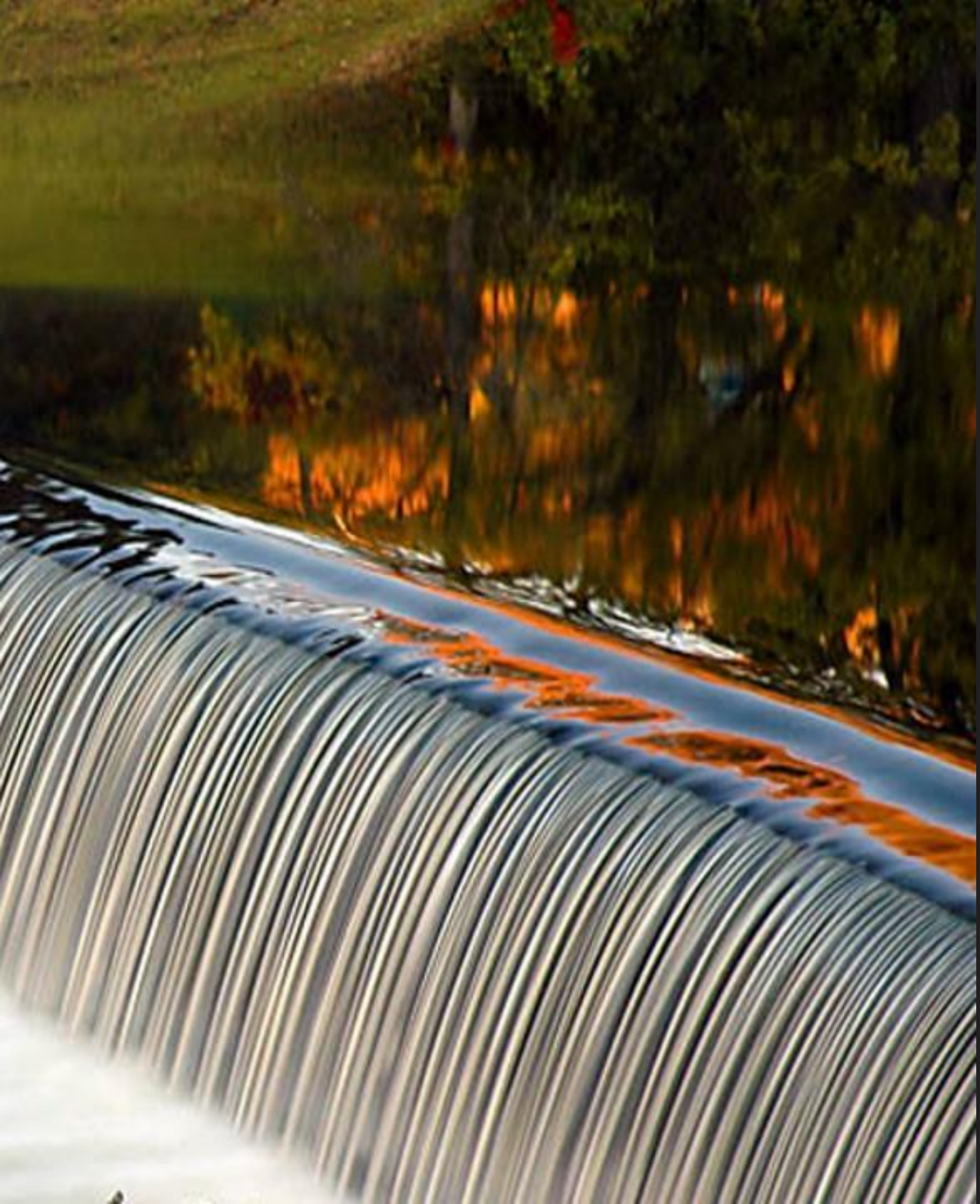

Water New Zealand Conference 2019
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Disinfection Byproduct Control Strategies

Introduction

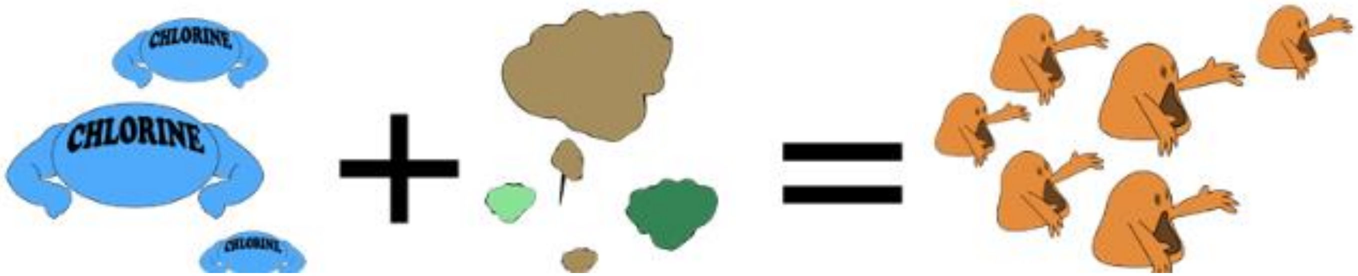
- Disinfection is an essential step for production of safe drinking water.

- Real, acute risks of waterborne disease can be overshadowed by concerns over chronic exposure to Disinfection Byproducts (DBPs)

- Current regulations balance these competing objectives by taking a precautionary stance by minimizing DBP formation while ensuring adequate disinfection

