Disinfection Byproducts

Erin Hammer

Alloway

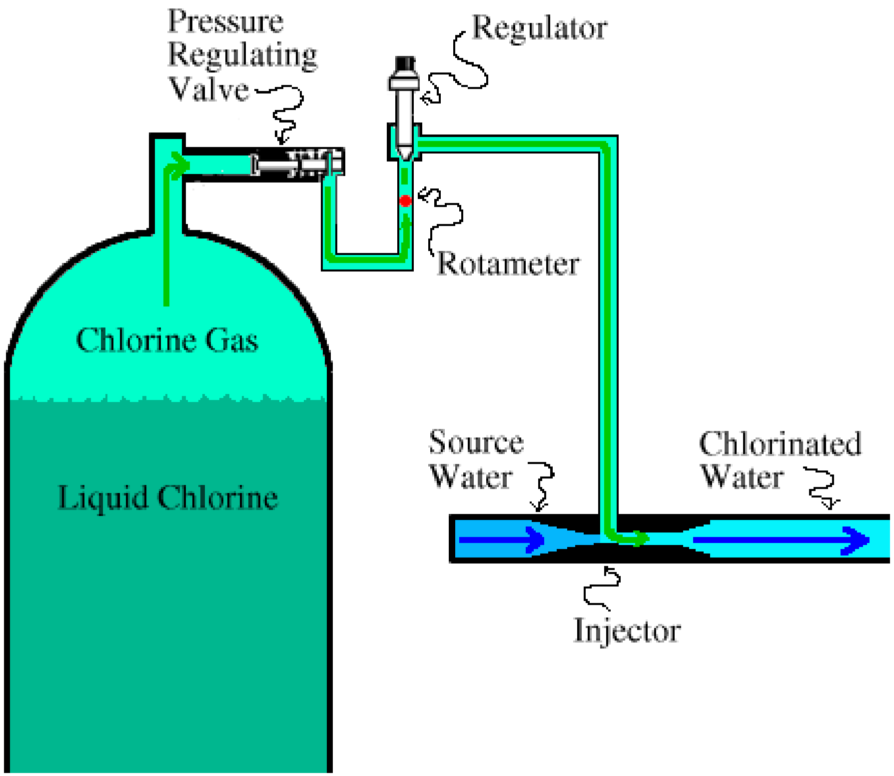
Your Resource for Defensible Data

Topics to Be Covered

- Disinfection
- Disinfection Byproducts
  - What they are
  - Health risks
- Regulations
- Influencing Factors
  - What factors affect THM and HAA5
  - How factors affect THM and HAA5
- Application

Disinfection

- Chemicals added to water to kill or inactivate disease-causing microorganisms in raw water
  - Chlorine
  - Chlorine dioxide
  - Chloramine
  - Ozone



Disinfection Byproducts

- Disinfectants react with inorganic and organic material in water to produce disinfection byproducts (DBPs)
- Over 500 DBPs have been identified but only 11 are currently regulated

NOM + Cl2 → DBPs

Disinfection Byproducts

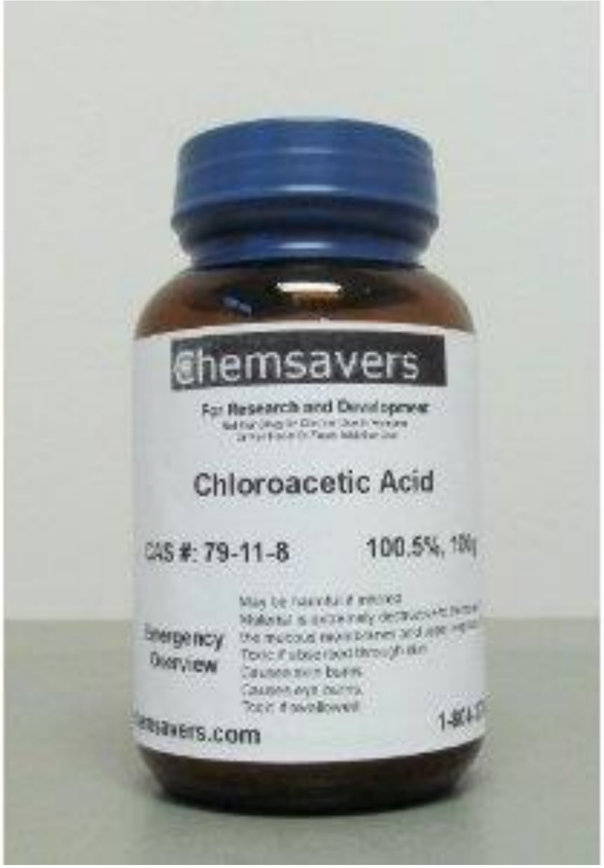
Disinfection Byproducts	Disinfectants
Bromate	Ozone
Chlorite	Chlorine Dioxide
Haloacetic acids	Chlorine, Chloramine
Trihalomethanes	Chlorine, Chloramine

Trihalomethanes

- Constitute the majority of DBPs formed in chlorinated waters
- Trihalomethanes (THMs)
  - Bromodichloromethane
  - Bromoform
  - Chloroform
  - Dibromochloromethane

Haloacetic Acids

- Second most abundant DBPs
- Haloacetic acids (HAA5s)
  - Dichloroacetic acid
  - Trichloroacetic acid
  - Monochloroacetic acid
  - Monobromoacetic acid
  - Dibromoacetic acid



Health Effects

- High levels of HAA5s and THMs linked to:
  - Central nervous system damage
  - Increased risk of liver, kidney, bladder, and colon cancers
  - Increased risk of spontaneous abortions, birth defects, and low birth weights

DBP Regulation

- THMs first detected in chlorinated water by J.J. Rook in 1974
- In 1970s, a link was made between drinking chlorinated water and digestive and urinary tract cancers
- In 1979, U.S. EPA established the Interim Trihalomethane Rule
  - Set MCL at 100 µg/L for TTHMs
  - Only applied to water systems serving ≥10,000 people

DBP Regulation

- In 1998, U.S. EPA established Stage 1 Disinfectants and Disinfection Byproducts Rule
  - Set MRLs for disinfectants
    - Chlorine, chloramine, and chlorine dioxide
  - Set MCLs for DBPs
    - MCL reduced to 80 μg/L for TTHMs
    - MCL set at 60 μg/L for total HAA5s
  - Applied to all community water systems
  - Running average of entire water system

DBP Regulation

- In 2006, U.S. EPA established the Stage 2 Disinfectants and Disinfection Byproduct Rule
  - Built upon the Stage 1 D/DBP Rule
  - MCLs remained the same but tightened compliance monitoring for THMs and HAA5s
  - Monitored as running average at each sample location

Stage 1

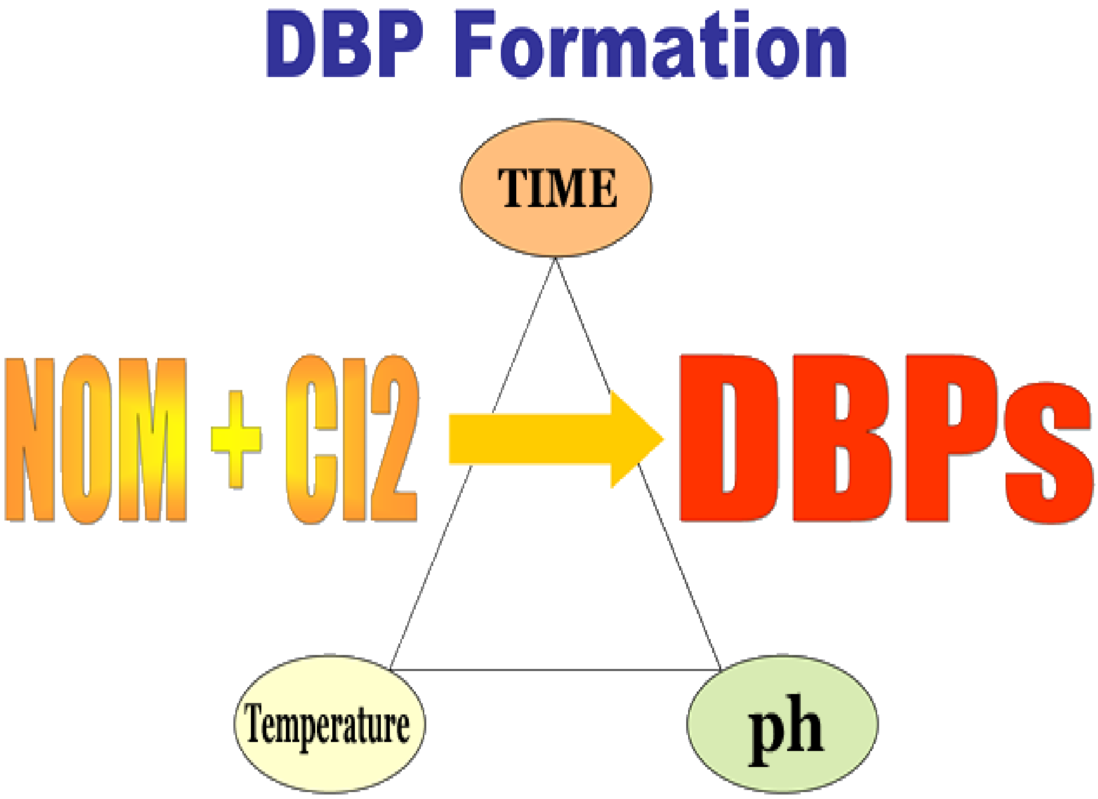
	Winter	Spring	Summer	Fall	Annual Average
Site 1	15.2	31.3	55.4	39.3	50.5
Site 2	14.1	33.5	48.1	26.3	
Site 3	21.3	43.9	**89.7**	64.3	
Site 4	51.5	72.4	**121.9**	79.8	
System	25.5	45.3	78.8	52.4	

Stage 2

	Winter	Spring	Summer	Fall	Annual Average
Site 1	15.2	31.3	55.4	39.3	35.3
Site 2	14.1	33.5	48.1	26.3	30.5
Site 3	21.3	43.9	**89.7**	64.3	54.8
Site 4	51.5	72.4	**121.9**	79.8	**81.4**

