Draft RoC Monograph on Haloacetic Acids Found as Water Disinfection By-Products

Properties & Exposure

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Background

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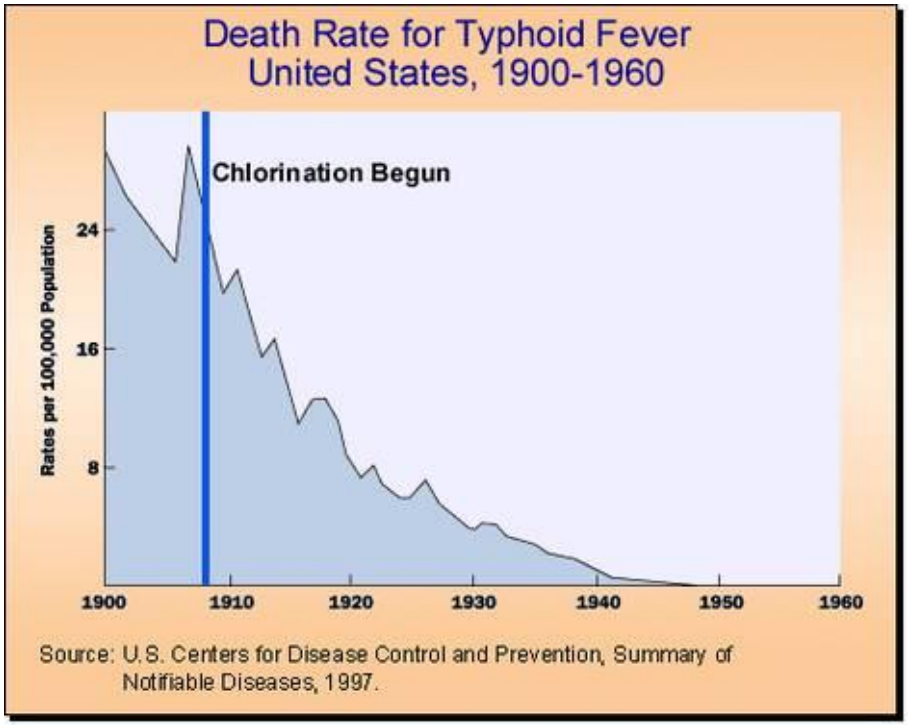
Physical-Chemical Properties

Water Disinfection: Background

Water disinfection provides great public health benefits

- Water treatment removes contaminants and disease-causing agents from drinking water
- Water disinfection has substantially reduced waterborne pathogens and incidences of disease for-
  - cholera (~90%)
  - typhoid (~80%)
  - amoebic dysentery (~50%)



Water Disinfection: Background

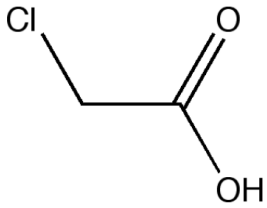
Water disinfection produces many different chemicals with potential toxic effects

- More than 500 disinfection by-products (DBPs) have been identified but even more remain unidentified
- The major classes (on a weight basis) include
  - Trihalomethanes (THMs)
  - Haloacetic acids (HAAs)
- U.S. EPA regulates the following groups of DBPs to protect public health
  - 4 Trihalomethanes (80 µg/L)
  - 5 Haloacetic acids (60 µg/L)
  - Bromate (10 µg/L)
  - Chlorite (1000 µg/L)

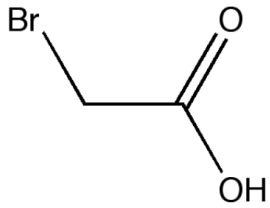
13 Haloacetic acids that vary by number and type of halogens have been identified in disinfected water

Mono-haloacetic acids

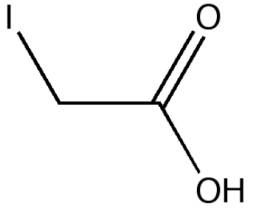
MCA



MBA



MIA



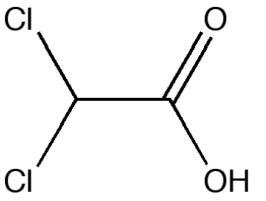
Cl = chlorine

B = bromine

I = iodine

Di-haloacetic acids

DCA



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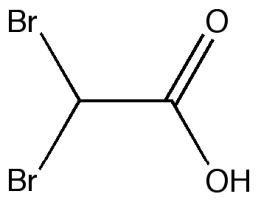
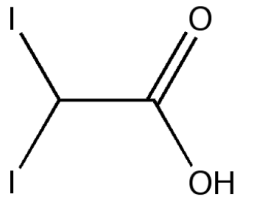
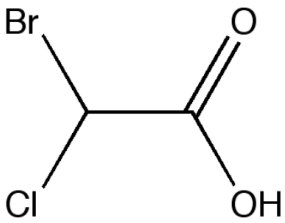


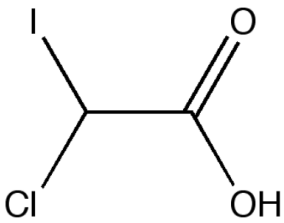
DIA



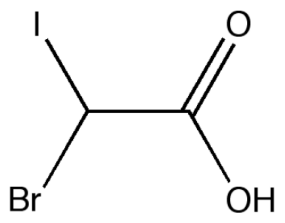
BCA



ClA



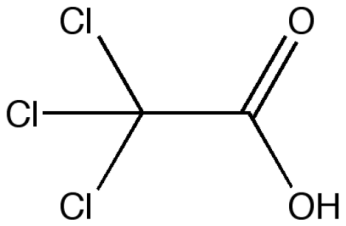
BIA



HAA5 components are shown in blue

Tri-haloacetic acids

TCA



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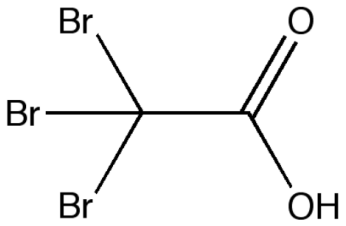
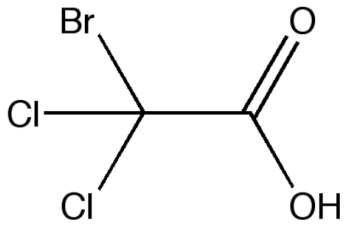


