Disinfection Byproducts

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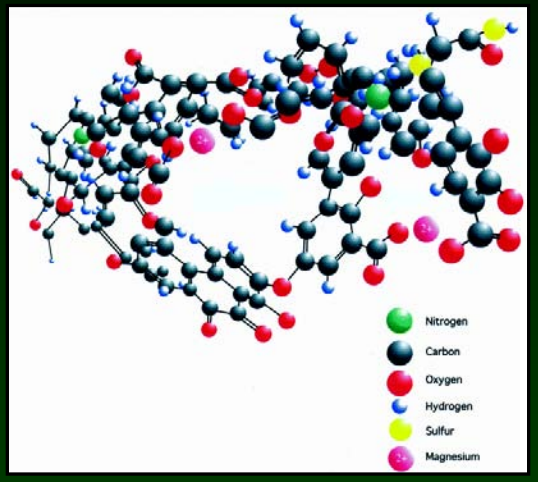
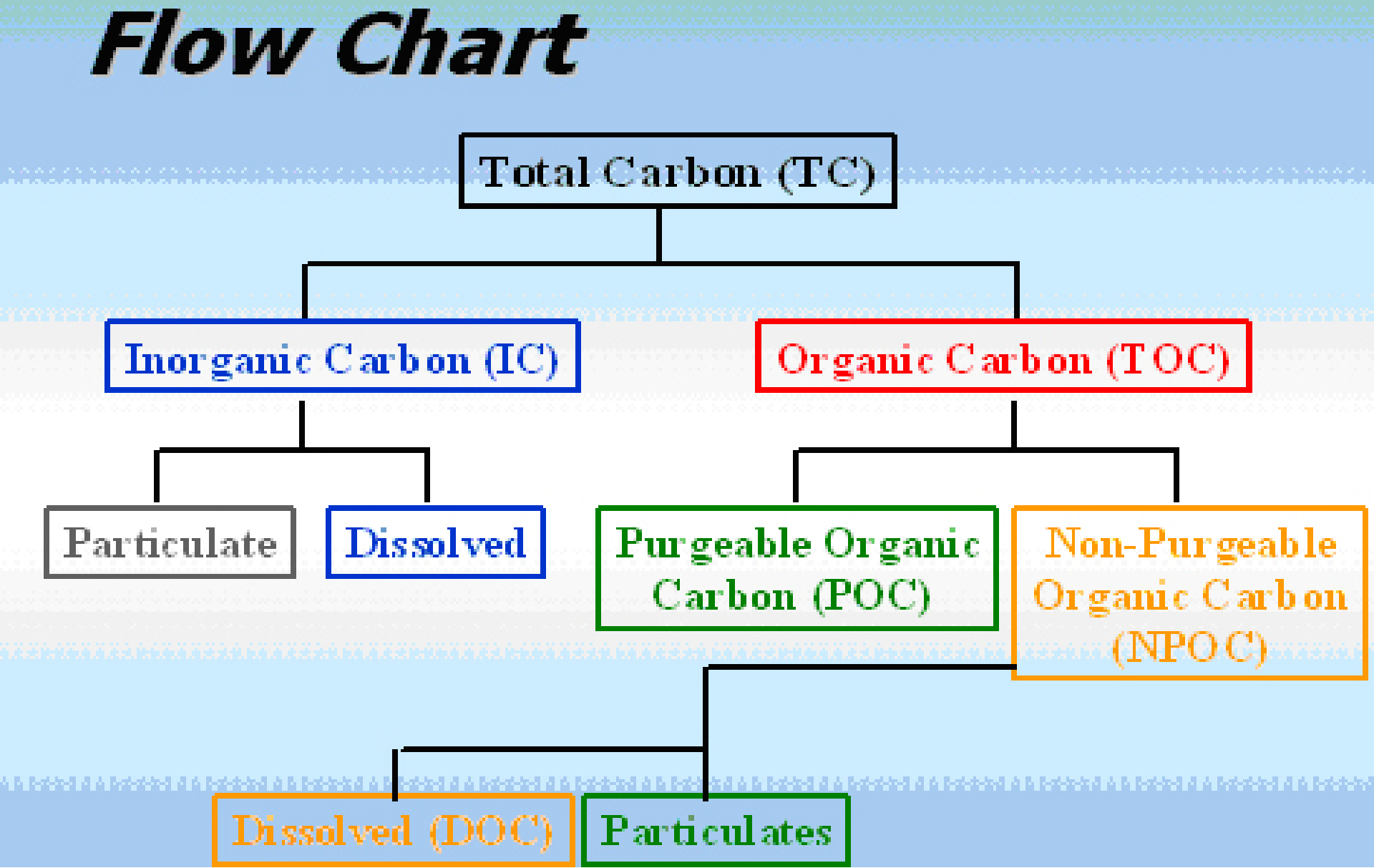
DBP Chemistry

