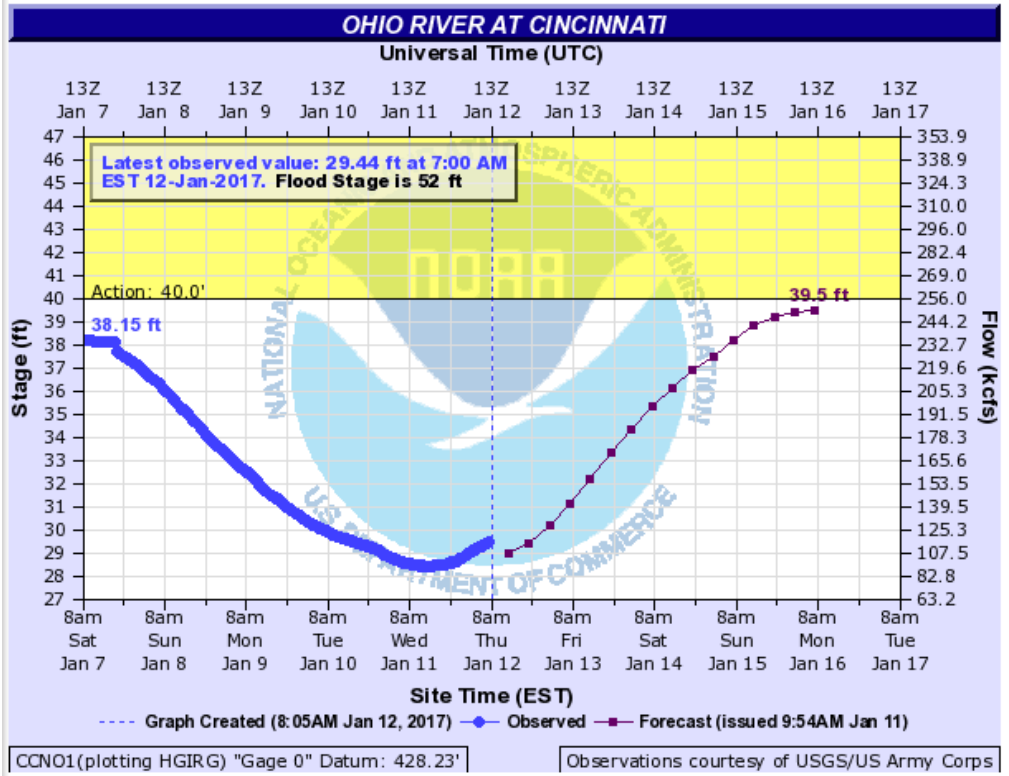
Miller treatment plant, Cincinnati, OH



1. Raw Water (RAW)
2. Lamella Effluent (LMEF)
3. Settling Reservoirs (SETT)
4. Sand Filter Influent (FLIN)
5. Granular Activated Carbon Influent (GACI)
6. Clear Well #1 Influent (CW1I)

Sampling procedure

- Targeted rain event with rainfall greater than 1 inch
- Samples collected hourly over 72 hour period
  - Stored with ice in coolers to keep < 4°C
  - Preservatives added for TOC
- THM samples collected at 1, 18, 36, 54, and 72 hours
  - Zero headspace
  - Preserved with phosphate and sodium sulfate



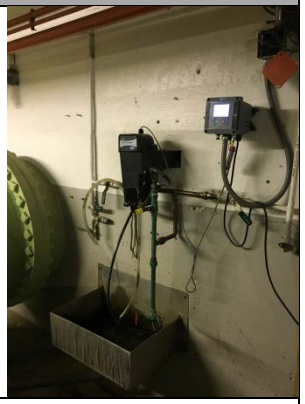
Water quality measurements

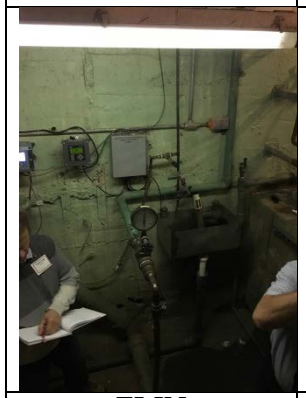
- *In situ* measurements of:
  - Turbidity
  - pH
  - Temperature
- Samples collected to measure:
  - THMs (Chloroform, bromoform, bromodichloromethane, and dibromochloromethane)
  - Non-purgeable organic carbon (NPOC)
  - Bromide concentration