BDCA



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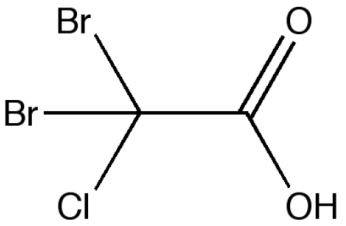

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Mono-haloacetic acids

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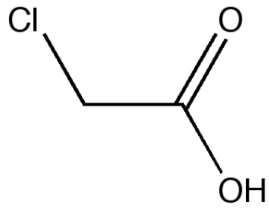

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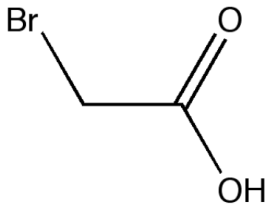

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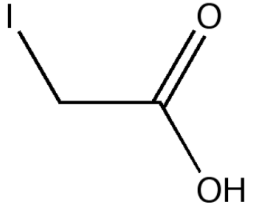

Cl = chlorine

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Di-haloacetic acids

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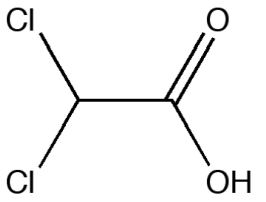

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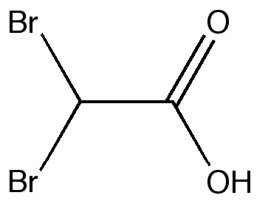
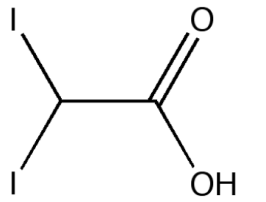


DIA



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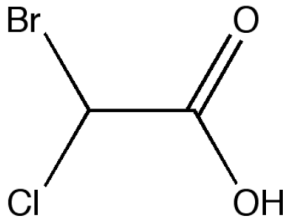
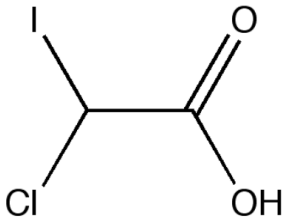
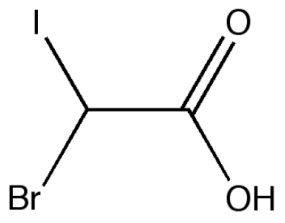


CIA



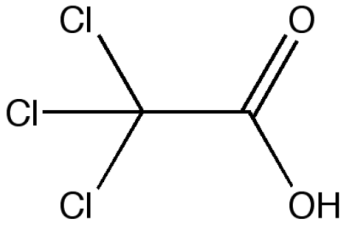
BIA



Additional compounds that make up HAA9 are shown in red

Tri-haloacetic acids

TCA



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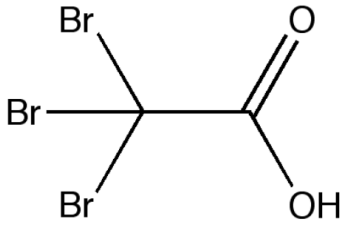

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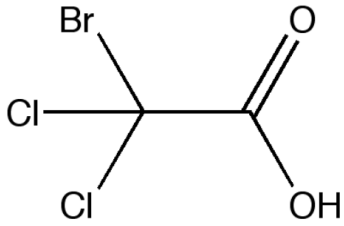

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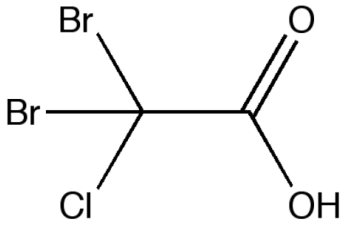
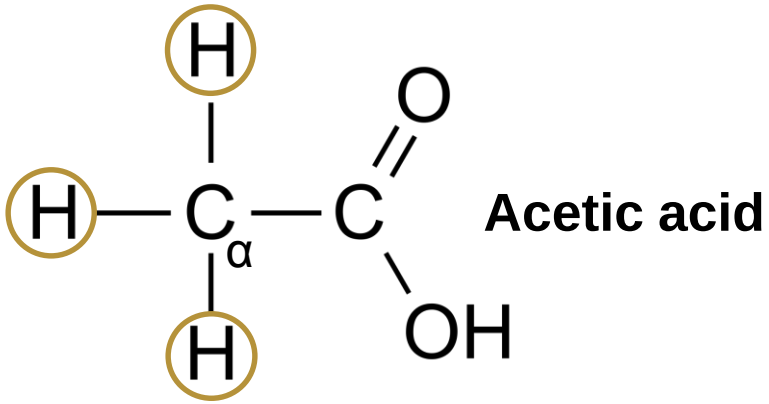


