Distribution System Nitrification: Cometabolism and Nitrification Index

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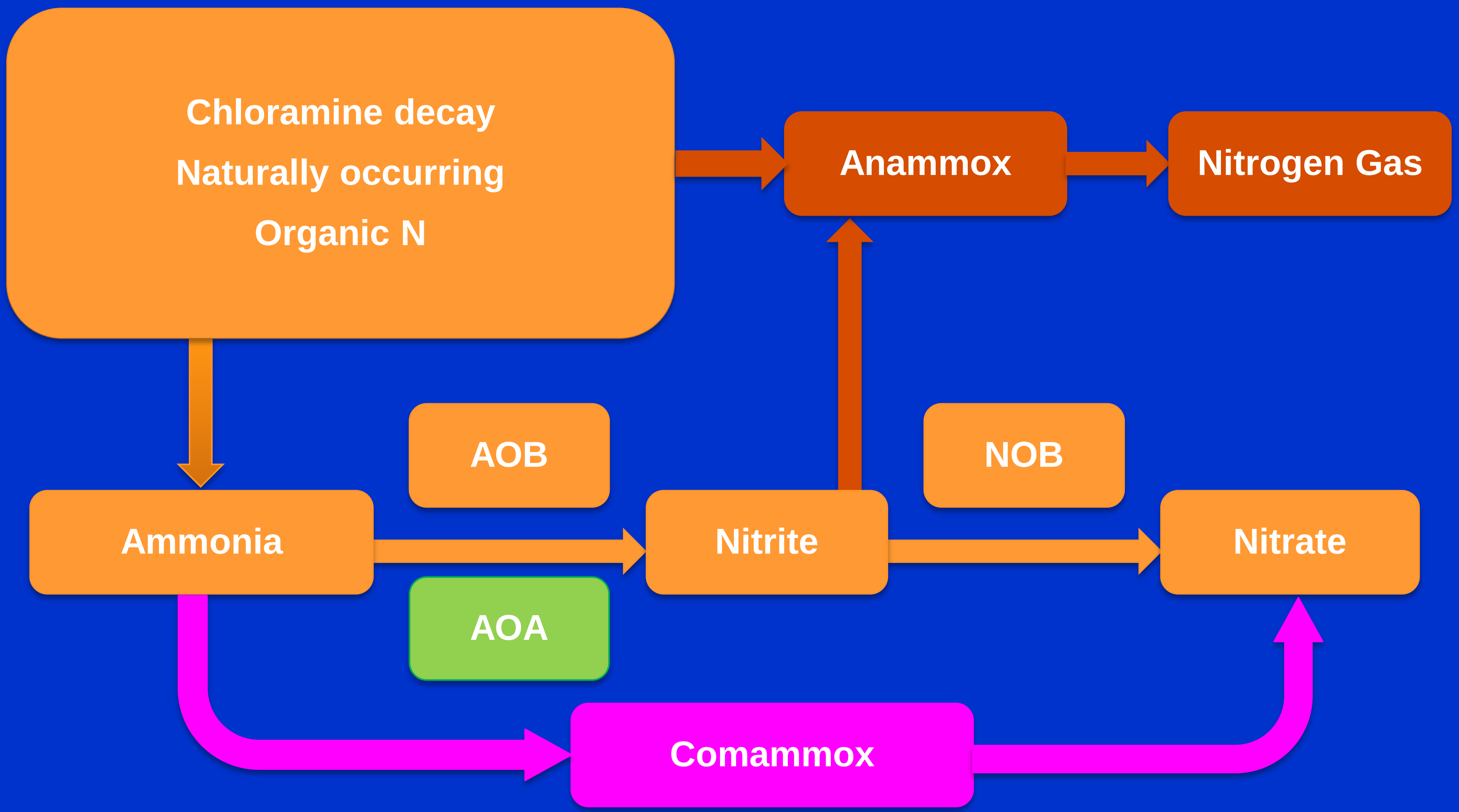
Nitrifier Classifications