Organic Matter



- Natural Organic Matter (NOM) is found in all surface water and comes from decaying plant and animal matter.
- Total Organic Carbon (TOC) is a measure of all organic carbon in water and includes NOM, petroleum products, pesticides, etc.
- Dissolved Organic Carbon (DOC) is that portion of TOC that is dissolved. It is usually the largest fraction of TOC and of the most concern.

Flow Chart Illustrating Total Carbon Constituents



Total Carbon Constituents

- **Total Carbon (TC)**: all the carbon in the sample, including both inorganic and organic carbon
- **Total Inorganic Carbon (TIC)**: often referred to as inorganic carbon (IC), carbonate, bicarbonate, and dissolved carbon dioxide (CO_2)
- **Total Organic Carbon (TOC)**: material derived from decaying vegetation, bacterial growth, and metabolic activities of living organisms or chemicals
- **Non-Purgeable Organic Carbon (NPOC)**: commonly referred to as TOC; organic carbon remaining in an acidified sample after purging the sample with gas
- **Purgeable (volatile) Organic Carbon (POC)**: organic carbon that has been removed from a neutral, or acidified sample by purging with an inert gas. These are the same compounds referred to as Volatile Organic Compounds (VOC) and usually determined by Purge and Trap Gas Chromatography
- **Dissolved Organic Carbon (DOC)**: organic carbon remaining in a sample after filtering the sample, typically using a 0.45 micrometer filter
- **Suspended Organic Carbon (SOC)**: also called particulate organic carbon (PtOC); the carbon in particulate form that is too large to pass through a filter

DBP Chemistry

- Disinfection Byproducts (DBPs) are caused by the reaction of a disinfectant with DBP precursors. The most significant precursor is NOM:

$$\text{Disinfectant} + \text{NOM} \rightarrow \text{DBPs}$$

- There are hundreds of different DBP compounds, many of which can have serious human health impacts (e.g. birth defects and carcinogenicity).
- Only a few DBPs are regulated:
  - Trihalomethanes (THM)
  - Haloacetic Acids (HAA)
  - Chlorite
  - Bromate

DBP Chemistry

Trihalomethanes

- The MCL is for the combined concentration of 4 trihalomethanes, Total Trihalomethanes (TTHM)
- Results from use of Chlorine as disinfectant

Haloacetic Acids

- The MCL is for the combined concentration of 5 Haloacedic Acids (HAA5)
- Results from use of Chlorine as disinfectant