GCWW Sampling Location

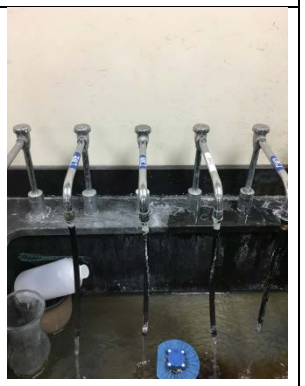

RAW


LMEF


SETT


FLIN


GACI

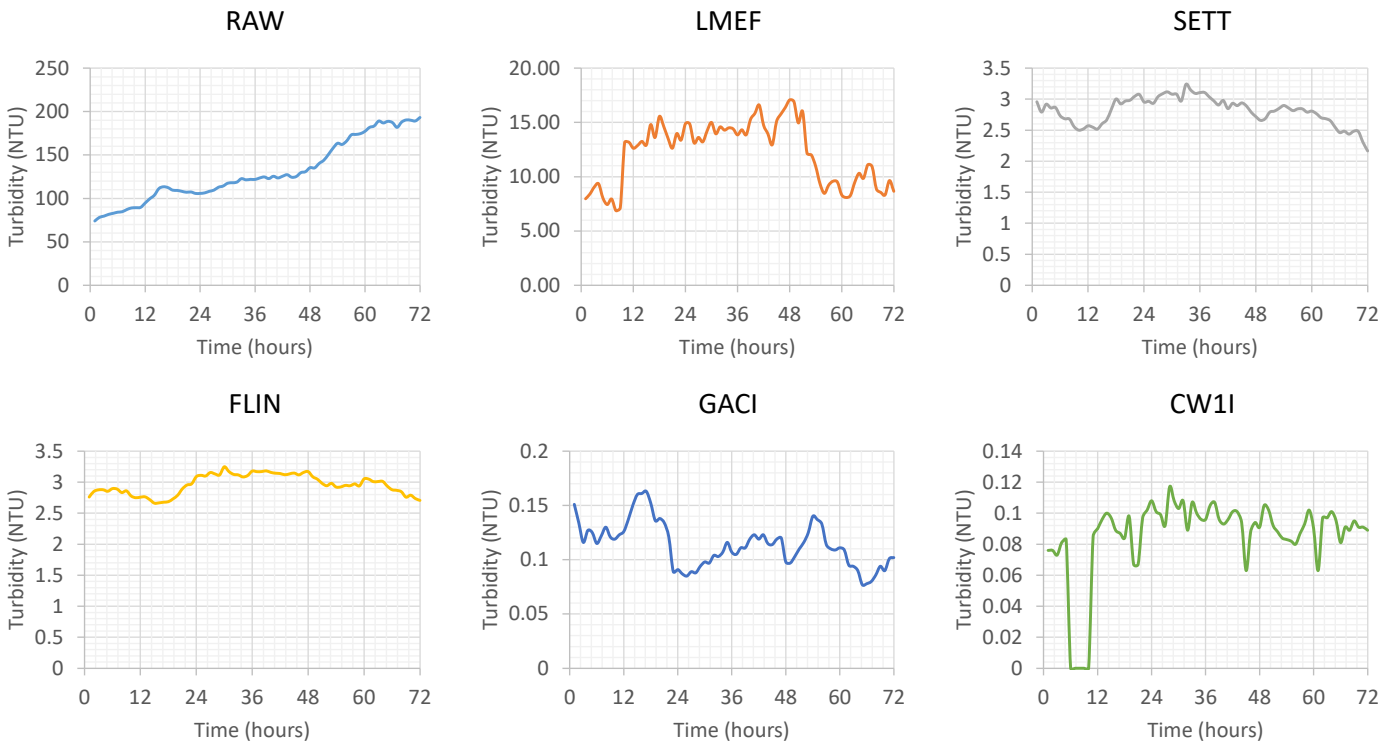

CW1I

Spiking experiments

- Large batches of THM samples collected at 1, 18, 36, 54, and 72 hours
- Spiking procedure:
    1. Shaken well and spiked to 1mg/L free available chlorine (FAC) using Clorox (sodium hypochlorite)
    2. Inverted several times after spiking
    3. Initial free chlorine was measured
    4. 60 mL of the bottle contents were removed for THM measurement
    5. After 36 hours, the free chlorine was measured again
    6. Additional 60 mL set aside for THM analysis

Water Quality Results

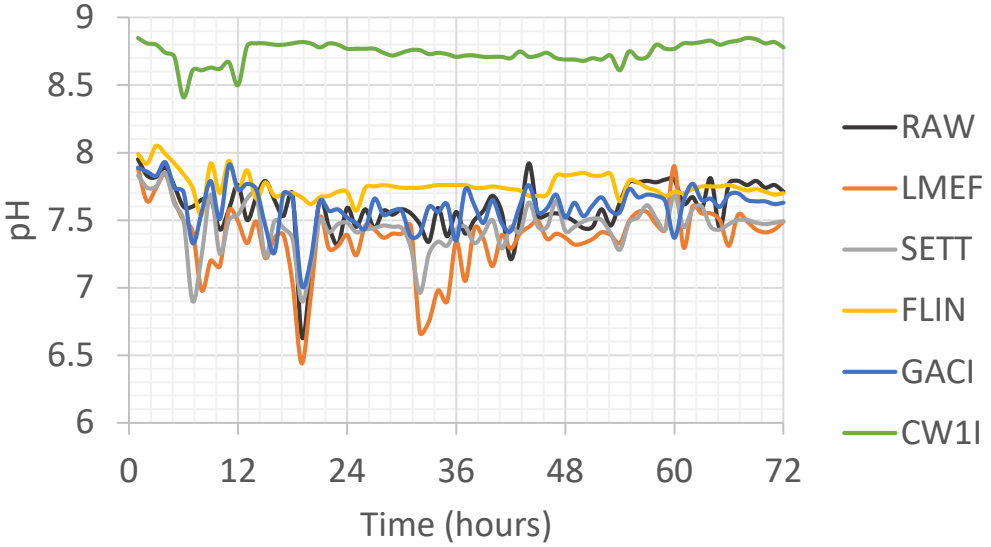
Turbidity changes



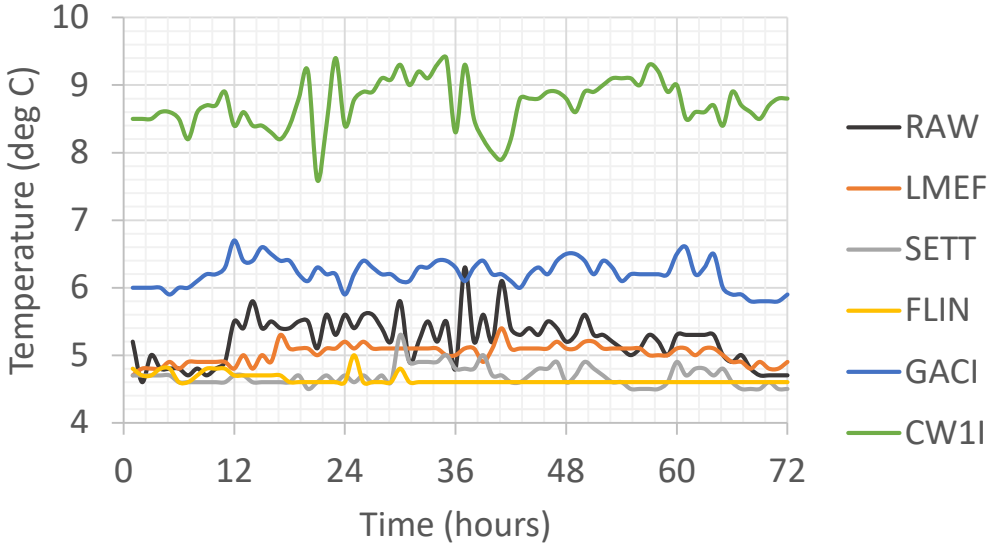
- Steady increase in turbidity in RAW samples
- Significant decreases between RAW and LMEF, LMEF and SETT, and SETT and FLIN
- Final product water did not show any propagation of turbidity changes

