Arkansas Department of Health

Disinfectants and Disinfection Byproducts Rules

ADH Compliance Short School

Disinfection Byproducts Definition

Disinfection Byproducts (DBPs) are chemical compounds that are formed as an unintended result of drinking water disinfection.

When a disinfection chemical, usually chlorine, is added as part of water treatment, chemical reactions can produce contaminants that are regulated due to health concerns.

Many DBPs are the result of chlorine reacting with organic compounds such as leaf decay.

Disinfection Byproducts Definition

Systems using surface water sources will often have more DBP formation in their treated water since lakes and rivers may have forested watersheds.

Forested watersheds are overall most protective of drinking water quality, but leaf decay presents a challenge in controlling some of the disinfection by products due to being a naturally occurring source of carbon.

Disinfection Byproducts Definition

- Some other DBPs are inorganic compounds formed by the oxidative power of the disinfectants and can be affected by various factors that include presence of bromide in the raw water and dosage of the disinfectant being employed.
- This presentation will discuss the various regulated DBPs but it is well understood that there are many unregulated DBPs, known and unknown, that may also be harmful.
- It is believed that controlling regulated DBPs serves to also limit the formation of many unregulated DBPs.

Disinfection Byproduct Rules Applicability

- There are 2 DBP Rules that have been issued by EPA.
  - The Stage 1 Disinfection Byproduct Rule (2002)
  - The Stage 2 Disinfection Byproduct Rule (2012)
- These rules apply to All Community water systems, and Non-transient Non-community water systems, that deliver water which has been treated with a primary or residual disinfectant other than ultraviolet light. (As a practical matter this is all of the Community and Non-transient Non-Community water systems in Arkansas.)
- The following slides will present all current requirements and will not differentiate between Stage 1 and Stage 2 rule requirements.

Disinfection Byproduct Rules

Terms & Acronyms

- TOC – Total Organic Carbon
- Disinfectants
- DBPs – Disinfection Byproducts
- TTHM – Total Trihalomethanes
- HAA5 – Haloacetic Acids
- MCL – Maximum Contaminant Level
- MRDL – Maximum Residual Disinfectant Level
- MCLG – Maximum Contaminant Level Goal
- MRDLG – Maximum Residual Disinfectant Level Goal
- Entry point
- RAA – Running Annual Average
- LRAA – Locational Running Annual Average
- OEL – Operational Evaluation Level
- Subpart H water system

Concept: Running Annual Average

- DBP Rules routinely use the concept of “running annual average” (RAA) to determine compliance with contaminant limitations.
- Typically, compliance is based on the average of the previous 1-year of monitoring results.
- Monitoring frequency may vary depending upon contaminant.
- The results of each new monitoring period replaces the monitoring results that are no longer within the new 1-year period but have aged out.
- Example: Quarterly Monitoring includes previous 4 quarters, Monthly monitoring includes previous 12 months, etc. when calculating a RAA.

Concept: MCL and MCLG

- For regulated contaminants, EPA normally issues a Maximum Contaminant Level (MCL) and also a Maximum Contaminant Level Goal (MCLG).
- The MCL is the required limit for the contaminant but the MCLG, normally lower than the MCL, is the level at which no adverse health effects are expected.
- When an MCL is higher than the MCLG, it is normally because it is either not feasible or cost effective to provide treatment to meet the lower MCLG.

Disinfection Byproduct Rule
Regulated Contaminants

- The following regulated contaminants will be discussed individually.
  - Total Organic Carbon (TOC) Removal Requirements
  - Disinfectant Level Limitations
  - THMs and HAA5s Limitations
  - Bromate Limitations
  - Chlorite Limitations
- Monitoring and Operational Evaluation Level (OEL)
- Operational Evaluation Level (OEL) is an analytical and reporting requirement that will be discussed in detail later in this presentation.

Total Organic Carbon Removal Requirements

- Disinfection byproducts (THMs and HAA5s) are formed when Total Organic Carbon (TOC), which is usually naturally occurring organic material (NOM), combines with a disinfectant.
- Removing TOC, prior to addition of a disinfectant, is required and is effective in reducing DBP formation.