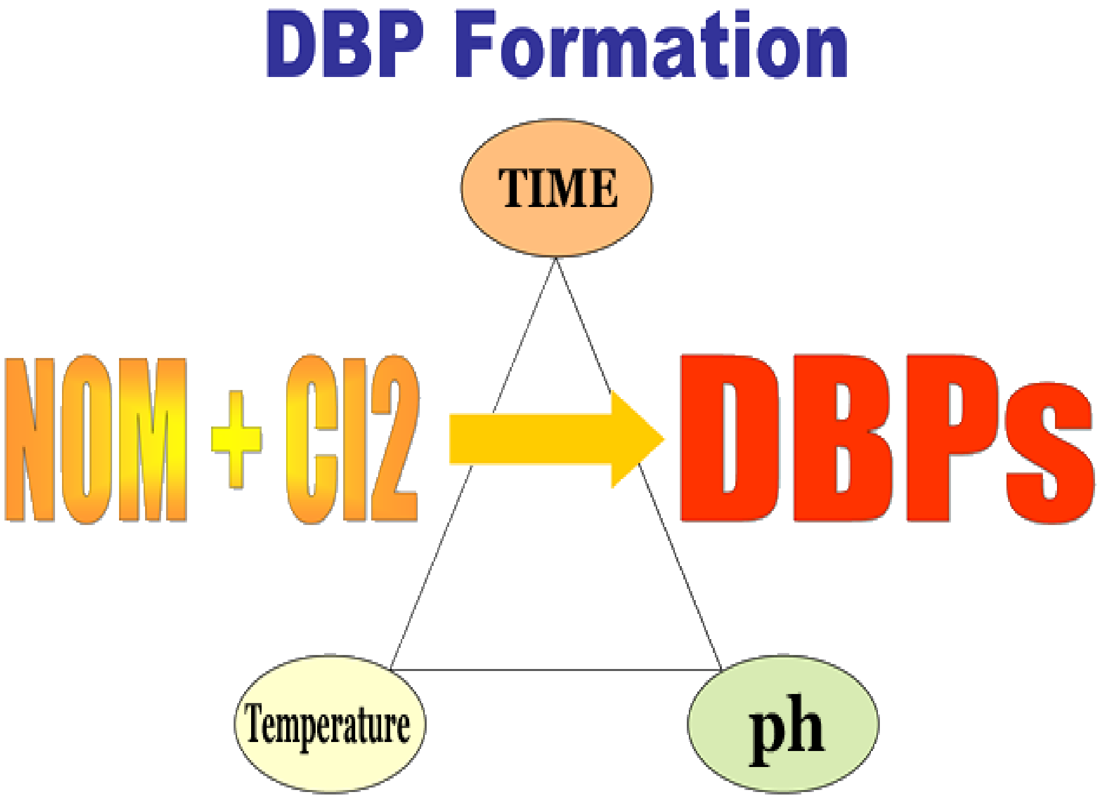
Influencing Factors

- Disinfectant
- NOM
- Contact time
- Temperature
- pH
- Bromide



Influencing Factors

- Disinfectant
- NOM
- Contact time
- Temperature
- pH
- Bromide



Disinfectant

- Type and amount of disinfectant used can have a significant affect on amount of THMs and HAA5s produced
  - Chlorine
  - Chloramine
  - Chlorine dioxide
- All produce some form of DBP

Chlorine

- Free chlorine is the most common disinfectant used in water treatment
  - Gas – chlorine (Cl_2)
  - Liquid – sodium hypochlorite (NaClO)
- The higher the dose of Cl_2 added, the greater the THM and HAA5 formation potential

Chlorine

- Use of chloramine or chlorine dioxide as disinfectant lower the amount of Cl_2 added to the water
  - Significantly reduce the potential for HAA5 and THM formation
- Each has its own set of disadvantages

Chloramine

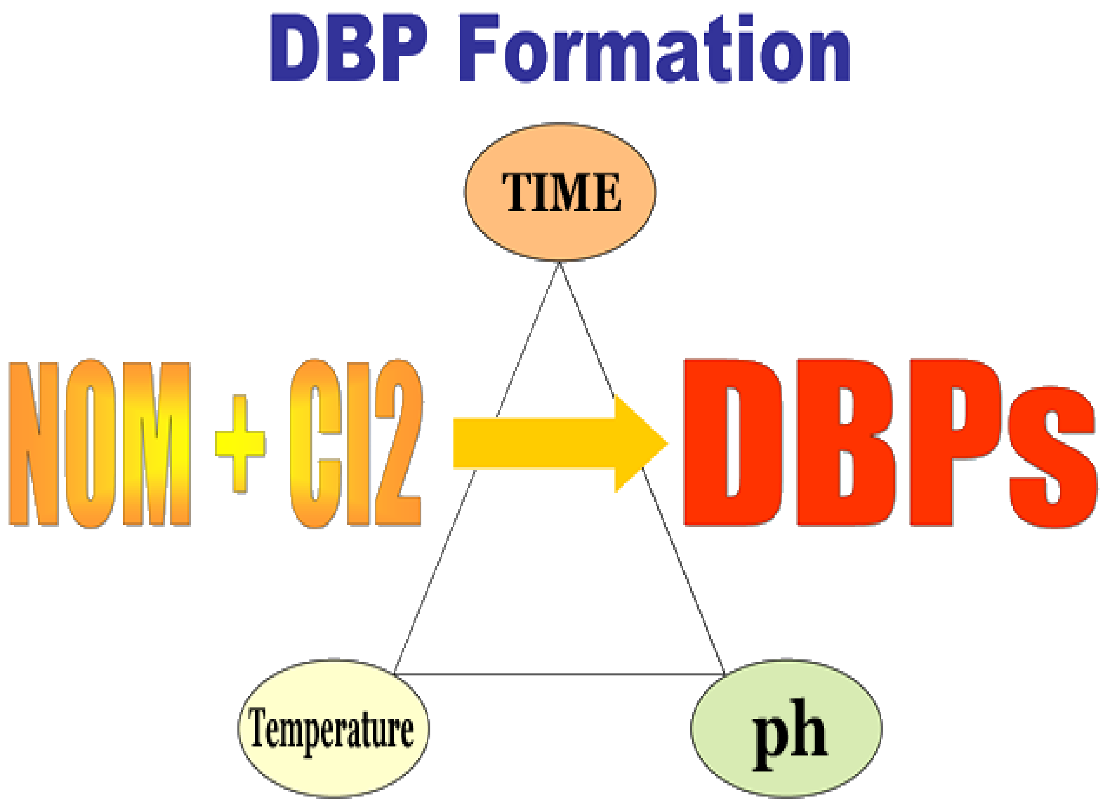
- If chlorine is added before ammonia or mixing is inefficient, THM and HAA5 formation still possible
- Disadvantages
  - Higher ammonia
  - High cyanogen chloride production
  - Longer distribution system residence times

Chlorine Dioxide

- If Cl_2 was added during the production of chlorine dioxide, small amounts of HAA5s and THMs can be produced
- Oxidizes bromide ions which can react with NOM to form brominated THMs and HAA5s
- Disadvantage
  - Forms chlorite which must be closely monitored
    - MCL = 1.0 mg/L

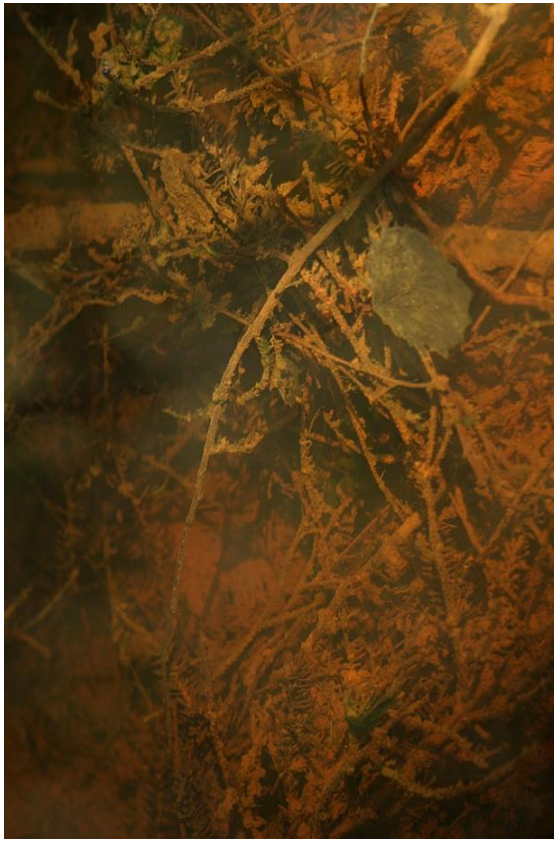
Influencing Factors

- Disinfectant
- NOM
- Contact time
- Temperature
- pH
- Bromide



NOM

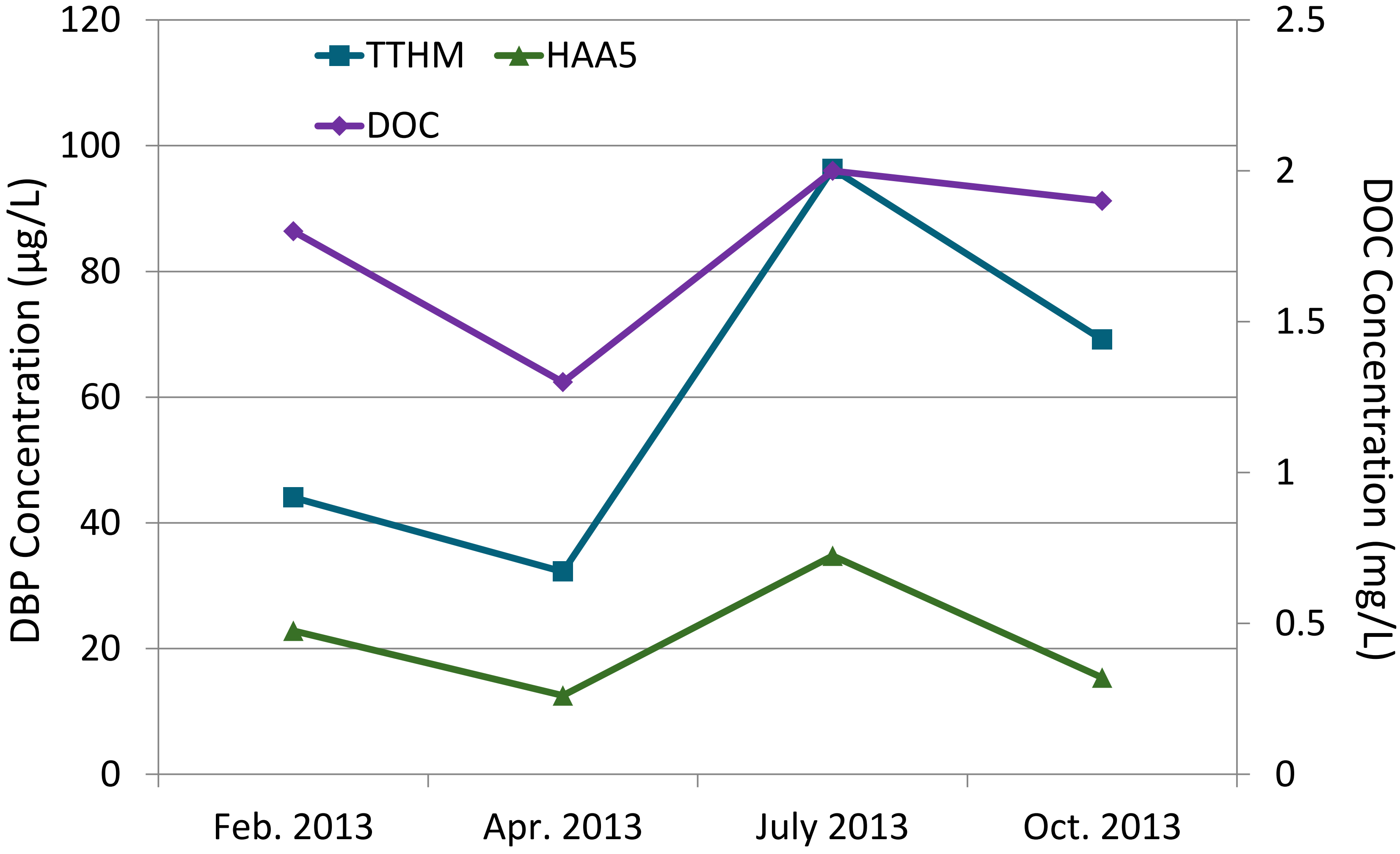
- Organic matter naturally in the water from decaying vegetation
- Both the amount and quality of NOM can impact DBP formation
  - Amount indicated by TOC or DOC
  - Quality indicated by UV_{254} or SUVA