Water Quality Results

pH changes during sampling



Temperature changes during sampling

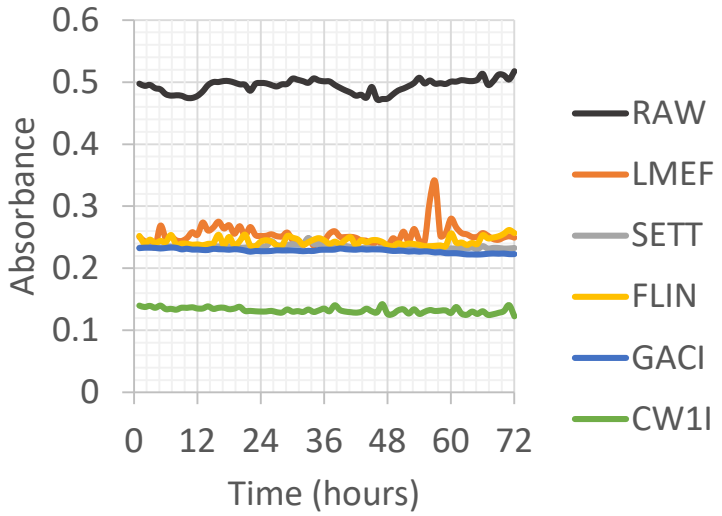


- pH fluctuated but did not change significantly until final pH adjustment before CW1I
  - Final water pH was between 8.5 and 9
- Temperature increased slightly before GACI from ~ 5 to ~6°C
  - Increased to ~8-9 °C between GACI and CW1I
  - Higher T = faster rate of THM formation

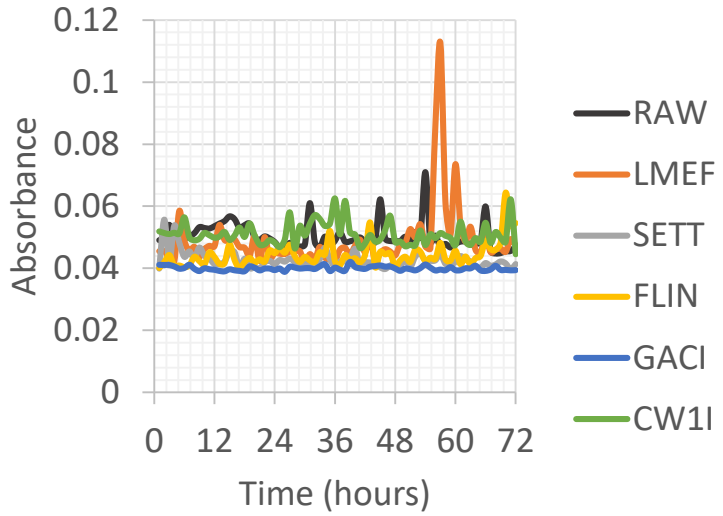
UV-vis measurements

- UV scans (200-700) give insight into different reactive NOM portions
  - UV-254 = more reactive organics which form DBPs
  - UV-472 = organic material at the beginning of humification
  - UV-664 = strongly humified material with a high degree of aromatic groups