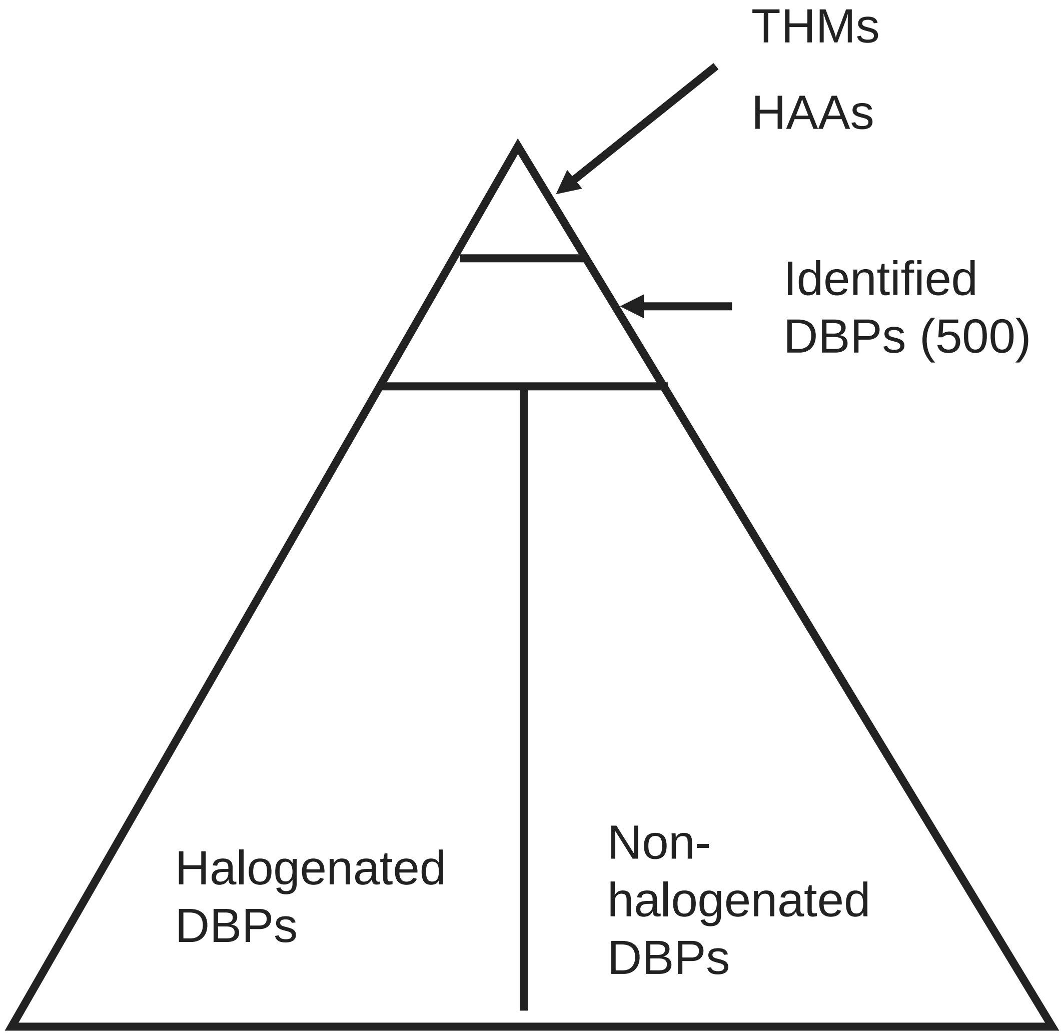
Chemistry of DBPs

- All chemical oxidants form DBPs: Cl_2, NH_2Cl, O_3, ClO_2
  - UV at germicidal doses appears to form very few DBPs
- Disinfectant + Precursors = DBPs
- Formation affected by:
  - Precursor material
  - pH, temperature, time
  - Dose, residual



DBP Iceberg

- THMs and HAAs are the largest group of DBPs commonly found in drinking water
- THMs and HAAs treated as “indicator species” for other DBPs
- Regulated DBPs represent very small portion of DBPs formed



THMs

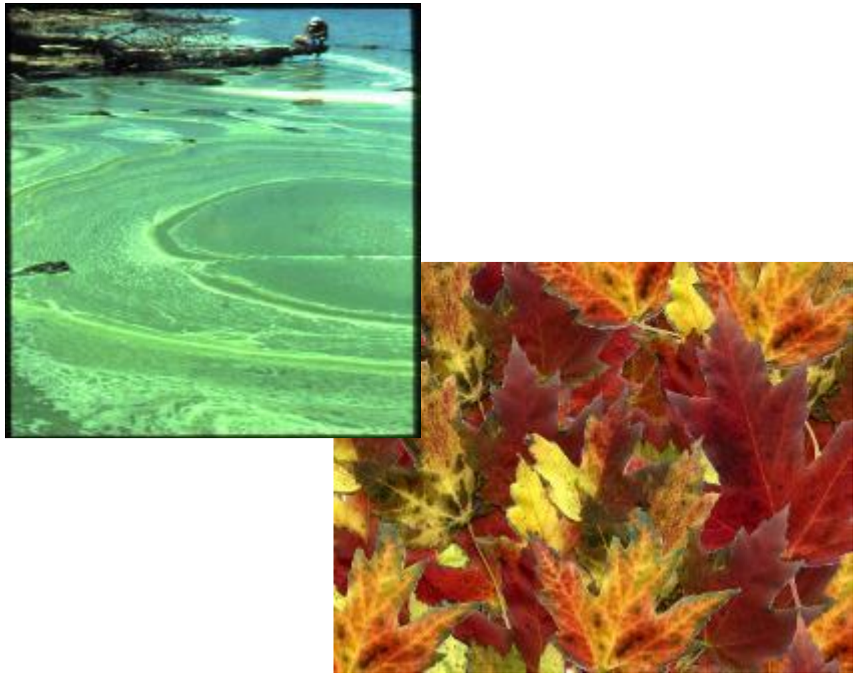
HAAs

Identified DBPs (500)

Halogenated DBPs

Non-halogenated DBPs

DBP Precursors

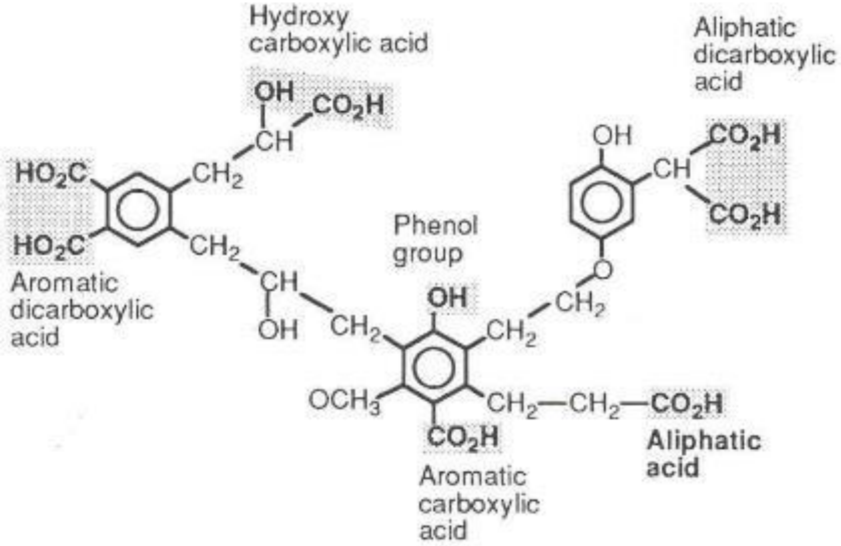


Natural Organic Matter (NOM)