NOM Quantity

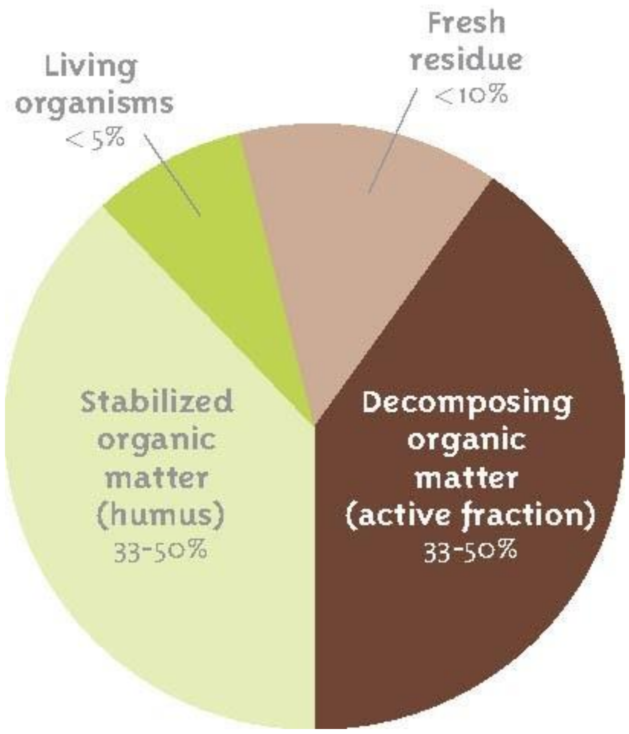
- High quantities of NOM (DOC > 5mg/L) lead to an higher THM and HAA5 formation
  - More fuel for the reaction
  - Increases the Cl_2 demand of water, requiring a higher Cl_2 dosage
- NOM quantity varies seasonally
  - Increases in spring due to increased runoff from snow melt and heavy rains
  - More vegetation and algae present in surface waters in summer

NOM Quantity

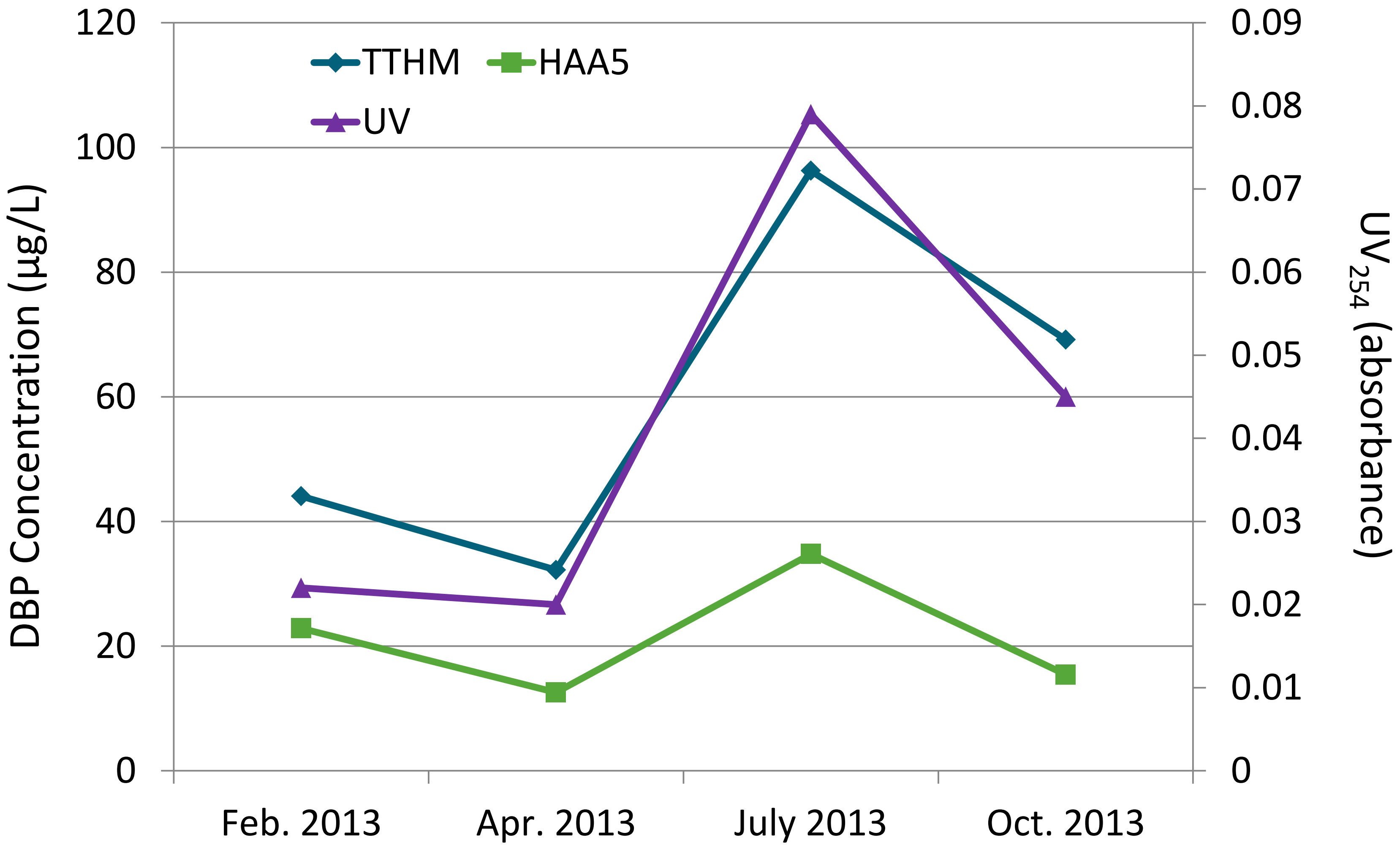


NOM Quality

- Quality depends on vegetation in watershed and species of algae in water
- NOM with higher aromatic content tend to form more DBPs
  - Higher UV_{254}
  - Higher soluble humic material



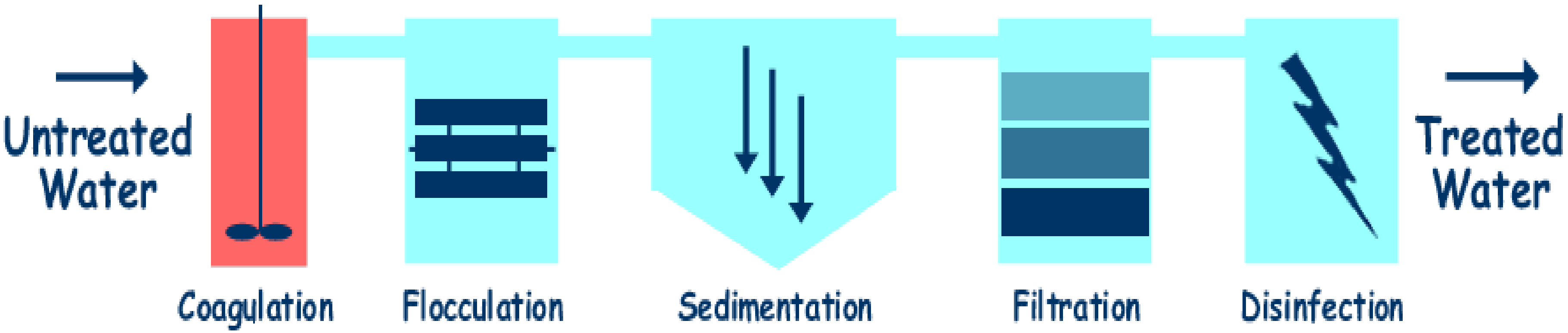
NOM Quality



TTHM
HAA5
UV
DBP Concentration (µg/L)
UV254 (absorbance)
120
100
80
60
40
20
0
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Feb. 2013
Apr. 2013
July 2013
Oct. 2013

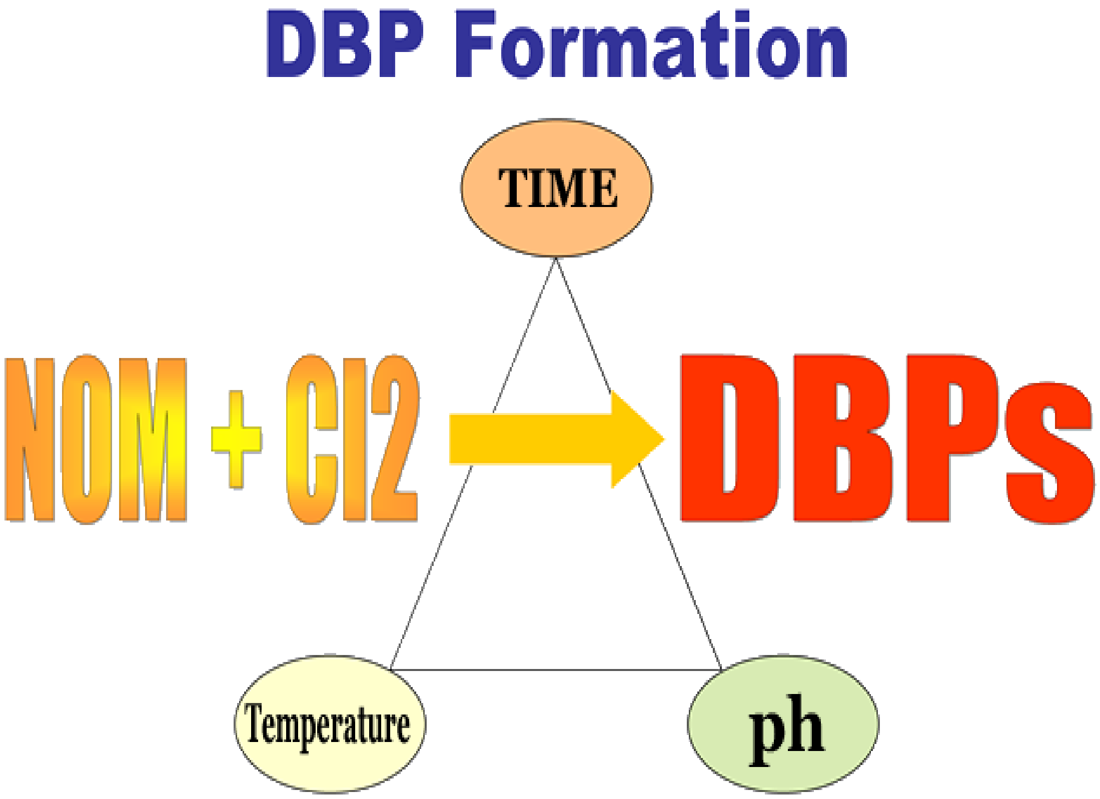
NOM

- Both quantity and quality of NOM can be reduced prior to chlorination
  - Alum coagulation
  - Ozonation
  - Lime softening
  - Ultrafiltration