Distribution System Nitrification

- Free ammonia source = AOB food

  1. Chloramines = free chlorine + ammonia
     - Stage 1 & 2 D/DBP rules (THMs & HAAs)
       - Free chlorine → chloramines
       - 57% surface & 7% groundwater
     - 30–63% nitrification
  2. Source water ammonia

Water Quality & Regulatory Issues

- AOB → not pathogenic or regulated
- Nitrification → "gateway bug" → other issues

Water Quality Issues	Regulatory Issues
Disinfectant depletion	SWTR, TCR
Nitrite/nitrate formation	Maximum Contaminant Level
Reduced pH and alkalinity	Lead & Copper Rule
Coliform occurrences	SWTR, TCR
HPC increase	SWTR, TCR
DBP formation via mitigation	DBP Rules

SWTR – Surface Water Treatment Rule

TCR – Total Coliform Rule

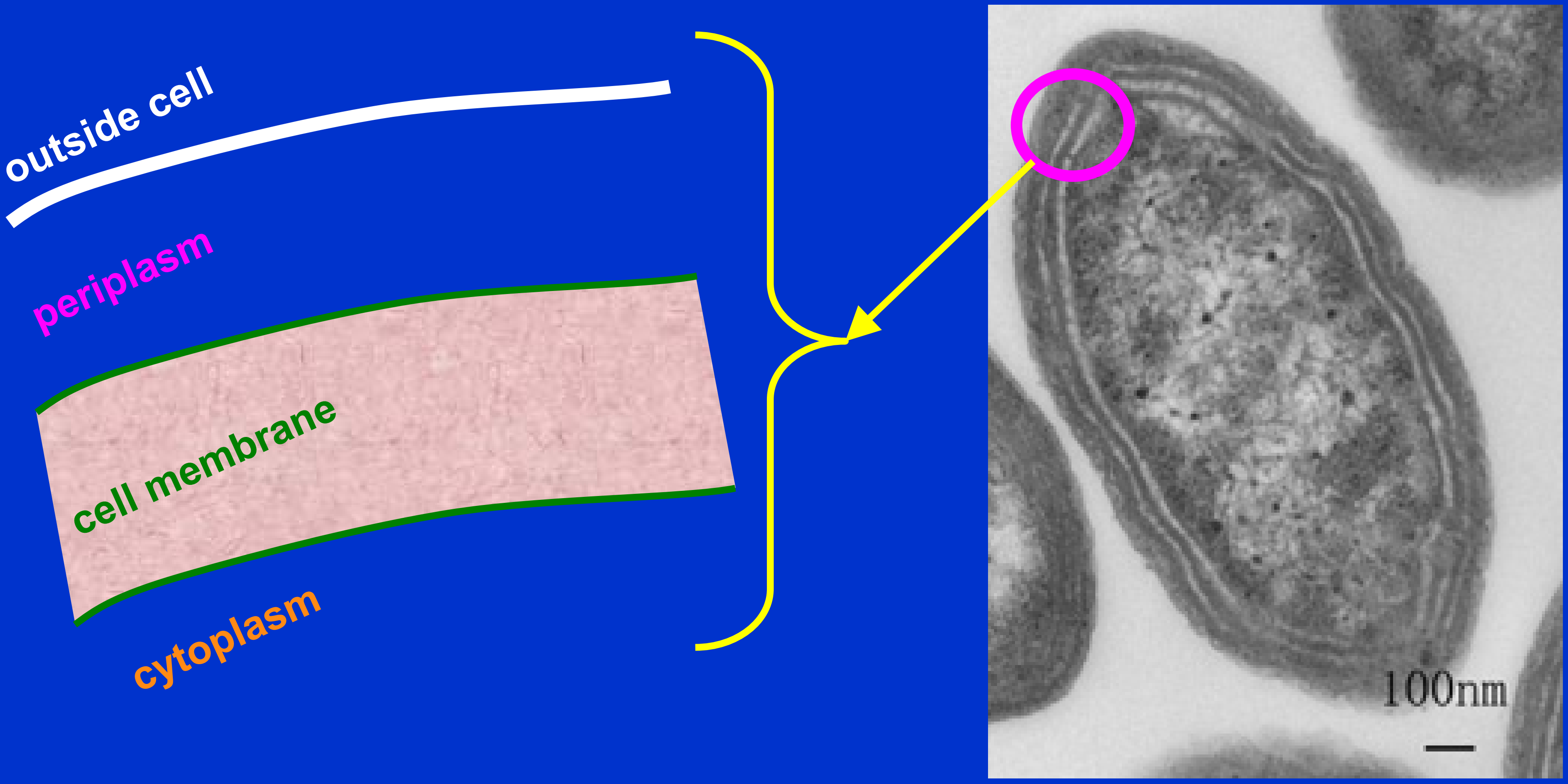
Source: AWWA (2013)