- dissolved-phase organic chemicals present in natural water supplies
- Originate from decaying vegetation, algae, municipal wastewater
- Measured with:
  - Colour, TOC, UV absorbance

Others:

- Bromide: often associated with seawater intrusion into aquifers



NOM and Chlorinated DBPs

Humic Fraction:

- Higher molecular weight
- Higher SUVA
- Higher yields of THM, HAA

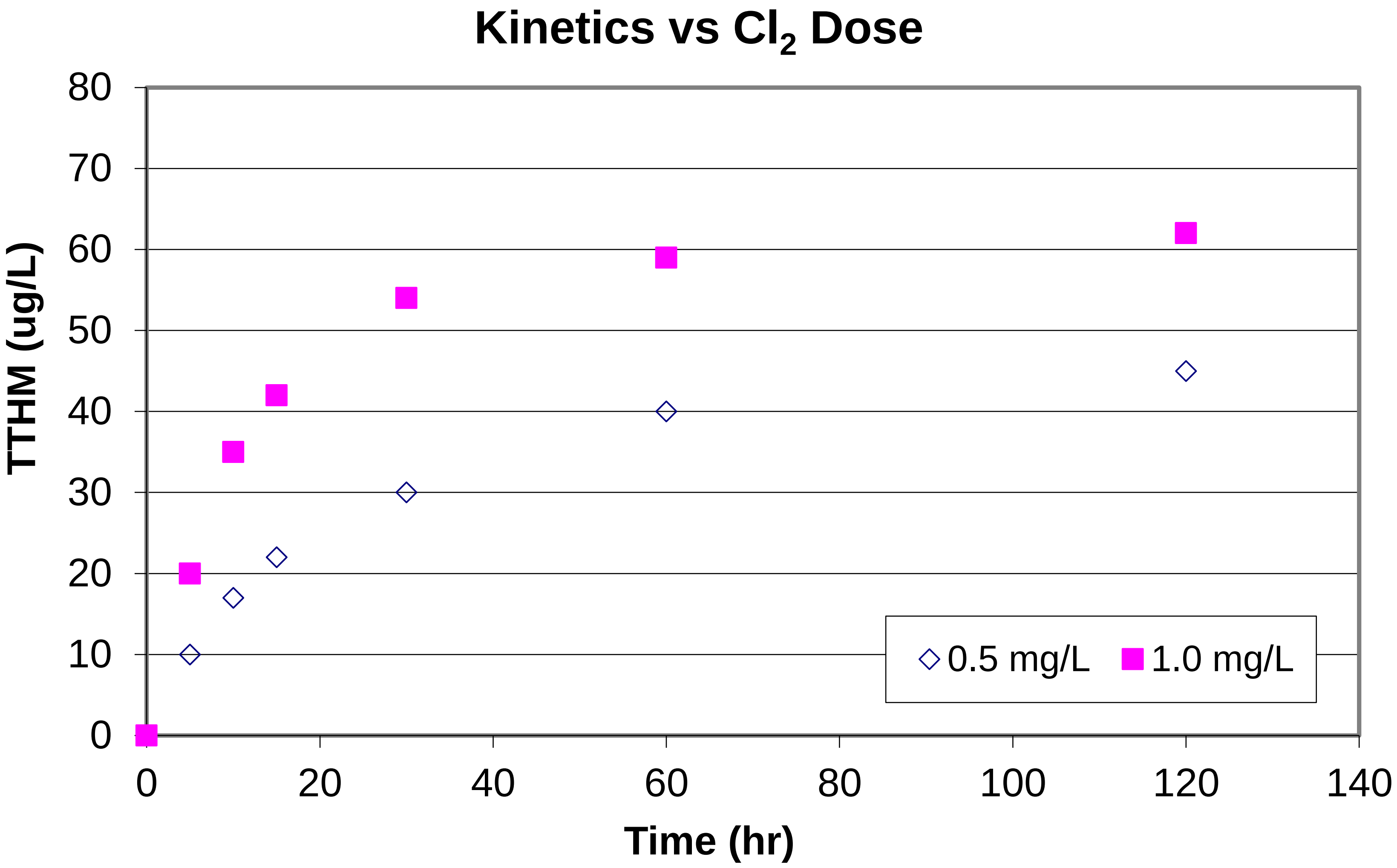
$$SUVA = \frac{UV_{254}(cm^{-1}) \times 100}{DOC(mg/L)}$$

NOM Fraction	Chlorine Demand (mg Cl_2/mgC)	THMFP (µg$CHCl_3$/mgC)	SUVA (L/mg-m)
Humic Acids	3 ± 0.2	51 ± 2	4.6
Fulvic Acids	1.4 ± 0.12	26 ± 2	3.1
Hydrophilic Acids	1.2 ± 0.2	21 ± 1.4	2.0
Hydrophobic Neutrals	0.27	12	2.0

Adapted from Krasner et al. (1996)

THM Formation Kinetics

Reducing chlorine dose good strategy for control
(Maintain CT!)



DBP Control Techniques

Remove Precursors

- Coagulation
- Softening
- GAC adsorption
- Membrane treatment

Change disinfection practices

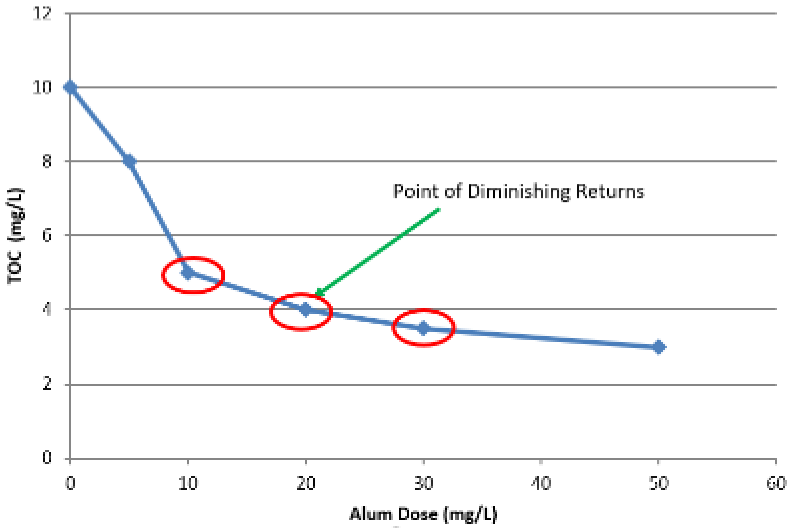
- Switch to alternative disinfectant (non-Cl_2)
- Move point of chlorination
- Fine-tune disinfection chemistry

