DBPs and Biofilm Interactions in Distribution Systems

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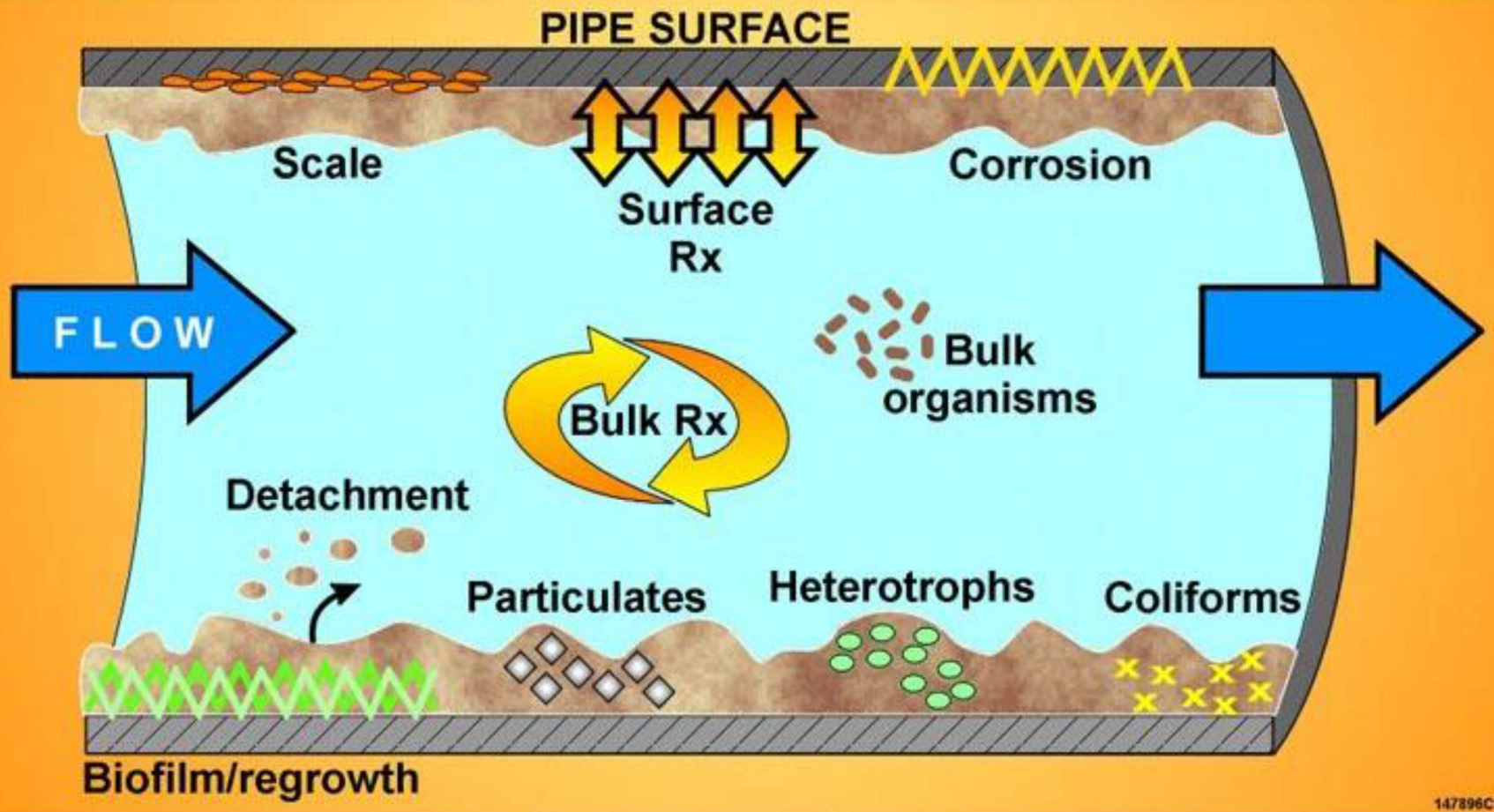
Drinking Water Biofilm

- Structure
  - Thin (1- 100 µm)
  - Patchy and non-uniform (low nutrient environment)
  - Cells embedded in extracellular matrix (EPS)
  - Diverse microbial community
- Location
  - Pipe walls
  - Storage tank walls
  - Sediment (“thicker biofilms”)
- Impact (water quality degradation)
  - Corrosion/metals release
  - Residual loss
  - Harbor pathogens
  - DBP formation from reactions with disinfectants

The Distribution System as Reactor



DBP Interactions with Biofilm

- DBP biodegradation by metabolism or cometabolism
- DBP concentrations likely to be too low to support microbial growth in the absence of other carbon and energy sources such as NOM and ammonia
- DBP formation from reactions between disinfectants and metabolic intermediates, soluble metabolic products (SMPs) and extracellular polymeric substances (EPS)
- Toxicity to biofilm from intermediate products of DBP cometabolism
- Competing formation and degradation reactions: some DBPs may increase while others may decrease

Types of Metabolism

1. Primary Metabolism (AOC, Ammonia)
   - Contaminant is a carbon and/or energy source for microbial growth (organic chemicals typically both; ammonia is an energy source)

2. Secondary Metabolism (DBPs)
   - Chemical is a carbon and/or energy source
   - Concentration is too low ($<S_{min}$) to support microbial growth
   - Another growth substrate is required to sustain organisms

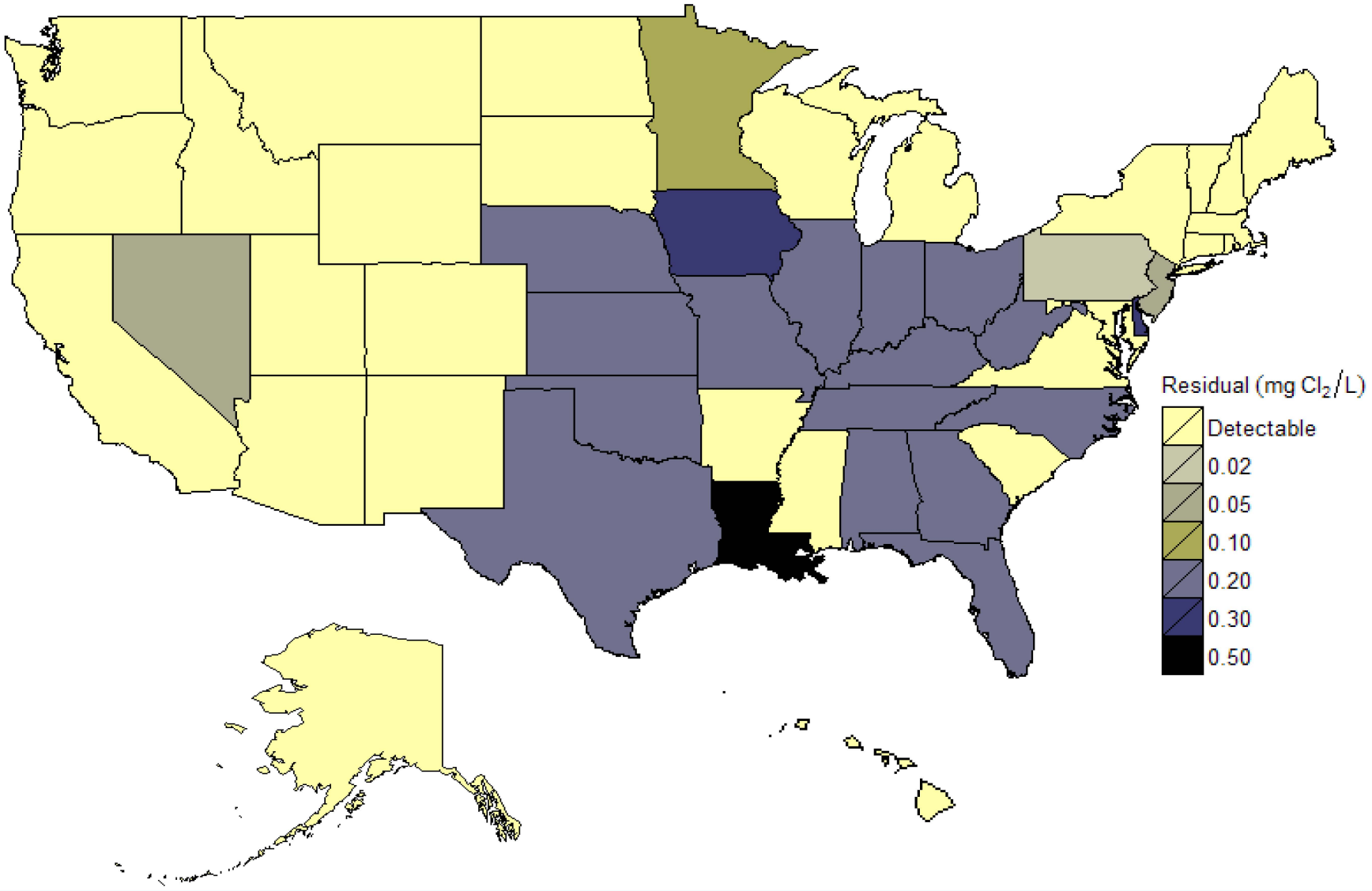
Types of Metabolism

3. Cometabolism (DBPs)
   - Not a carbon and energy source
   - Fortuitous degradation by non-specific enzymes (AMO)
   - A growth substrate is required
   - May harm bacteria
     - Toxic intermediates
     - Reductant depletion
     - Enzyme competition

Reason for Disinfectant Residual

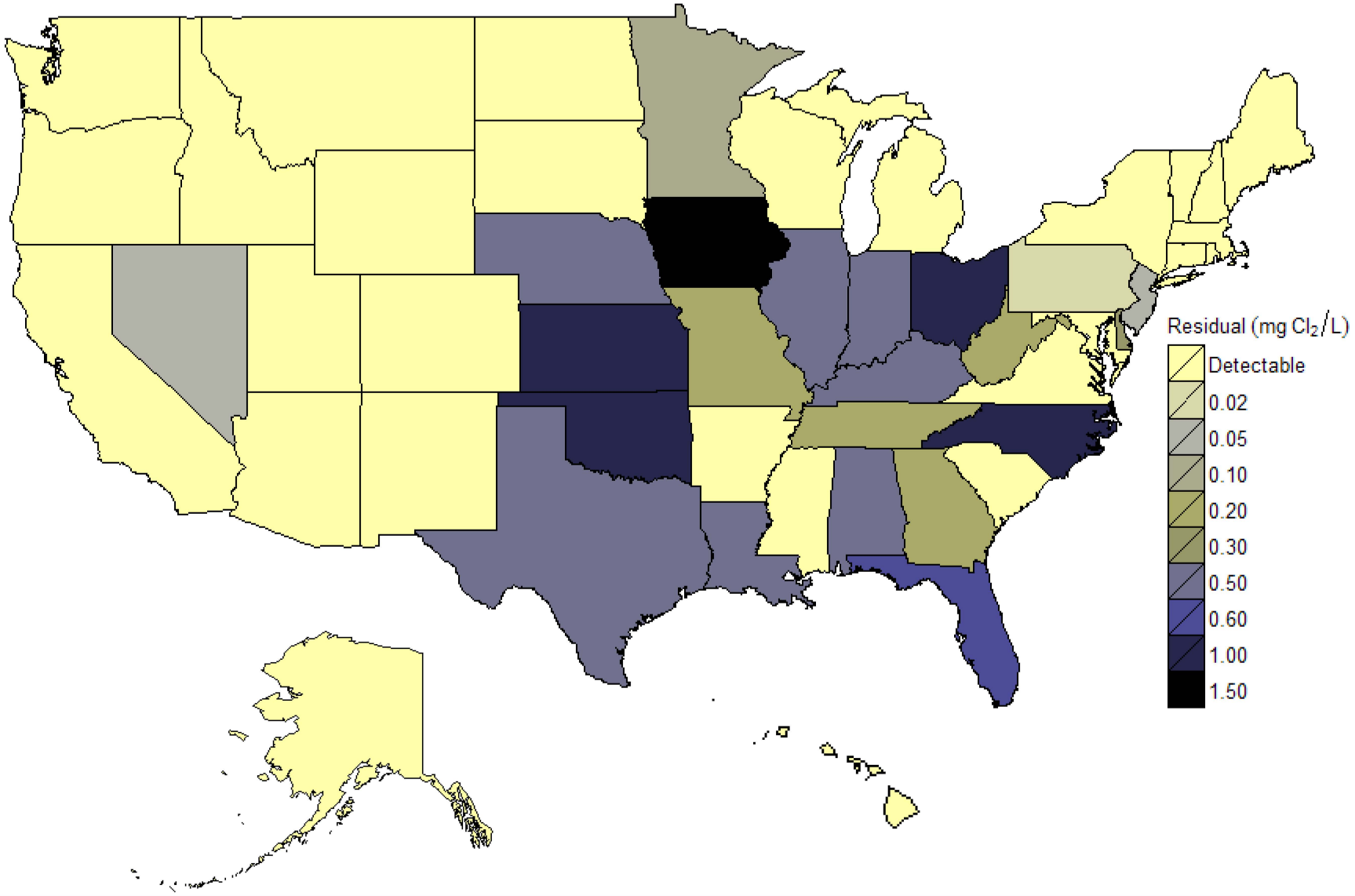
- US regulatory requirement → "detectable"
  - Surface water (SW)
  - Groundwater under direct influence (GWUDI) of SW
  - Heterotrophic plate count (HPC) < 500/mL ≡ "detectable"
- Intent behind regulations
  - Distribution system integrity
    - ❖Proper system maintenance
    - ❖Identify & limit outside contamination
  - Limit heterotrophic bacteria & *Legionella* growth
  - Provide quantifiable minimum target → action