Influencing Factors

- Disinfectant
- NOM
- Contact time
- Temperature
- pH
- Bromide

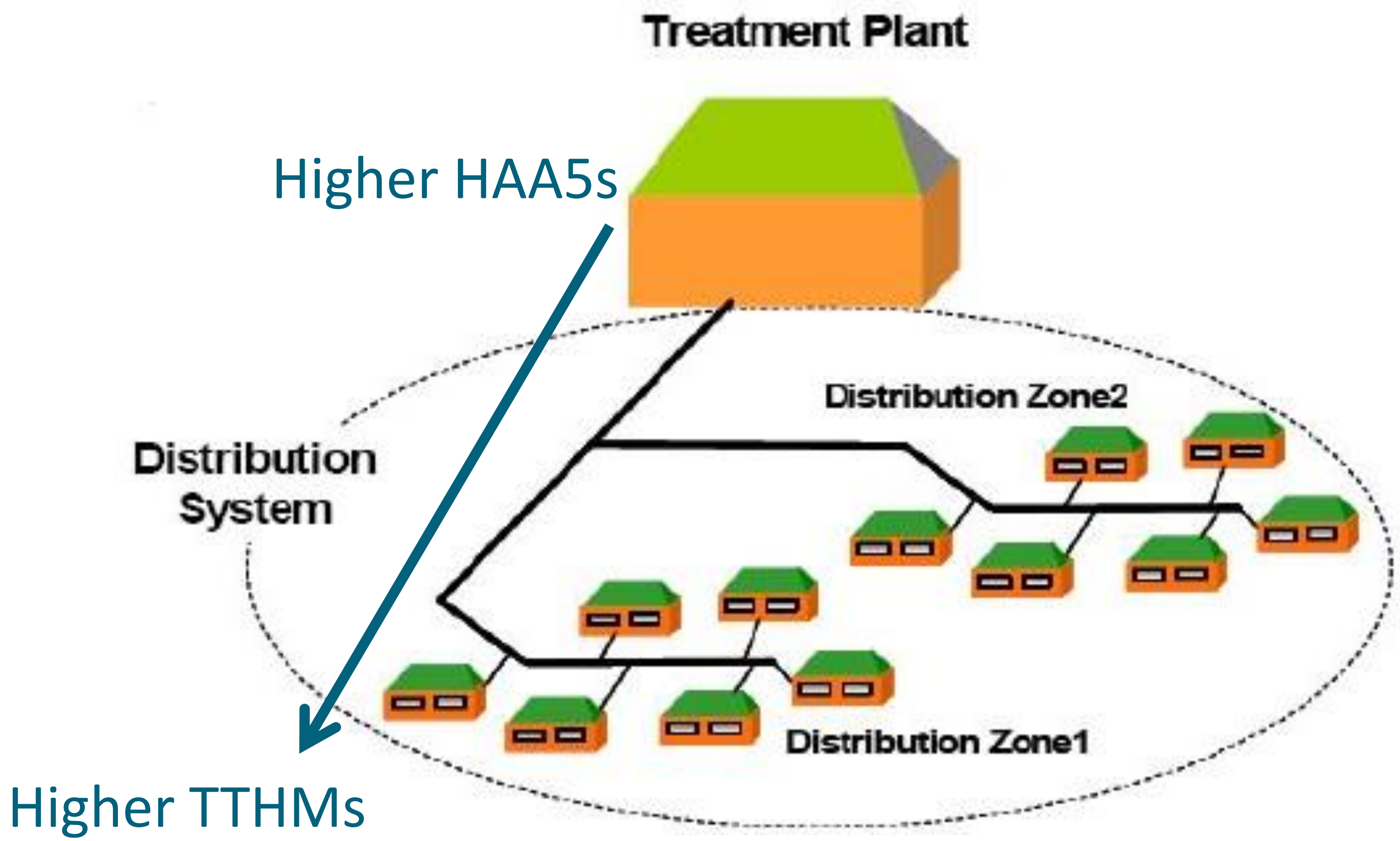


Contact Time

- Free Cl_2 and Br_2 react with NOM within minutes of disinfection
- DBPs form rapidly and then stabilize as Cl_2 is depleted
  - 41% of THM formation occurs within the first 4 hours
  - Within 5 days, 90% THM formation is complete

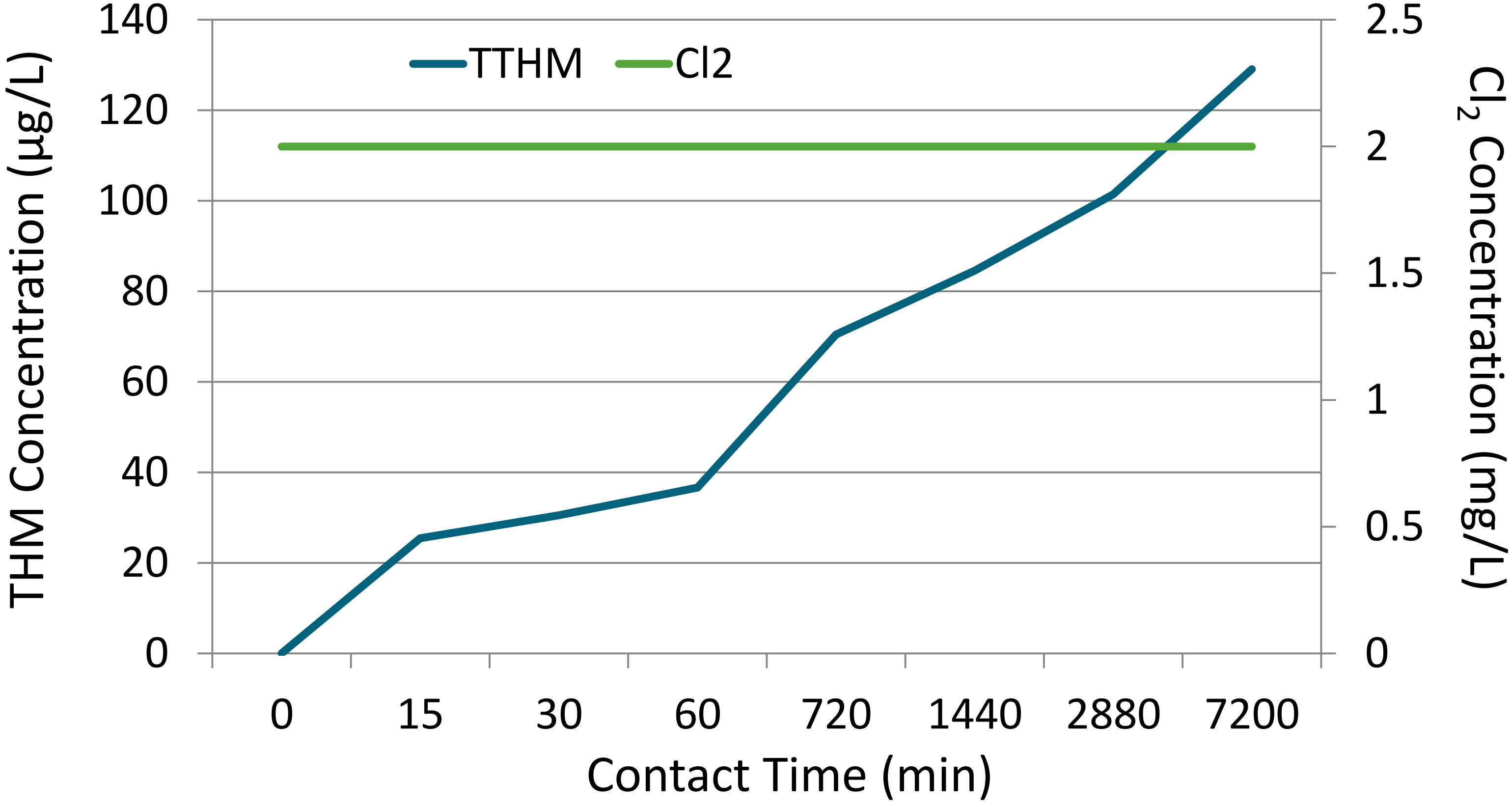
Contact Time

- HAA5s generally form faster than THMs



Contact Time

- DBPs will continue to form as long as residual free Cl_2 and NOM are present in the water

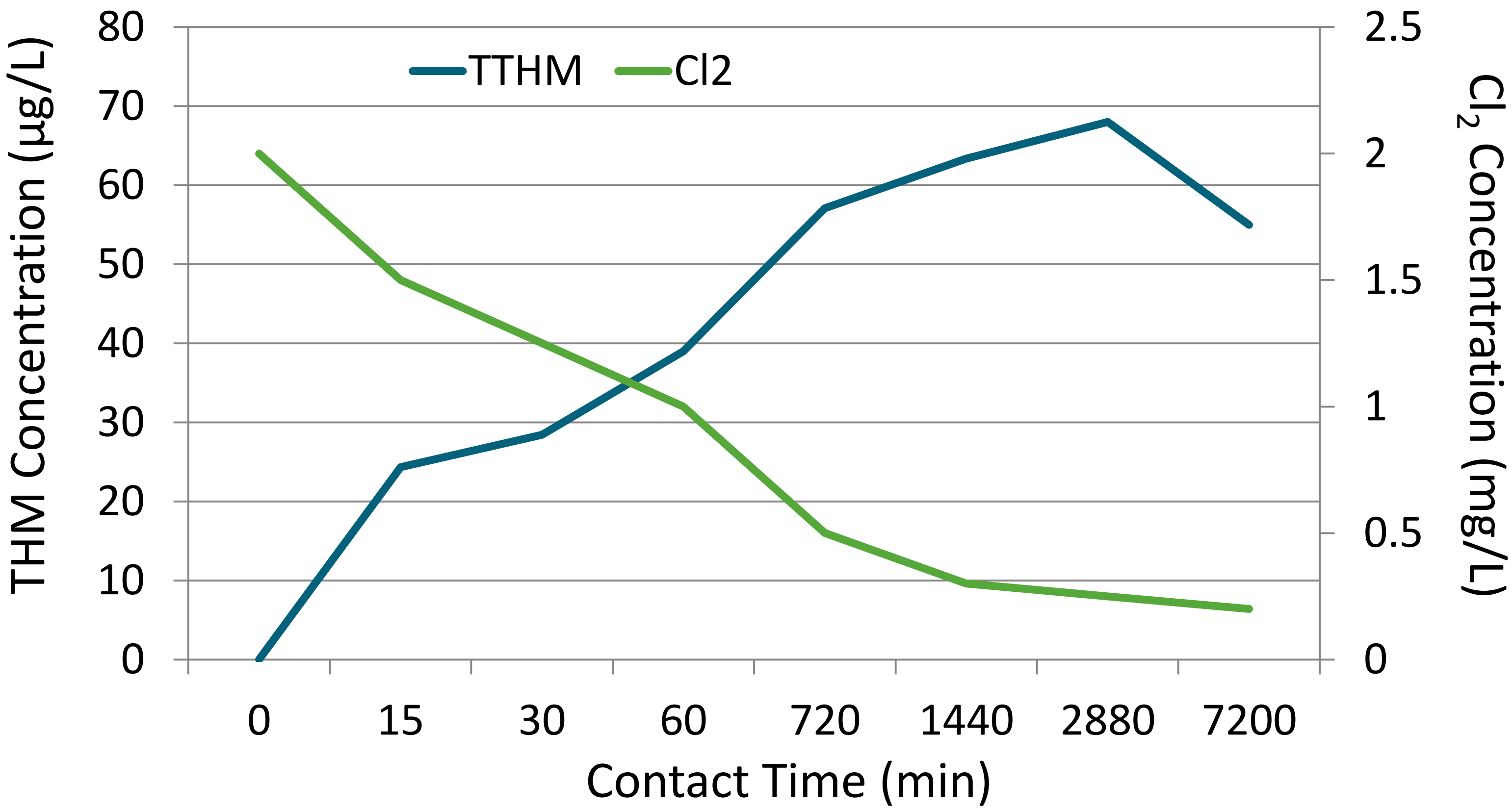


Contact Time

- If residual Cl_2 levels are low, DBPs can decrease over time
  - Below 0.3 mg/L Cl_2, HAA5s will begin to biodegrade
  - THMs can begin to volatilize