amoA Detections in Distribution Systems (Starke et al. 2013)

Most commonly detected amoA OTUs in 78 samples collected from full-scale and pilot-scale distribution systems

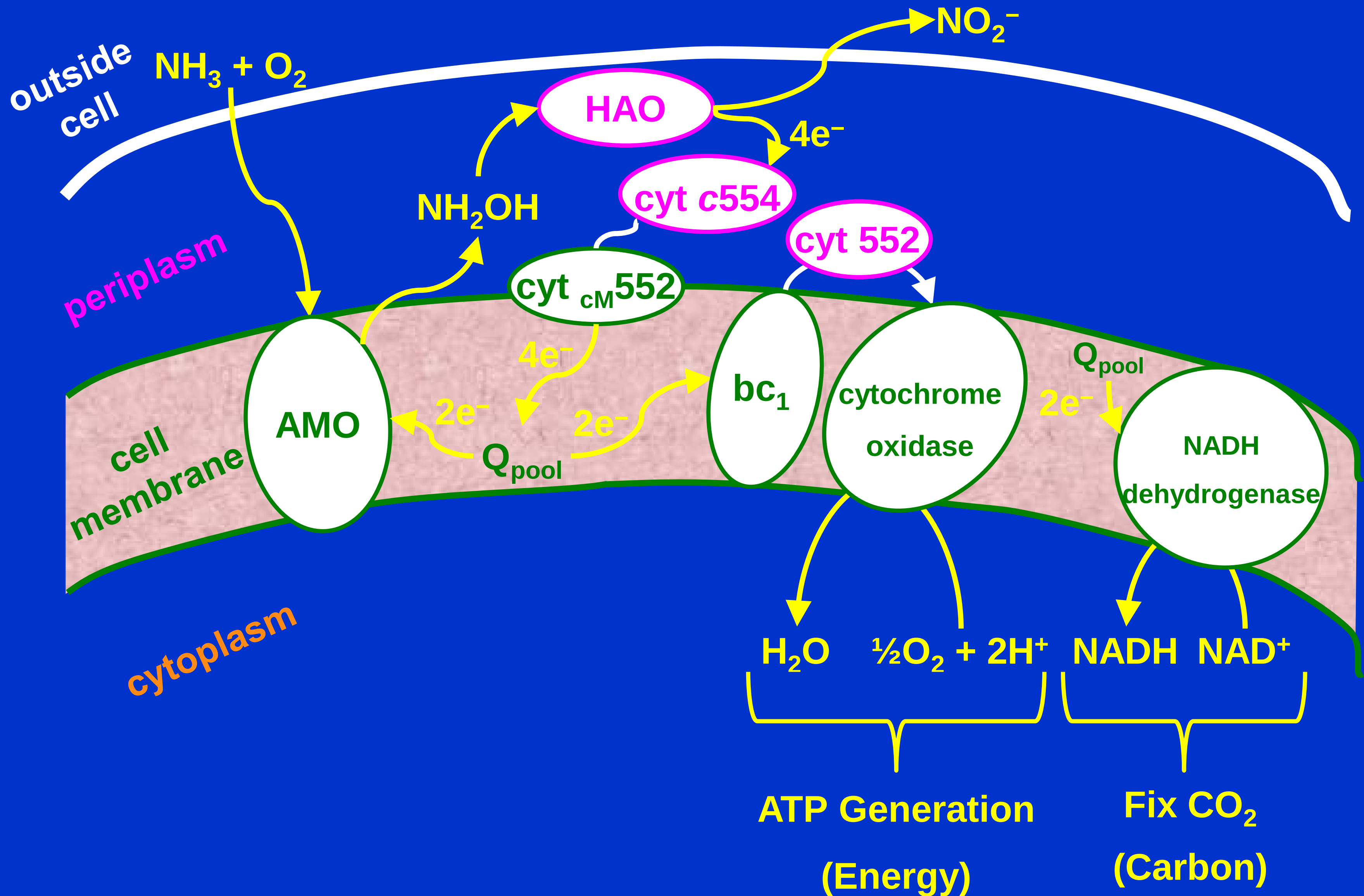
Organism	Accession Number	OTU Number	Percentage of samples with OTU
Nm. oligotropha	AY356516	AOB 5	91
Nm. oligotropha	AY026907	AOB 106	88
Nm. oligotropha	EU616619	AOB 284	54
Nm. oligotropha	AY050678	AOB 170	47
AOA 1.3.3.2	FJ227695	AOA 95	47
AOA 1.3.3.2	EU651294	AOA 341	46
AOA 1.3.3.2	AB529744	AOA 83	44
Nm. oligotropha	EU770906	AOB 297	41
AOA 2.1.8.1	ARPLA59	AOA 184	33
AOA 1.3.3.1	GQ390324	AOA 70	32