Haloacetic acids (HAAs) & Halogen Chemistry

Halogen atom substitutions to acetic acid determine reactivity of HAAs



Acetic acid

Haloacetic acids include one or more halogen atoms on the alpha carbon

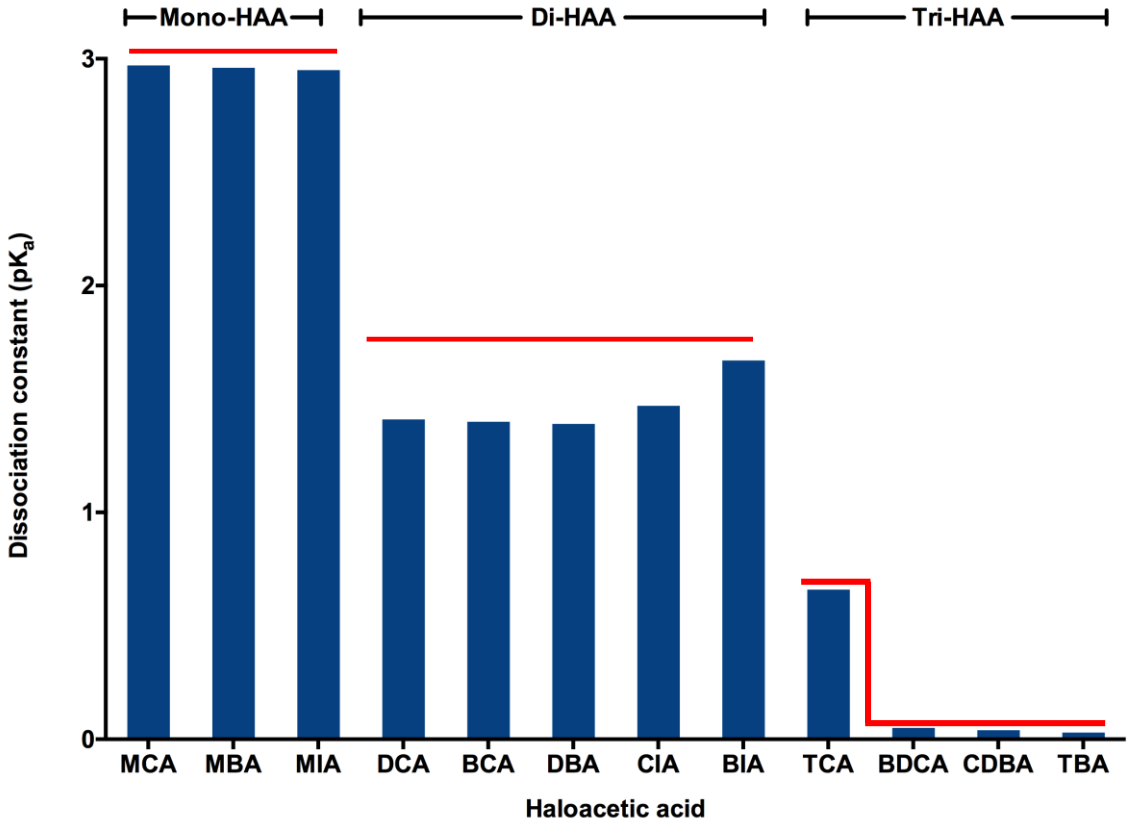
Trends across halogens with increasing atomic weight

- Decrease in power to attract an electron to form a negative ion
- Increase in likelihood to be a leaving group
- Decrease in reactivity

Biological reactivity of HAAs varies with number and type of halogens

- At physiological pH, all HAAs exist primarily in their ionized form
- Two important physical-chemical properties affecting potential toxicity are:
  - **pK_a** (the negative log of the acid dissociation constant), which indicates the strength of the acid form (lower pK_a = stronger acid)
  - **E_{LUMO}** (the energy of the lowest unoccupied molecular orbital), which is a measure of electrophilicity and potential reactivity with other molecules

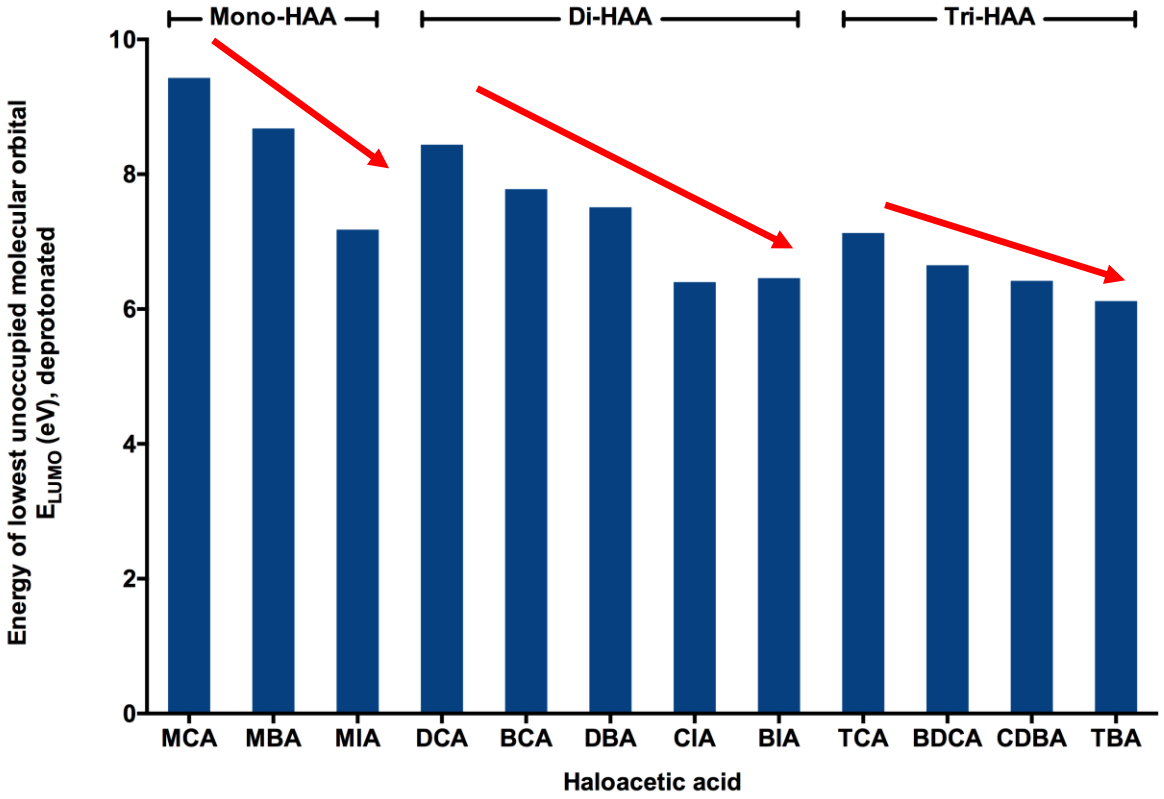
Bioavailability of HAAs* and their transport into cells varies with pK_a



- pK_a decreases markedly with the number of halogens
- pK_a varies less with the type of halogens within the mono-, di-, and tri-HAAs

*Values are shown for 12 HAAs; no value identified for DIA.