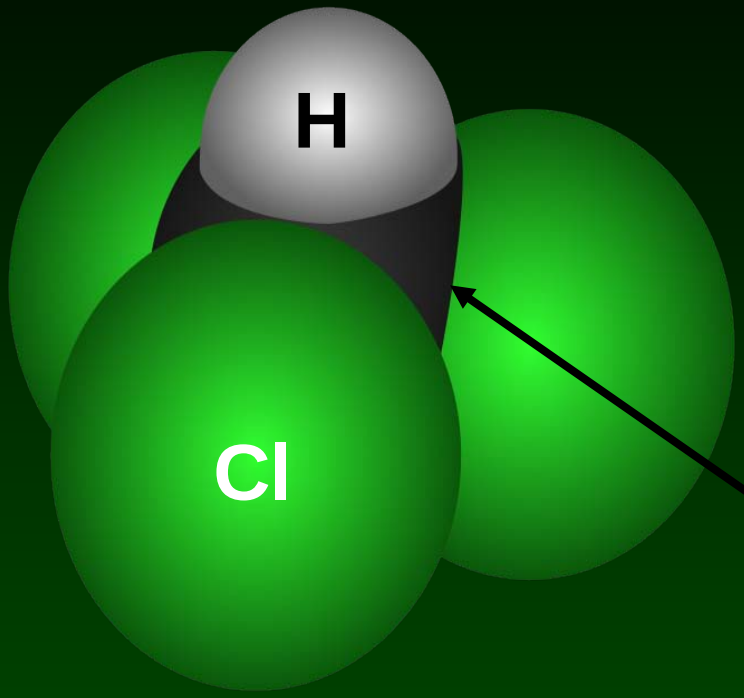
Chlorite

- Results from dissociation of Chlorine dioxide as disinfectant (doesn't require NOM)

Bromate

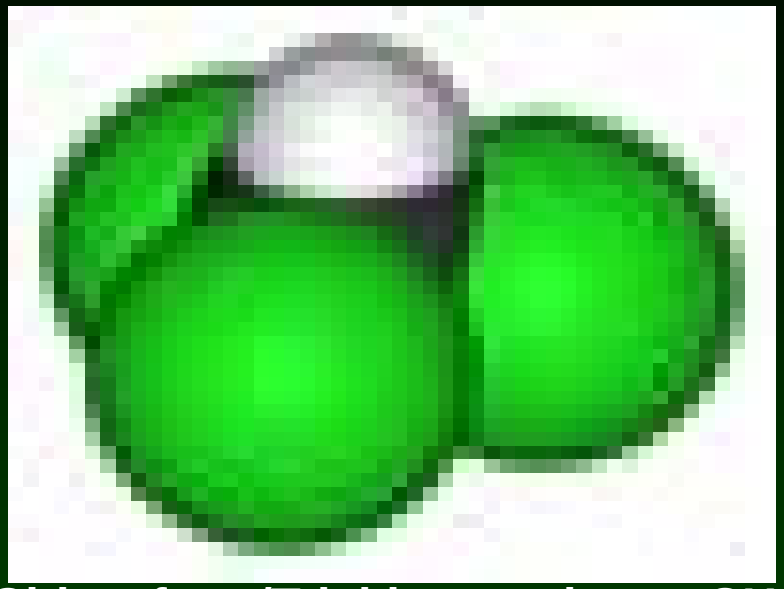
- Results from use of Ozone and requires Bromide as a precursor