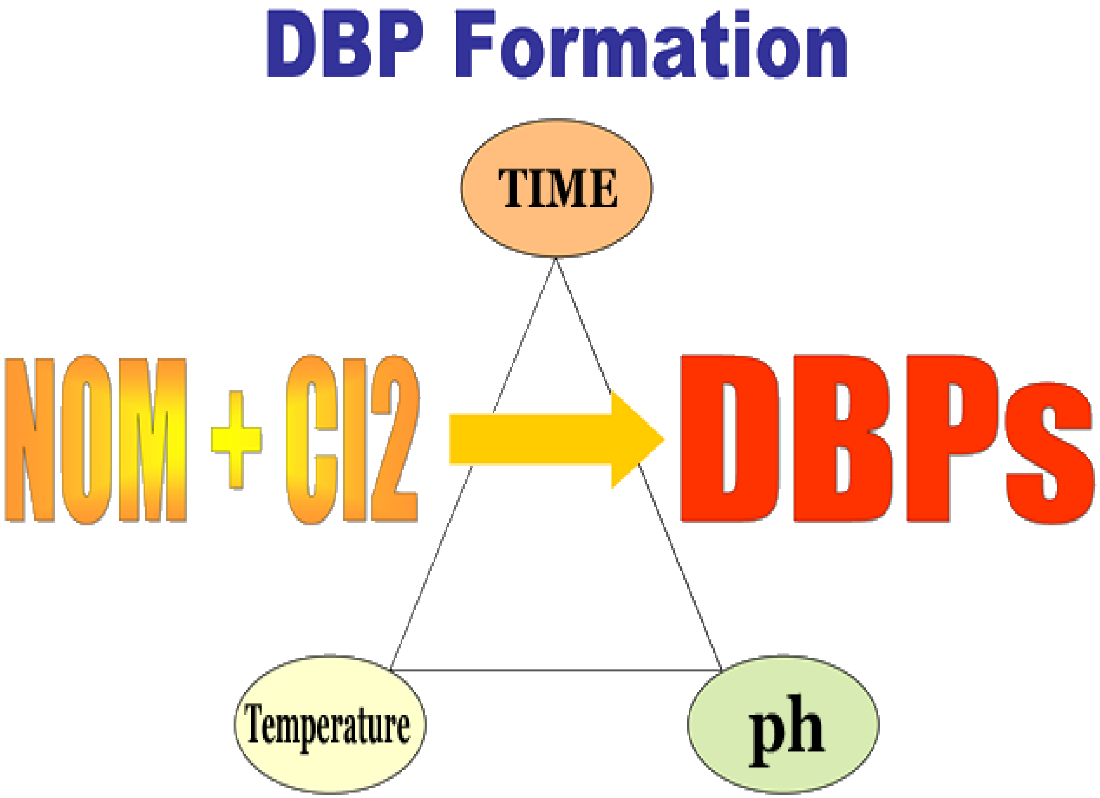
Contact Time

- DBPs will continue to form as long as residual free Cl_2 and NOM are present in the water



Influencing Factors

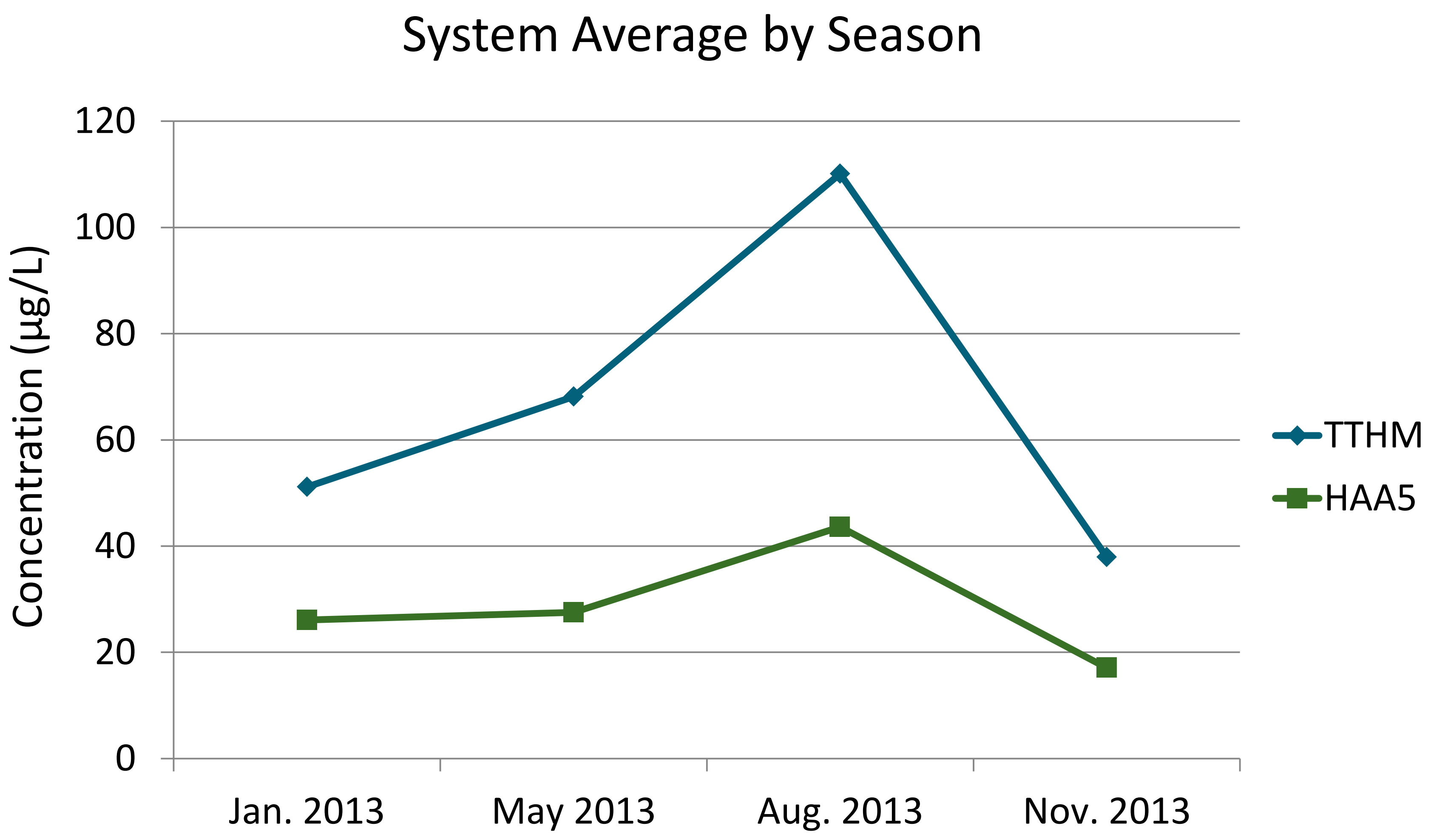
- Disinfectant
- NOM
- Contact time
- Temperature
- pH
- Bromide



Temperature

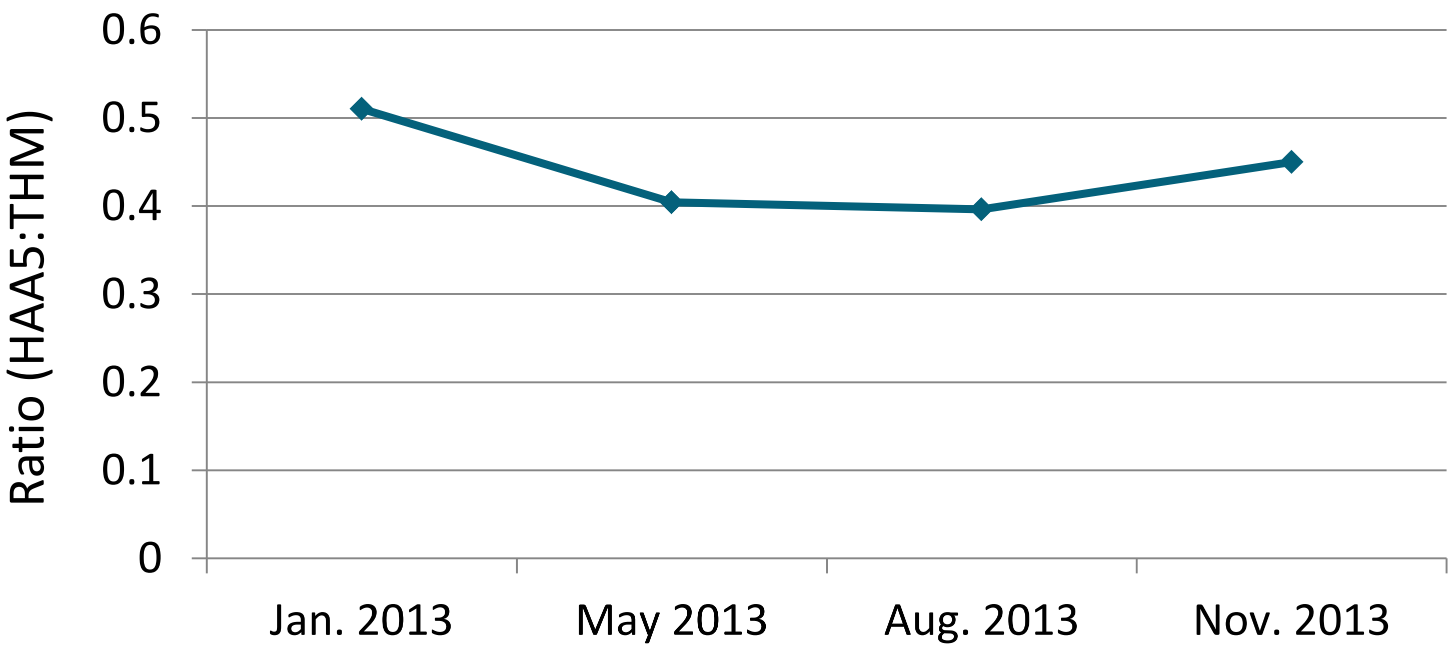
- As temperature increases, formation of DBPs increases
  - At 25°C, THM concentrations are twice the amount as at 10°C for a 24 hour contact time
  - THM and HAA5 concentrations generally higher in warm summer months
- More chlorine is consumed therefore a higher dosage is needed to achieve disinfection

Temperature



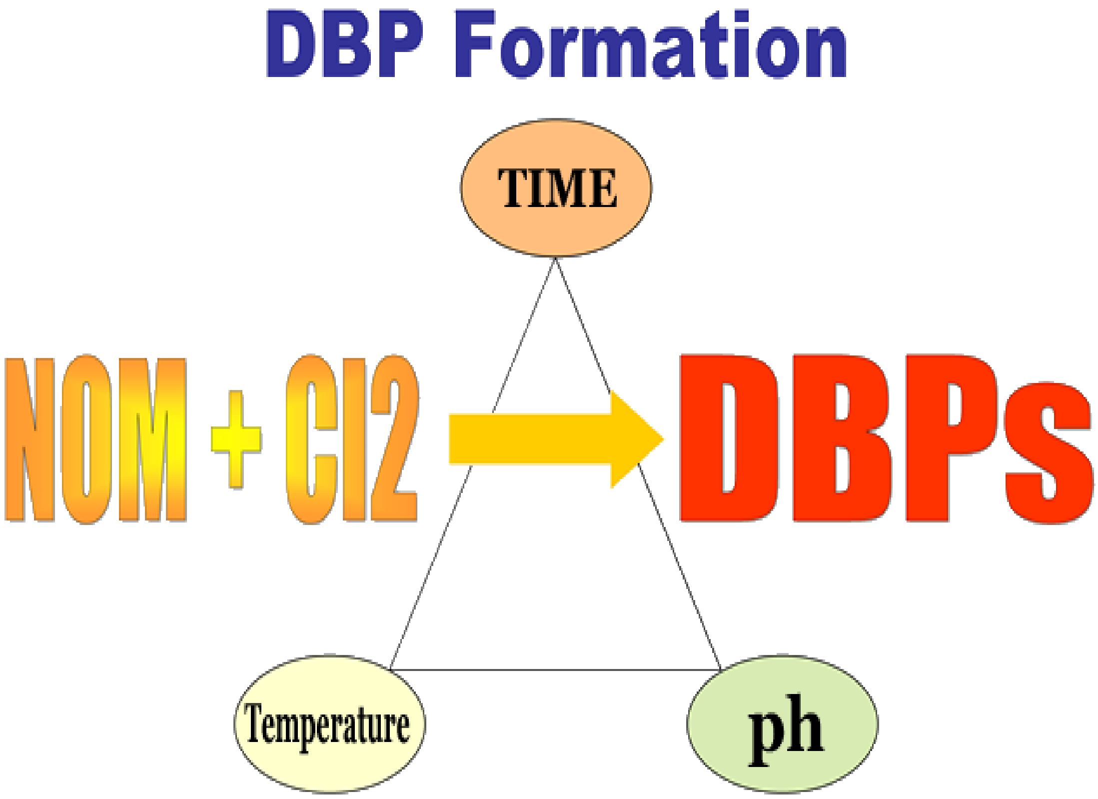
Temperature

- HAA5s are less sensitive to temperature changes than THMs
  - May see a higher ratio of HAA5s compared to THMs in colder months