Ammonia Oxidizing Bacteria (*Nitrosomonas europaea*)



Source: X. Fang et al. (2010)

Biological Ammonia Oxidation



Source: Adapted from Sayavedra-Soto and Arp (2011)

Nitrification Occurrence

- Free ammonia (food) → chloramines
- Ammonia-oxidizing microorganisms (AOM) → AOB
- Growth rate $\geq$ Inactivation rate
  - Growth rate → Free ammonia concentration
  - Inactivation rate
    - Endogenous decay
    - THM cometabolism
    - Monochloramine inactivation
    - Monochloramine concentration impacts
      - Cometabolism
      - Hydroxylamine
      - Nitrite
      - Cellular & utilization associated product (UAP) reactions

Metabolism vs. Cometabolism

Metabolism

- Contaminant is a carbon and/or energy source for microbial growth (organic chemicals typically both; ammonia is an energy source)

Cometabolism

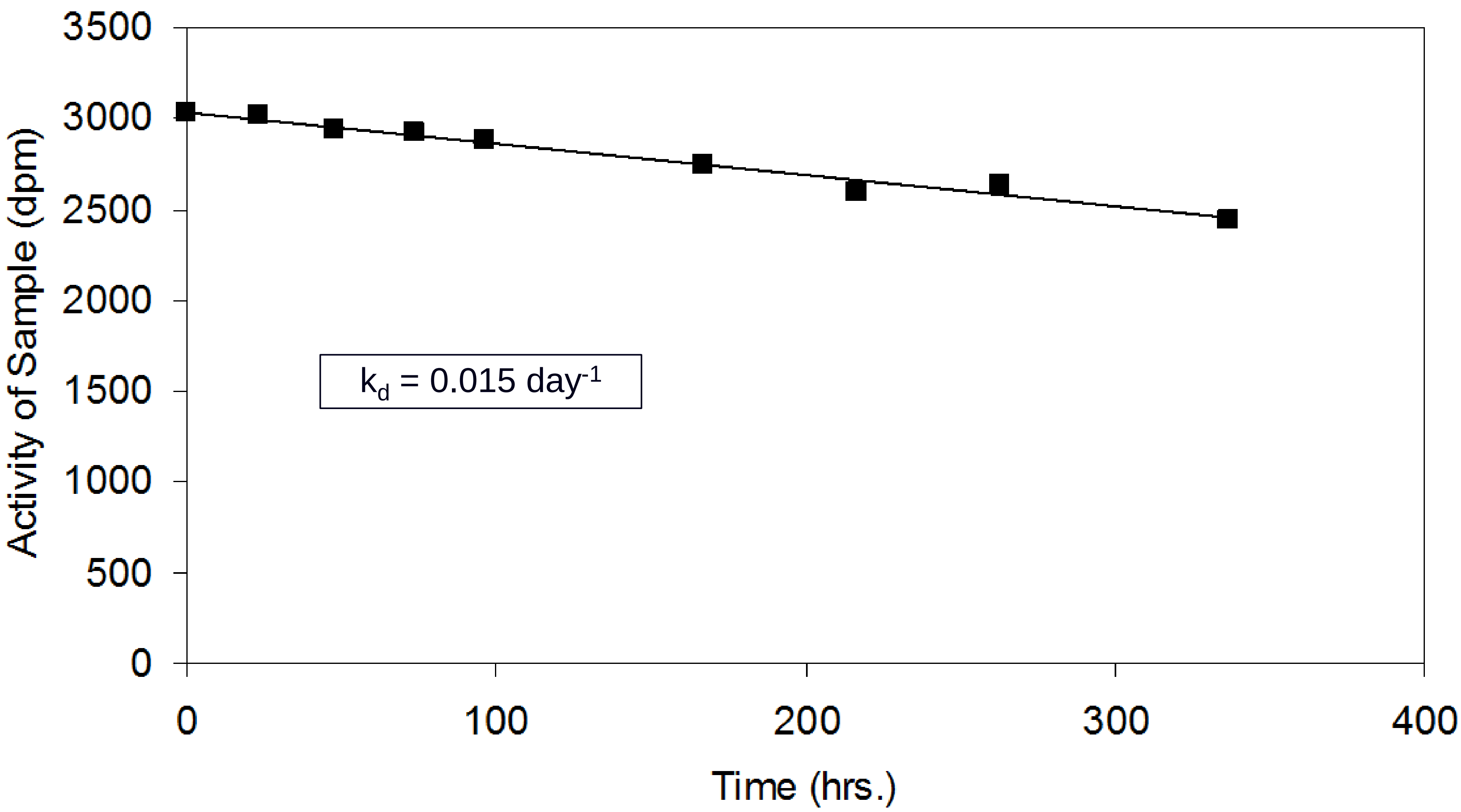
- Not a carbon and energy source
- Fortuitous degradation by non-specific enzymes (AMO)
- A growth substrate is required
- May harm bacteria
  - Toxic intermediates
  - Reductant depletion
  - Enzyme competition