Reactivity of HAAs* may vary with E_{LUMO}



- E_{LUMO} decreases with the number of halogens, (e.g. MCA, DCA, TCA)
- E_{LUMO} also decreases with addition of less electrophilic halogens within the mono-, di-, and tri-HAAs

*Values are shown for 12 HAAs; no value was identified for DIA.

Exposure

Potential Sources of Exposure

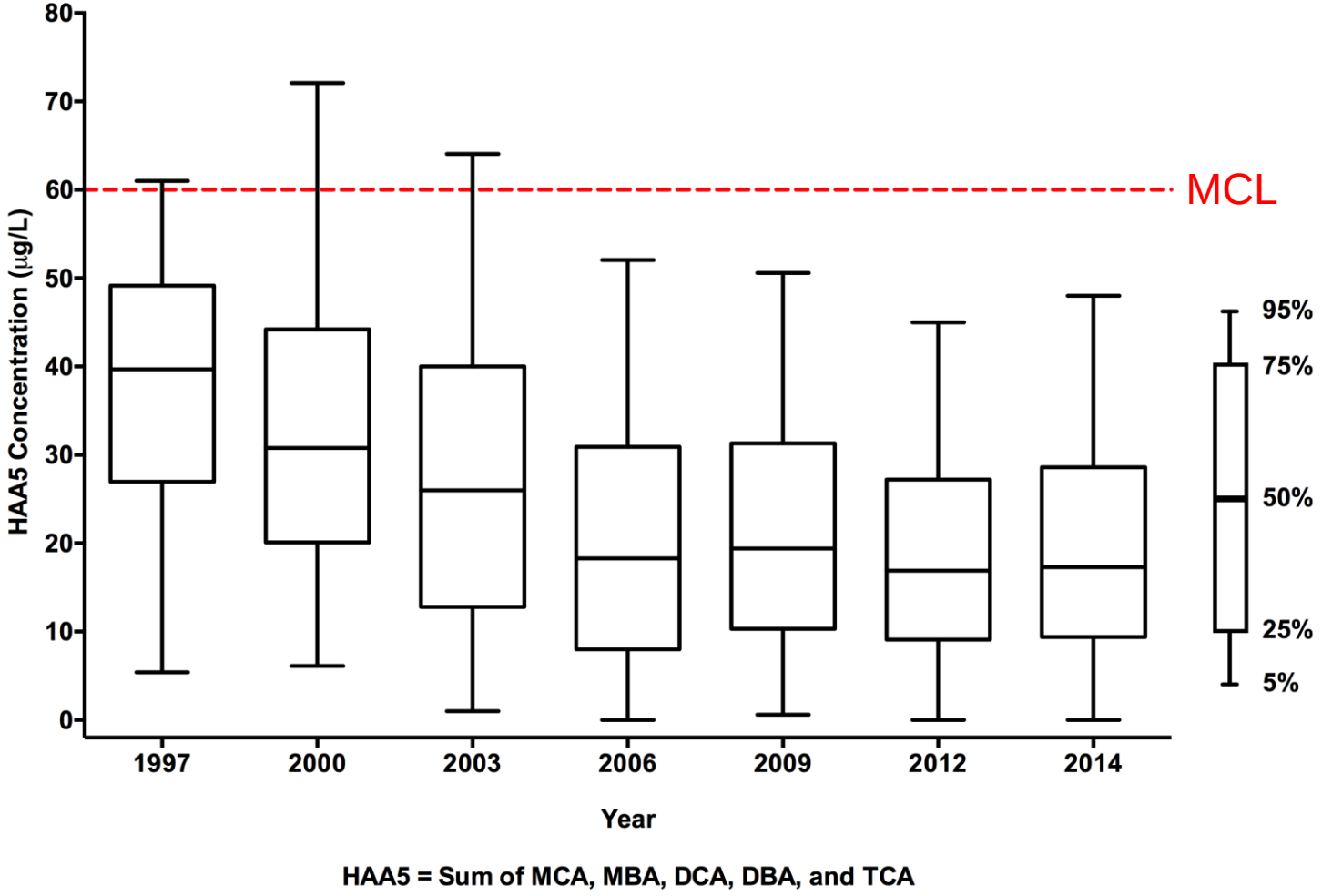
Drinking water is the primary source of exposure to HAAs

Potential Exposure in the United States

A significant number of people residing in the United States are exposed to HAAs

- Exposure to HAAs from drinking water is widespread
  - ~250 million people (> 80% of U.S. population) use disinfected water from community drinking water systems subject to EPA regulations
  - Levels of HAA5 range from ~2.0 to 59 µg/L depending on source water and disinfecting chemicals (EPA 2011 data)
  - Remediation methods may help decrease exposure
- People ingest ~ 5.5 to 205 µg of HAAs/day
  - Estimates are based on drinking 2.75 L (women) or 3. 5 L (men) of water a day and using the estimated range for HAA5 in drinking water (EPA 2011 data)