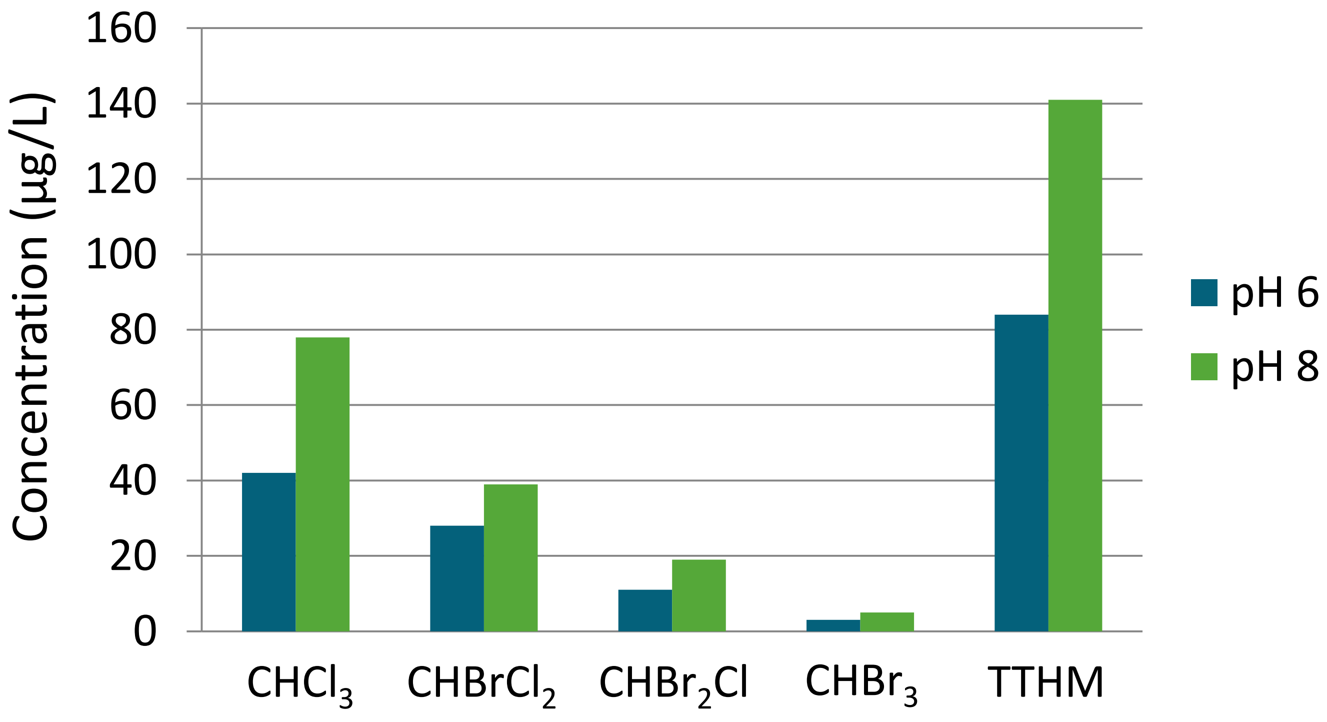
Influencing Factors

- Disinfectant
- NOM
- Contact time
- Temperature
- pH
- Bromide



pH

- Effect of pH dependant on type of DBP
  - Increasing pH increases THM formation
    - A 20-40% increase in TTHMs from pH 7 to 10

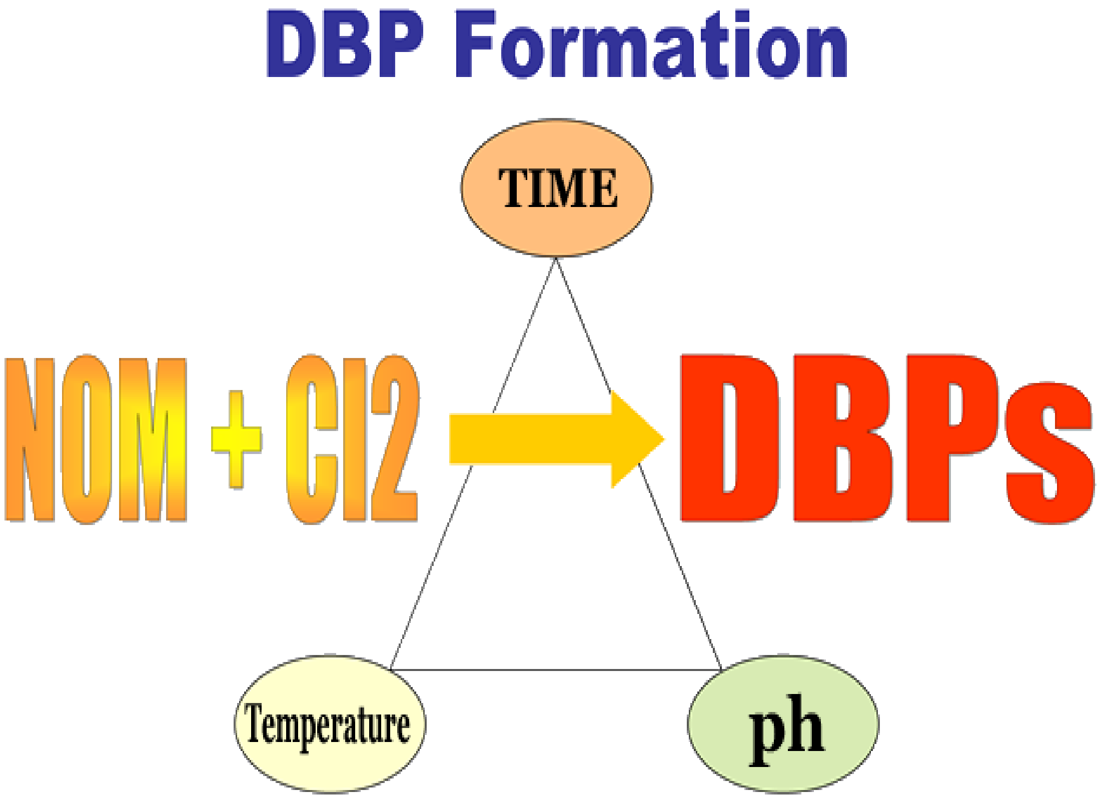


pH

- HAA5 formation less predictable
  - Different HAAs react differently to pH changes
    - As pH increases between pH 6 and 8, some HAA concentrations remain the same, slightly increase or decrease
  - Above pH 8, HAA5s generally decrease as pH increases
    - Most HAA5s biodegrade above pH 8

Influencing Factors

- Disinfectant
- NOM
- Contact time
- Temperature
- pH
- Bromide



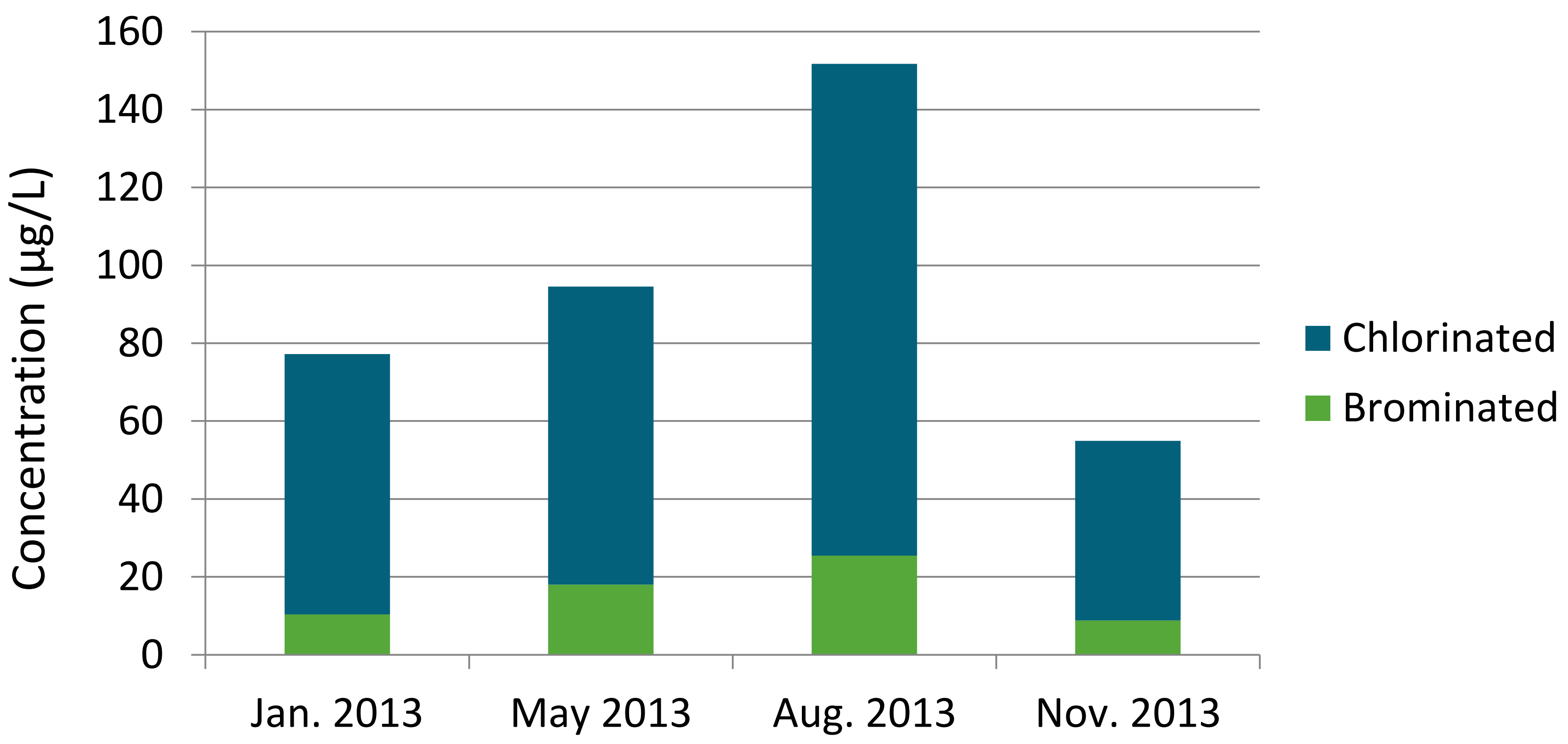
Bromide

- Chlorine oxidizes bromide to bromine
  - Bromine combines with NOM to form brominated DBPs

Brominated DBPs	**Chlorinated DBPs**
Bromoform ($CHBr_3$)	Chloroform ($CHCl_3$)
Dibromochloromethane ($CHBr_2Cl$)	Monochloroacetic acid ($ClCH_2COOH$)
Bromodichloromethane ($CHBrCl_2$)	Dichloroacetic acid ($Cl_2CHCOOH$)
Dibromoacetic acid ($Br_2CHCOOH$)	Trichloroacetic acid (Cl_3CCOOH)
Monobromoacetic acid ($BrCH_2COOH$)	