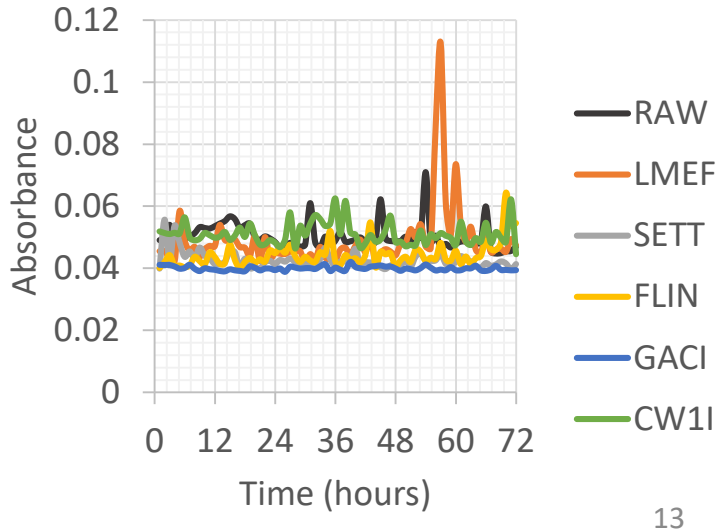
UV-254 measurements



UV-472 measurements



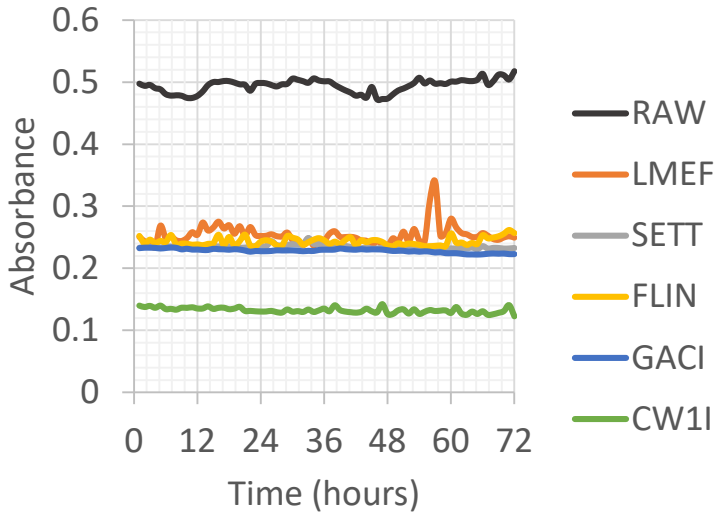
UV-664 measurements



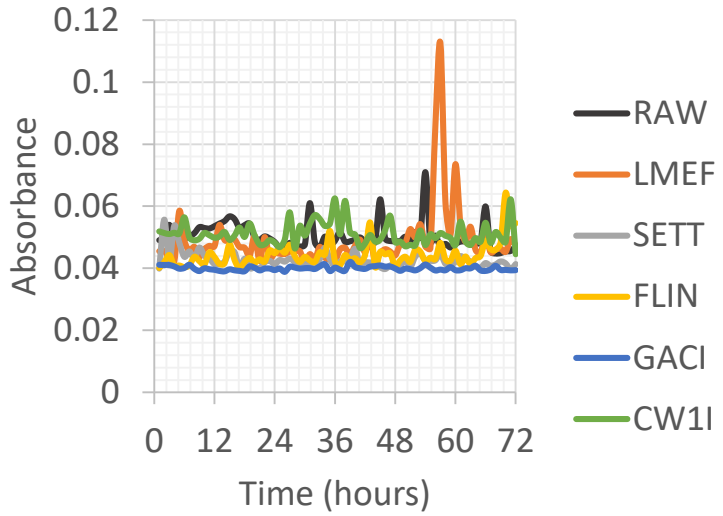
UV-vis measurements

- Presettling/Lamella and GAC unit are more effective at removing UV-254 fraction
- Presettling/Lamella removes some UV-472 fraction and settling evens spikes
- Very little removal of more humified UV-664 materials