Free Chlorine Residual Requirements



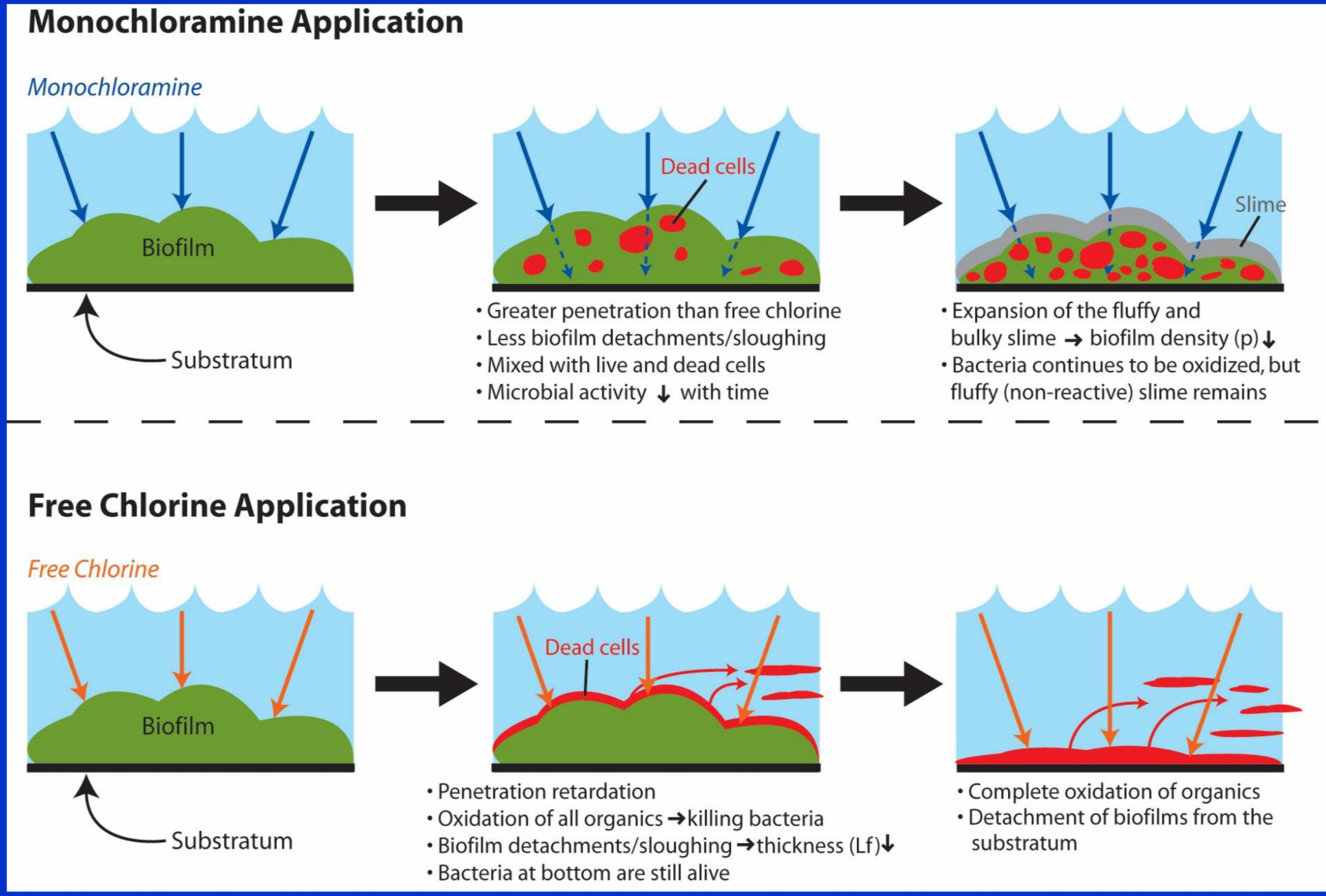
Wahman & Pressman (2015) *Journal American Water Works Association*

Total Chlorine Residual Requirements



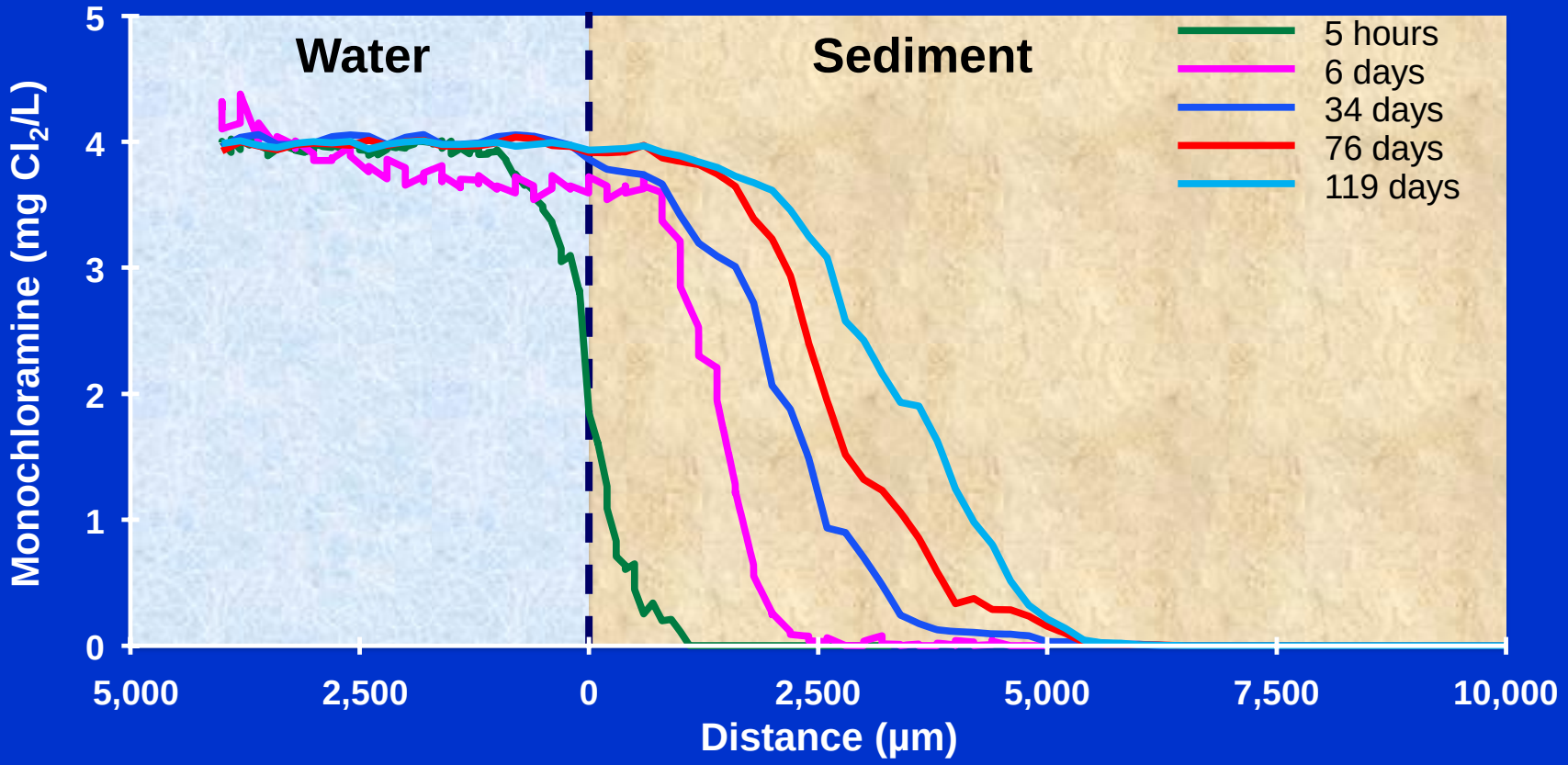
Wahman & Pressman (2015) *Journal American Water Works Association*

Disinfectant Interactions with Biofilm



Lee, Wahman, & Pressman (2012) WQTC proceedings

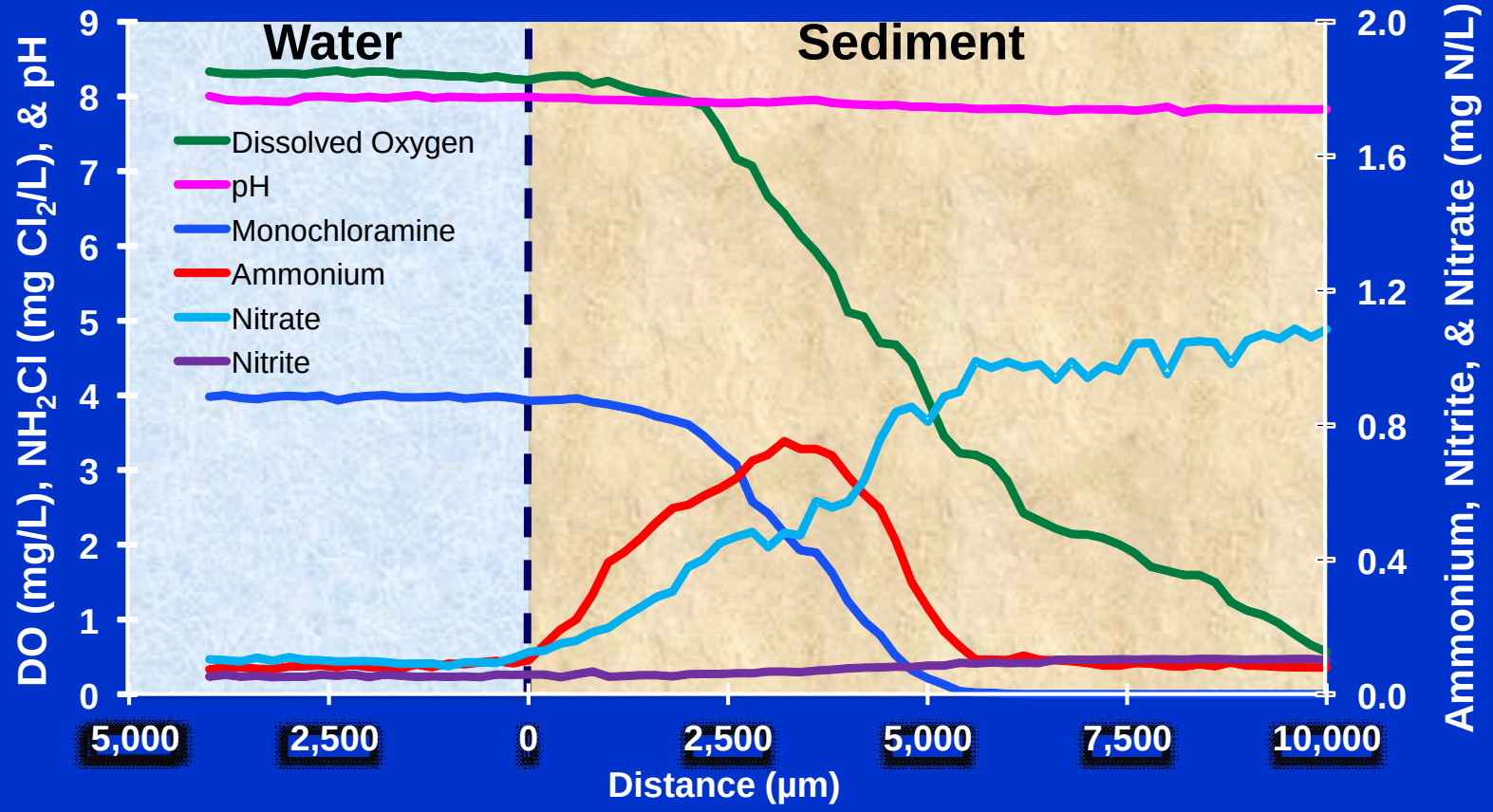
Phase 1 Monochloramine



- Slowly progressed inward
- 5 hours @ surface → 2 mg Cl_2/L
- 119 days @ 3,200 µm depth → 2 mg Cl_2/L
- Greater than 6,200 µm → no measurable monochloramine (30% penetration)

Liu, Wahman, & Pressman (2016) WQTC proceedings

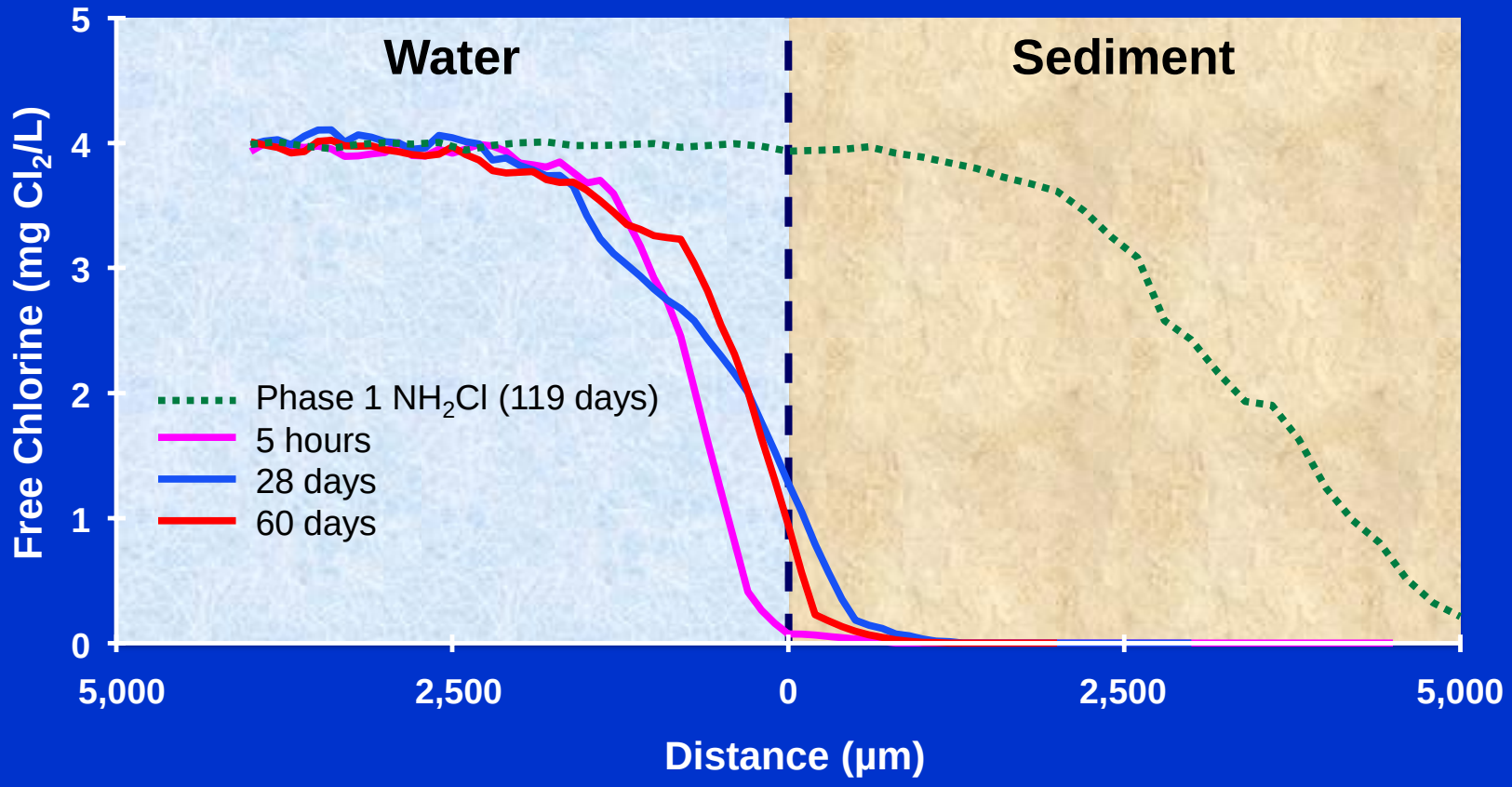
Phase 1 Final Profile Summary



- Minor pH decrease (8.0 → 7.8)
- DO consumption start corresponded with monochloramine decrease
- Complete nitrification → oxygen consumption corresponded
- DO consumption continued after ammonia removal → heterotrophic activity