TTHMs – Ex., Trichloromethane

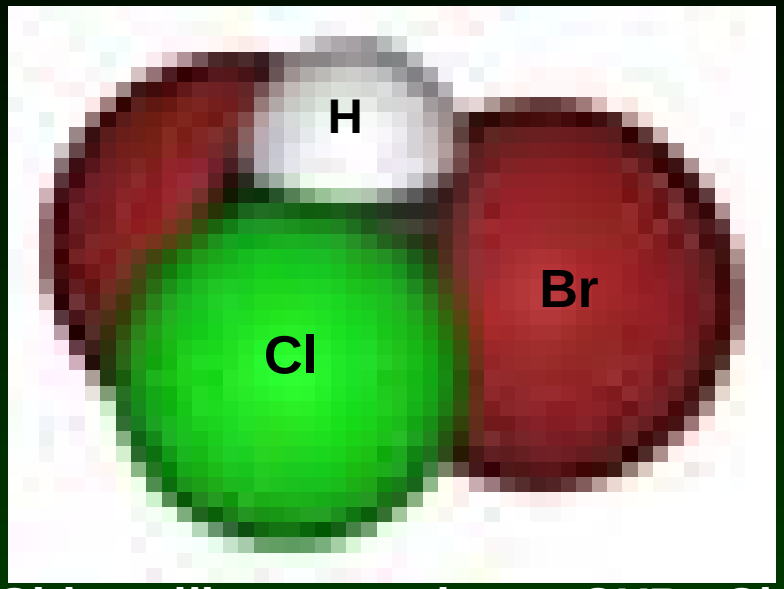


$CHCl_3$

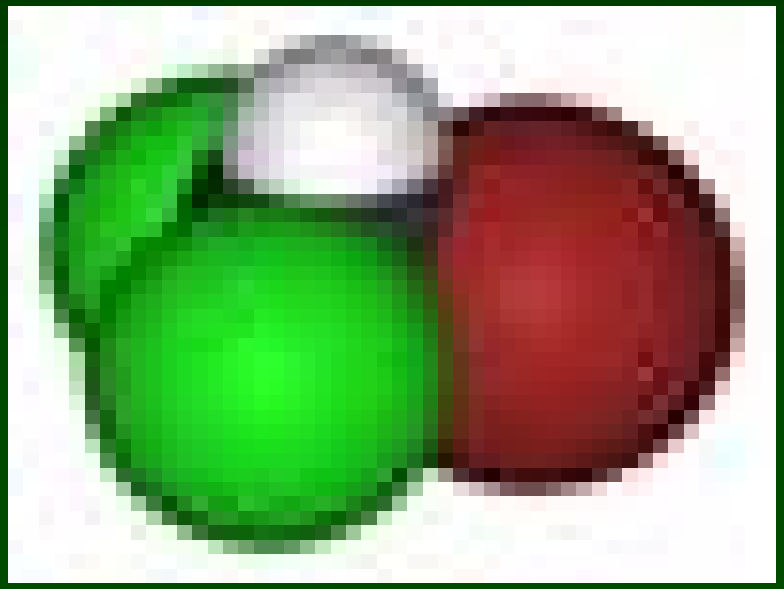
All Four (4) TTHMs



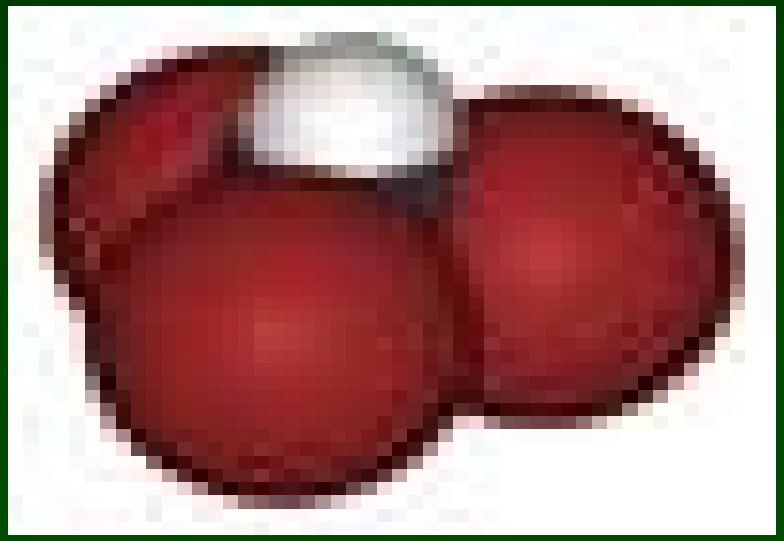
Chloroform/Trichloromethane - $CHCl_3$



Chlorodibromomethane - $CHBr_2Cl$

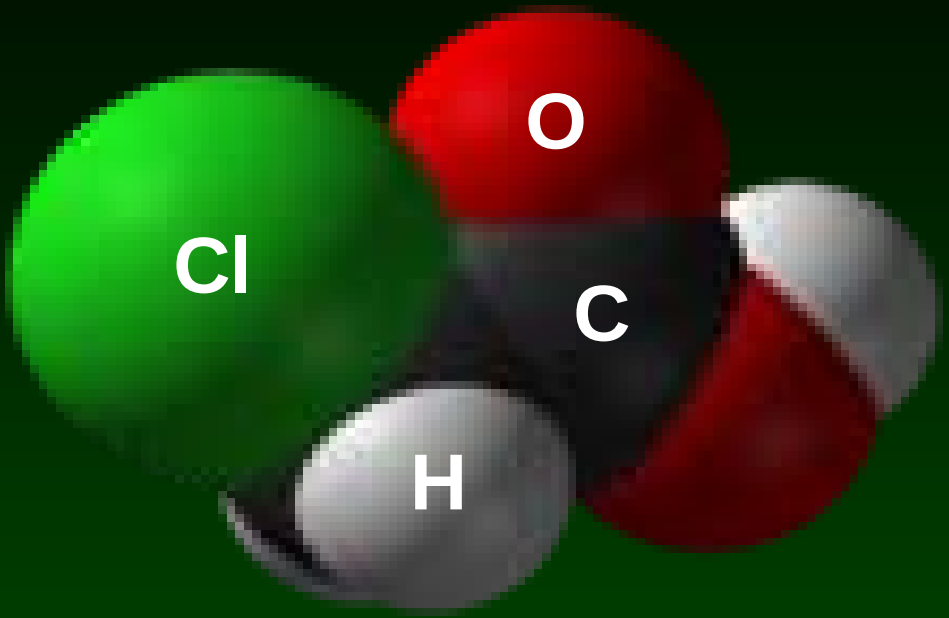


Bromodichloromethane - $CHBrCl_2$



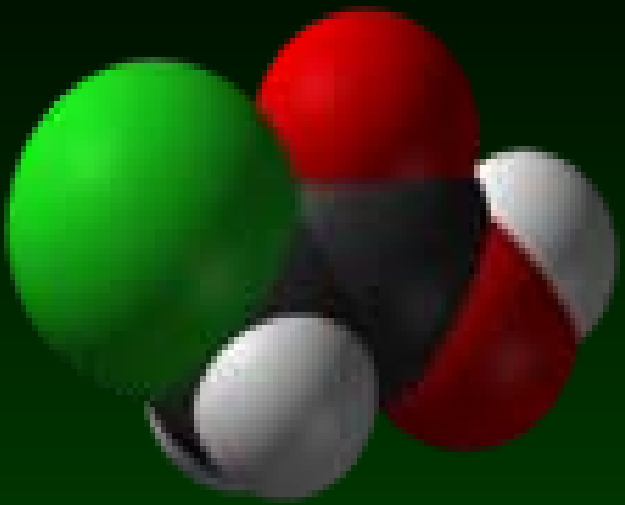
Bromoform/Tribromomethane - $CHBr_3$

HAA5s – Ex., Monochloroacetic Acid



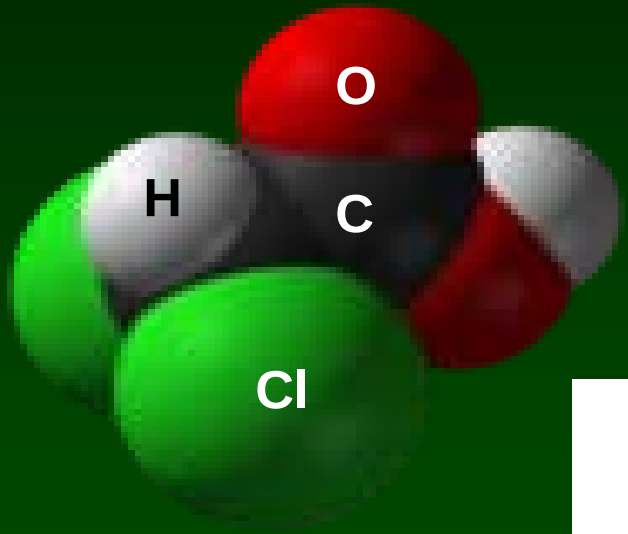
$C_2H_3ClO_2$

All Five (5) HAA5s

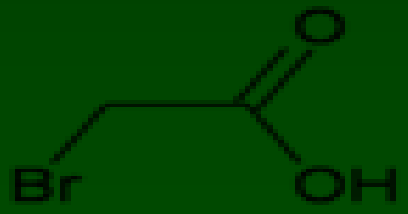


Monochloroacetic acid,
$C_2H_3ClO_2$

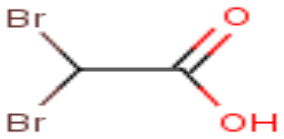
Dichloroacetic acid,
$C_2H_2Cl_2O_2$