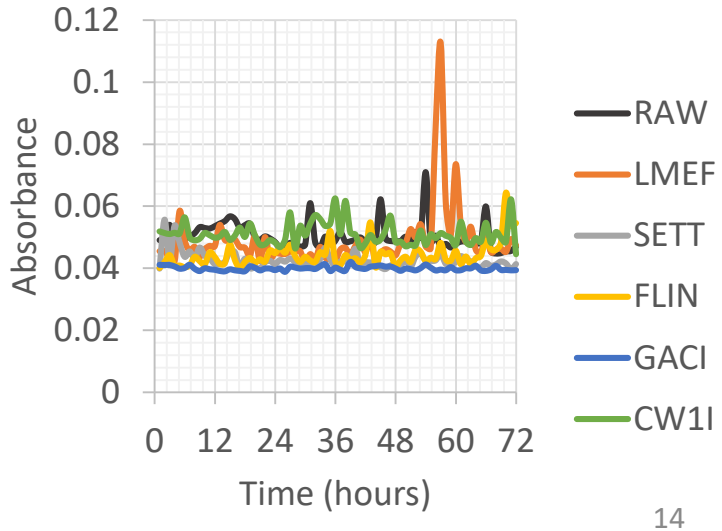
UV-254 measurements



UV-472 measurements

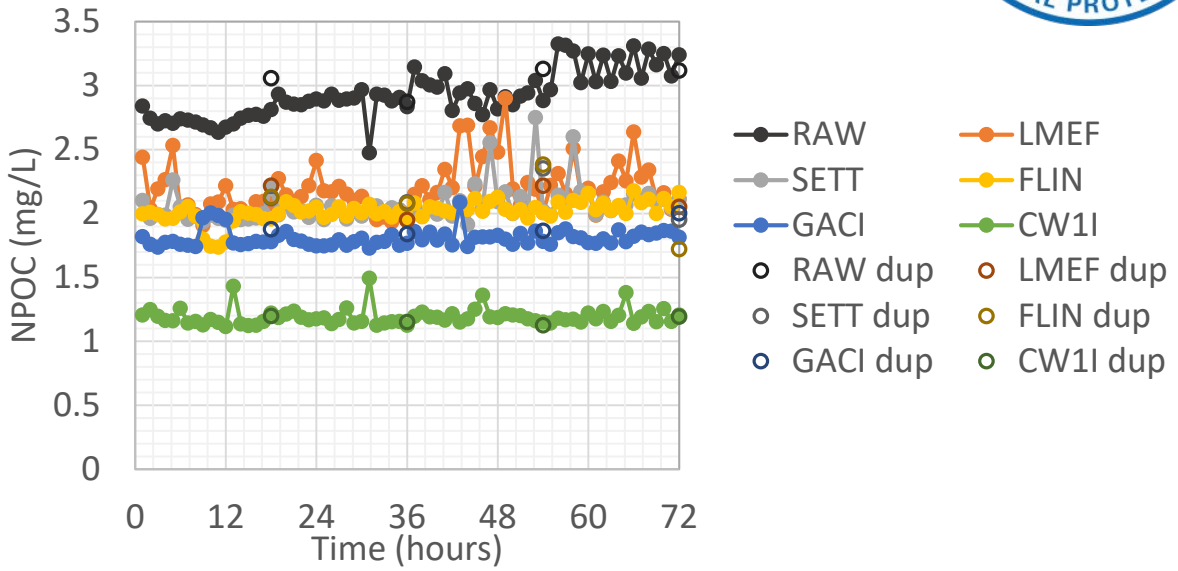


UV-664 measurements



NPOC measurements

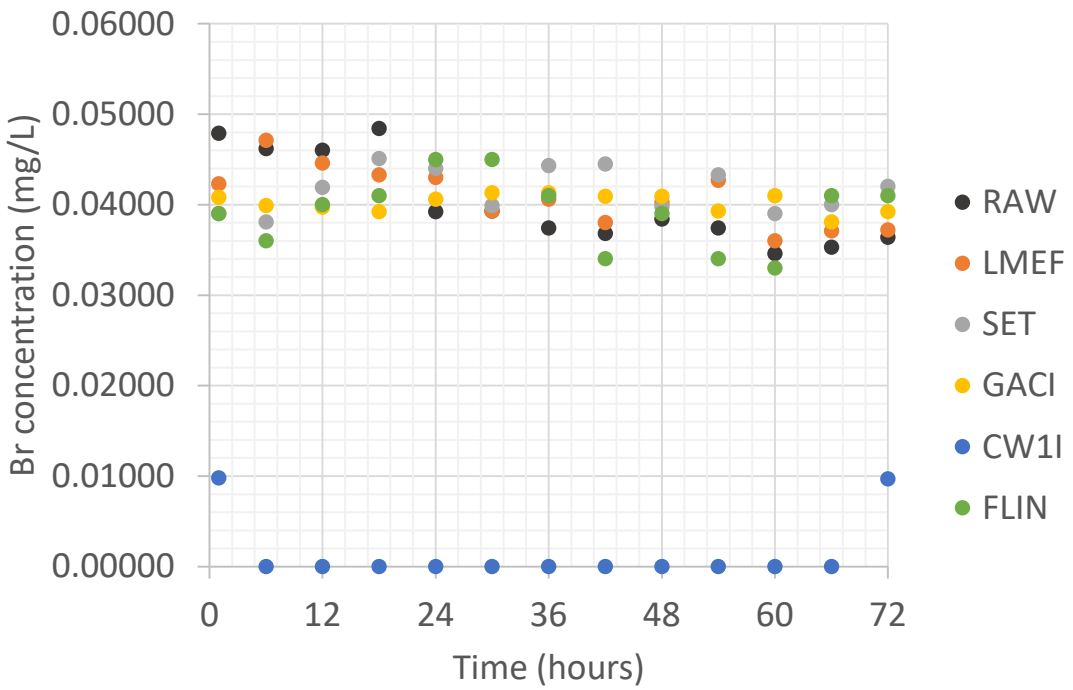
- Increase in RAW NPOC over reaction period due to storm event
  - Product water NPOC consistently low
- **Presettling/Lamella and GAC most effective barriers**
  - Slight decrease in filter
- Settling removes NPOC spiking



Unit process	*Percent removal*	*% of total removal*
RAW → LMEF	**24.7 ± 7.2%**	**32.3%**
LMEF → SETT	5.4 ± 7.8%	7.1%
SETT → FLIN	2.2 ± 5.5%	2.9%
FLIN → GACI	10.1 ± 6.1%	13.2%
GACI → CW1I	**34.0 ± 4.7%**	**44.5%**

Bromide measurements

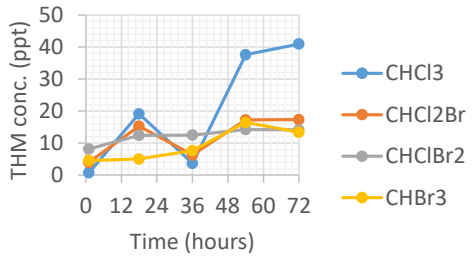
- Consistently between 0.04 – 0.05 mg/L bromide
- Only significant concentration drop between GACI and CW1I samples
  - Removal due to GAC treatment or formation of Br-THMs
- Mass balance with Br in THMs shows **87.5 - 91.2%** removed through GAC treatment



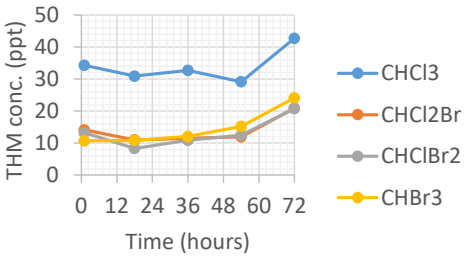
THM formation

- Significant formation only in CW1I samples
  - Less than 10 ppb TTHMs
- After chlorination, THM formation trend is dibromochloromethane > bromodichloromethane > chloroform > bromoform
  - More toxic Br-THMs forming
- Samples taken 20-30 min after chlorination
  - Br-incorporation decreases with time: 0.64, 0.47, and 0.39 at 30 minutes, 24 hours, and 72 hours, respectively (Tian *et al*. 2013)

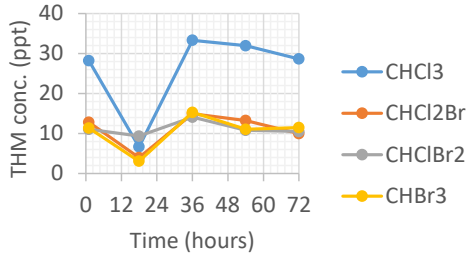
A. RAW samples



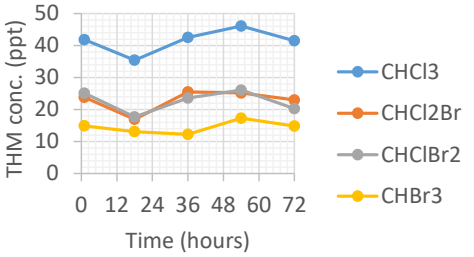
B. LMEF samples



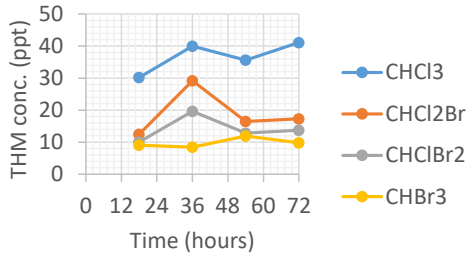
C. SETT samples



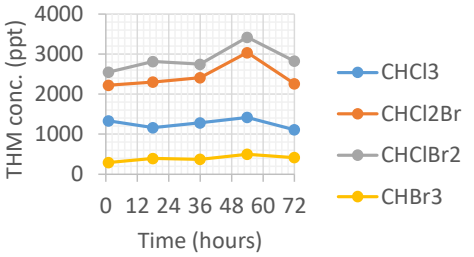
D. FLIN samples



E. GACI samples



F. CW1I samples



Research Questions

Which drinking water unit treatment processes safeguard against propagation of DBP precursor concentrations as source water quality changes?