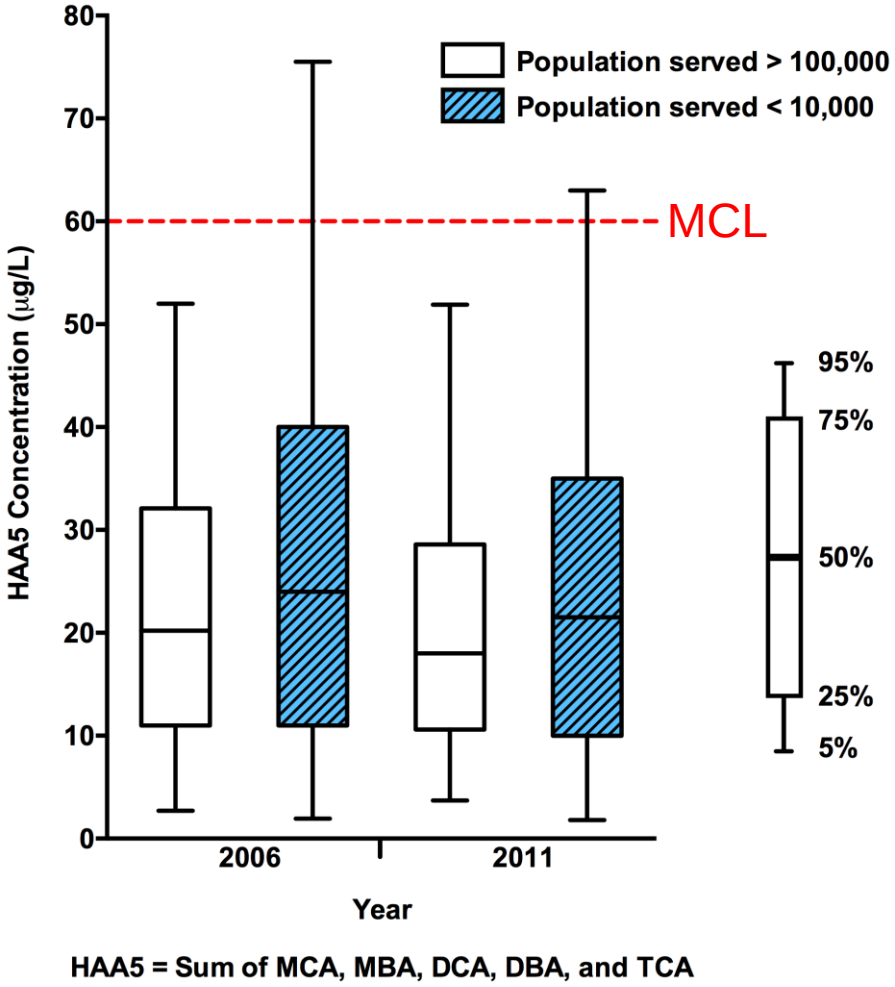
Compliance with EPA's HAA5 maximum contaminant level (MCL) has improved over time



Data from American Water Works Association (AWWA) for facilities serving > 100,000 individuals

HAA5 Levels

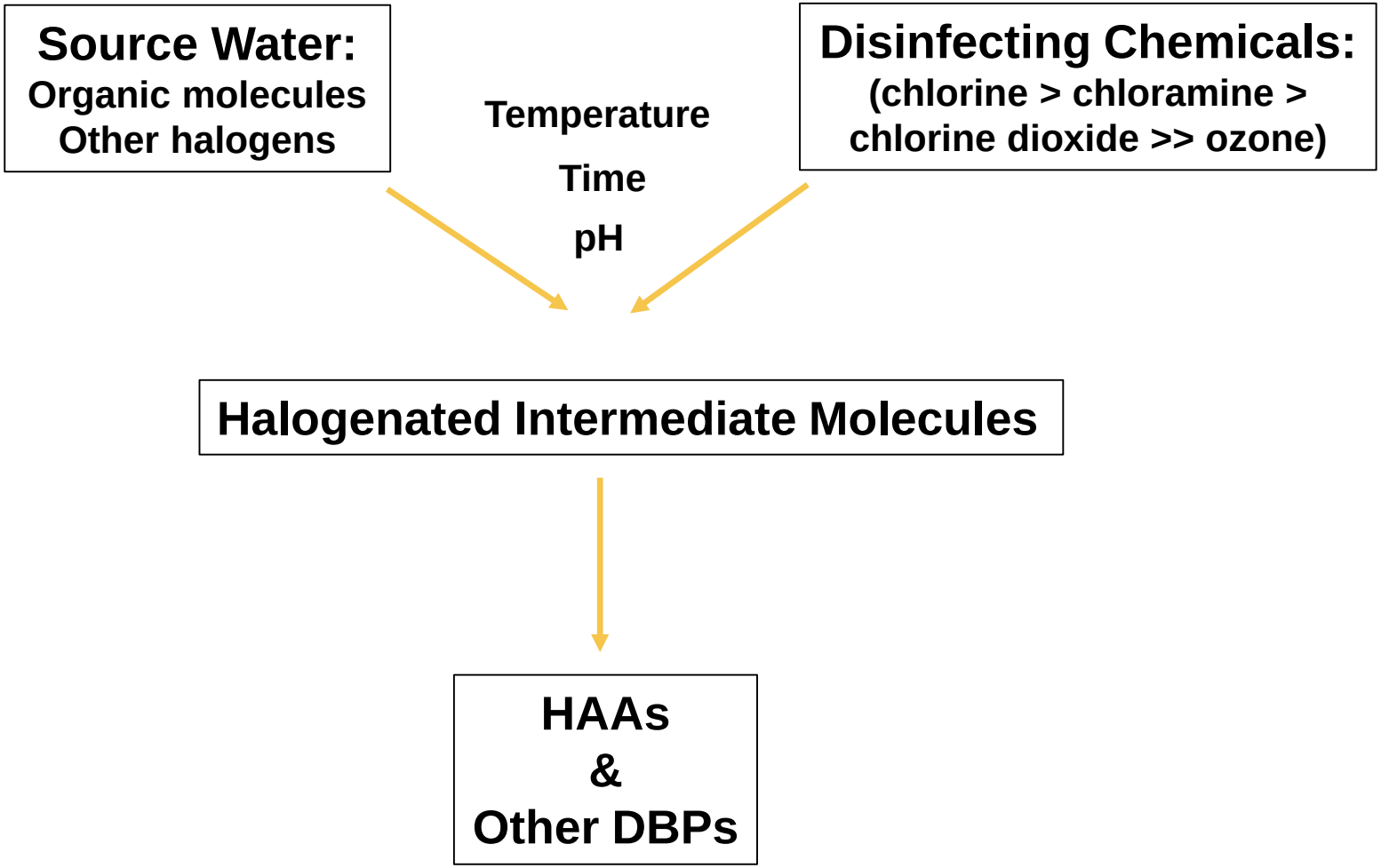
Smaller community water treatment facilities may have more difficulty meeting the HAA5 MCL