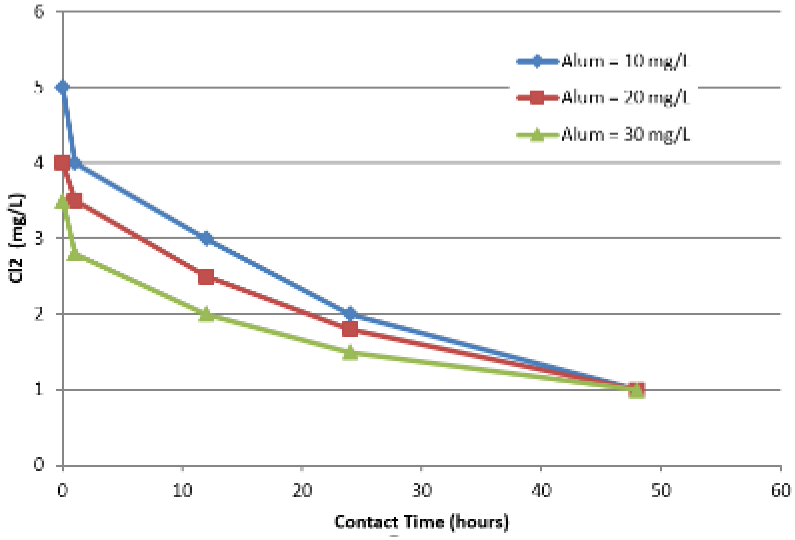
Remove DBPs

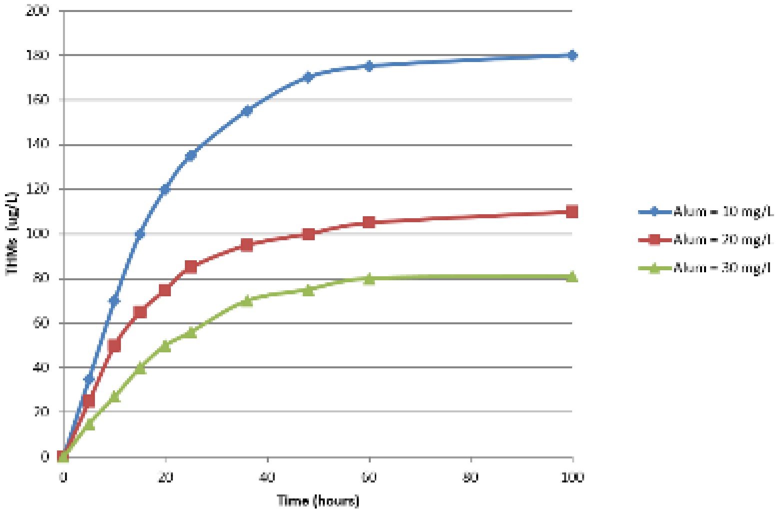
- Biofiltration
- GAC adsorption
- Air Stripping

Precursor Removal - Coagulation

- Coagulation is the least expensive process for NOM removal
- One of the best tools for removing bulk NOM
- Removes DBP precursors
- Reduces downstream Cl_2 or O_3 demand; improves UVT