Liu, Wahman, & Pressman (2016) WQTC proceedings

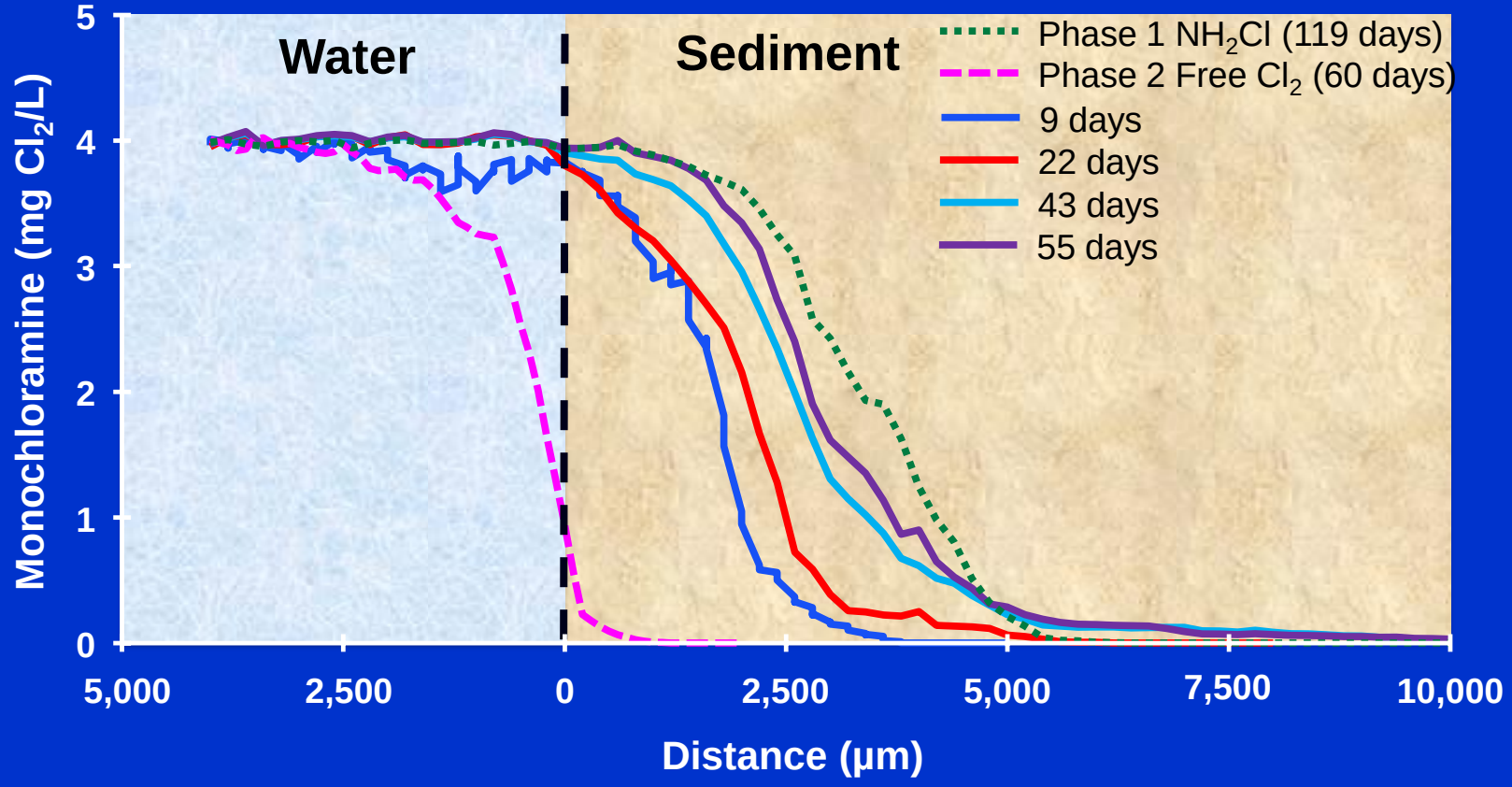
Phase 2 Free Chlorine



- Slow free chlorine penetration
- 5 hours @ surface → minimal free chlorine
- 60 days @ 250 µm depth → 0.2 mg Cl_2/L
- Greater than 500 µm → no measurable free chlorine (3% penetration)

Liu, Wahman, & Pressman (2016) WQTC proceedings

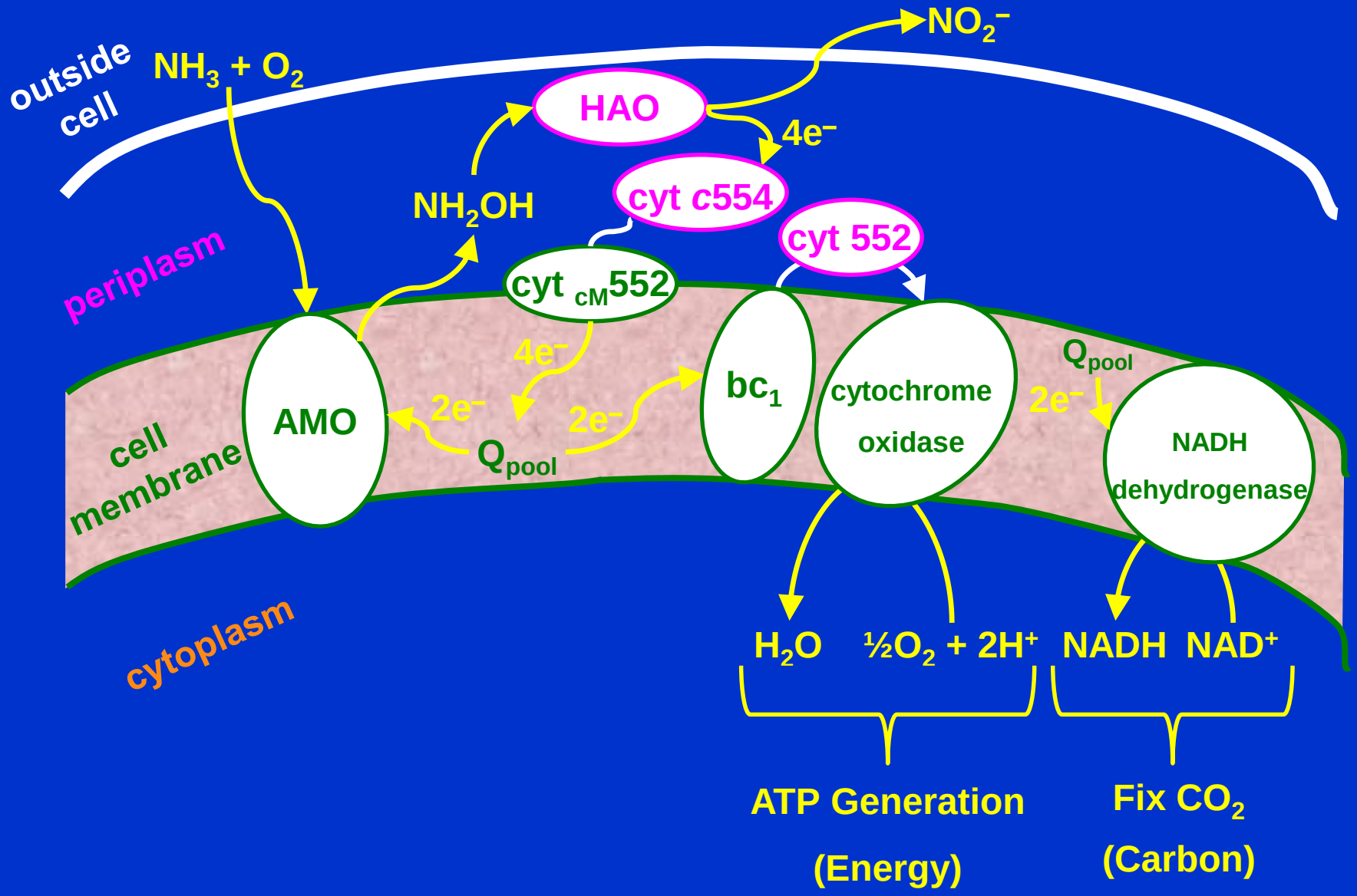
Phase 3 Monochloramine



- Final monochloramine penetration approaches Phase 1 end
- 9 days @ 1,700 µm depth → 2 mg Cl_2/L
- 55 days @ 2,700 µm depth → 2 mg Cl_2/L
- Greater than 7,500 µm → no measurable monochloramine (40% penetration)

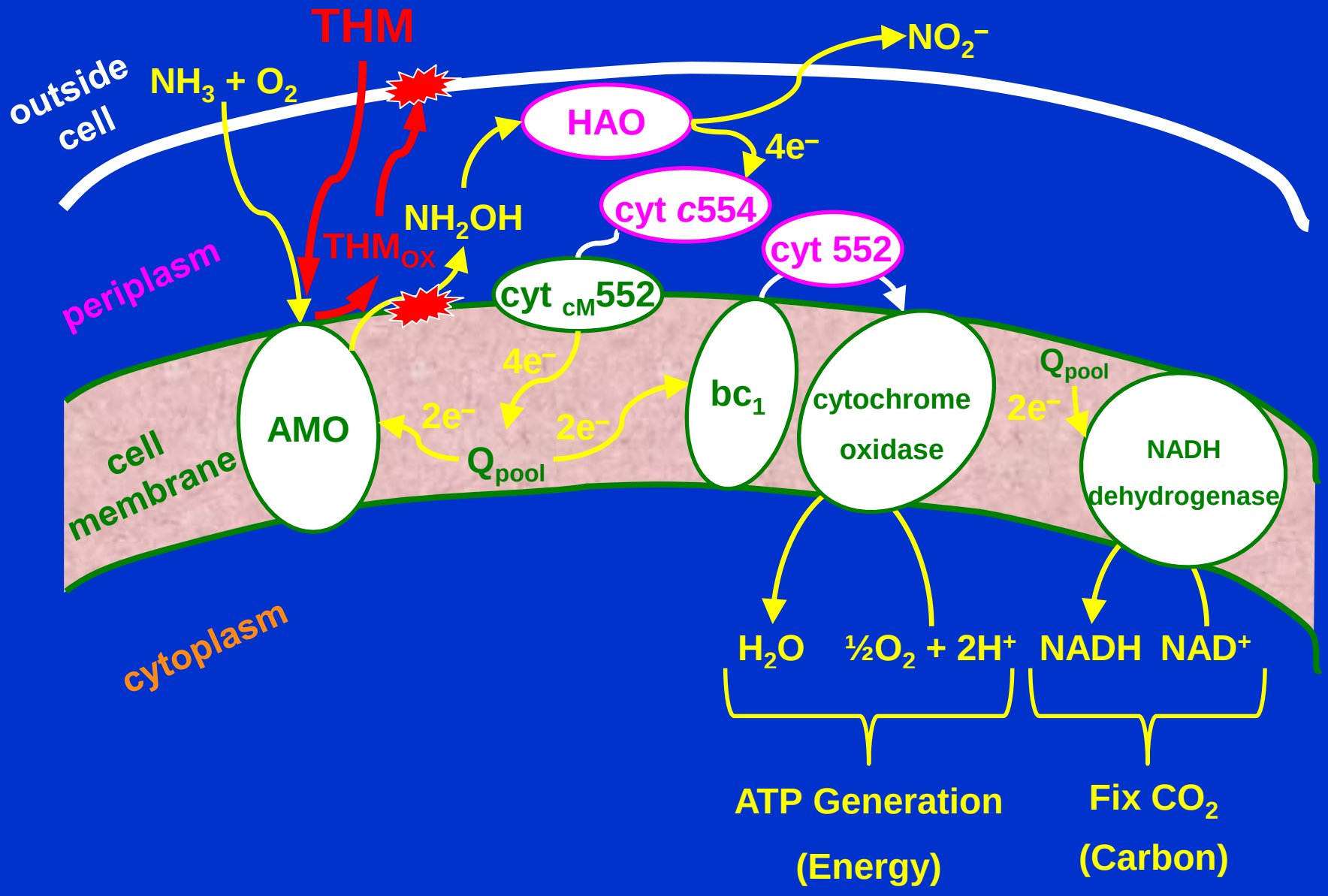
Liu, Wahman, & Pressman (2016) WQTC proceedings