Nitrification Index

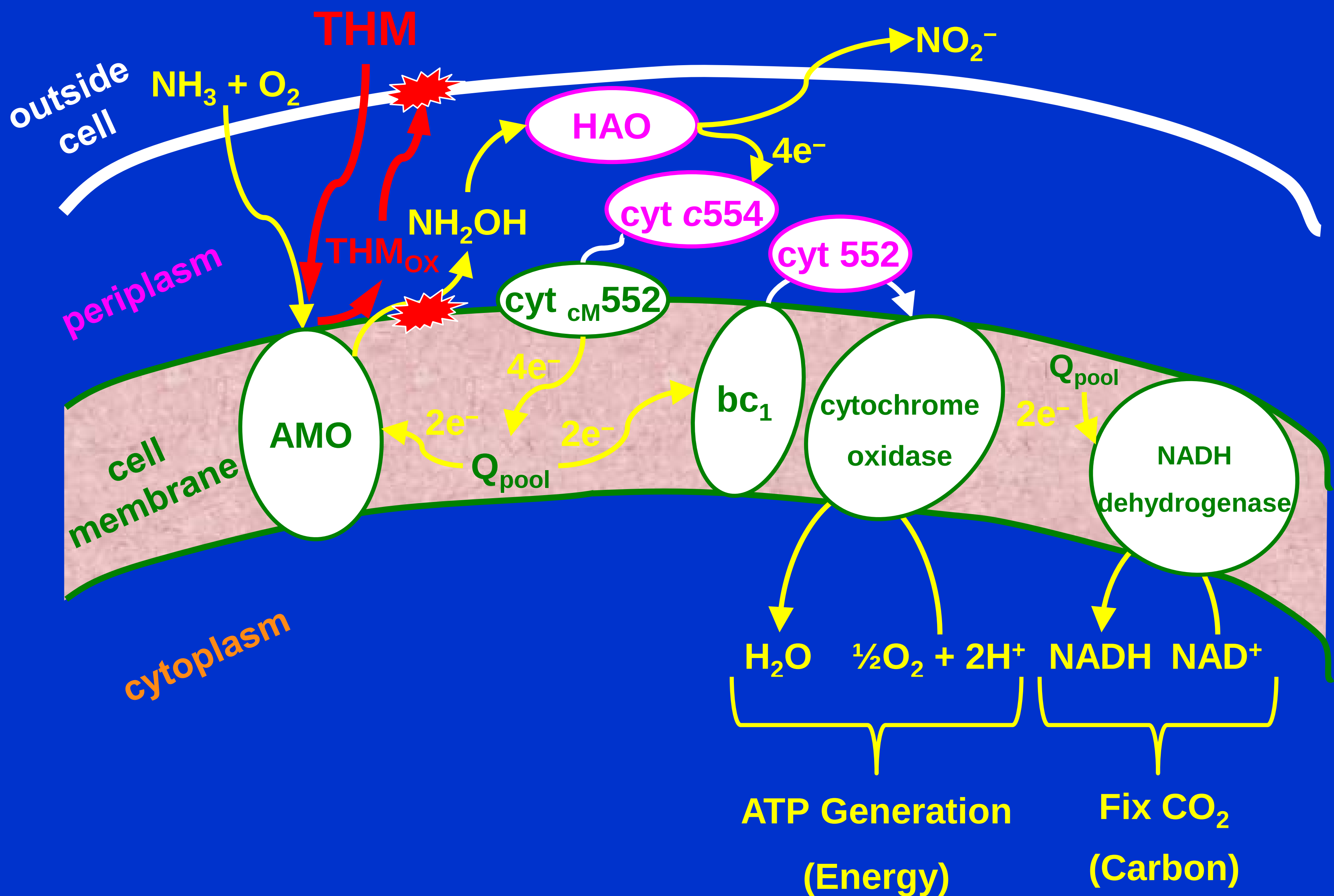
$$NI = \frac{r_g'}{r_i} = \frac{Yk_{TOTNH_3}\left(\dfrac{\alpha_1 S_{TOTNH_3}}{K_{s_{NH_3-N}} + \alpha_1 S_{TOTNH_3}}\right)}{k_d + k_{NH_2Cl}S_{NH_2Cl} + \left(\dfrac{k_{1_{TCM}}S_{TCM}}{T_{c_{TCM}}} + \dfrac{k_{1_{BDCM}}S_{BDCM}}{T_{c_{BDCM}}} + \dfrac{k_{1_{DBCM}}S_{DBCM}}{T_{c_{DBCM}}} + \dfrac{k_{1_{TBM}}S_{TBM}}{T_{c_{TBM}}}\right)\left(\dfrac{\alpha_1 S_{TOTNH_3}}{K_{s_{NH_3-N}} + \alpha_1 S_{TOTNH_3}}\right)}$$

- NI represents ratio of growth rate to the sum of the inactivation rates
  - Monod growth kinetics
  - Endogenous decay
  - Inactivation by monochloramine
  - Inactivation by THM cometabolism
- NI < 1 indicates that inactivation rate is faster than growth rate
- Importance of monochloramine and ammonia concentrations