How does the reactivity of DBP precursors change along the drinking water treatment train?

espite removal, still significant formation of HMs, particularly Br-THMs…

recommendations for water treatment plant operation in the face of source water quality uncertainty?

- GACI treatment removes 34.0 ± 4.7% of NPOC and 87.5 - 91.2% of bromide
- Source water NPOC increases did not propagate through water treatment
  - Settling prevented NPOC spiking

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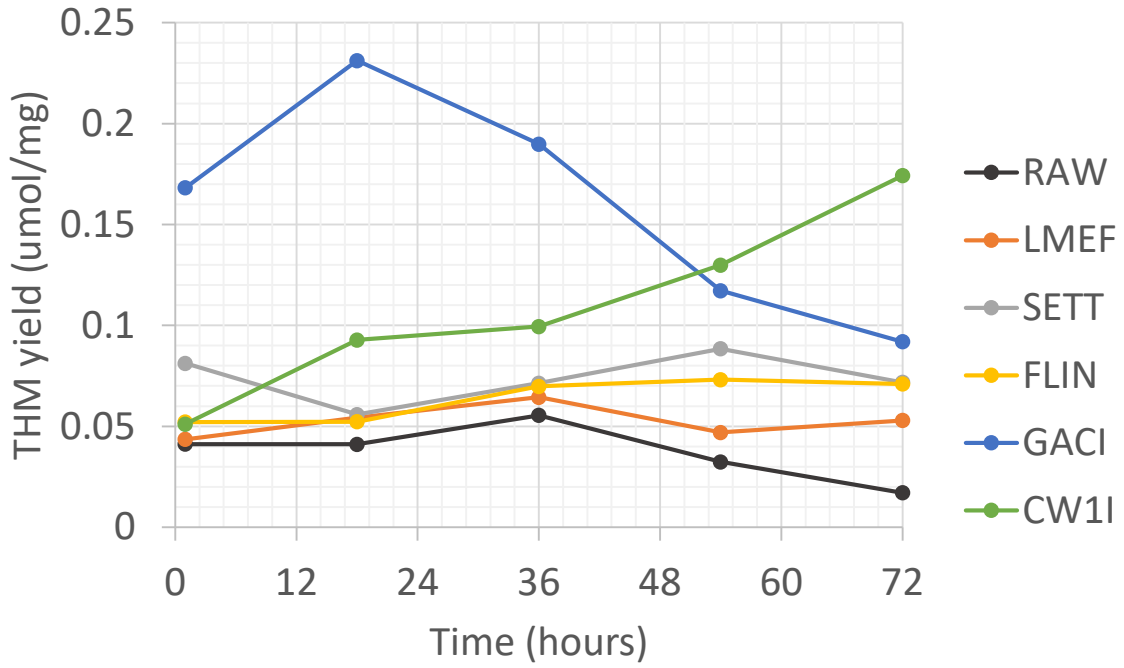
Spiking experiment results

- THM yield of NPOC in RAW, LMEF, SETT, and FLIN treatment units was similar
- High initial yield in GACI unit decreased with time
- Yield increased with time in CW1I

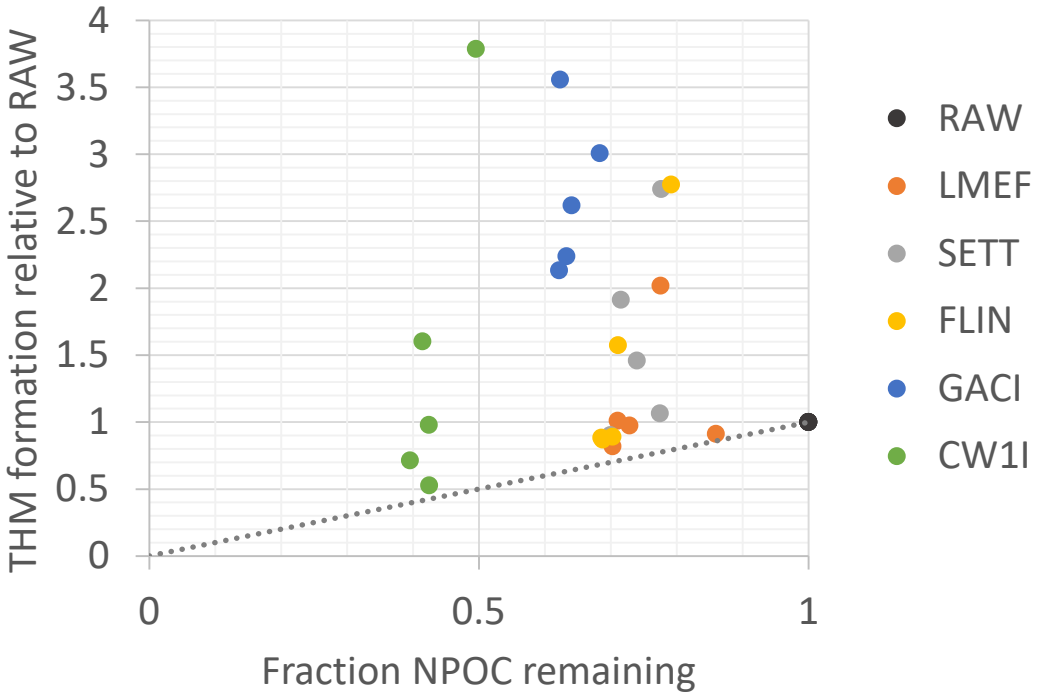
Conventional and GAC treatment did not remove most reactive portion of NPOC