Biological Ammonia Oxidation



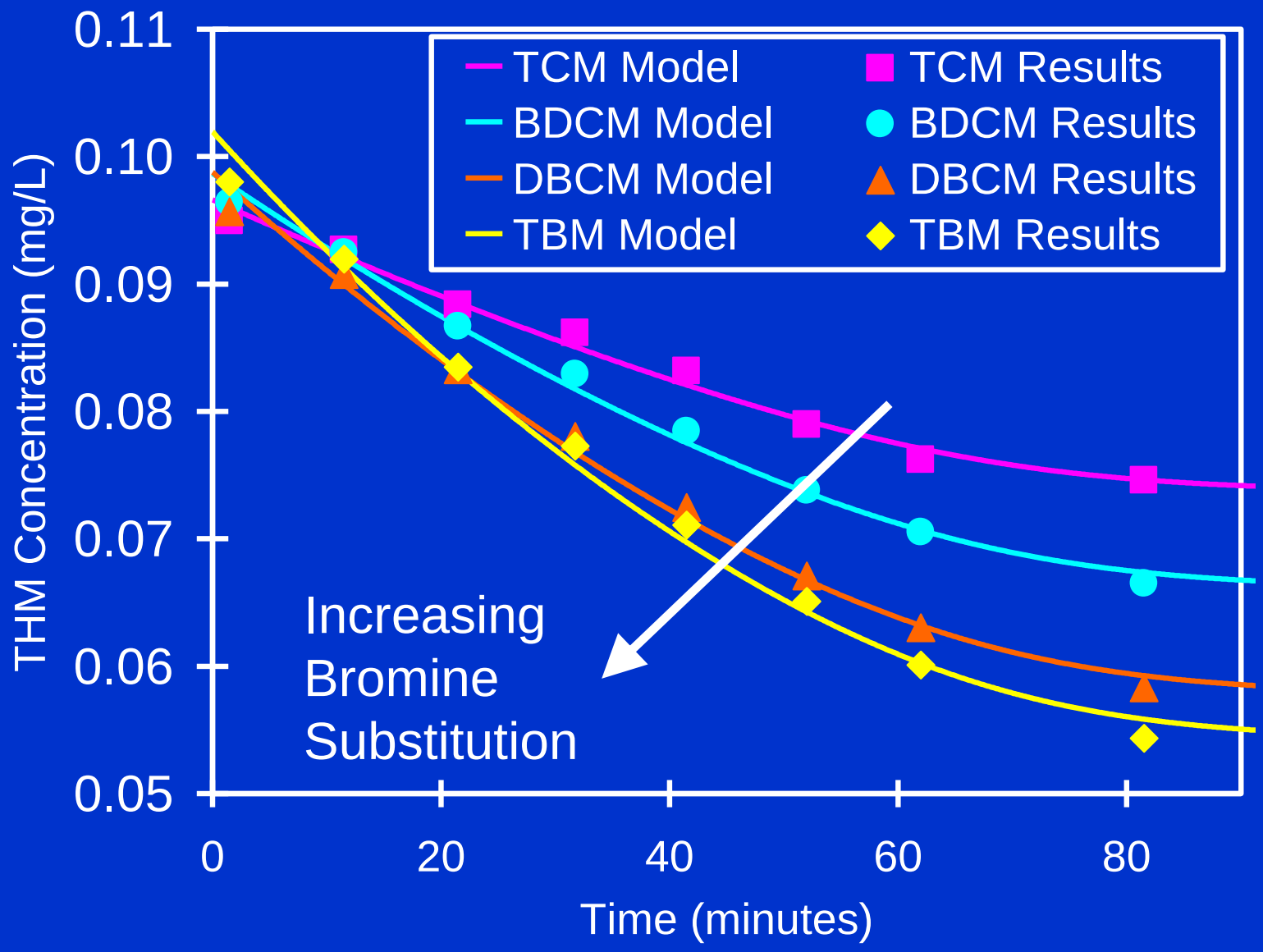
Adapted from Sayavedra-Soto and Arp (2011) *Nitrification*

Trihalomethane Cometabolism



Adapted from Sayavedra-Soto and Arp (2011) *Nitrification*

THM Kinetics – Experiment



Transformation Capacity (T_c)

$$T_c = \frac{S_{I_{THM}} - S_{F_{THM}}}{X}$$

UT Research		Literature Reported Values		
Chemical	T_c (nmol/mg)	Chemical	T_c (nmol/mg)	Source
TCM	77	TCM	92-150	Ely (1996)
BDCM	45	TCE	61-99	Alvarez-Cohen and Speitel (2001)
DBCM	31	1,1-DCE	24-45	
TBM	22	1,2-DCA	>3,500	

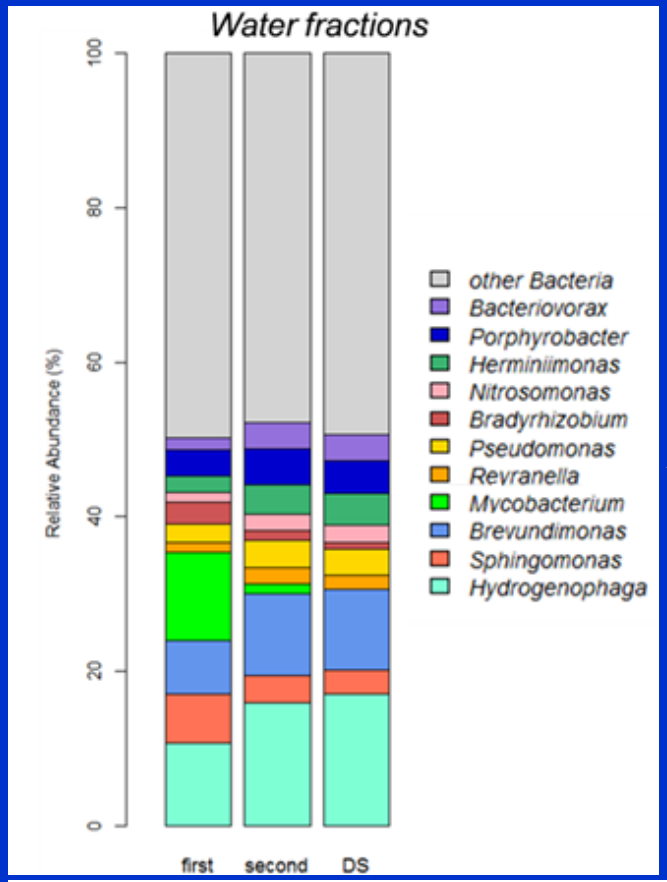
Iodine-Substituted THMs

- More toxic than corresponding chlorine and bromine-substituted analogues
- Formation favored as iodide concentration in source water increases
- Formation greater with monochloramine vs. chlorine because monochloramine oxidation of HOI is slower
- Expectations for cometabolism of Iodo-THMs
  - Kinetics should be faster than for Cl and Br-substituted THMs
  - Toxicity should be higher than for Cl and Br-substituted THMs (i.e., low transformation capacity)

Cometabolism of Other Chemicals

- Non-specific oxygenases from bacteria growing on simple aliphatics (CH_4), simple aromatics (phenol, toluene) and ammonia
- Range of chemicals include:
  - Halogenated alkanes
  - Halogenated alkenes
  - Halogenated aromatics
  - NDMA
  - Some pharmaceuticals
  - Monochloramine

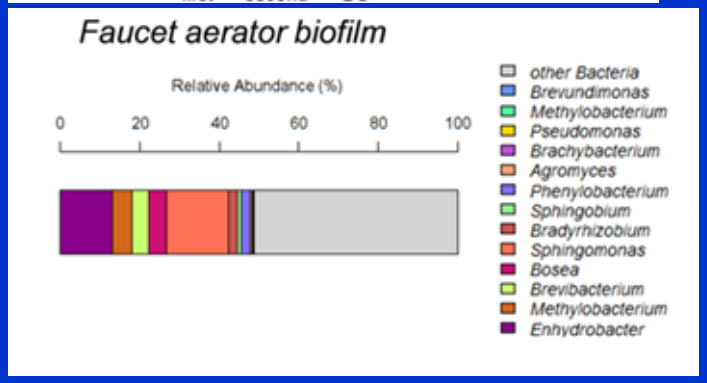
Microbial Diversity in Distribution Systems



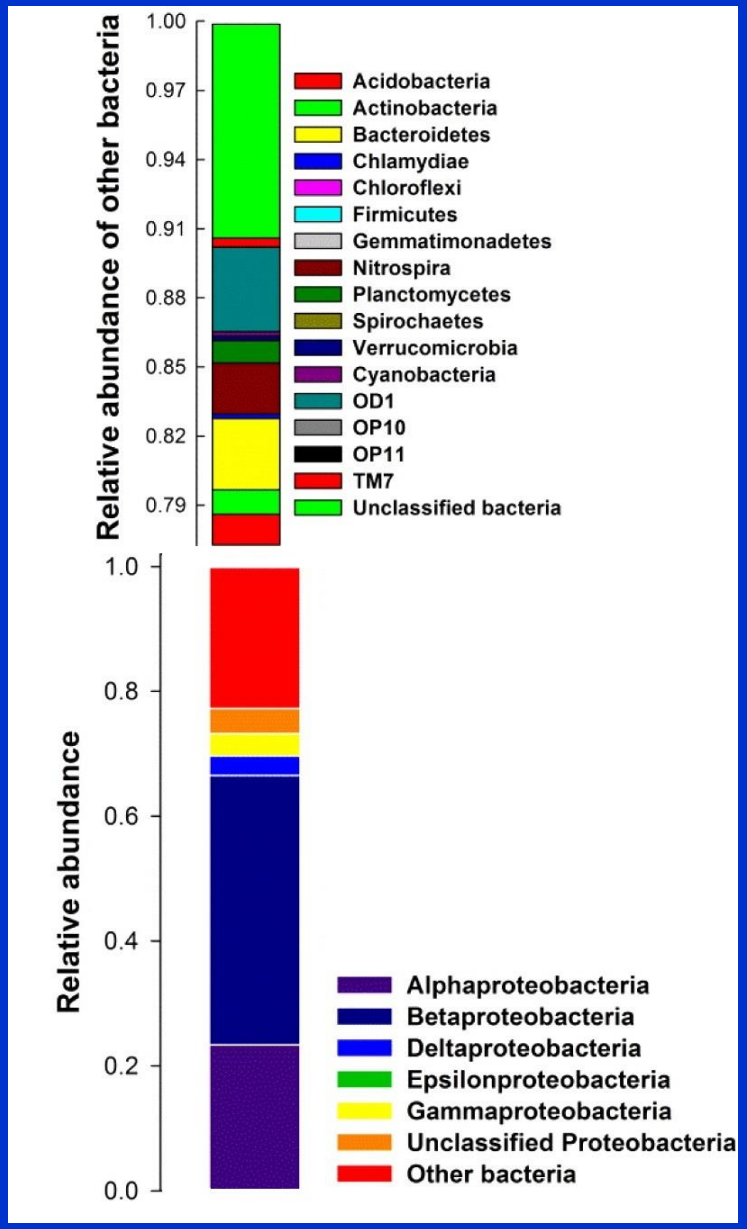
Ann Arbor, MI

Phyla →

← Genus

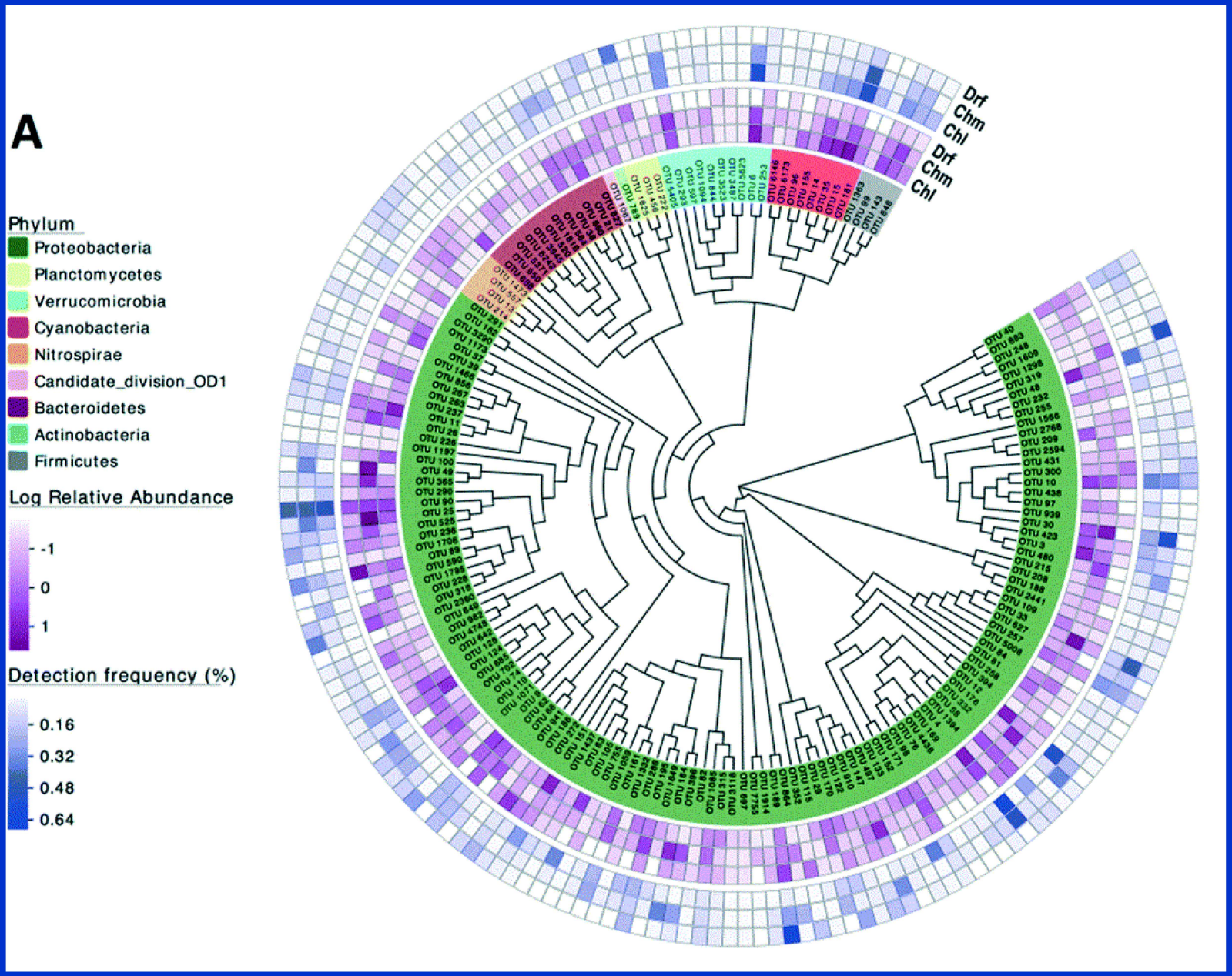


Kotlarz (Unpublished)