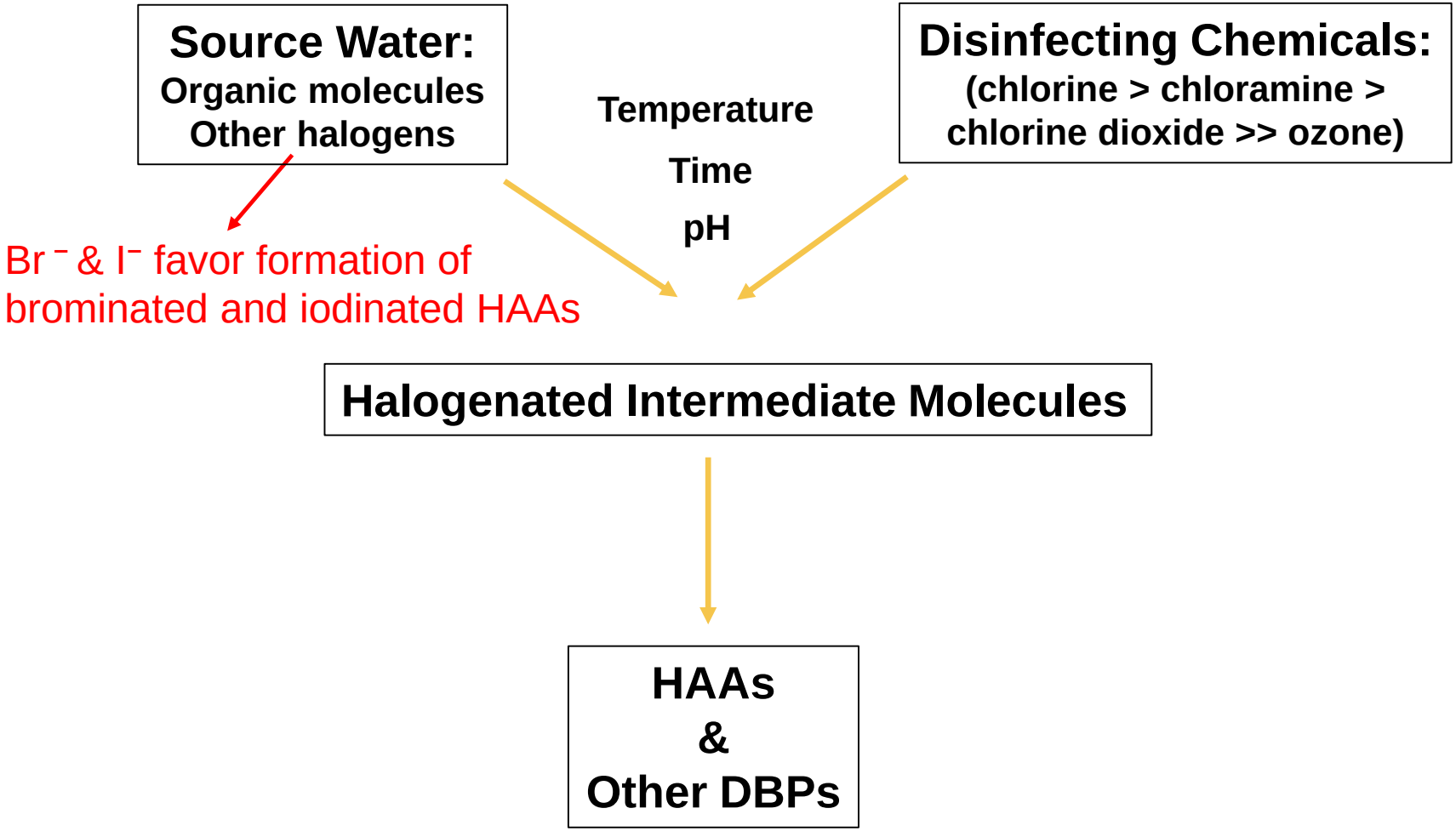
- Larger facilities (> 100,000 served) generally meet the MCL for > 95% of samples
- Smaller facilities (defined by EPA as serving < 10,000 individuals) may have limitations in resources and aging infrastructure and may not always meet the MCL

Data from monitoring for EPA Third Six-Year Review.

