Today we will discuss:

- Evolution of DBP Regulations
- Recent and Upcoming Regulatory Developments
- DBP Control Measures
Drinking water disinfection is a critical part of public health.

1908: Jersey City, NJ became the first US city to add chlorination to their normal operations.

1929: First use of chloramines in use in the US.
Disinfectants do not just react with pathogens

In 1974, Trihalomethanes (THMs) were the first group of DBPs to be identified.

In 1976, chloroform was classified as a suspected human carcinogen.

Disinfection Byproducts

- Disinfectant
- Organic Matter (DBP Precursors)
- Inorganic Ions
The 1979 Total Trihalomethanes (TTHM) Rule was the first DBP regulation in the US.

Quarterly samples in the drinking water distribution systems.

Compliance based on a running annual average.

Maximum Contaminant Level (MCL) of 100 μg/L.

- Chloroform
- Bromodichloromethane
- Dibromochloromethane
- Bromoform
The regulatory process changed with the 1996 Safe Drinking Water Act Amendments

Every 5 years:

Contaminant Candidate List (CCL) → Unregulated Contaminant Monitoring Rule (UCMR) → Regulatory Determinations on ≥ 5 contaminants → Propose Regulation → Finalize Regulation

Out-of-Cycle regulatory determinations can be made (perchlorate)

Other priority regulations were given their own deadlines in 1996 SDWA Amendments

DBPs were regulated under the Stage 1 and 2 Disinfectants/DBP (D/DBP) Rules

- Maximum Contaminant Levels (MCLs) for DBPs
- Maximum Residual Disinfectant Levels (MRDLs) for Disinfectants
- Monitoring frequency and # of required samples
- Enhanced coagulation requirements for conventional filtration plants
- Required initial distribution system evaluations to identify high DBP locations
- Required systems to determine operational evaluation levels
DBP regulations force utilities to balance public health goals.
DBP Rules have resulted in decreased TTHM concentrations in US drinking water

Water utilities must also balance formation of regulated and unregulated DBPs

Regulated

- 4 Trihalomethanes
- 5 Haloacetic Acids
- Bromate
- Chlorite

> 600 identified

- Halogenated
- Non-halogenated
- Nitrogen-containing DBPs

All DBPs

- Only ~50% of halogenated DBPs have been identified
- The percentage of unidentified N-DBPs is unknown
UCMR 2 included 6 nitrosamines

<table>
<thead>
<tr>
<th>Nitrosamine</th>
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<tbody>
<tr>
<td>N-nitroso-diethylamine (NDEA)</td>
</tr>
<tr>
<td>N-nitroso-dimethylamine (NDMA)</td>
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<tr>
<td>N-nitroso-di-n-butylamine (NDBA)</td>
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<tr>
<td>N-nitroso-di-n-propylamine (NDPA)</td>
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<tr>
<td>N-nitroso-methylethylamine (NMEA)</td>
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<tr>
<td>N-nitroso-pyrroolidine (NPyR)</td>
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CCL 3 and UCMR 3 focused on nitrosamines and chlorate

<table>
<thead>
<tr>
<th>CCL 3</th>
<th>UCMR 3</th>
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<tbody>
<tr>
<td>• Formaldehyde</td>
<td>• Chlorate</td>
</tr>
<tr>
<td>• N-nitrosodimethylamine (NDMA)</td>
<td></td>
</tr>
<tr>
<td>• N-nitrosodiethylamine (NDEA)</td>
<td></td>
</tr>
<tr>
<td>• N-nitroso-di-n-propylamine (NDPA)</td>
<td></td>
</tr>
<tr>
<td>• N-nitrosodiphenylamine</td>
<td></td>
</tr>
<tr>
<td>• N-nitrosopyrroloidine (NPYR)</td>
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https://www.epa.gov/ccl/contaminant-candidate-list-3-ccl-3#chemical-list,
DBPs on the CCL 3 list appeared on CCL 4, and UCMR 4 focused on brominated DBPs

<table>
<thead>
<tr>
<th>CCL 4</th>
<th>UCMR 4</th>
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<tbody>
<tr>
<td>• Formaldehyde</td>
<td>• HAA5</td>
</tr>
<tr>
<td>• N-nitrosodimethylamine (NDMA)</td>
<td>• HAA6Br</td>
</tr>
<tr>
<td>• N-nitrosodiethylamine (NDEA)</td>
<td>• HAA9</td>
</tr>
<tr>
<td>• N-nitroso-di-n-propylamine (NDPA)</td>
<td>• Bromochloracetic acid</td>
</tr>
<tr>
<td>• N-nitrosodiphenylamine</td>
<td>• Bromodichloroacetic acid</td>
</tr>
<tr>
<td>• N-nitrosopyrrolidine (NPYR)</td>
<td>• Chlorodibromoacetic acid</td>
</tr>
<tr>
<td></td>
<td>• Dibromoacetic acid</td>
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<tr>
<td></td>
<td>• Dichloroacetic acid</td>
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<td></td>
<td>• Monobromoacetic acid</td>
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<td></td>
<td>• Monochloroacetic acid</td>
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<td></td>
<td>• Tribromoacetic acid</td>
</tr>
<tr>
<td></td>
<td>• Trichloroacetic acid</td>
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</tbody>
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https://www.epa.gov/ccl/chemical-contaminants-ccl-4,
https://www.epa.gov/sites/production/files/2017-03/documents/ucmr4-fact-sheet-general.pdf
Reclaimed water expected to impact DBP formation in drinking water systems