- Formation of DBPs is dependent upon:
  - Amount of TOC
  - Amount and Type of disinfectant
  - Contact Time
  - Temperature
  - pH
  - Various raw water qualities

Total Organic Carbon Removal Requirements Applicability

- All Community and Non-Transient Non-Community Subpart H systems using conventional filtration treatment must:
  - Monitor TOC levels
  - Monitor Alkalinity
  - Ensure that monitoring is done under normal operating conditions
  - Comply with TOC removal requirements
  - Be operated by qualified personnel
  - Monitor Magnesium Hardness levels in the raw water & in the finished water (softening plants only)

Total Organic Carbon Removal Requirements Monitoring Frequency

- A complete TOC sample set consists of a pair of TOC samples (1 source water sample & 1 finished water sample) and a source water alkalinity sample.
  - Routine monitoring: 1 sample set per month

- A system may be placed on a reduced monitoring schedule if the treated water TOC level is < 2.0 mg/L for 2 years, or < 1.0 mg/L for 1 year.
  - Reduced monitoring: 1 sample set per quarter

Total Organic Carbon Alkalinity Monitoring

- Alkalinity monitoring should be performed by water system personnel and must be done on the same day as TOC sample collection.
- Operators at surface water treatment plants in Arkansas analyze for alkalinity using either electrometric or color titration.
- The raw water alkalinity level must be recorded on the water system's Monthly Operating Report.

Alkalinity (ppm)			
Date	Raw	Set	Fin
1	54		
2	54		
3	52		
4	51		
5	52		
6	54		
7	54		
8	54		

Total Organic Carbon
Step 1 Removal Requirements

- **The raw water alkalinity and TOC levels determine the required removal percentage from the table.**

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as calcium carbonate)		
	0 – 60	**> 60 – 120**	**> 120**
> 2.0 – 4.0	**35%**	**25%**	**15%**
> 4.0 – 8.0	**45%**	**35%**	**25%**
> 8.0	**50%**	**40%**	**30%**

Note: Source waters with TOC levels less than 2.0 mg/L have no removal requirement.

Total Organic Carbon
Step 2 Removal Requirements

- System failed to meet Step 1 removal requirements. System petitions the state to accept a lower TOC removal requirement based on jar testing.
- Application made to the State within 3 months of failure to meet step 1 requirements.
- Jar testing to determine maximum TOC removal. Specific jar testing procedures are required.
- If maximum removal percentage is documented to be less than the Step 1 removal requirement, a new minimum removal requirement is set.
- State may make results retroactive.

Total Organic Carbon
Alternative Criteria for TOC Removal

1. Source water TOC < 2.0 mg/L (annual average)

2. Treated water TOC < 2.0 mg/L (annual average)

3. Source water TOC < 4.0 mg/L, and
   - Source water alkalinity is > 60 mg/L, and
   - Total Trihalomethanes level is < 40 ug/L, and
   - Haloacetic Acids level is < 30 ug/L

4. For systems using only chlorine as a disinfectant:
   - Total Trihalomethanes level is < 40 ug/L, and
   - Haloacetic Acids level is < 30 ug/L

Note: 40 ug/L is half the MCL for Total Trihalomethanes &
30 ug/L is half the MCL for Haloacetic Acids

Total Organic Carbon Removal Compliance Recap

To achieve compliance, systems must do one of the following:

- Achieve Step 1 TOC removal requirements
- Establish and Achieve Step 2 TOC removal requirements
- Meet one or more Alternative Compliance Criteria

Total Organic Carbon
Removal Compliance Calculations

- After each quarterly TOC sampling, the water system will receive a letter indicating whether the TOC removal requirement has or has not been met based on a RAA of the 4 most recent quarters.
- The requirement is expressed as a ratio of the measured removal (RAA) divided by the required removal.
- A ratio of 1.00 or greater indicates compliance with removal requirements.
- A ratio of less than 1.00 indicates noncompliance.

Disinfection Byproduct Rule
Monitoring for Regulated Contaminants

- Sample collection and sample analysis for various disinfection-by-products requires correct technique and expensive analytical equipment.
- The Ark. Dept. of Health's Drinking Water Program conducts the required sample collection and analysis for: THMs, HAA5s, TOC, Bromate, and distribution system Chlorite. Water systems are required to conduct the sample collection and analysis for required chlorine, chlorine dioxide, and entry point chlorite monitoring.
- Some water systems have acquired the ability to analyze for some or all of these for their own quality control purposes.