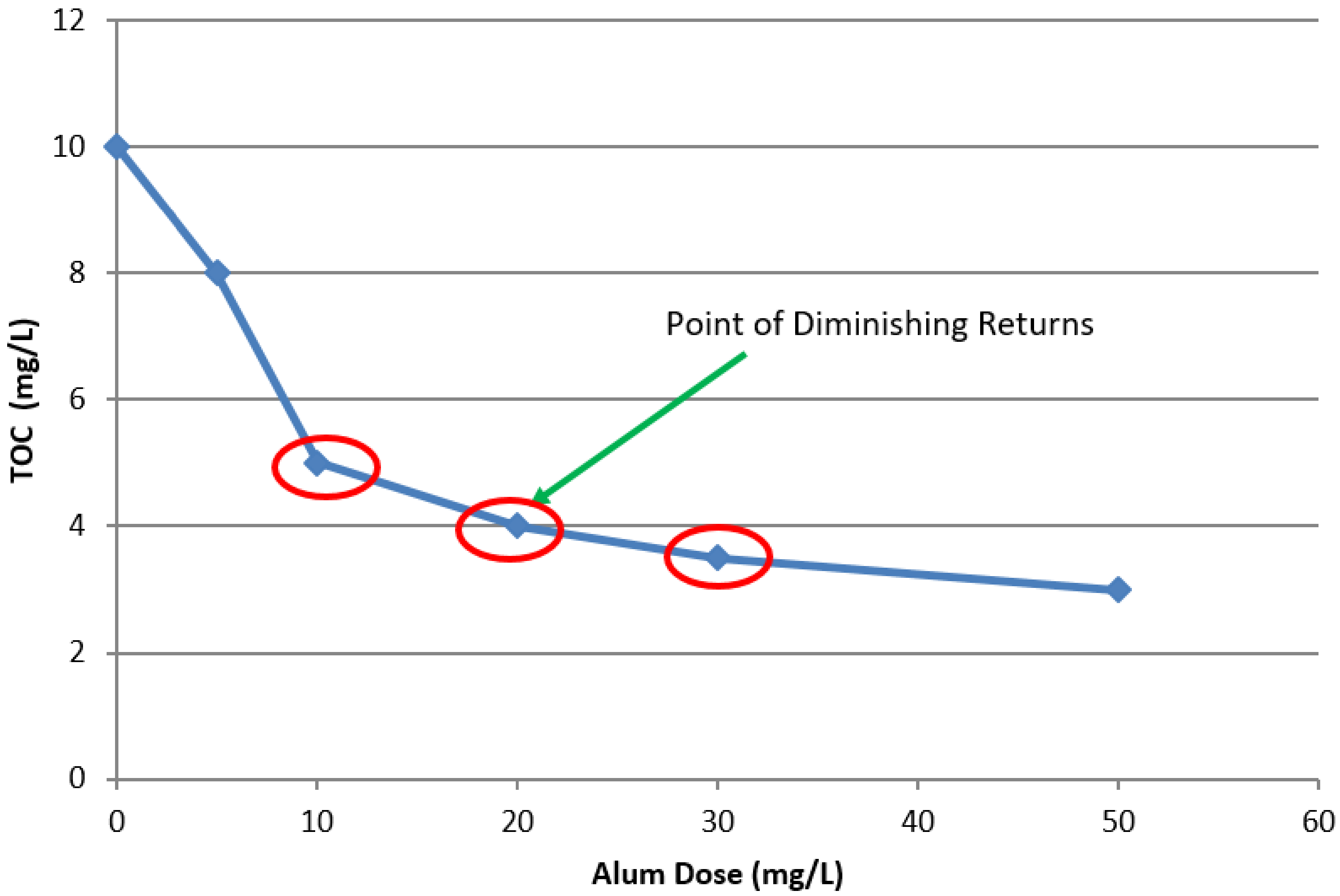






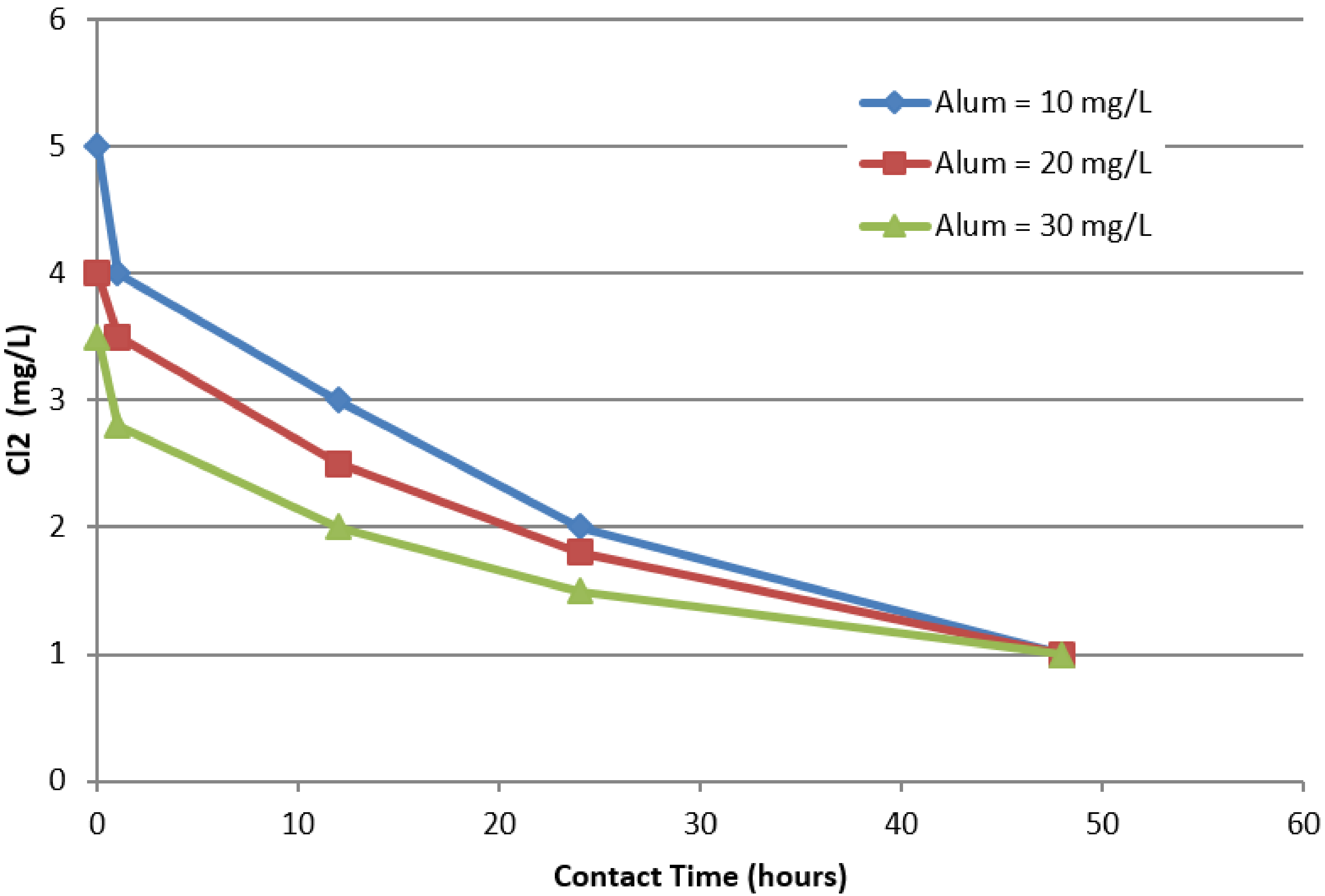
Bench-Scale SDS Tests to Assess Coagulation

- Jar test is conducted to measure the removal of TOC.
- Three coagulant doses (10, 20, 30 mg/L alum) near the point of diminishing returns are selected for further analysis



Bench-Scale SDS Tests to Assess Coagulation

- Chlorine demand/decay tests done to determine chlorine dose needed for each water
- An applied chlorine dose that yields the desired chlorine residual after the desired time (in this case a 1.0 mg/L residual after 48 hours) is determined