Major factors affecting HAA formation

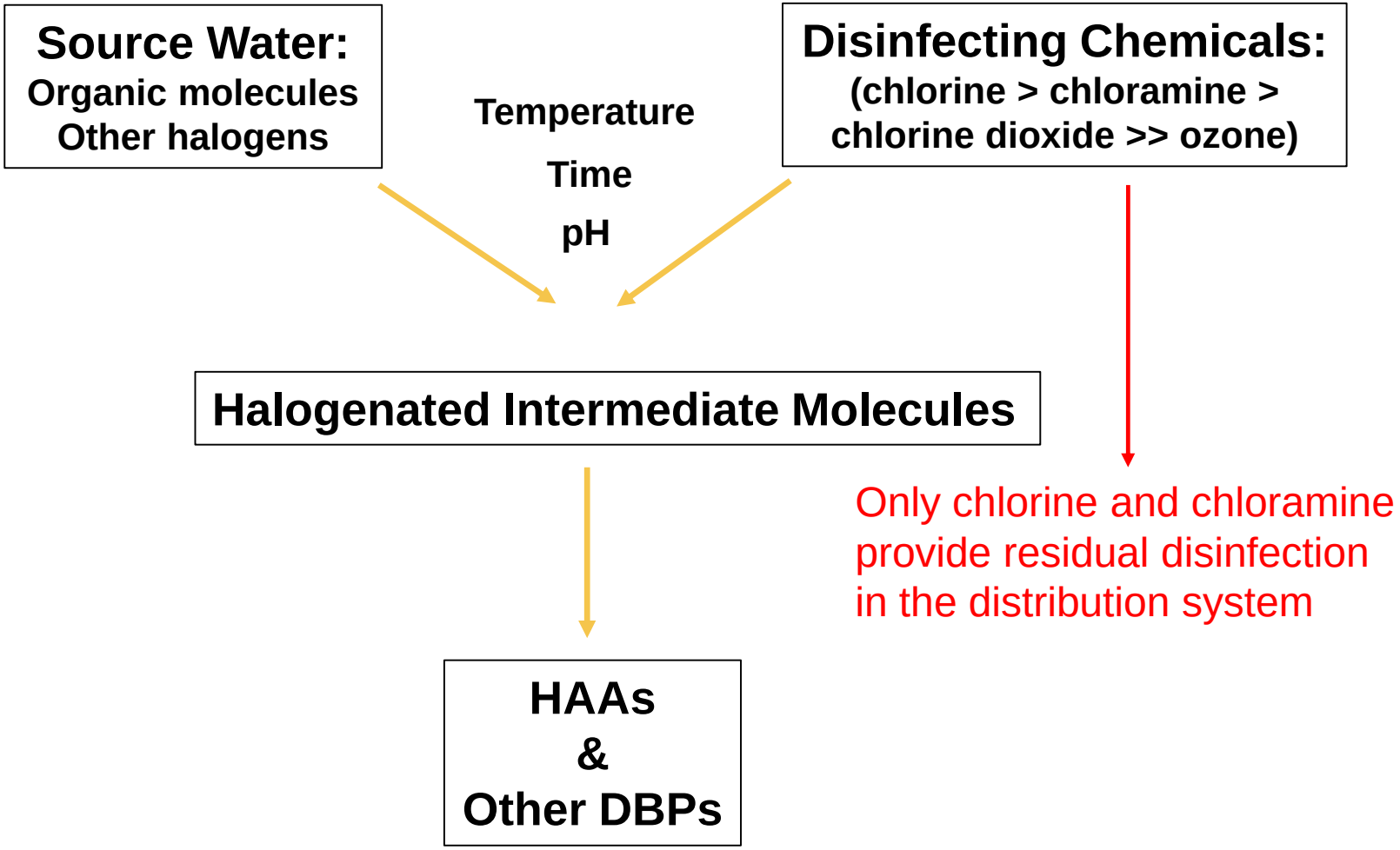


Other halogens can alter formation of HAAs



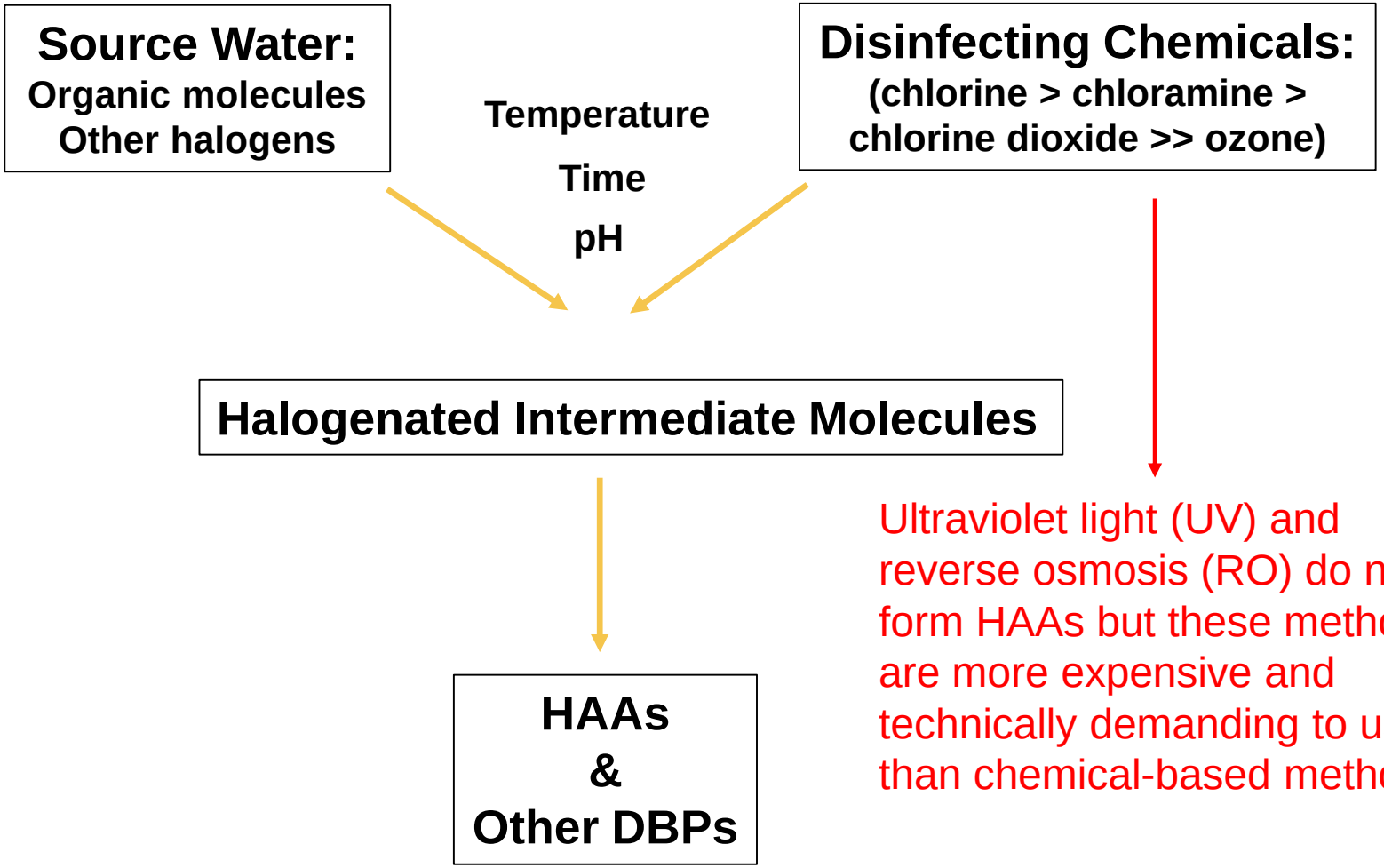
Formation of HAAs

Residual disinfection is an advantage



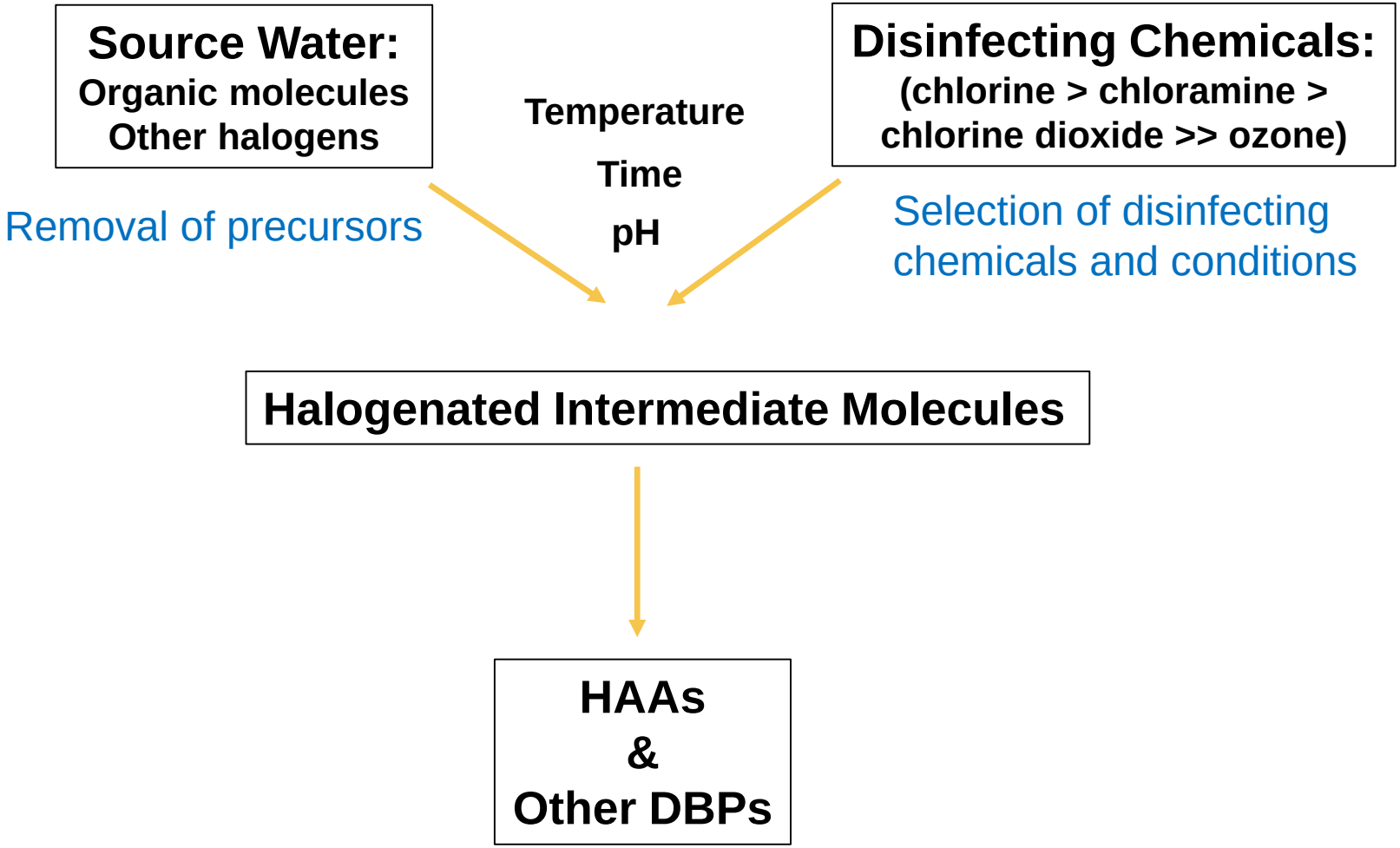
Formation of HAAs

Some methods do not form DBPs



Potential Remediation of HAAs

Methods to reduce HAAs and other DBPs in water



Summary

- Physical-chemical properties of HAAs and their potential reactivity and toxicity vary with number and type of halogen substitutions.

- Exposure to HAAs is widespread in the United States with more than 250 million people provided with disinfected water, which primarily involves use of chlorine-based chemicals that form HAAs.

- Most facilities currently meet the MCL for HAA5, but several strategies exist for remediation of HAAs and other DBPs that might reduce exposure further.

Questions?

Reviewer Questions

- Comment on whether the chemical identity and description of haloacetic acids found as water disinfection by-products (Section 1: Properties) are clear and technically accurate.
- Comment on whether the information on use, production, and human exposure to haloacetic acids found as water disinfection by-products (Section 2: Human Exposure) is clear and technically accurate.
  - Identify any information that should be added or deleted.
- Comment on whether adequate information is presented to document past and/or current human exposure in the United States to haloacetic acids found as water disinfection by-products. Exposure can be inferred by data on usage, production, or evidence for exposure in the workplace, from the environment or consumer products, diet, or medical products.