Disinfection Byproduct Rule
Monitoring for Regulated Contaminants

- All systems must develop a monitoring plan.
- Monitoring must be performed according to the plan, and the plan must:
  - Include monitoring locations & schedule
  - Explain compliance calculation methodology
  - Reflect the entire distribution system

Chlorine and Chloramine Limitations

- Most water systems utilize either chlorine or chloramines as disinfectants.
- DBP Rules limit the amount of chlorine and chloramine that can be present in the finished water based upon a Running Annual Average.
- Compliance data is obtained from disinfectant residuals measured when distribution system bacteriological monitoring is conducted and reported on the monthly Bacteriological Monitoring Report (BMR).
- Chlorine MCL: 4.0 mg/L based on a RAA
- Chloramine MCL: 4.0 mg/L based on a RAA

Chlorine and Chloramine Limitations

- Chlorine and Chloramines are regulated due to concerns that higher levels may cause nose and eye irritation.
- The MCL is based upon a yearly average (RAA) and this allows for a water system to occasionally exceed 4.0 mg/L to appropriately respond to contamination in the distribution system, or other unusual/emergency situations where a higher disinfectant residual is warranted.
- Do not hesitate to raise disinfectant residuals if needed if appropriate for the specific situation. Always consult with the ADH during these types of situations.

Chlorine Dioxide Limitations

- Chlorine Dioxide is a more powerful oxidant than chlorine or chloramines and is used in some surface water treatment plants.
- The SDWA limits the amount of chlorine dioxide that consumers can be exposed to due to concerns of anemia in infants and young children and also adverse neurological effects.
- Chlorine Dioxide MCL: 0.8 mg/L
- Chlorine Dioxide MCLG: 0.8 mg/L
- Monitoring is only required at treatment plants that add Chorine Dioxide.

Chlorine Dioxide Limitations Monitoring

- **Monitoring Requirements:**
  - Treated water at the entry point to the distribution system must be checked for chlorine dioxide levels once per day.
  - If any daily sample is > 0.8 mg/L, then
    - Systems without booster chlorination will collect 3 samples at > 6 hour intervals as close as possible to the first customer.
    - Systems providing booster chlorination in their distribution system must monitor at the first customer, and at the average and maximum residence time locations.

Chlorine Dioxide Limitations
Compliance Criteria

Compliance Criteria

Non-acute violation:

- 2 consecutive entry point samples > 0.8 mg/L
- All distribution samples are < 0.8 mg/L

Acute violation is based on samples collected on consecutive days:

- Entry point sample is > 0.8 mg/L
- 1 or more distribution system samples > 0.8 mg/L

- The water system will monitor the residuals at the entry point to the distribution system, and if triggered, in the distribution system, and report them on its Monthly Operating Report.

Disinfection Byproducts

Suspected Health Hazards

Toxicological and Epidemiological evidence shows a strong possibility of DBPs in drinking water contributing to cancer and reproductive problems.

Reduction in exposure to:

- Total Trihalomethanes (TTHM)
- Haloacetic Acids (HAA5)
- Chlorite
- Bromate

Reduced risks from:

- Cancer
- Reproductive effects
- Developmental effects

Total Trihalomethanes and Haloacetic Acids Limitations

- Trihalomethanes are undesired byproducts of adding chlorine or chloramines to the water typically for disinfection purposes.
- Chlorine and chloramines can react with naturally occurring organic material (NOM) and produce trihalomethanes which are comprised of the following compounds.
  - Chloroform ($CHCl_3$)
  - Bromodichloromethane ($CHBrCl_2$)
  - Dibromochloromethane ($CHBr_2Cl$)
  - Bromoform ($CHBr_3$)

Total Trihalomethanes and Haloacetic Acids Limitations

- Haloacetic acids are also undesired byproducts of adding chlorine or chloramines to the water typically for disinfection purposes.
- Chlorine and chloramines can react with naturally occurring organic material (NOM) and produce haloacetic acids which are comprised of the following compounds.
- Monochloroacetic acid ($ClCH_2CO_2H$)
- Dichloracetic acid ($CHCl_2CO_2H$)
- Trichloricacetic acid (CCl_3CO_2H)
- Monobromoacetic acid (CH_2BrCO_2H)
- Dibromoacetic acid ($CHBr_2CO_2H$)

TTHM & HAA5

Maximum Contaminant Levels & Maximum Contaminant Level Goals

Disinfection Byproduct	mg/L
Total Trihalomethanes (TTHM) MCL	**MCL = 0.080**
• Chloroform	MCLG = 0.07
• Bromodichloromethane	MCLG = 0
• Bromoform	MCLG = 0
• Dibromochloromethane	MCLG = 0.06

80 ppb

Haloacetic Acids (HAA5) MCL	**MCL = 0.060**
• Monochloroacetic Acid	MCLG = 0.07
• Dichloroacetic Acid	MCLG = 0
• Trichloroacetic Acid	MCLG = 0.02
• Bromoacetic Acid	No MCLG established
• Dibromoacetic Acid	No MCLG established