THM yield from spiked samples



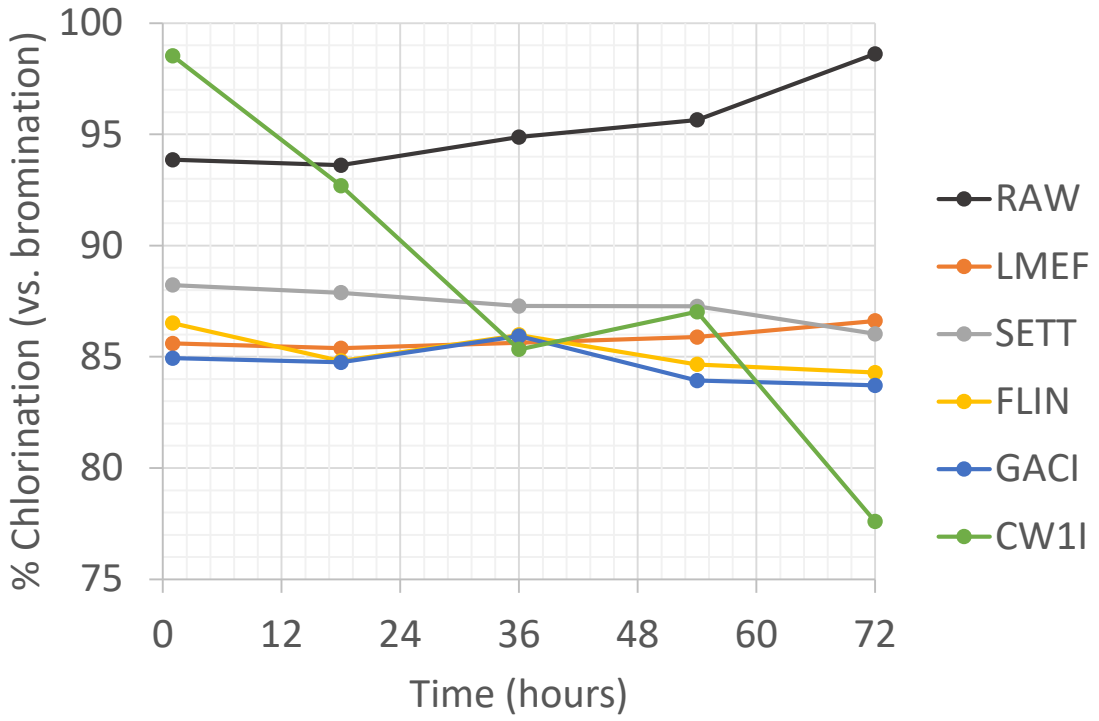
Reactivity changes of NPOC

- All samples along the treatment train had increased THM formation relative to RAW samples
  - Particularly increased for GACI and late CW1I samples, despite low fraction of TOC remaining
- **Important to characterize why reactive NPOC remains despite treatment**



Bromination of spiked samples

- More chlorination (vs. bromination) relative to in situ samples
  - Longer reaction time of 36 hours
- Increased bromination of THMs after RAW samples
  - May correlate with increase reactivity of NPOC
- Nearly linear decrease in chlorination with time in CW1I samples matches THM yield trend

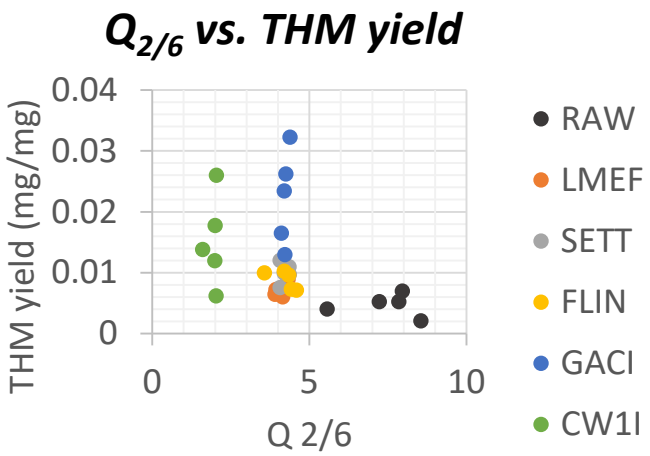


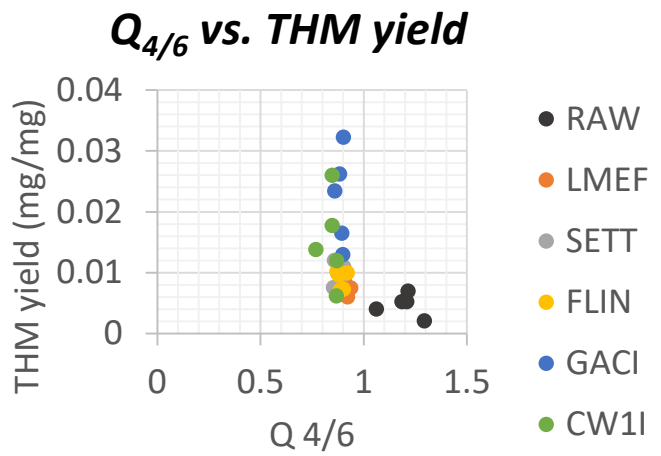
Q-ratios

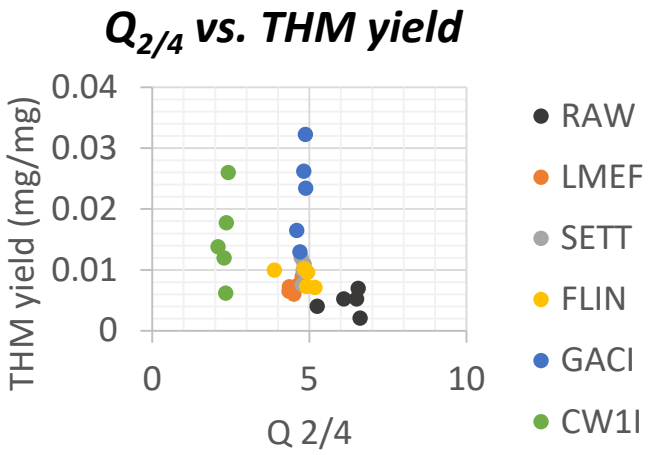
- $Q_{2/4} = A_{280}/A_{472}$; $Q_{2/6} = A_{280}/A_{664}$; $Q_{4/6} = A_{472}/A_{664}$
- Low $Q_{2/6}$ or low $Q_{4/6}$ ratio indicates a high degree of aromatic condensation
  - a larger fraction of strongly humified material
- High $Q_{2/6}$ or $Q_{4/6}$ ratio = compounds with more phenolic and benzene-carboxylic groups, e.g. less humified compounds
- $Q_{2/4}$ indicates the point where organic matter transitions to begin humification.