Trichloroacetic acid,
$C_2HCl_3O_2$



Monobromoacetic acid,
$C_2H_3BrO_2$



Dibromoacetic acid, $C_2H_2Br_2O_2$

DBP Chemistry

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DBP Chemistry

DBP Formation Factors

- Temperature – Increasing temperature results in increased DBP formation rate.
- pH – THMs increase somewhat with pH, HAAs increase with decreasing pH.
- Time – Reaction is rapid for the first few hours and then decreases. Reaction will continue as long as there is disinfectant and precursors.
- Disinfectant Dose – Increasing dose results in increasing DBP formation
- Type and concentration of NOM

Stage 1 DBPR

- Published in 1998.
- Stage 1 DBPR regulates the allowable levels of disinfectants, DBPs, and DBP precursors in drinking water.
- Applies to CWS and NTNC systems that add a disinfectant, and transient systems using chlorine dioxide.

Stage 1 DBPR

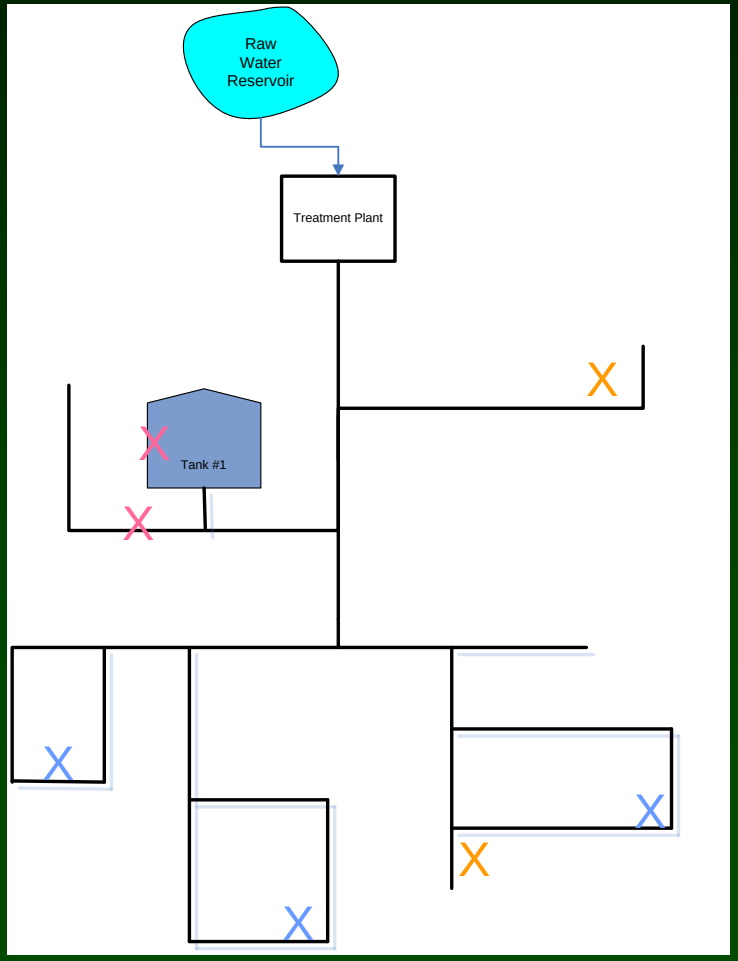
Monitoring

- Systems required to monitor must have and follow a monitoring plan, to include specific locations and schedules.
- Monitoring must include:
  - DBPs
  - Disinfectant residuals
  - TOC and alkalinity (conventional treatment only)
- DBP sampling locations must be representative of Maximum Residence Time (MRT)

Stage 1 DBPR

Find active locations of MRT:

- Locations most distant from point of chlorination
- Areas of low usage
- Water within or downstream of tanks