Pinto, Xi, & Raskin (2012) *ES&T*

Microbial Diversity in Distribution Systems

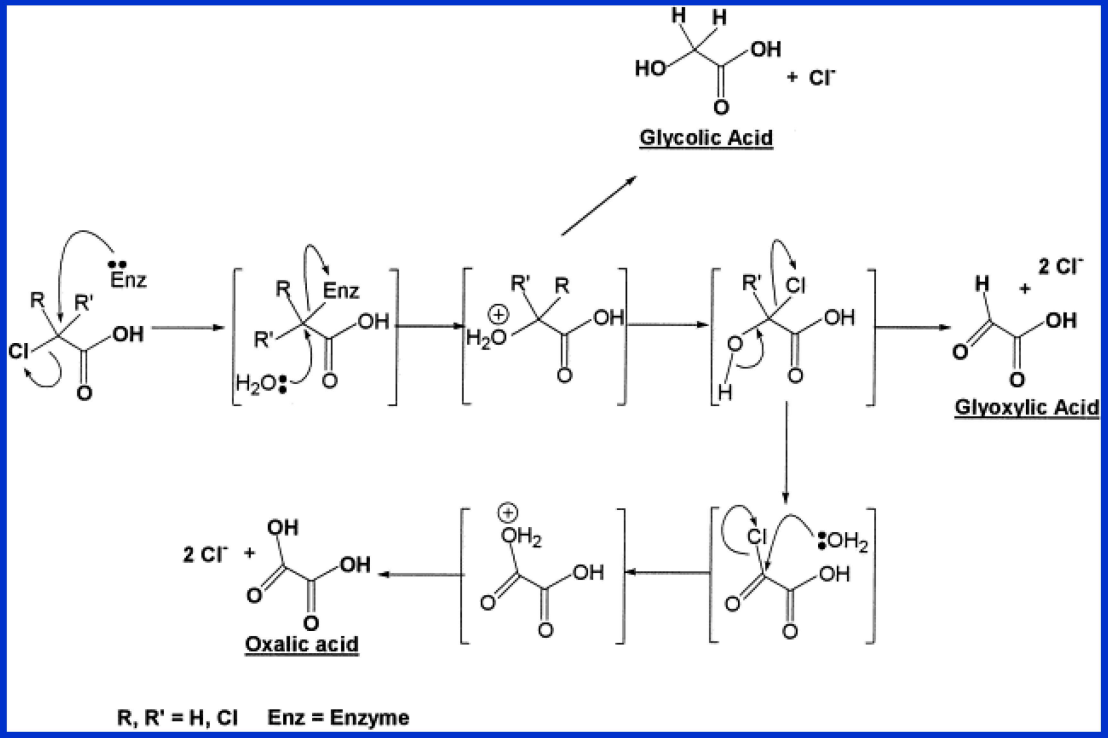


Bautista-de los Santos, Schroeder, Sevillano–Rivera, Sungthong, Ijaz, Sloana, & Pinto (2016) *Env. Sci: Water Res. & Tech.*

Heterotrophs

- Much phylogenic diversity in distribution systems; *Alpha-* and *Betaproteobacteria* typically dominate
- Metabolic diversity a characteristic common to some phyla found (e.g., *Betaproteobacteria*)
- Organisms also likely to be oligotrophic
- Influencing factors:
  - Upstream treatment processes
  - Disinfectant type and concentration
  - Environmental conditions (e.g., temperature, pH)
  - Hydraulic conditions
  - Distribution system and premise plumbing materials
  - Nutrient availability

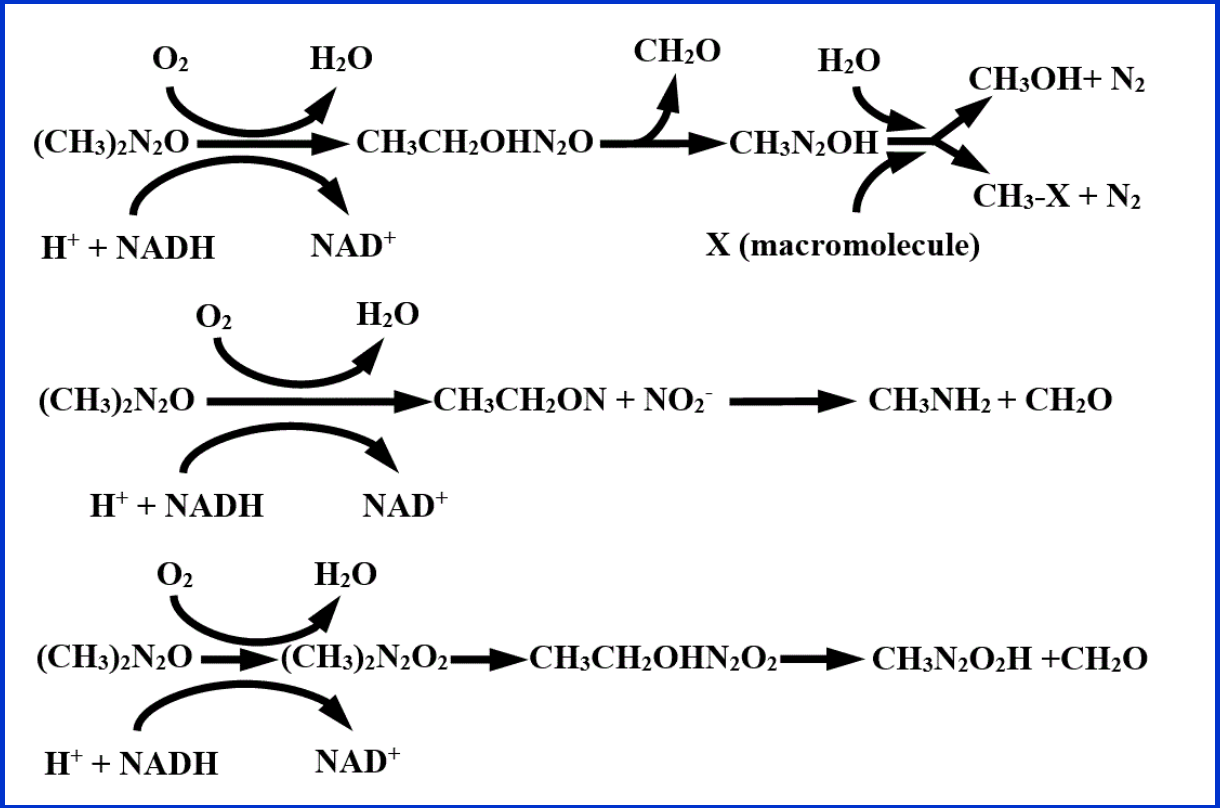
HAA Biodegradation



- Initial steps are dehalogenation reactions; products highly biodegradable
- Bacteria can grow on HAAs; concentration high enough in drinking water?
- Rates: ClAA > Cl_2AA >> Cl_3AA; Br substitution increases rates relative to Cl
- Considerable evidence that mono- and dihalo-AA's can biodegrade in distribution systems; disinfectant concentration, temperature, and pH control likelihood
- By analogy, monoiodo- and diido-acetic acids should be readily biodegradable

Ellis, Hanson, Sibley, Shahid, Fineberg, Solomon, Muir, & Mabury (2001) *Chemosphere*

NDMA Biodegradation

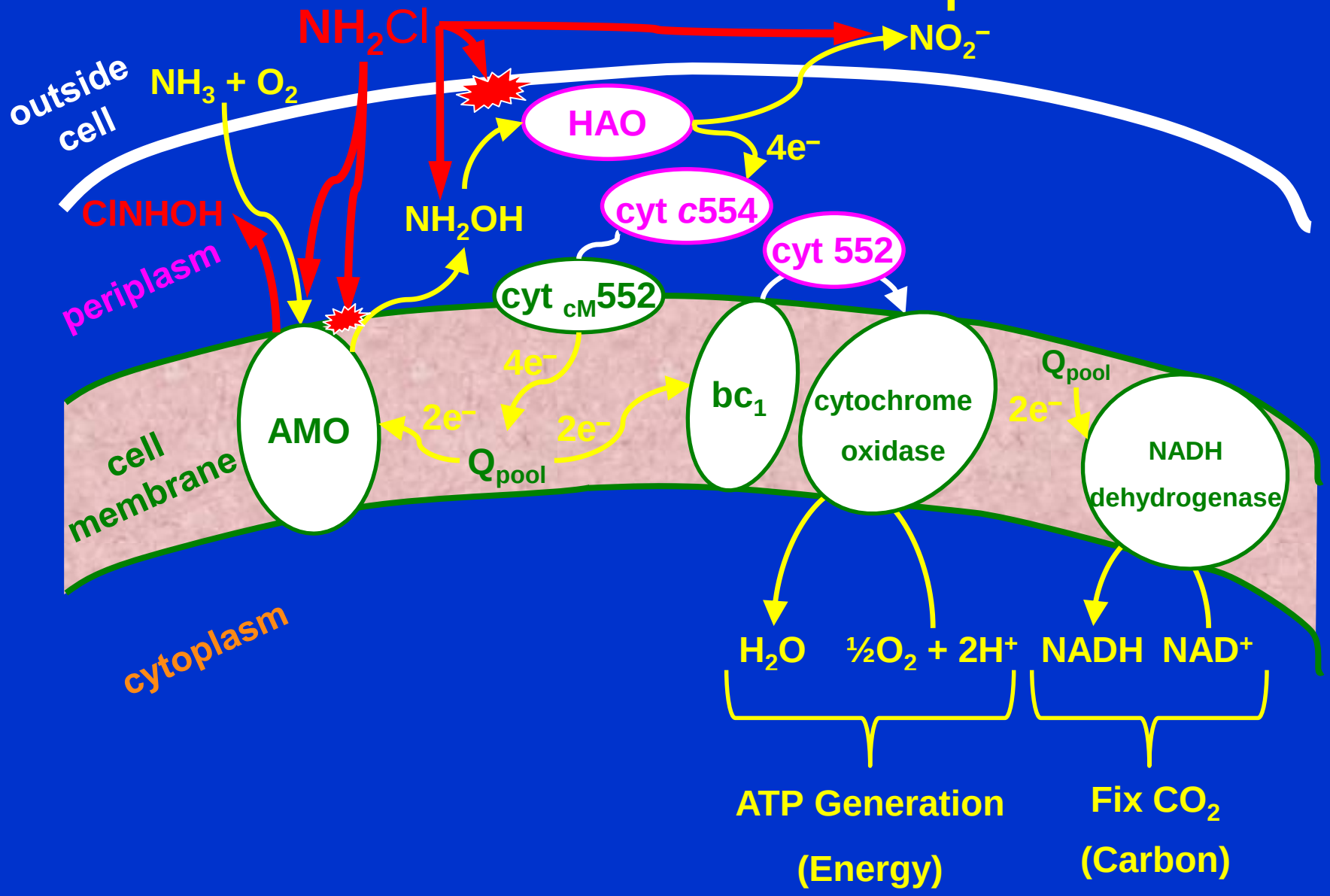


- First step is oxygenation via an oxygenase enzyme
- Evidence for both metabolism and cometabolism in the environment (e.g., riverbank filtration)
- Products may include formaldehyde and methylated macromolecules
- Primary metabolism not likely under drinking water concentrations

Speitel (Unpublished)

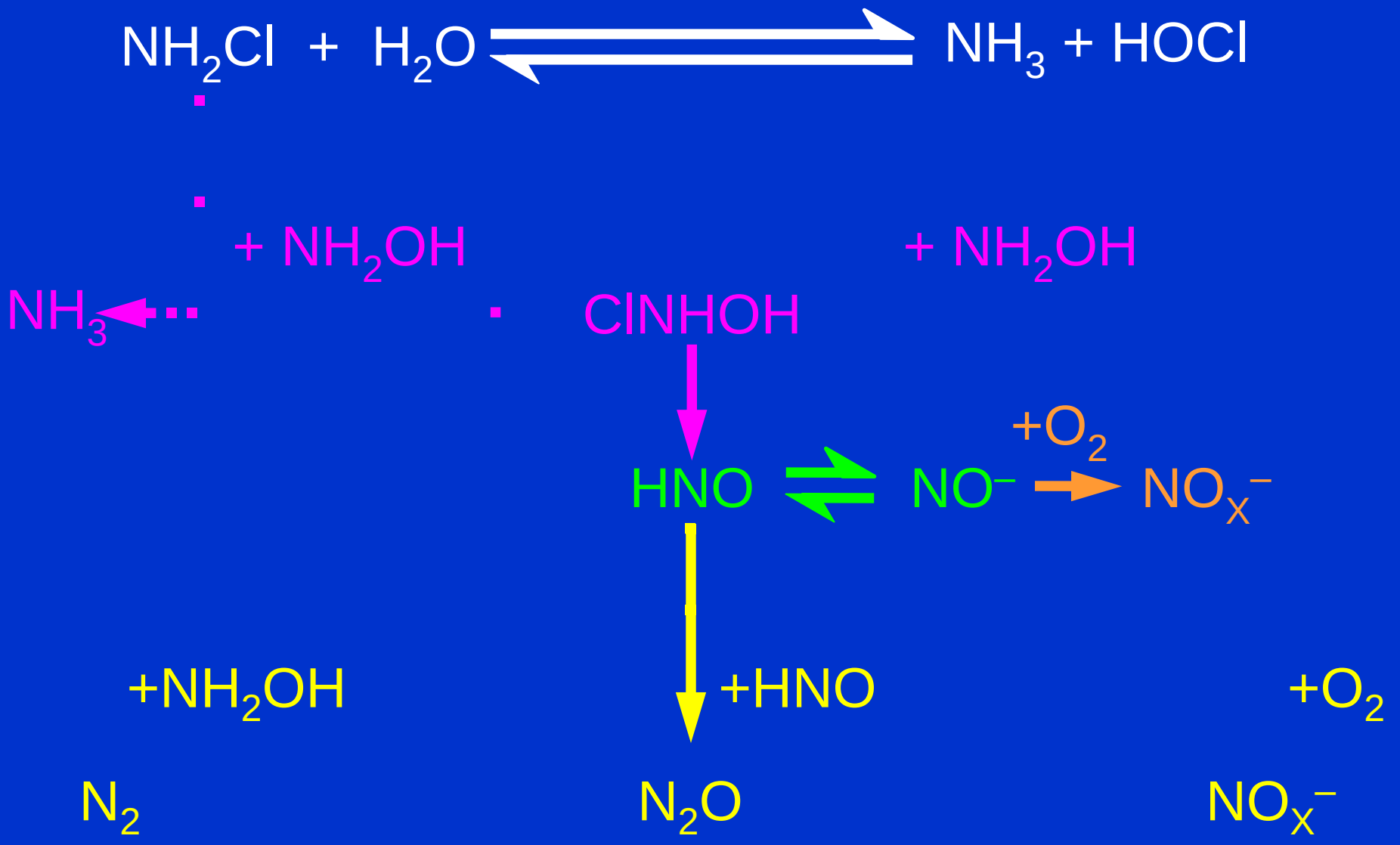
Disinfectant Interactions with Metabolites