60 ppb

Total Trihalomethanes and Haloacetic Acids Routine Monitoring Frequency

Source Type	Population	Number of Sites & Frequency
Surface	<500	2 per year*
	500 – 3,300	2 per quarter
	3,301 – 9,999	2 per quarter
	10,000 – 49,999	4 per quarter
	50,000 – 249,999	8 per quarter
	250,000 – 999,999	12 per quarter
	1,000,000 – 4,999,999	16 per quarter
	≥ 5,000,000	20 per quarter
Ground	< 500	2 per year*
	500 – 9,999	2 per year
	10,000 – 99,999	4 per quarter
	100,000 – 499,999	6 per quarter
	≥ 500,000	8 per quarter

Dual sample set = 1 THM & 1 HAA sample.

Quarterly monitoring is a dual sample set at each monitoring location every 90 days.

For systems serving < 500, only one site is needed if the highest THM & HAA levels occur at the same location.

Total Trihalomethanes and Haloacetic Acids

Example Compliance Calculation for Trihalomethanes

Compliance will be based on Locational Running Annual Averages (LRAAs) for each sampling site.

TTHM *Results in ug/L (ppb)*	First Quarter	Second Quarter	Third Quarter	Fourth Quarter	LRAA
Site 1	45	50	59	49	51
Site 2	78	**84**	**88**	79	82
Site 3	42	48	57	50	49
Site 4	55	62	81	75	68

TTHM MCL = 80 ppb
Calculated quarterly as a locational running annual average
Site #1, 3, & 4 are in compliance
Site # 2 is not in compliance

Calculations are similar for HAA5s except HAA5 MCL = 60 ppb

Bromate Limitations

- Bromate can be present when a source water contains bromide (usually naturally occuring) and the treatment plant uses ozone as an oxidant/disinfectant. Bromate is an unintended byproduct.
- The SDWA limits the amount of bromate that consumers can be exposed to due to multiple health concerns including kidney damage.
- Bromate MCL: 0.010 mg/L
- Bromate MCLG: 0 mg/L
- Monitoring is only required at community or non-transient non-community treatment plants that add ozone.

Bromate Limitations
Monitoring and Compliance

- Systems that are required to monitor for bromate, due to the addition of ozone, are required to monitor once a month at the entry point to the distribution system.
- Compliance is based upon a 12 month Running Annual Average (RAA).

Chlorite Limitations

- Chlorite can be present when chlorine dioxide (an oxidant) is added to the water. Chlorite forms as chlorine dioxide decays.
- The SDWA limits the amount of chlorite that consumers can be exposed to due to multiple health concerns including anemia and nervous system effects.
- Chlorite MCL: 1.0 mg/L
- Chlorite MCLG: 0.8 mg/L
- Monitoring is only required at community or non-transient non-community treatment plants that add chlorine dioxide.

Chlorite Formation

- Chlorine dioxide rapidly decomposes into chlorite, chlorate and chloride ions in treated water, chlorite being the predominant species.
- Chlorine dioxide cannot be shipped to a site due to chemical instability. Chlorine dioxide has to be generated on-site by sophisticated feeder equipment.
- Over feeding chlorine dioxide can lead to a treated water exceedance of the chlorite limit.

Chlorite Limitations
Monitoring and Compliance

Daily - at entry point

Monthly - first customer, average and maximum residence times

Triggered - if daily sample > MCL, immediately notify the health department. A sampler will be sent the following day to collect the required 3-sample compliance set from the monthly monitoring points.

Disinfection Byproducts

Chlorite Monitoring and Reporting

The entry point chlorite levels must be recorded on the system's Monthly Operating Report.

Chlorite Monitoring (For Systems using Chlorine Dioxide)		DATE
Entry Point Chlorite	Dist. Samples Collected (Y/N)	
0.52	N	1
0.61	N	2
0.67	N	3
0.75	N	4
0.35	N	5
0.49	N	6

Disinfection Byproducts

Compliance with Chlorite MCL

Chlorite compliance is based on an Arithmetic Average of each monthly 3 sample set.