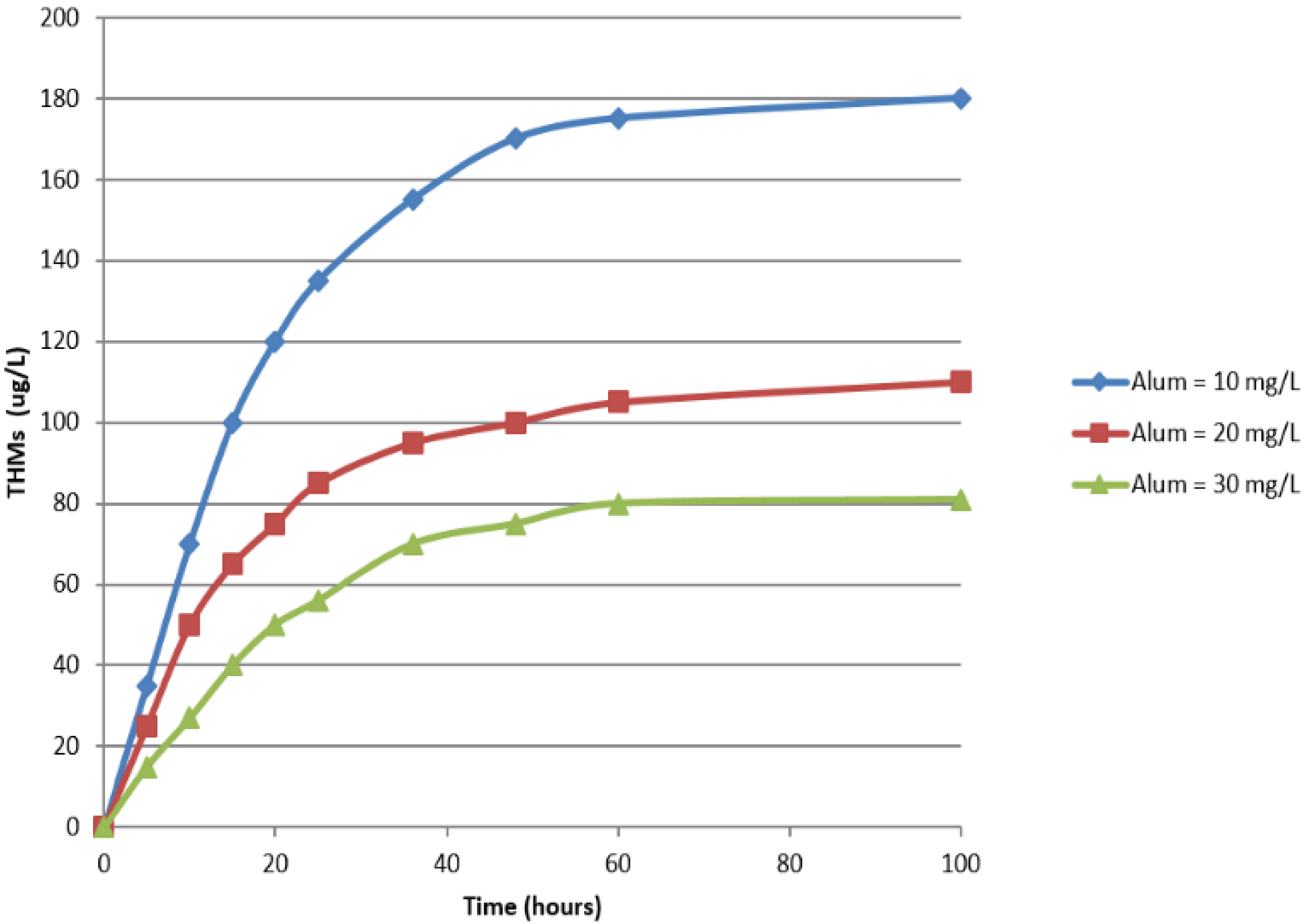
Bench-Scale SDS Tests to Assess Coagulation

Another sample of treated water is chlorinated with the appropriate applied chlorine dose

- 10 mg/L alum plus 5 mg/L Cl_2
- 20 mg/L alum plus 4 mg/L Cl_2
- 30 mg/L alum plus 3.5 mg/L Cl_2

DBPs are measured over time

- 30 mg/L alum needed to comply with regulations



Precursor Removal - GAC

Generally expensive for NOM removal

- Short bed life (6 weeks to 6 months)
- Poor bed usage

Best applied after coagulation to minimize NOM loading

GAC adsorbs high molecular weight, hydrophobic (non-polar) compounds

Pilot scale evaluation required

Membrane Precursor Removals

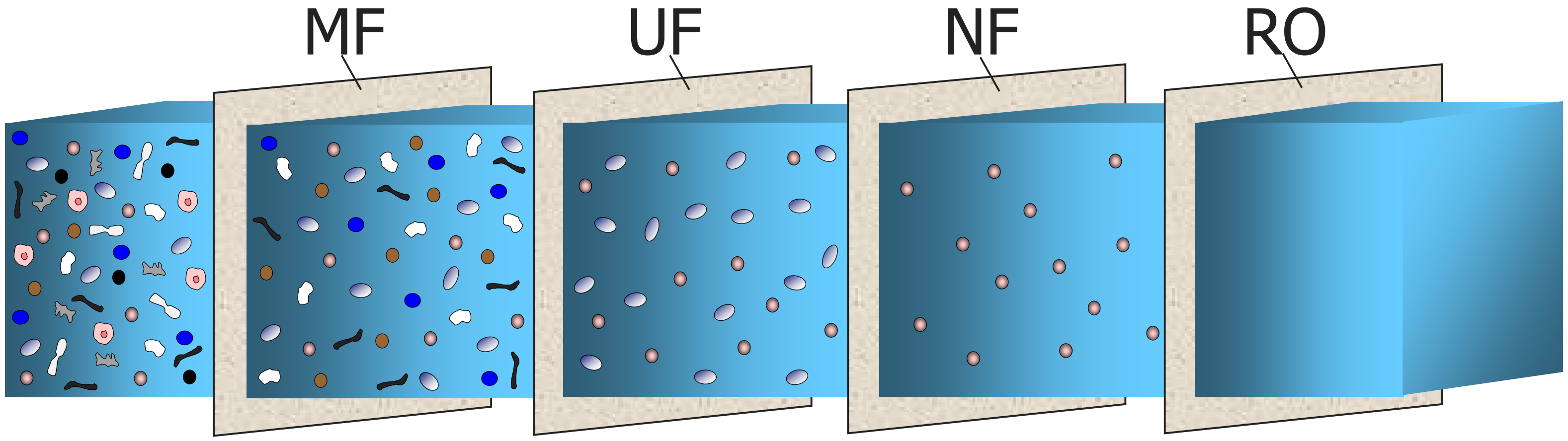
MF/UF designed to remove particulates

  - Will not remove dissolved NOM

NOM must be converted to solid phase (coagulation or PAC) prior to membranes

NF/RO membranes will remove NOM and DBP precursors in dissolved phase

  - Typically require MF/UF treatment upstream of NF/RO to prevent particulate fouling



MF	UF	NF	RO
0.1 - 0.2 Micron	13k - 100k MWCO	200 - 400 MWCO	0.001 Micron
- Turbidity - Particles - Bacteria - Cysts/Oocysts - Some Viruses	- Turbidity - Particles - Bacteria - Cysts/Oocysts - Viruses	- Dissolved Organics - Color - TOC - DBP-FP - Hardness Ions - Some TDS	- Dissolved Organics - Color - TOC - DBP-FP - Hardness Ions - TDS

Headingly, Canada

- 150 L/s (population 15,000)
- Key raw water quality parameters:
  - Settled Turbidity: 10 ~ 60 NTU
  - True Color: 15 ~ 41
  - Hardness: 300 ~ 600 mg/L as $CaCO_3$
  - TDS: 724 ~ 890 mg/L
  - TOC: 11 ~ 15 mg/L
  - Iron: 0.22 ~ 1.71 mg/L
  - Manganese: 0.033 ~ 0.193 mg/L
  - Total Alkalinity: 180 ~ 360 mg/L
- UF for Pathogens
- Low pressure RO for organics, hardness
- No coagulant sludge