Stage 1 DBPR

Monitoring Schedule

Analyte	Applicability	Frequency
TTHM/HAA$_5$	Surface water and GWUDI serving ≥ 10,000	4/plant/quarter
	Surface water and GWUDI serving 500 - 9,999	1/plant/quarter
	Surface water and GWUDI serving < 500	1/plant/year in month of warmest water temperature
	Ground water serving ≥ 10,000	1/plant/quarter
	Ground water serving < 10,000	1/plant/year in month of warmest water temperature
Bromate	Ozone plants	Monthly
Chlorite	Chlorine dioxide plants	Daily at entrance to distribution system; monthly in distribution system
Chlorine Dioxide	Chlorine dioxide plants	Daily at entrance to distribution system
Chlorine/Chloramines	All systems	Same location and frequency as TCR sampling
DBP Precursors	Conventional filtration plants	Monthly for total organic carbon and alkalinity

Stage 1 DBPR

Compliance Requirements:

- Maximum Contaminant Levels are:
  - 0.08 mg/l for TTHM
  - 0.06 mg/l for HAA5
  - 0.01 mg/l for Bromate
  - 1.0 mg/l for Chlorite
- Systems collecting quarterly samples base MCL on a running annual average (RAA) of 4 consecutive quarters.
- Systems collecting more than 1 sample per quarter average all samples over past year for RAA.

Stage 1 DBPR

RAAs are calculated each quarter using the most recent 4 quarters of data for all samples. Is the following system in compliance?

Quarter	Q1	Q2	Q3	Q4	Q5	Q6
TTHM	47 µg/l	108 µg/l	94 µg/l	52 µg/l	67 µg/l	95 µg/l
RAA	n/a	n/a	n/a	75.2 µg/l	80.25 µg/l	77.0 µg/l

Stage 1 DBPR

- Maximum Residual Disinfectant Level (MRDL) for chlorine is 4 mg/l.
- Compliance with MRDL is based on RAA of one consecutive year's worth of monthly averages of all samples.
- Total chlorine residual cannot be undetectable in distribution in more than 5% of samples/month.

Stage 1 DBPR

- TOC must be monitored monthly at conventional treatment systems.
- A source water sample must be tested for TOC and alkalinity and a CFE sample must be tested for TOC at the same time.
- Rules of thumb:
  - The lower the TOC, the lower the percentage removal of TOC
  - The higher the alkalinity, the lower the percentage removal of TOC

Stage 1 DBPR

- The table gives the percent TOC removal required for conventional treatment systems:

Source Water TOC, mg/l	Source Water Alkalinity, mg/l as CaCO3		
	0 - 60	> 60 - 120	> 120
> 2.0 – 4.0	35%	25%	15%
> 4.0 – 8.0	45%	35%	25%
> 8.0	50%	40%	30%

- Removal is based on the RAA of monthly samples.
- Failure to meet removal will require:
  - Step 1: Adjustments to treatment
  - Step 2: Determination of alternative removal requirement

Stage 2 DBPR

- Published in 2006.
- Stage 2 builds on Stage 1 and accomplishes the following:
  - Broadens applicability
  - Requires Initial Distribution System Evaluation (IDSE) to identify locations of greatest DBP concentrations
  - Requires routine monitoring plan be adjusted to reflect results of IDSE
  - Stricter compliance requirements

Stage 2 DBPR

- Stage 2 applies to all CWS and NTNC that deliver water that has been treated with a disinfectant (other than UV).
- Therefore, consecutive systems (i.e. purchase systems) are subject to Stage 2.
- For combined systems, the wholesale and consecutive systems are on the same schedule.

Stage 2 DBPR

- IDSE has 4 options for determining Stage 2 sampling locations:
  - Standard Monitoring, which is one year of DBP samples. The number of locations and the sampling frequency varies with the size of the system.
  - System Specific Study using either sufficient existing data or modeling.
  - 40/30 certification means there were no sampling violations under Stage 1 and all samples analyzed were less than 40 µg/l TTHM and 30 µg/l HAA5. No additional sampling required.
  - Very Small System Waiver for systems serving < 500 and have collected all Stage 1 samples. No additional sampling required.