Bromide

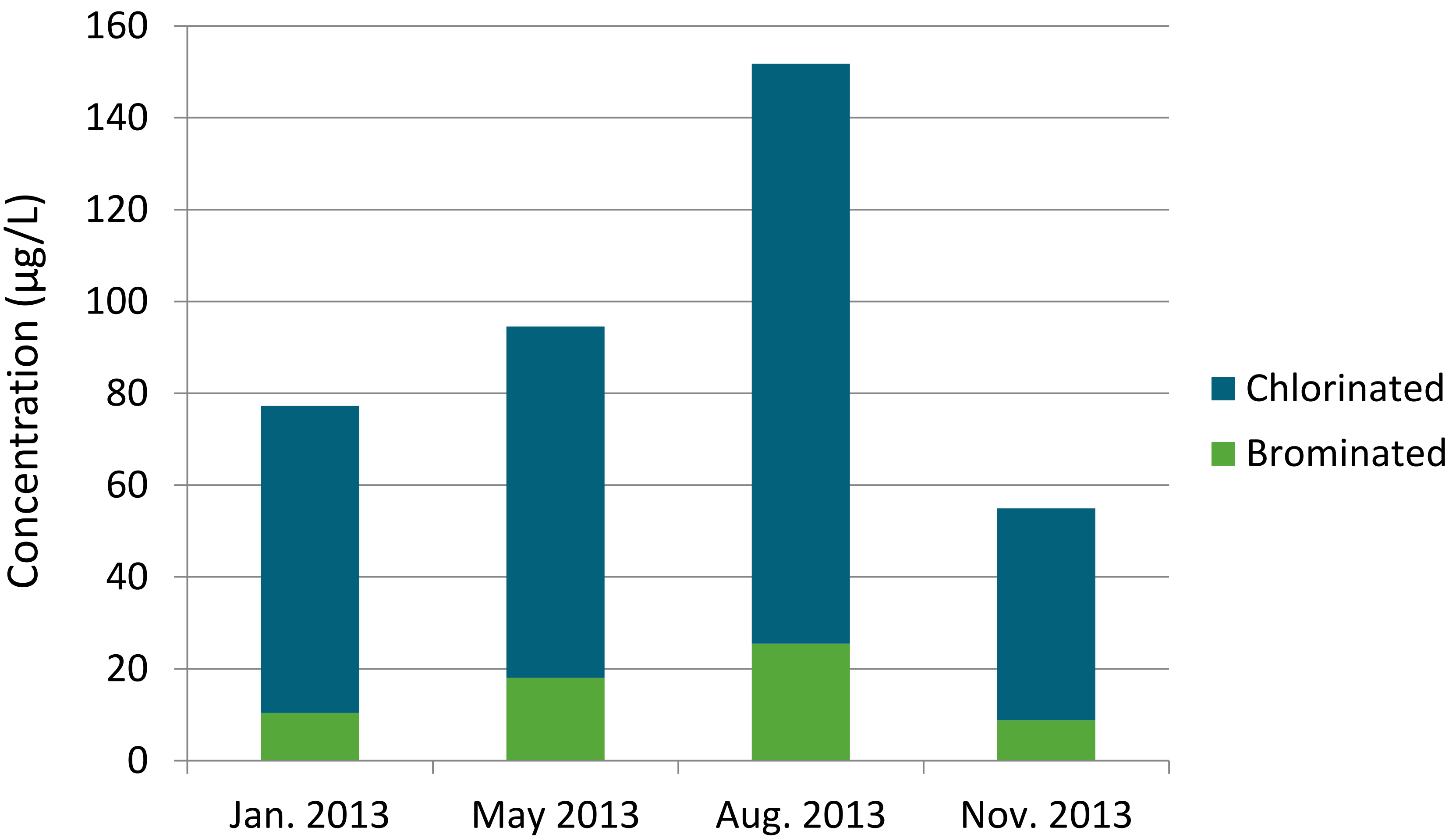
- Bromide concentrations generally low in surface and ground waters (<0.5 mg/L)



Bromide

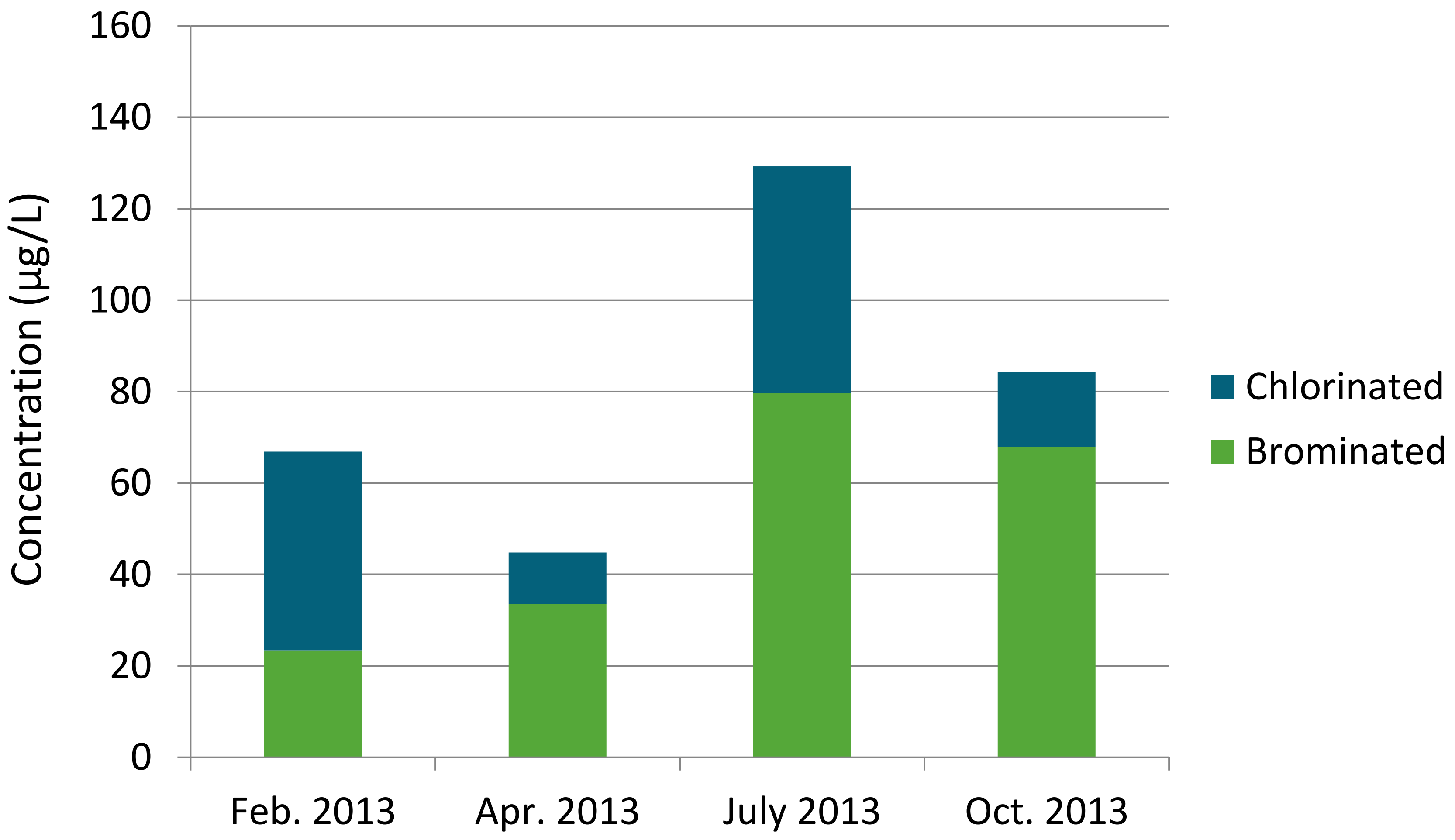
- An increase in bromide concentration does not necessarily cause an increase in total THM and HAA5 concentrations
- It does increase the ratio of brominated to chlorinated DBPs

Bromide



Concentration (μg/L)
160
140
120
100
80
60
40
20
0
Jan. 2013
May 2013
Aug. 2013
Nov. 2013
Chlorinated
Brominated

Bromide



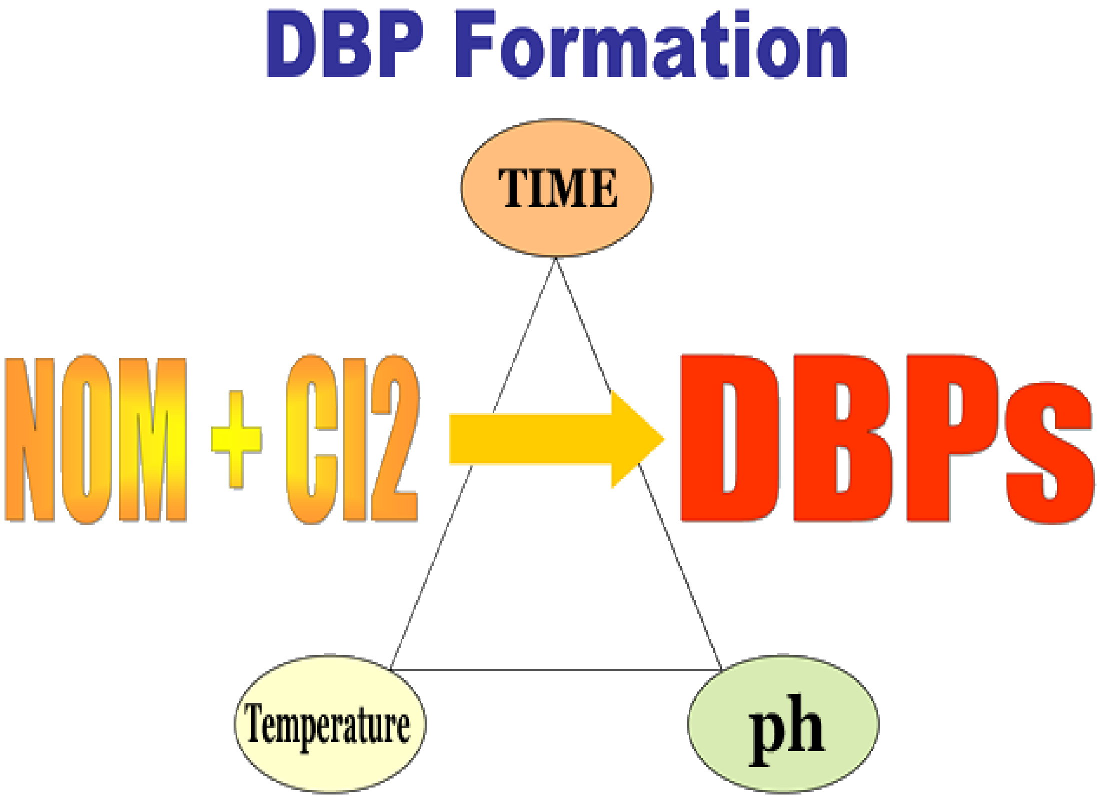
Concentration (µg/L)
160
140
120
100
80
60
40
20
0
Feb. 2013
Apr. 2013
July 2013
Oct. 2013
Chlorinated
Brominated