Moving Point of Chlorination

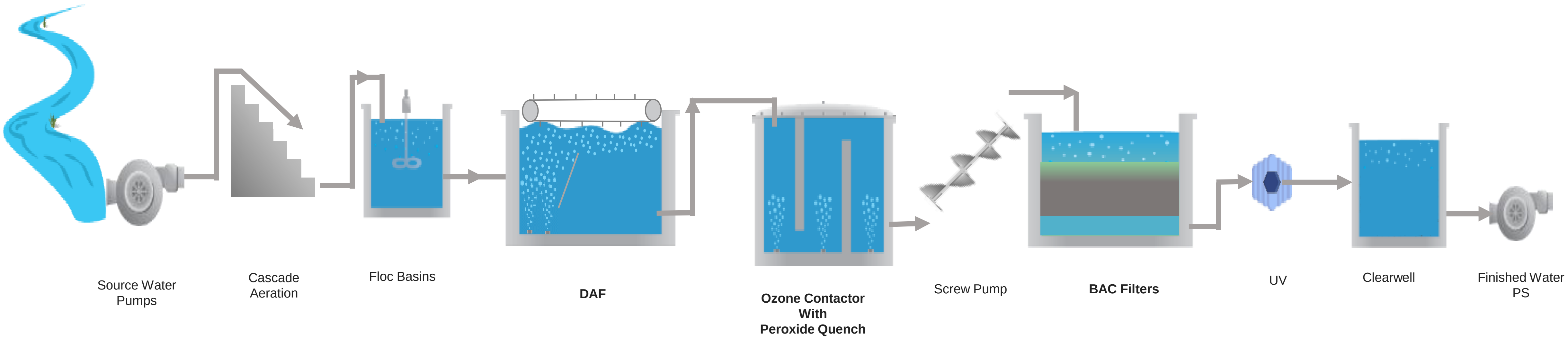
Pre-chlorination should be avoided for any water with high NOM

Move point of chlorination to downstream of coagulation/clarification

- Removes bulk of DBP precursors
- Retains benefits of oxidation prior to filtration (if necessary)
- Results in chlorination at low pH; lower CT’s required, lower Cl_2 doses possible

Biofiltration

- Generally, NOM in raw water not amenable to biodegradation
- Biofiltration performance marginal for DBP precursor removal in non-oxidized waters
- Oxidation required to break NOM into smaller, easily biodegradable, lower m.w. compounds
- Biofiltration needed after ozonation to ensure finished water is biologically stable



GAC Adsorption for DBP Removal

GAC can be effective for removal of DBPs after formation

Usually not cost effective

- Most DBPs are not well adsorbed
  - THMs: moderate
  - HAAs: poor
- Significant competing adsorption from NOM
- Bed life short

Removal of precursors much better approach…

Air Stripping for DBP Removal

- THMs are volatile
- Aeration inside distribution system storage tanks can remove THMs after formation.
- HAAs are not volatile – air stripping not effective

Bench-Scale Testing

- DBP chemical reactions lend themselves well to bench-scale testing (unlike physical-chemical filtration processes)

- Money and time can be saved by using bench-scale evaluation techniques, compared to pilot studies

- Bench-scale testing more accurate than pilot testing due to precision of chemical dosing and batch analysis

Disinfection and DBP Health Risk Facts

1. Cotruvo, J.A. and Amato, H. 2019. Trihalomethanes: Concentrations, Cancer Risks, and Regulations. *Journal of the American Waterworks Association* 111:1:12-20
    - https://awwa.onlinelibrary.wiley.com/doi/full/10.1002/awwa.1210

2. Hrudey, S.E., and Hrudey, S.J. 2019. Common themes contributing to recent water disease outbreaks in affluent nations
    - https://iwaponline.com/ws/article-pdf/19/6/1767/578191/ws019061767.pdf

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Questions

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DBP Regulations

Jurisdiction	THM Limit (µg/L)	HAA Limit (µg/L)	Other Regulated DBPs
New Zealand	Chloroform 40 Bromoform 100 BDCM 60 DBCM 15	MCAA 20 DCAA 50 TCAA 200	Bromate < 0.010 µg/L Chlorate < 0.8 mg/L Cyanogen chloride < 0.4 mg/L Dibromoacetonitrile < 80 µg/L Dichloroacetonitrile < 80 µg/L Dichloromethane < 20 µg/L
United States	TTHMs 80	HAA5 60	Bromate < 0.010 µg/L A goal of zero is included for BDCM, bromoform, bromate, and DCAA. Goals for chloroform (<70 µg/L), DBCM (<60 µg/L), MCAA (<70 µg/L) and TCAA (<20 µg/L).
Canada	TTHMs 100	HAA5 80	
United Kingdom	TTHMs 100	none	
European Union	TTHMs 100	HAA9 80	

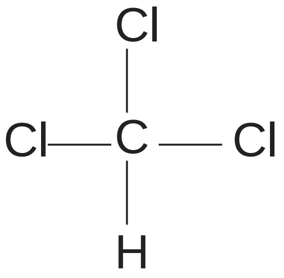
Trihalomethanes

Chloroform: $CHCl_3$

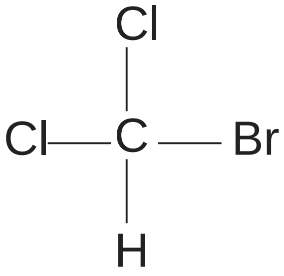
Bromodichloromethane (BDCM): $CHCl_2Br$

Dibromochloromethane (DBCM): $CHClBr_2$

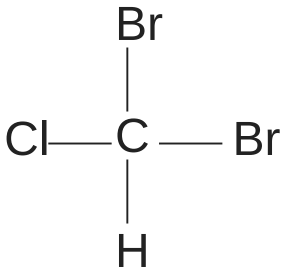
Bromoform: $CHBr_3$



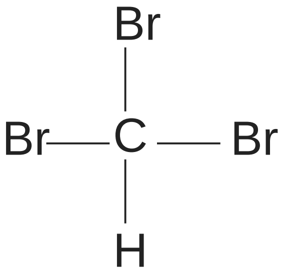
Chloroform



BDCM



DBCM

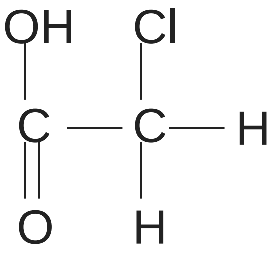


Bromoform

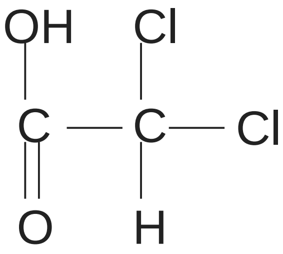
Haloacetic Acids

HAA5:

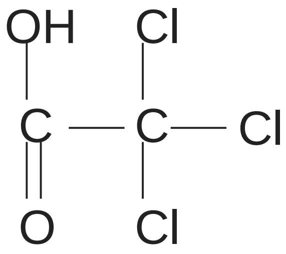
- Mono, di, tri- chloroacetic acid
- Mono, di- bromoacetic acid



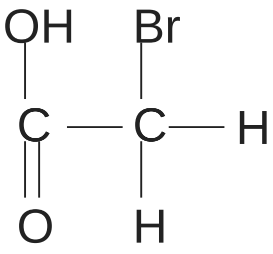
MCAA



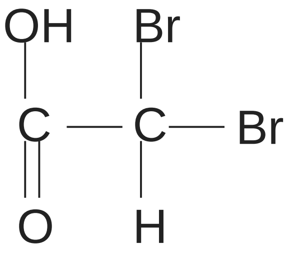
DCAA



TCAA



MBAA



DBAA

Chloramine Chemistry

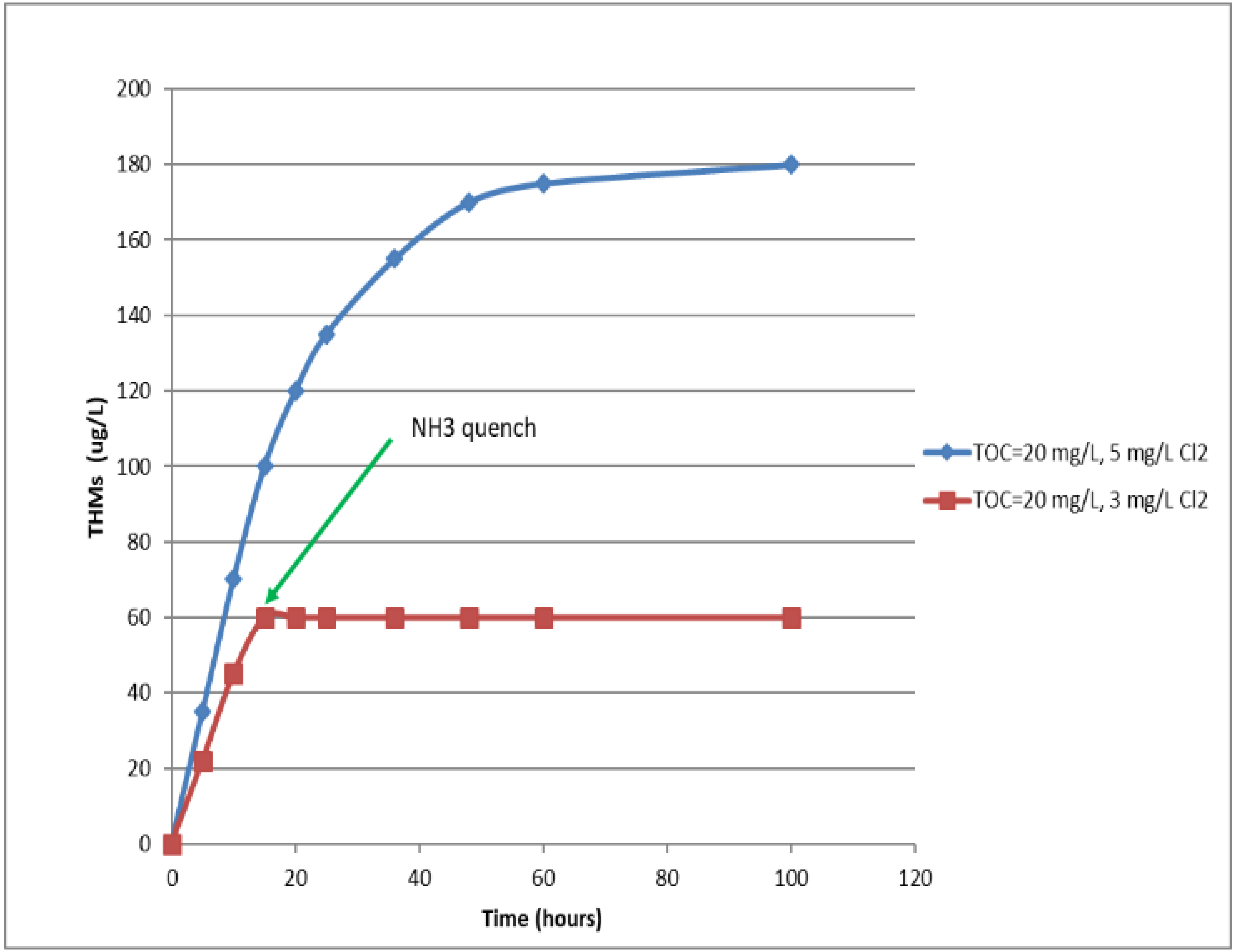
Cl_2 - NH_3 rxns out-compete Cl_2 - NOM rxns

Greatly reduces formation of THMs/HAAs

- 10 to 20% of TOX compared to Cl_2

THMs typically < 20 ug/L

HAAs typically < 40 ug/L



Chloramine DBPs

Known DBPs:

- Halogen-substituted amines
- Cyanogen chloride
- Chlorinated aldehydes
- Other Nitrogenous DBPs

NDMA ($C_2H_6N_2O$):

- probable human carcinogen
- Formation via interaction of chlorine/chloramines with polymers with amine functional groups

Current USEPA CCL contains several Nitrogenous DBPs

Krasner, S.W., Mitch, W.A., McCurry, D.L., Hanigan, D., Westerhoff, P. 2013. Formation, precursors, control, and occurrences of nitrosamines in drinking water. *Water Research* 47: 4433-4450.

Krasner, S.W., Mitch, W.A., Westerhoff, P., Dotson, A. 2012. Formation and control of emerging C- and N-DBPs in drinking water. *Journal of the American Waterworks Association* 104,11: E582-E595.