Stage 2 DBPR

- Results of IDSE are used to determine routine monitoring locations. Monitoring frequency is:

Source Water Type	Population Size	Monitoring Frequency	Distribution System Monitoring Locations
Subpart H	< 500	Per year*	2
	500 – 3,300	Per quarter	2
	3,301 – 9,999		2
	10,000 – 49,999		4
	50,000 – 249,999		8
	250,000 – 999,999		12
	1,000,000 – 4,999,999		16
	≥ 5,000,000		20
Groundwater	< 500	Per year*	2
	500 – 9,999		2
	10,000 – 99,999	Per quarter	4
	100,000 – 499,999		6
	≥ 500,000		8

* During warmest time of year

Stage 2 DBPR

- Compliance based on a Locational Running Annual Average (LRAA) which is an RAA, but computed for each monitoring location. If any of the LRAAs are above MCL, system is out of compliance.
- If a system monitors once per year, compliance is determined by the one sample.

Stage 2 DBPR

- Operational Evaluation Levels were introduced to try and reduce peaks in DBPs.
- Operational Evaluation Levels (QEL) must be computed quarterly for each sample location for TTHM and HAA5:

$$QEL = (Q_1 + Q_2 + 2 \bullet Q_3)/4$$

where Q_3 is the current quarterly result, and Q_1 and Q_2 are the results from the two previous quarters.

- If the QELs exceed the MCLs, the system must perform an operational evaluation to include consideration of treatment and distribution operational practices.
- An operational evaluation report must be submitted to the state within 90 days of receiving the analytical results. Failure to submit report is a M&R violation

DBP Reduction

- System review for addressing high disinfection byproducts should include the following:
  - Treatment modifications
  - Disinfectant usage
  - Storage design, operation and maintenance
  - Distribution management

DBP Reduction

Treatment:

- Goal is to reduce DBP precursors prior to chlorination.
- Modifications to process control should be reviewed:
  - Is the operator properly adding coagulant?
  - Is there a better coagulant option?
  - Should a coagulant aid be used?
- Does the operator have sufficient time at the plant?

DBP Reduction

Disinfectant:

- Is the system pre-chlorinating? If so, can this be eliminated?
- Can the chlorine dose be decreased?
  - Make sure CT is being met
  - Would this require a new disinfection profile?
  - Can booster chlorination be considered?
  - Do consecutive systems need to be considered?

DBP Reduction

Storage:

- Goal is to reduce water age.
- Are tanks poorly mixed? Possible solutions include
  - Decreasing inflow/outflow pipe diameter
  - Baffling tank
- Can tank operation be modified to increase turnover rate?
- Is there excessive storage capacity?

DBP Reduction

Distribution:

- Goal is to minimize residence time in distribution.
- Ensure an adequate flushing program.
- Looping dead ends when appropriate.
- Ensure proper valving.

Questions

- What are the minimum and maximum chlorine residuals allowed in distribution? At the system entry point?
- If the RAA of a system collecting annual samples for TTHM is 80.51 mg/l, are they in compliance?

Quick Reference Guides

Stage 1 D/DBP Rule
http://www.epa.gov/safewater/mdbp/qrg_st1.pdf

Stage 1 D/DBP Rule for Laboratories
http://www.epa.gov/safewater/mdbp/pdfs/st1labqrg-final02rev.pdf

Stage 2 D/DBP Rule for Schedule 1-4 systems (population based)
http://www.epa.gov/safewater/disinfection/stage2/pdfs/qrg_stage_2_dbpr_qrg_sch1_final.pdf (>100,00)

http://www.epa.gov/safewater/disinfection/stage2/pdfs/qrg_stage_2_dbpr_qrg_sch2_final.pdf (50,000-99,999)

http://www.epa.gov/safewater/disinfection/stage2/pdfs/qrg_stage_2_dbpr_qrg_sch3_final.pdf (10,000-49,999)

http://www.epa.gov/safewater/disinfection/stage2/pdfs/qrg_stage_2_dbpr_qrg_sch3_final.pdf (<10,000)

Distribution Systems: A Best Practices Guide
http://www.epa.gov/safewater/smallsystems/pdfs/guide_smallsystems_dist_system_08-25-06.pdf