Monochloramine Impacts



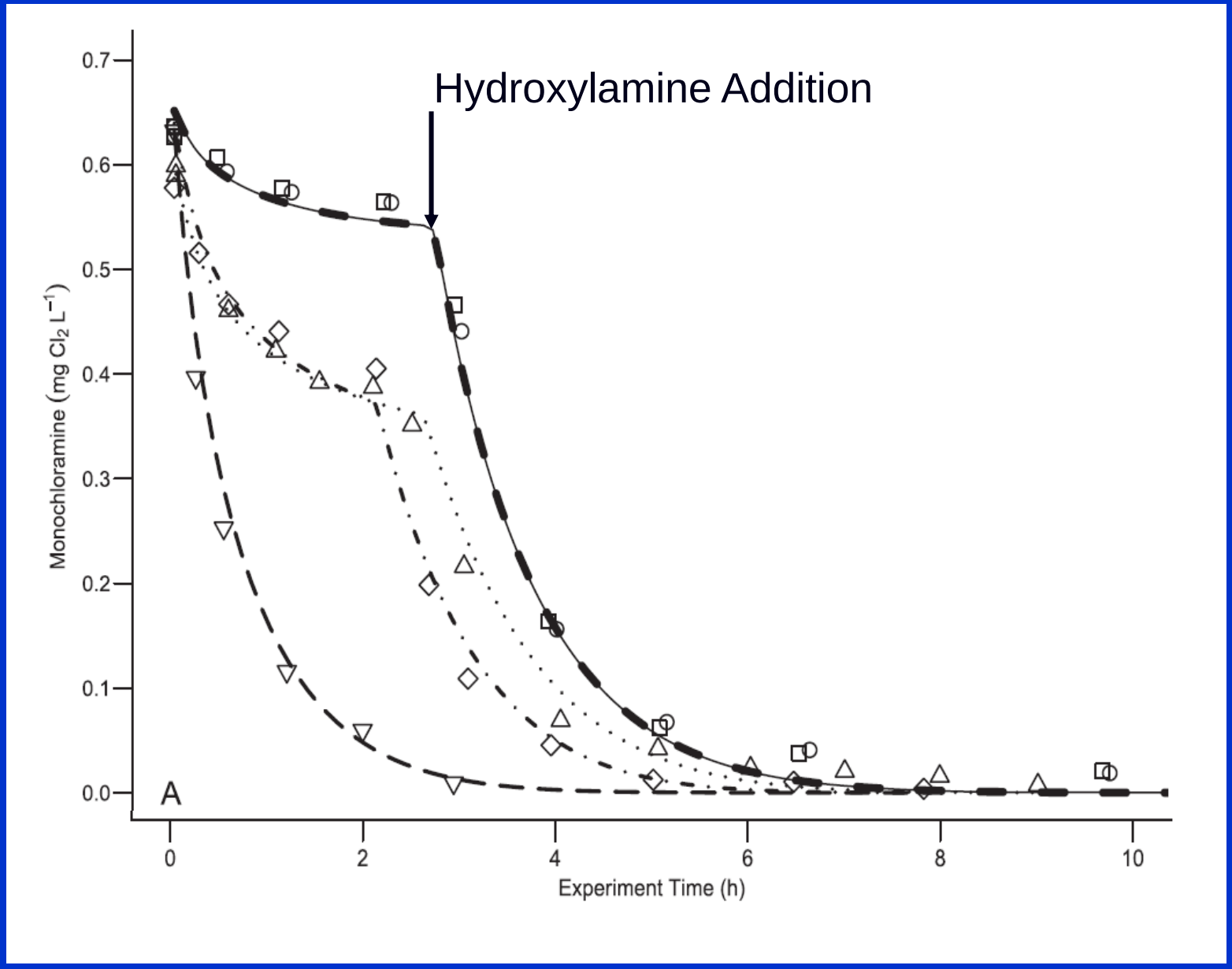
Adapted from Sayavedra-Soto and Arp (2011) *Nitrification*

Hydroxylamine Oxidation



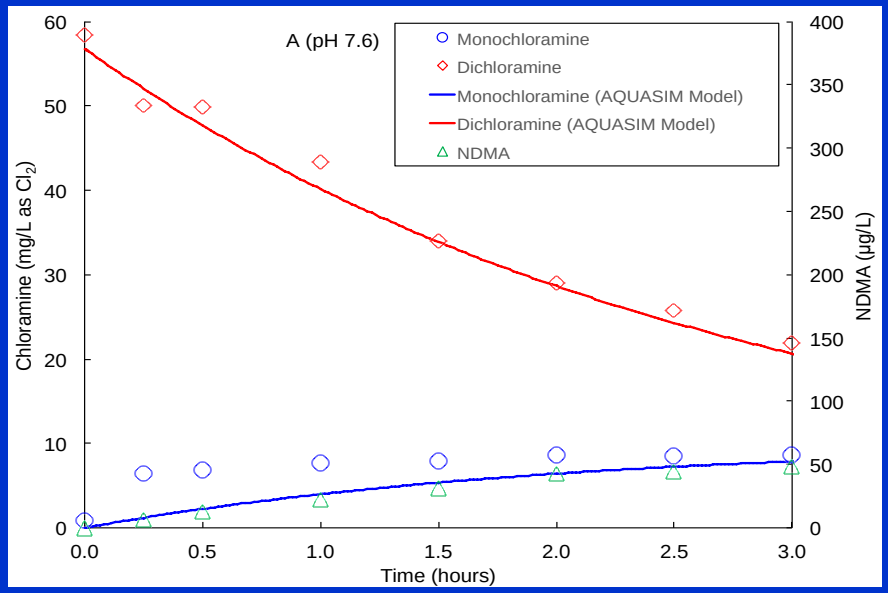
Wahman, Speitel, & Machavaram (2014) *Water Research*

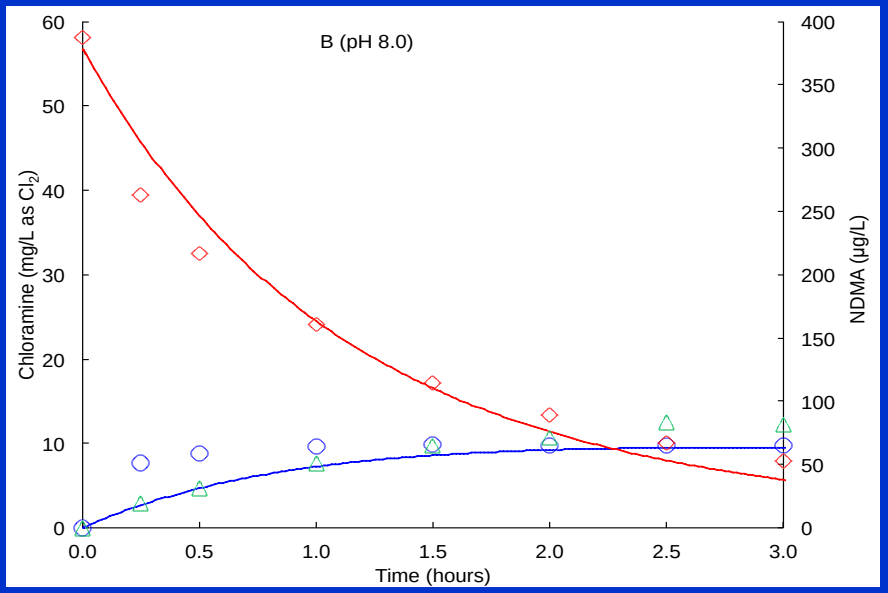
Monochloramine & Hydroxylamine Reaction

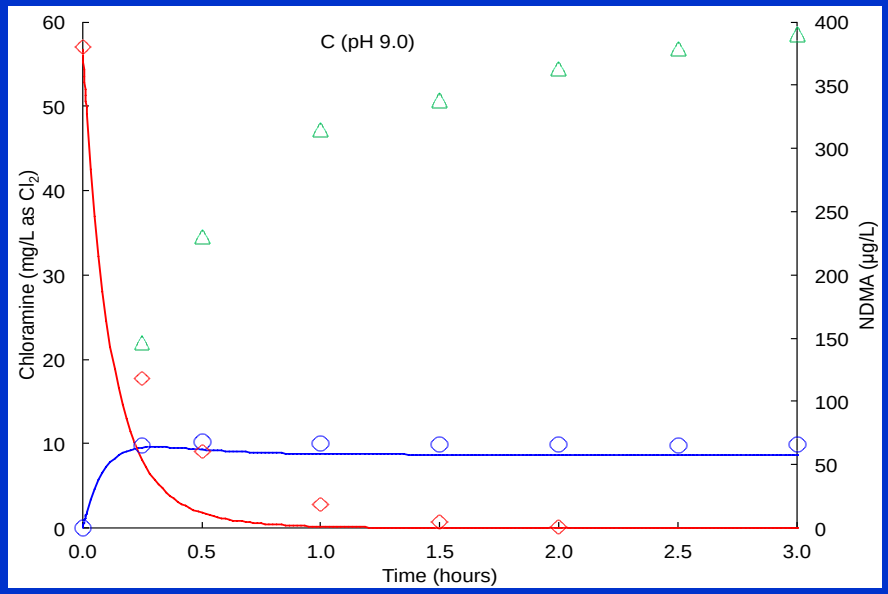


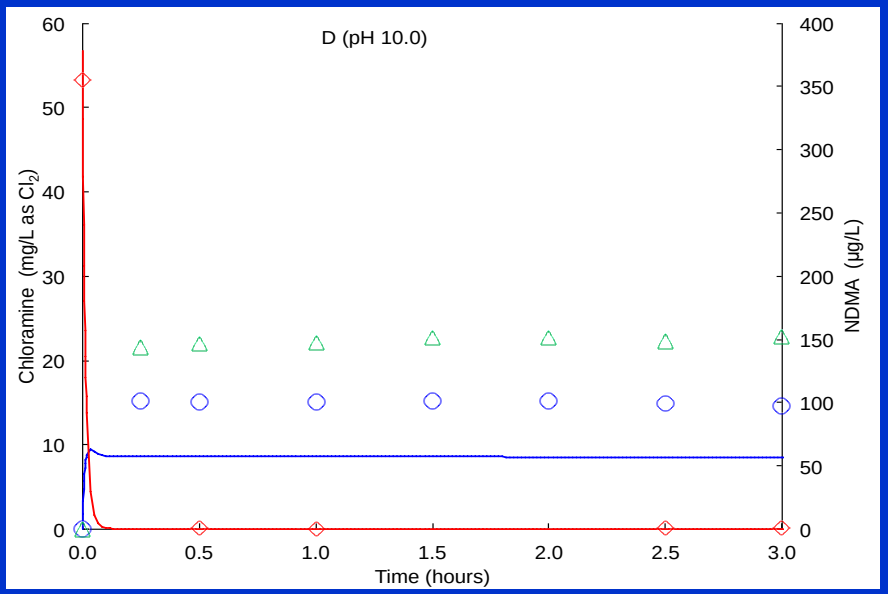
Wahman & Speitel (2015) *Water Research*