Endogenous Decay – Lake Austin AOB

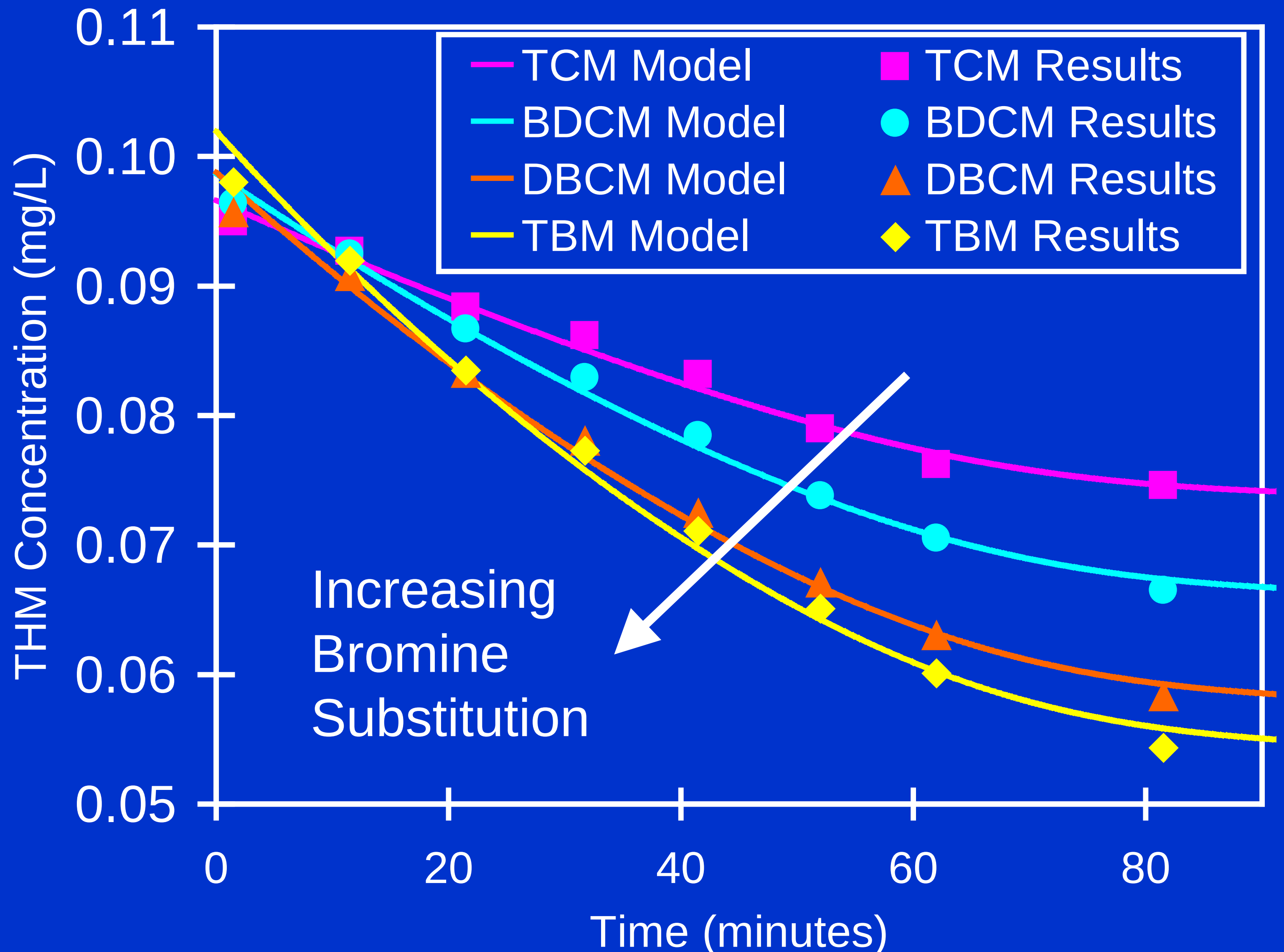


Trihalomethane Cometabolism



Source: Adapted from Sayavedra-Soto and Arp (2011)