Bromide

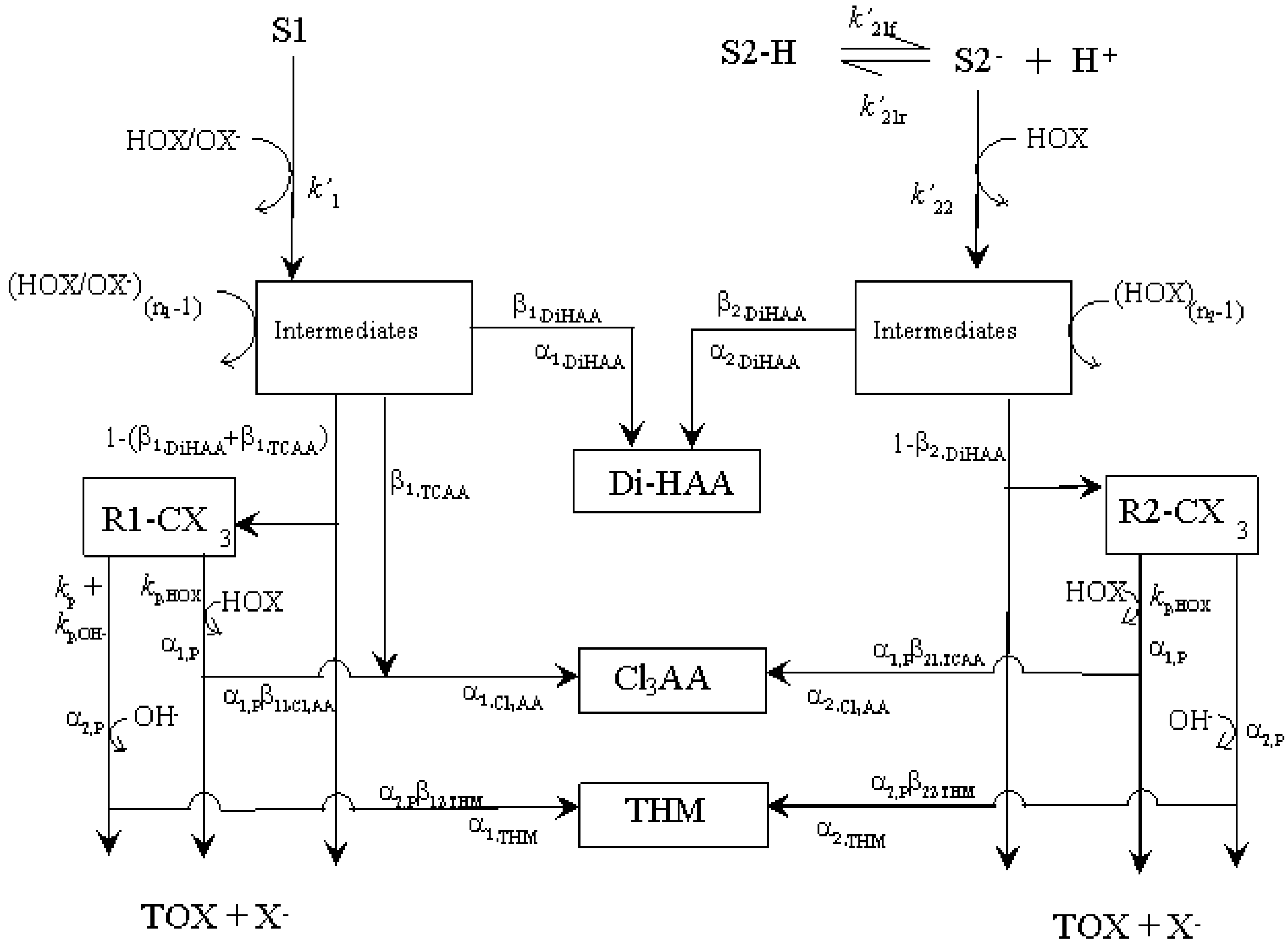
- Brominated DBP concentrations may spike in winter
  – Runoff from roadways de-iced with rock salt
- Speculation about high bromide concentrations in flowback waters from hydraulic fracturing
  – Elevated DBPs in drinking water along Allegheny River may be linked to increased bromide discharge from WWTP receiving flowback wastes

Application

- Disinfectant
- NOM
- Contact time
- Temperature
- pH
- Bromide



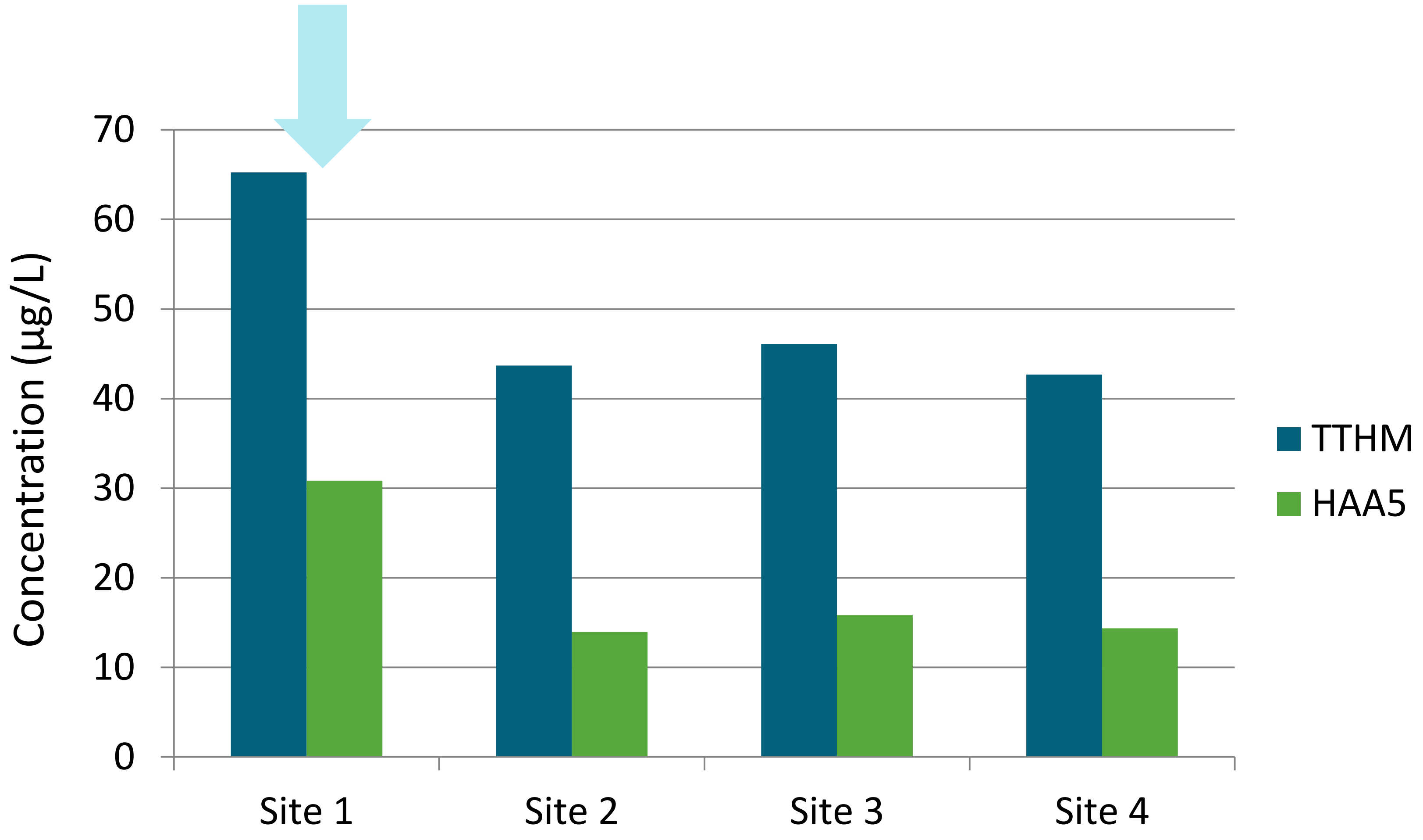
Application



Application

- Understanding relationships between water conditions and DBP formation can be used to:
  - **Understand THM and HAA5 results and patterns**

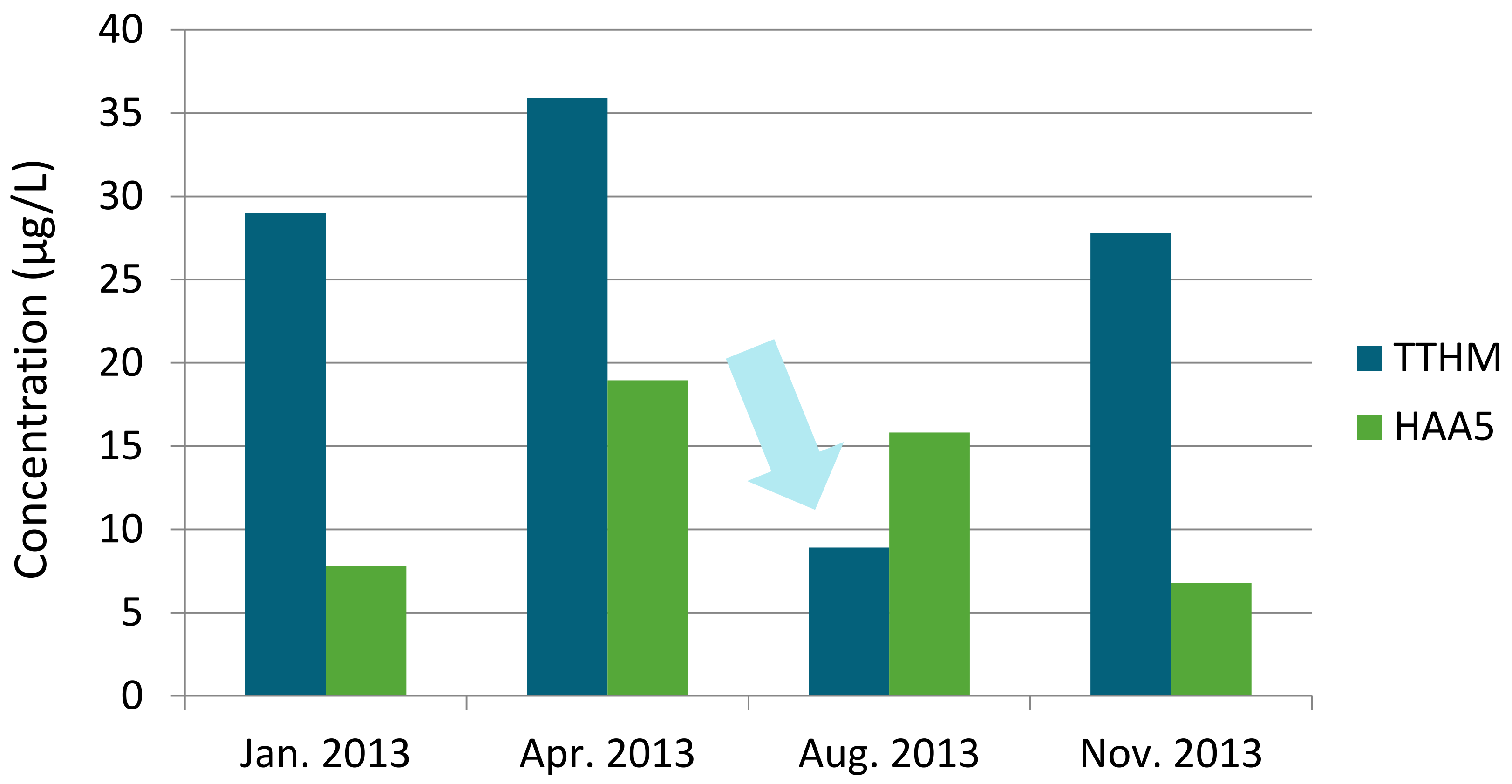
Spatial Variation



Application

- Understanding relationships between water conditions and DBP formation can be used to:
  - Understand THM and HAA5 results and patterns
  - **Detect if problems are present in the system**

Data Error



40
35
30
25
20
15
10
5
0
Concentration (µg/L)
Jan. 2013
Apr. 2013
Aug. 2013
Nov. 2013
TTHM
HAA5

Application

- Understanding relationships between water conditions and DBP formation can be used to:
  - Understand THM and HAA5 results and patterns
  - Detect if problems are present in the system
  - **Design or modify disinfection processes**
    - **Selecting appropriate disinfectants**
    - **Selecting appropriate disinfectant doses**
    - **Implementing appropriate pre-chlorination treatment methods**

Questions?