NDMA Formation



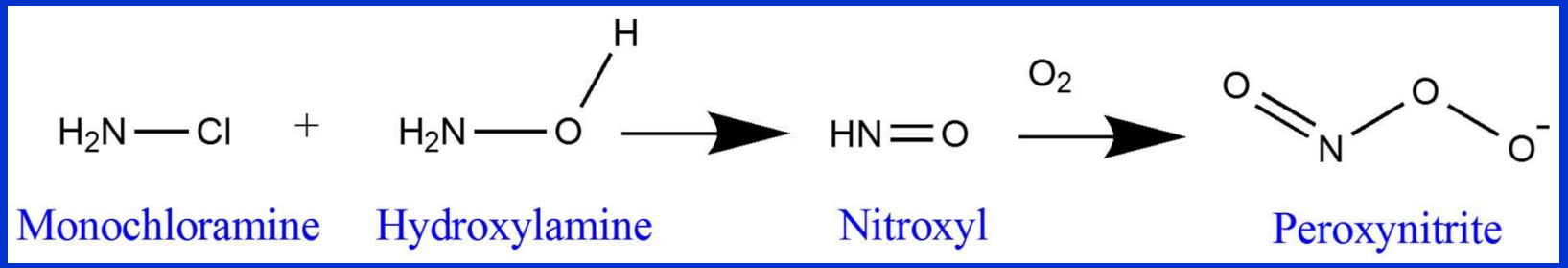




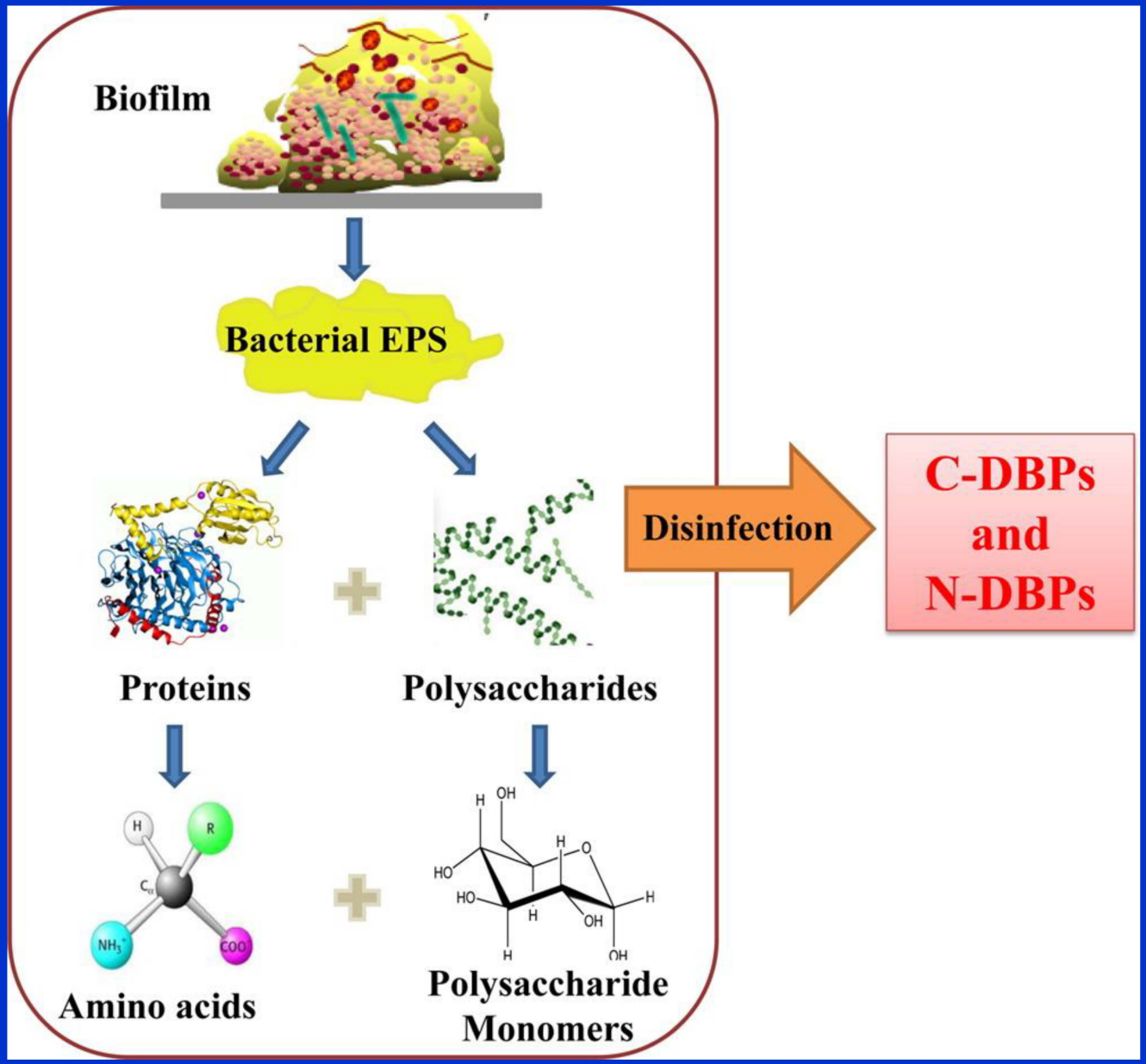


NDMA Formation

- Proposed monochloramine decay pathway



Disinfectant Interactions with EPS & SMP



Wang, Choi, & Seo (2013) *ES&T*

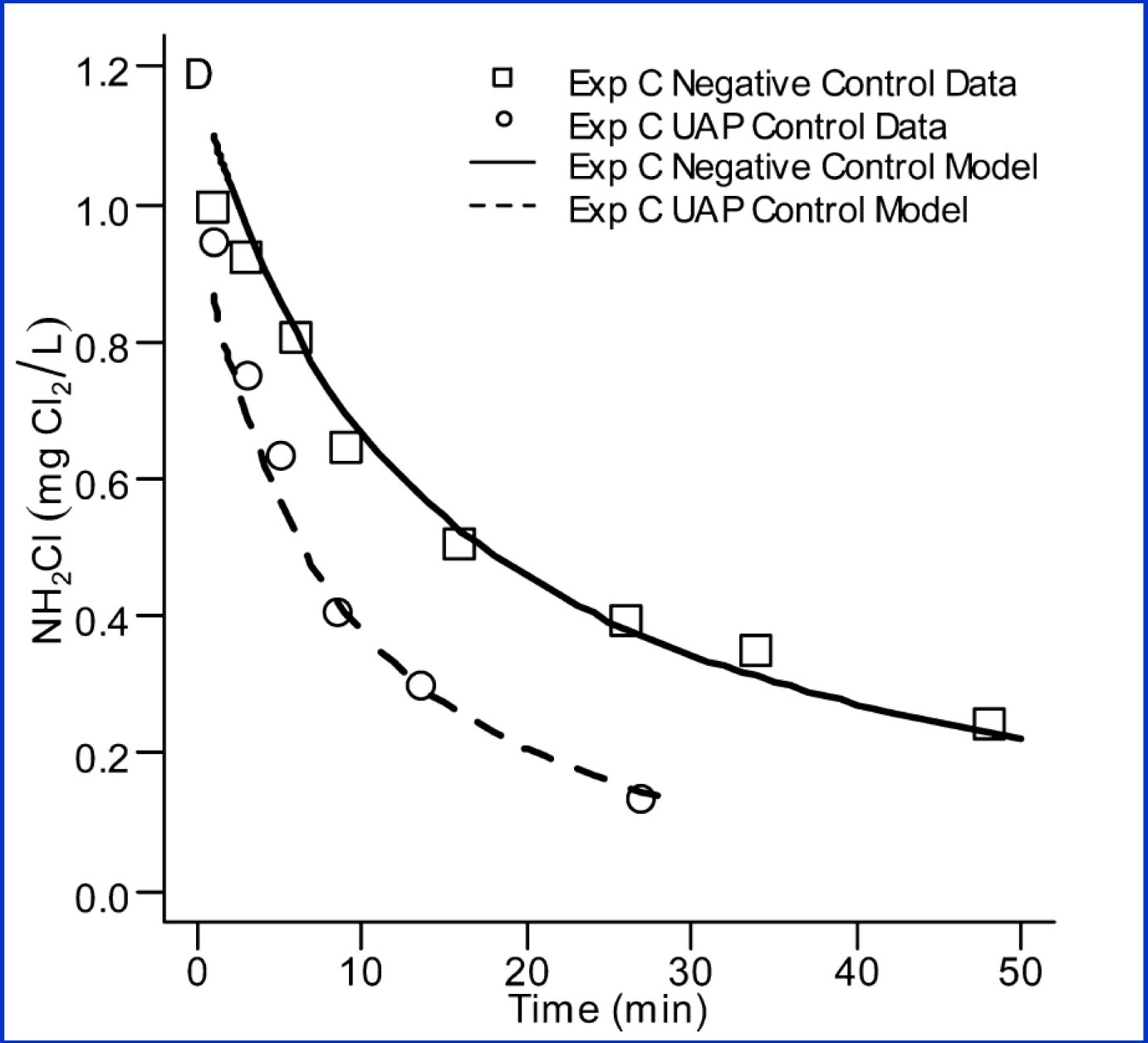
Soluble Microbial Products (SMP)

- SMP: soluble organic compounds released during normal biomass metabolism and decay
- Lower molecular weight than EPS but similar: proteins, polysaccharides, humic-like materials
- Biomass-Associated Products (BAP): SMP produced from hydrolysis of biomass, in particular from extracellular polymeric substances (EPS)
- Utilization Associated Products (UAP): SMP produced directly as part of electron-donor oxidation
- SMP is biodegradable, UAP more readily so than BAP
- Nitrifying bacteria produce SMP, which in turn can support the growth of heterotrophic bacteria
- SMP can also exert a disinfectant demand and lead to the formation of DBPs

Monomer Composition

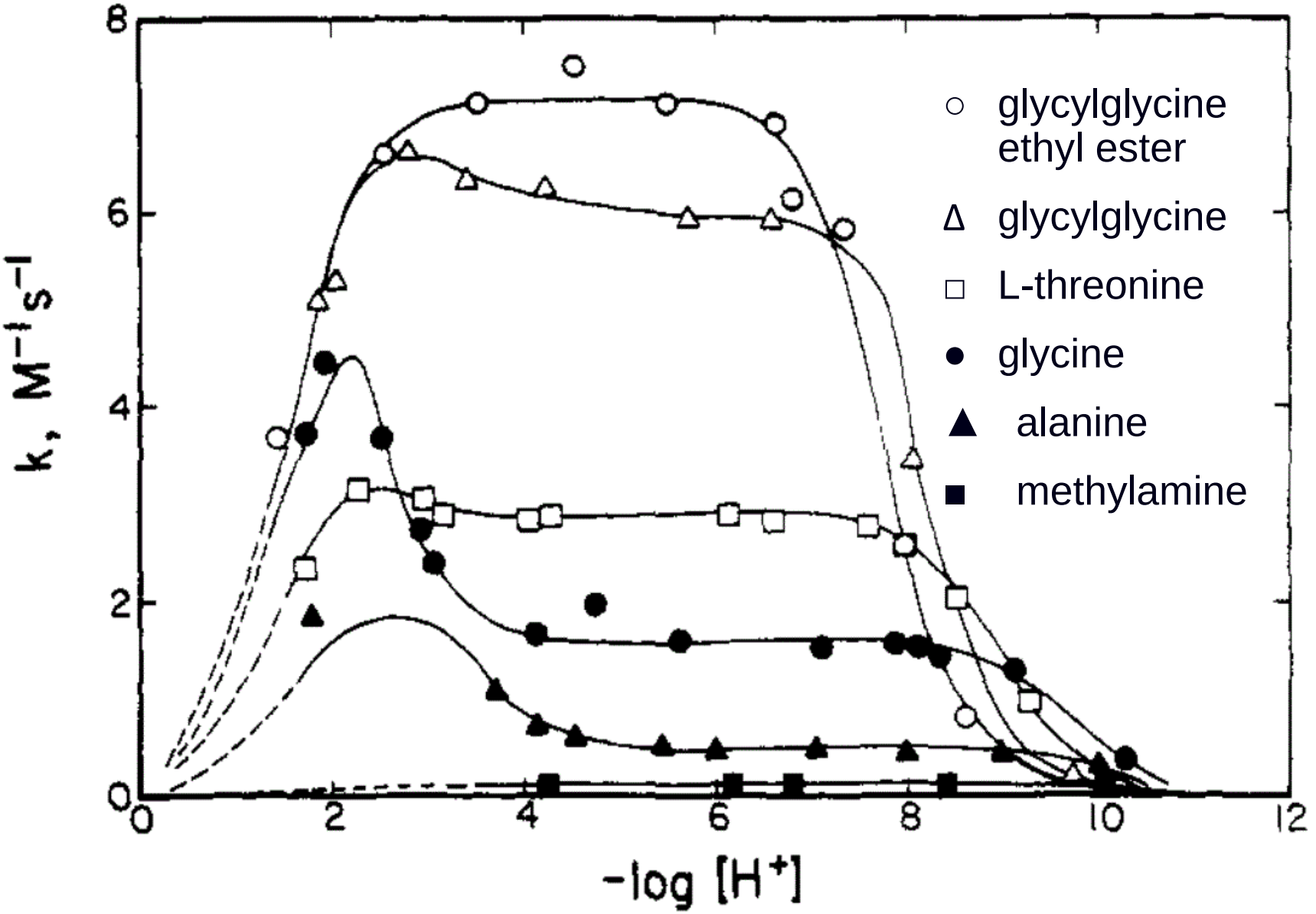
- Wide variety of amino acids
  - Glycine
  - Aspartic Acid
  - Glutamic Acid
  - Alanine
- Polysaccharide monomers:
  - D-glucosamine
  - D-glucuronic acid
  - D-glucose
  - L-fucose

Cellular & UAP Reactions with Monochloramine



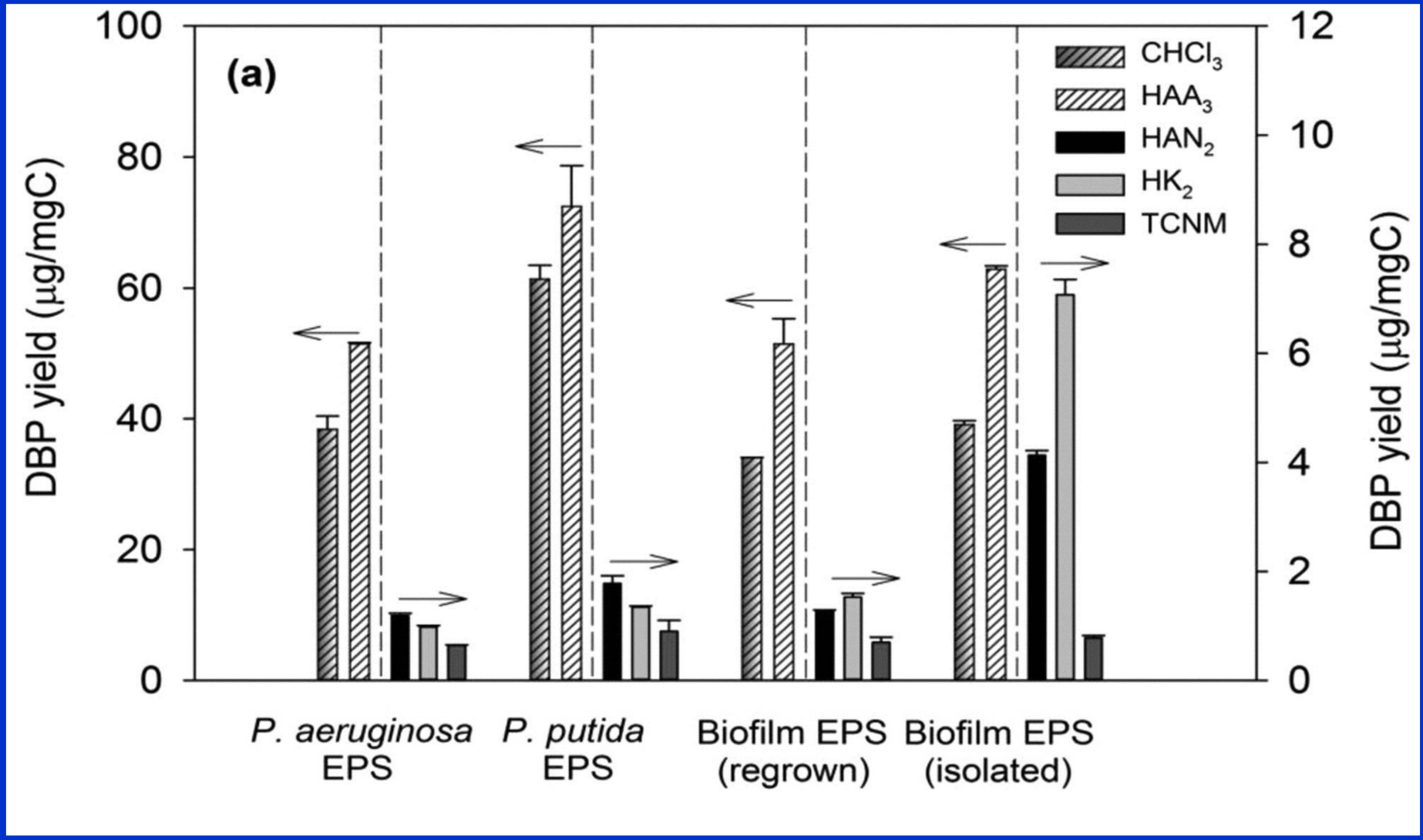
Maestre, Wahman, & Speitel (2016) *ES&T*