**Indirect Potable Reuse**
- Nitrogen and Phosphorus fuel algae blooms
- Nitrogen-rich organics

**Direct Potable Reuse**
- Nitrogen-rich organic matter
- DBPs formed at the Water Reclamation Facility
Saltwater intrusion increases concentrations of inorganic ions in coastal regions

- Groundwater use depletes freshwater aquifers
- Saltwater moves in to fill the void
- Bromide and iodide concentrations increase
- Bromate, brominated and iodinated organic DBPs form

Hydraulic fracturing can have a similar effect by introducing bromide
DBP CONTROL STRATEGIES
Four general strategies can be used to maintain compliance with the Stage 2 D/DBP Rule:

1. Control disinfection conditions
2. Use a disinfectant that does not form regulated DBPs
3. Remove organics prior to disinfection
4. Remove disinfection byproducts after they form
Step 1: Minimize chlorine dose by optimizing the injection point

- Are iron and manganese present? Taste and odor?
- Does this provide adequate CT?

Raw Water → Coagulation/Flocculation → Sedimentation → Filtration → Clearwell → Distribution

DBP Precursors → Cl₂ → DBP Precursors
Changing disinfection pH can decrease dose required for CT

Corrosion Concerns:
- pH adjustment may be needed prior to distribution
- Phosphate-based corrosion inhibitors can also help
Alternative disinfectants are not one-size-fits-all

**Pre-Oxidation**
- Ozone
- Chlorine Dioxide
- Potassium Permanganate
- Hydrogen Peroxide

**Primary Disinfection**
- Ozone
- Chlorine Dioxide
- Monochloramine

**Secondary Disinfection**
- Monochloramine
Ozone can provide disinfection and taste and odor control.

Regulated DBP: Bromate
Emerging DBPs: Formaldehyde, ketoacids, carboxylic acids

Biofiltration or activated carbon needed for assimilable organic carbon removal.
Chlorine dioxide is typically used as a pre-oxidant or primary disinfectant.
Monochloramine is formed by reacting free chlorine and ammonia in a controlled ratio. Monochloramine provides a stable disinfectant residual. Dichloramine and trichloramine are associated with taste and odor issues. Monochloramine provides a stable disinfectant residual. Dichloramine leads to formation of di-halogenated HAAs and nitrosamines. Breakpoint
Nitrification is a challenge for chloraminated systems

Free chlorine burns to control nitrification can form high levels of TTHM and HAA5

If the chlorine:ammonia ratio exceeds 5:1, nitrosamines and DXAAs can form
DBP precursor removal can be achieved by several processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Methods</th>
</tr>
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<tbody>
<tr>
<td>Coagulation</td>
<td>• Using alum, PACI, ACH, ferric sulfate</td>
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<tr>
<td>Adsorption</td>
<td>• Granular activated carbon (GAC) in multi-media filters or contactors</td>
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<tr>
<td></td>
<td>• GAC can also remove DBPs</td>
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<tr>
<td>Biofiltration</td>
<td>• Conventional media</td>
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<tr>
<td></td>
<td>• GAC</td>
</tr>
<tr>
<td></td>
<td>• Biofiltration can remove DBPs</td>
</tr>
<tr>
<td>Membranes</td>
<td>• Nanofiltration</td>
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<tr>
<td></td>
<td>• Ultrafiltration with coagulant addition</td>
</tr>
<tr>
<td>Preoxidation</td>
<td>• Chlorine dioxide and ozone can improve DBP removal in subsequent</td>
</tr>
<tr>
<td></td>
<td>coagulation processes</td>
</tr>
<tr>
<td></td>
<td>• Chlorine and ozone can oxidize nitrosamine and I-THM precursors</td>
</tr>
</tbody>
</table>
Tank aeration has been proposed as a means of removing DBPs

- Regulated trihalomethanes could be removed by >86%

Not all DBPs are equally volatile

- Haloacetic acids would not be removed
- DBPs remaining in solution may be far more toxic than THMs

What’s next in DBP research and regulations?

DBP speciation research – bromine- and iodine-containing DBPs

Nitrogen-containing DBPs
Conclusions

Maintaining disinfection and controlling DBPs requires a balanced strategy

Current DBP regulations may favor selection of “DBP control processes” that promote formation of unregulated DBPs

DBP control processes should be carefully selected based on system-specific conditions to minimize unintended consequences
QUESTIONS?