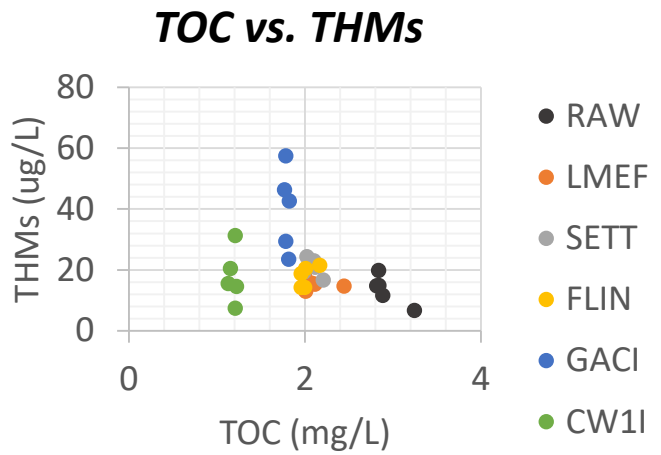
Q-ratios vs. THM yield

- RAW, LMEF, SETT and FLIN had slight increase in THM yield as Q ratio decreased
- GACI and CW1I samples had large variation in yield despite similar Q ratios
  - Other factors impacting reactivity
- **More sensitive techniques needed**









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How does the reactivity of DBP precursors change along the drinking water treatment train?

How can these observations be used to make recommendations for water treatment plant operation in the face of source water quality uncertainty?

- More reactive portions of NPOC will persist through treatment units, despite overall decrease in NPOC
- Additional research into NOM structure needed to determine cause

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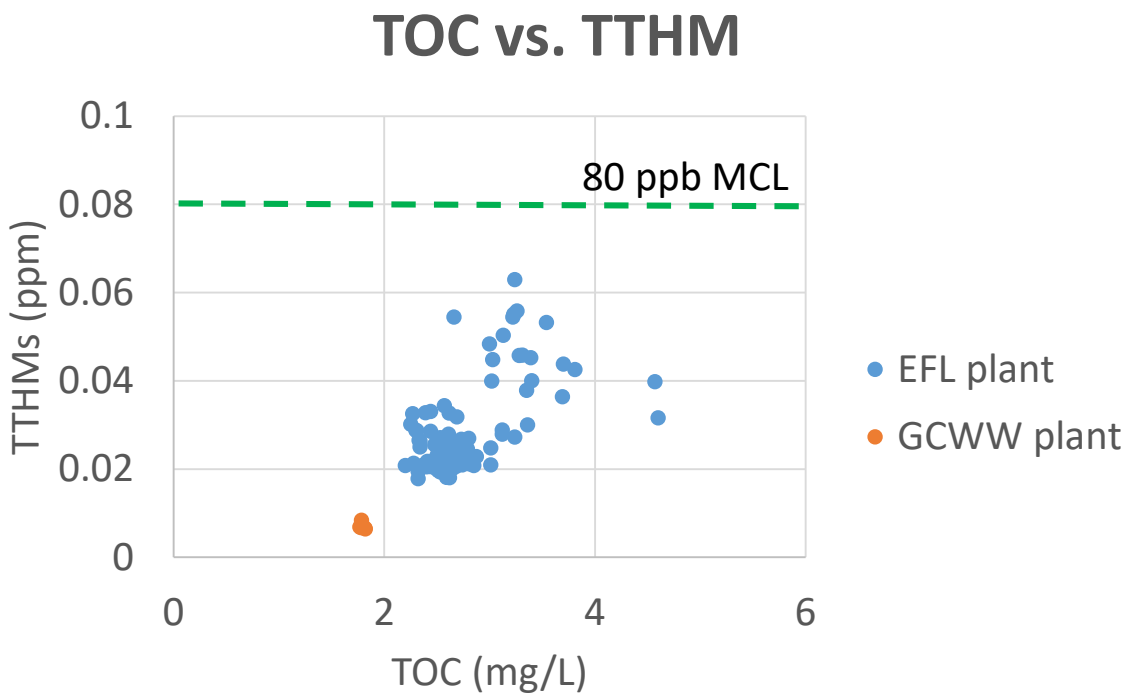
How does the reactivity of DBP precursors change along the drinking water treatment train?

How can these observations be used to make recommendations for water treatment plant operation in the face of source water quality uncertainty?

Water treatment plant operation

- Miller plant adapted to source water quality variation due to the storm event
  - Increased turbidity/NPOC did not propagate through treatment plant
  - GAC unit especially well suited for dealing with increased NPOC
- Recommendations for a non-stationary environment
  - More widespread use of GAC for THM precursor removal
  - Settling process important to remove spikes in NPOC



Future research directions

- Examine **seasonal changes** in precursor removal and reactivity
  - Temperature changes in source water
  - Different sources for turbidity/NPOC
- Characterize NPOC in more detail
  - Better understand reactive portion to ensure effective removal
  - Particular focus on formation of **Br-THMs**
- Improve models of THM formation for WTP models
  - Help WTPs optimize to **minimize use of chemicals and energy**

Thank you!

Questions or comments?

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