Chlorite *Results in mg/L (ppm)*	Nearest to First Customer Site	Average Residence Time Site	Maximum Residence Time Site	Distribution System Arithmetic Average
January	0.863	0.766	0.694	0.8
February	0.392	0.394	0.609	0.5
March	0.572	0.598	0.606	0.6
April	0.526	0.417	0.491	0.5
May	0.598	0.530	0.541	0.6
June	0.492	0.500	0.441	0.5
July	0.222	0.220	0.213	0.2
August	0.246	0.139	0.178	0.2
September	0.526	0.020	0.020	0.2
October	0.310	0.300	0.069	0.2
November	1.070	0.561	0.563	0.7
December	0.659	0.562	0.575	0.6

Operational Evaluation Levels (OELs) THMs and HAA5s

- The purpose of the operational evaluation level (OEL) is to allow a system to take action, if possible, to reduce the elevated disinfection byproduct levels in the system before a violation of the maximum contaminant level (MCL) occurs.
- The OEL is a calculation that is performed following each quarterly monitoring for THMs and HAA5s. The ADH performs this calculation and informs the water system of the results.
- Conceptually, the OEL indicates whether or not a water system will maintain compliance with THM and HAA5 MCLs if the most recent quarterly results are repeated in the next quarter.
- The purpose for water systems to take corrective actions before a violation actually occurs.

Operational Evaluation Levels (OELs)

Operational Evaluation Level formula:

$$\frac{[(2 \times \text{current quarter THM or HAA results}) + \text{previous two quarters THM or HAA results}]}{4} = \text{OEL}$$

The OEL should not exceed the Maximum Contaminant Level.

TTHM MCL = 80 ppb
HAA5 MCL = 60 ppb

Operational Evaluation Levels (OELs)

Operational Evaluation Level example for TTHM:

$$\frac{[(2 \times Q1) + Q4 + Q3]}{4} = \textbf{OEL}$$

TTHM *Results in ug/L (ppb)*	Third Quarter (Q3)	Fourth Quarter (Q4)	First Quarter (Q1)		OEL
Site 1	46	51	52 x 2	/4 =	50
Site 2	72	79	87 x 2	/4 =	**81**

TTHM MCL = 80 ppb

Operational Evaluation Levels (OELs)

What does the OEL tell us?

TTHM *Results in ug/L (ppb)*	Third Quarter (Q3)	Fourth Quarter (Q4)	First Quarter (Q1)		OEL
Site 1	46	51	52 x 2	/4 =	50
Site 2	72	79	87 x 2	/4 =	**81**

TTHM MCL = 80 ppb

Site 1 is OK

Site 2 needs improvement

Operational Evaluation Levels (OELs)

Follow-up Actions

Site 2 TTHM OEL = 81 ppb (from previous slide)

When an OEL is exceeded, the water system must:

- Conduct an *Operational Evaluation* to determine the cause of the exceedance
- Submit a written *Operational Evaluation Report* to the State no later than 90 days after being notified of the analytical result that caused the exceedance
- Keep a copy of the OEL Report and make it available to the public upon request

Operational Evaluation Levels (OELs)

Follow-up Actions, Content

The Operational Evaluation must include an examination of system treatment and distribution operational practices that may contribute to TTHM & HAA5 formation, including:

- Sources of supply and source water quality
- Treatment processes and finished water quality
- Storage tank operations and excess storage capacity
- Distribution system flushing

The Operational Evaluation must also include what steps could be considered to minimize future exceedances.

Disinfection Byproducts Control

Best Available Technology (BAT)

EPA has identified the following as the best technologies, treatment techniques, or other means available for achieving compliance with the maximum contaminant levels for TTHM & HAA5.

For systems treating their own source water:

- Enhanced coagulation or enhanced softening
- GAC 10
- GAC 20
- Nanofiltration

Consecutive systems serving at least 10,000 people

- Chloramination
- Management of hydraulic flow and storage to minimize residence time in the distribution system

Consecutive systems serving fewer than 10,000 people

- Management of hydraulic flow and storage to minimize residence time in the distribution system

Review Questions

What is TOC?

A. Treated Organic Compounds

B. Total Organic Carbon

C. Tertiary Ozone Classification

Who performs TOC and DBP sampling and analyses?

A. The Water System

B. USGS

C. Health Department

What is the MRDL for chlorine in the distribution system?

A. 80 ppb

B. 0.8 mg/L

C. 4.0 mg/L

What is the MCL for TTHMs?

A. 80 ppb

B. 8 ppb

C. 4 mg/L

Compliance for TOCs, TTHMs, and HAAs is based on what?

A. Monthly sample results

B. Chlorine residual

C. Running Annual Averages (RAAs)

What are some disinfection byproducts other than TTHMs & HAAs?

A. Chlorine, Chloramines

B. Lime

C. TOC

D. Bromate, Chlorite