Chlorine Transfer from NH_2Cl to Amine Nitrogen



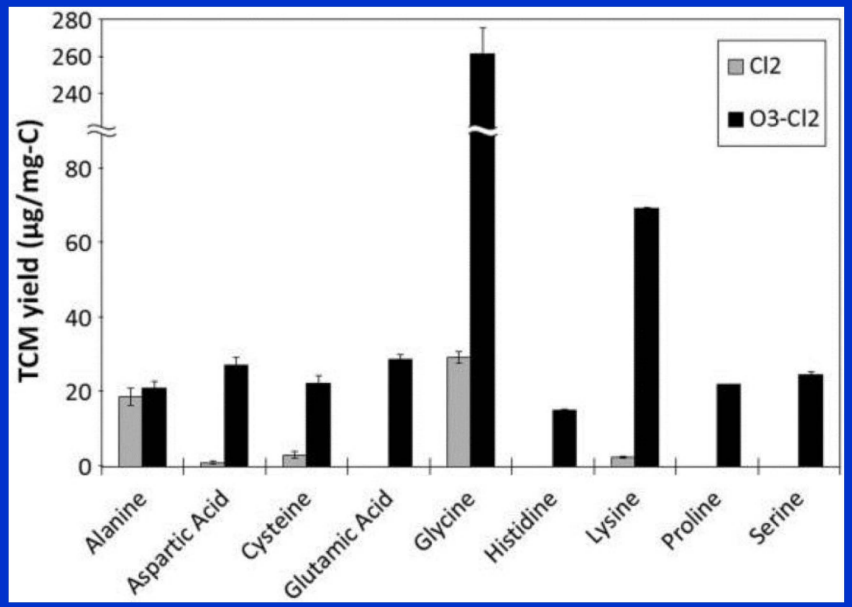
Snyder & Margerum (1982) *Inorganic Chemistry*

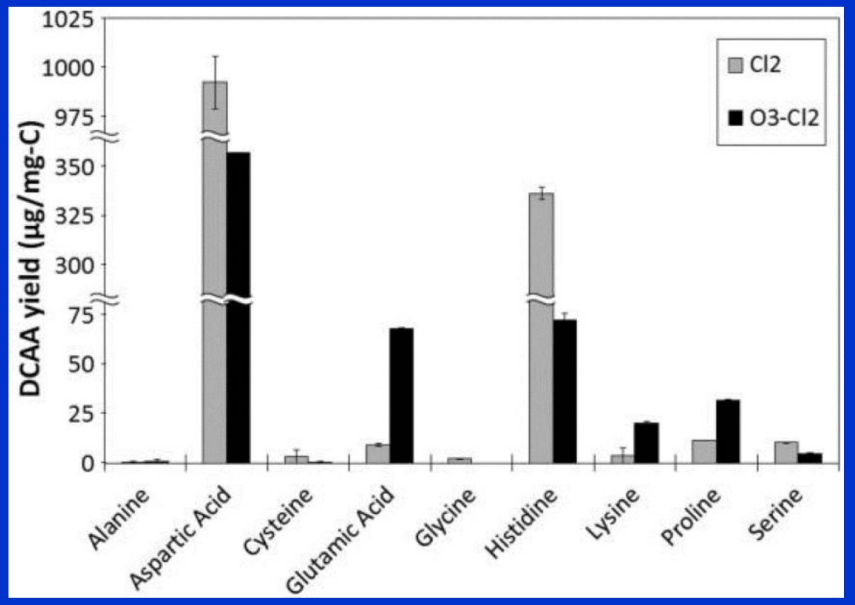
DBP Formation

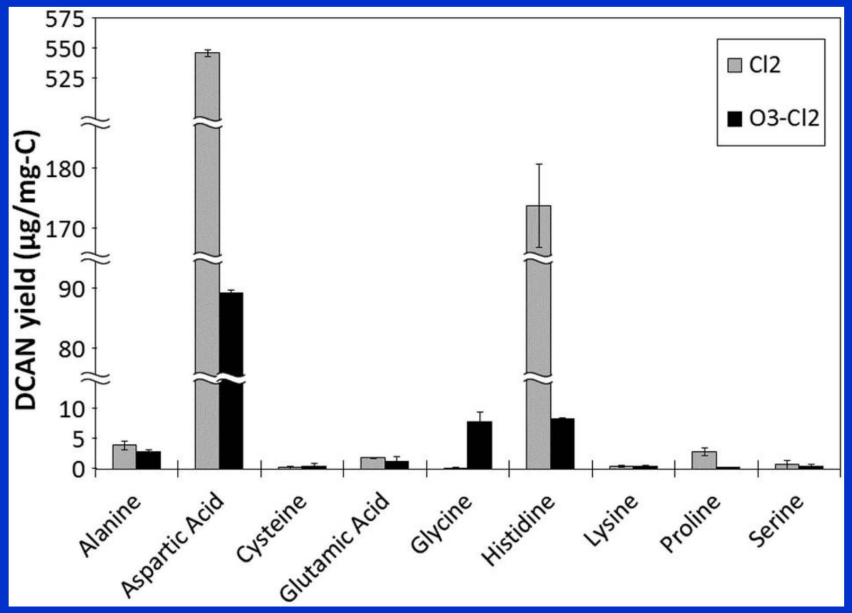


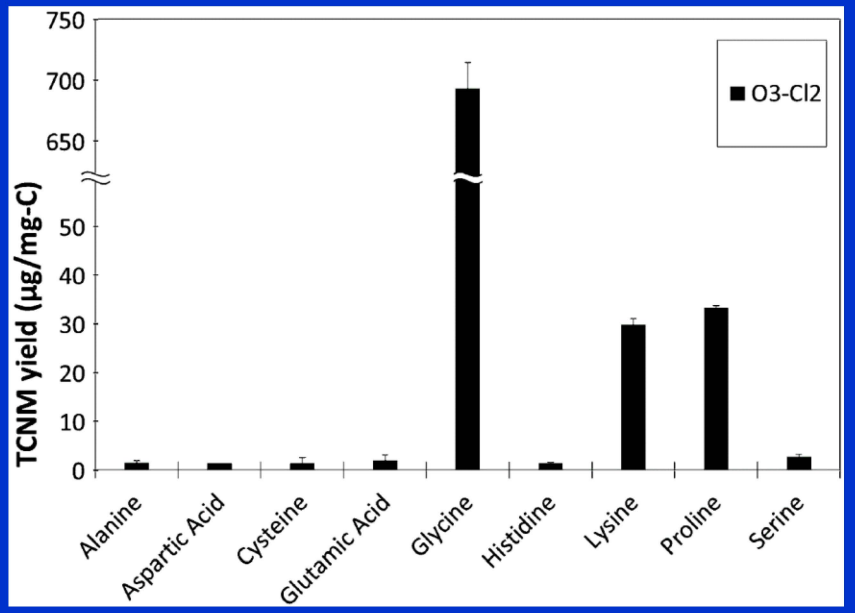
Wang, Choi, & Seo (2013) *ES&T*

DBP Formation from Amino Acids



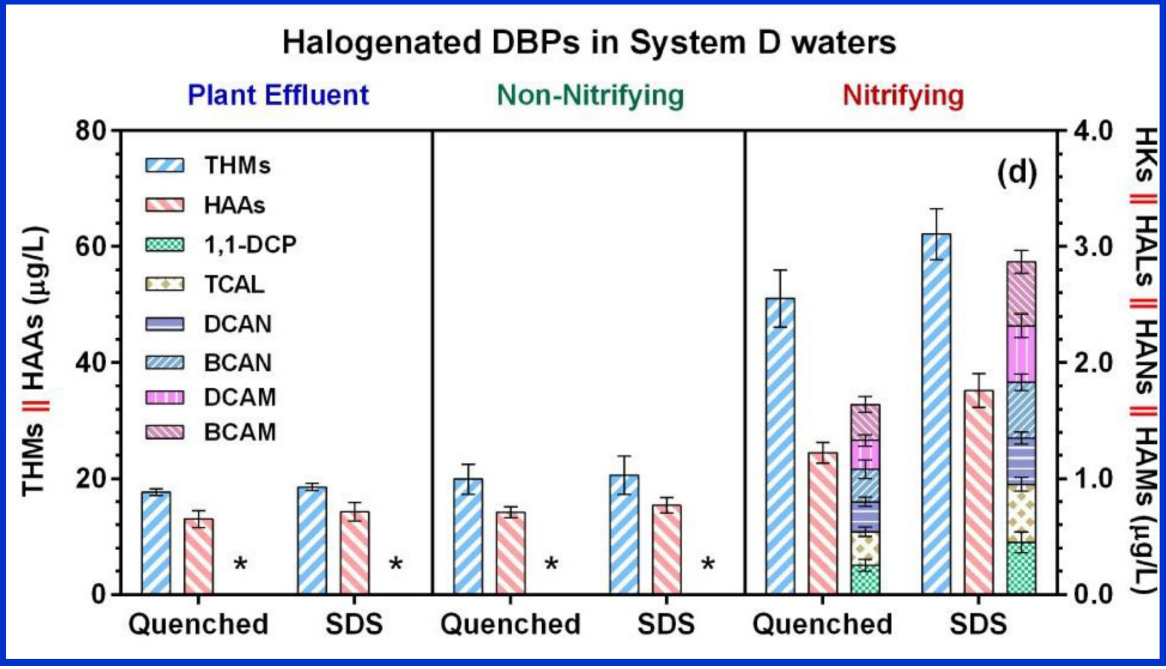


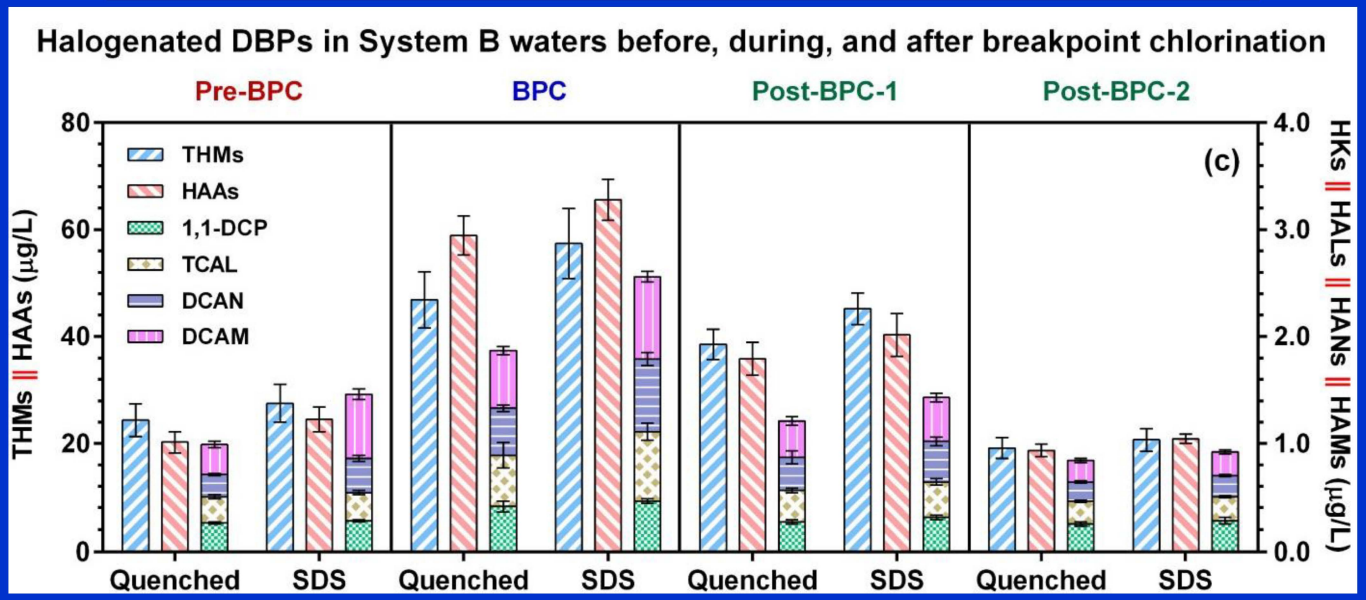




Selbes, Shan, Bekaroglu & Karanfil (2015) *Recent Advances in Disinfection By–Products*

Nitrification & Breakpoint Chlorination Impacts





Zeng & Mitch (2016) *ES&T*

Significance of UAP & EPS as DBP Source

Growth Substrate	UAP Formed (mg C/L)	EPS Formed (mg C/L)	Max. Reactive SMP Formed (mg C/L)	Max. Chloroform (µg/L)	Max. HAA_3 (µg/L)	Max. HAN_2 (µg/L)	Max. TCNM (µg/L)
1 mg N/L	0.13	0.20	0.33	13	17	0.41	0.21
0.1 mg C/L	0.012	0.018	0.030	1.2	1.6	0.04	0.02

HAA_3 = monochloroacetic acid + dichloroacetic acid + trichloroacetic acid

HAN_2 = dichloroacetonitrile + trichloroacetonitrile

TCNM = trichloronitromethane

DBP yields from Wang, Choi, & Seo (2013) *ES&T*

UAP/EPS yields from Merkey, Rittmann, & Chopp (2009) *Journal of Theoretical Biology*

Greater Challenges

- Disinfectant residual regulations (i.e., measurable concentration) in contradiction to nature of concentration gradients in biofilms
- Are we fighting a losing battle in the US with current approaches?
- Are disinfectant residuals in distribution systems a net benefit?
- Or, should we commit to treating water to a greater extent as in some European countries, so that it is sufficiently “stable” to not need residual disinfection?

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- Hong Liu

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Questions?

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