THM Kinetics – Experiment

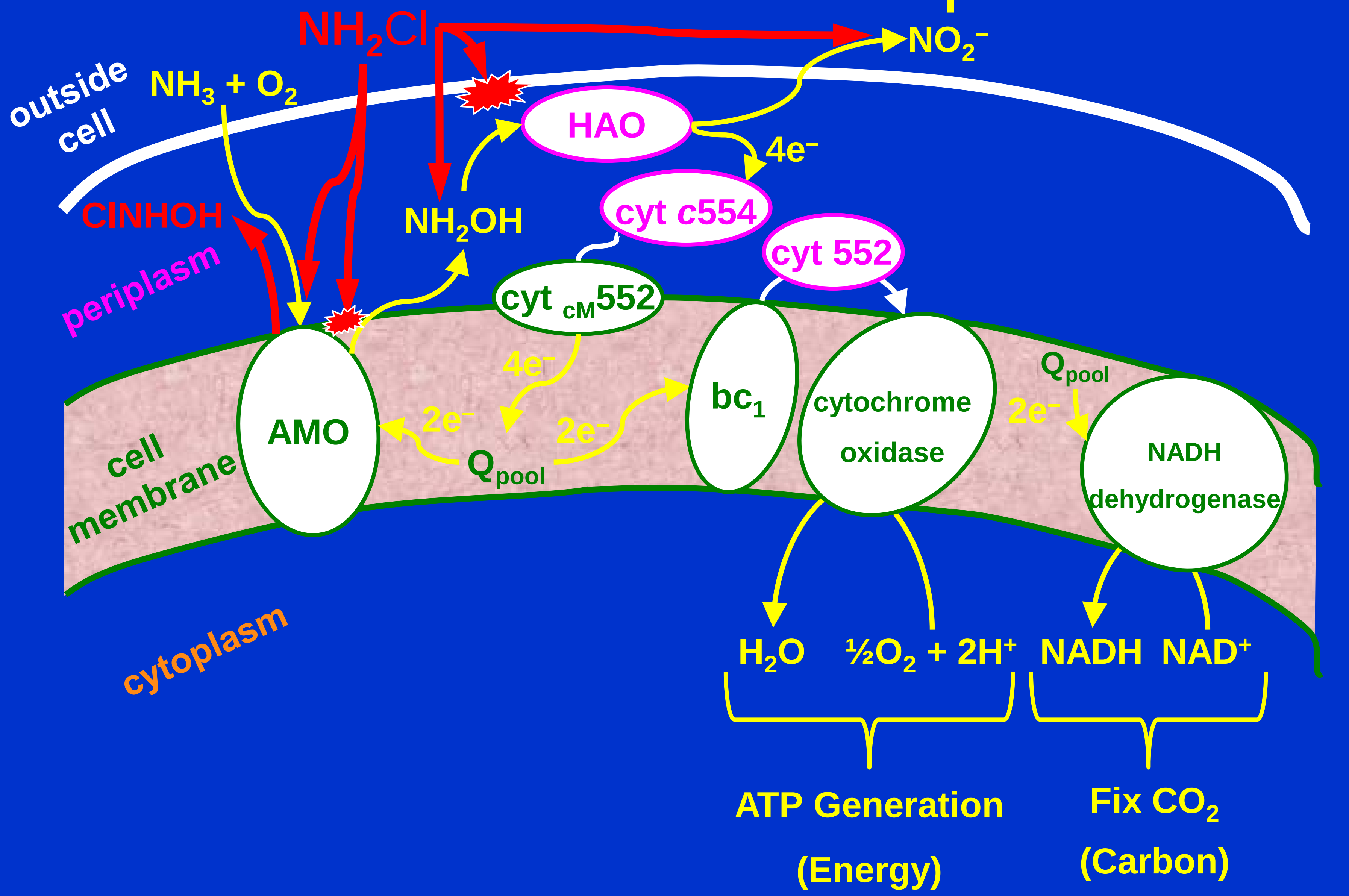


Transformation Capacity (T_c)

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

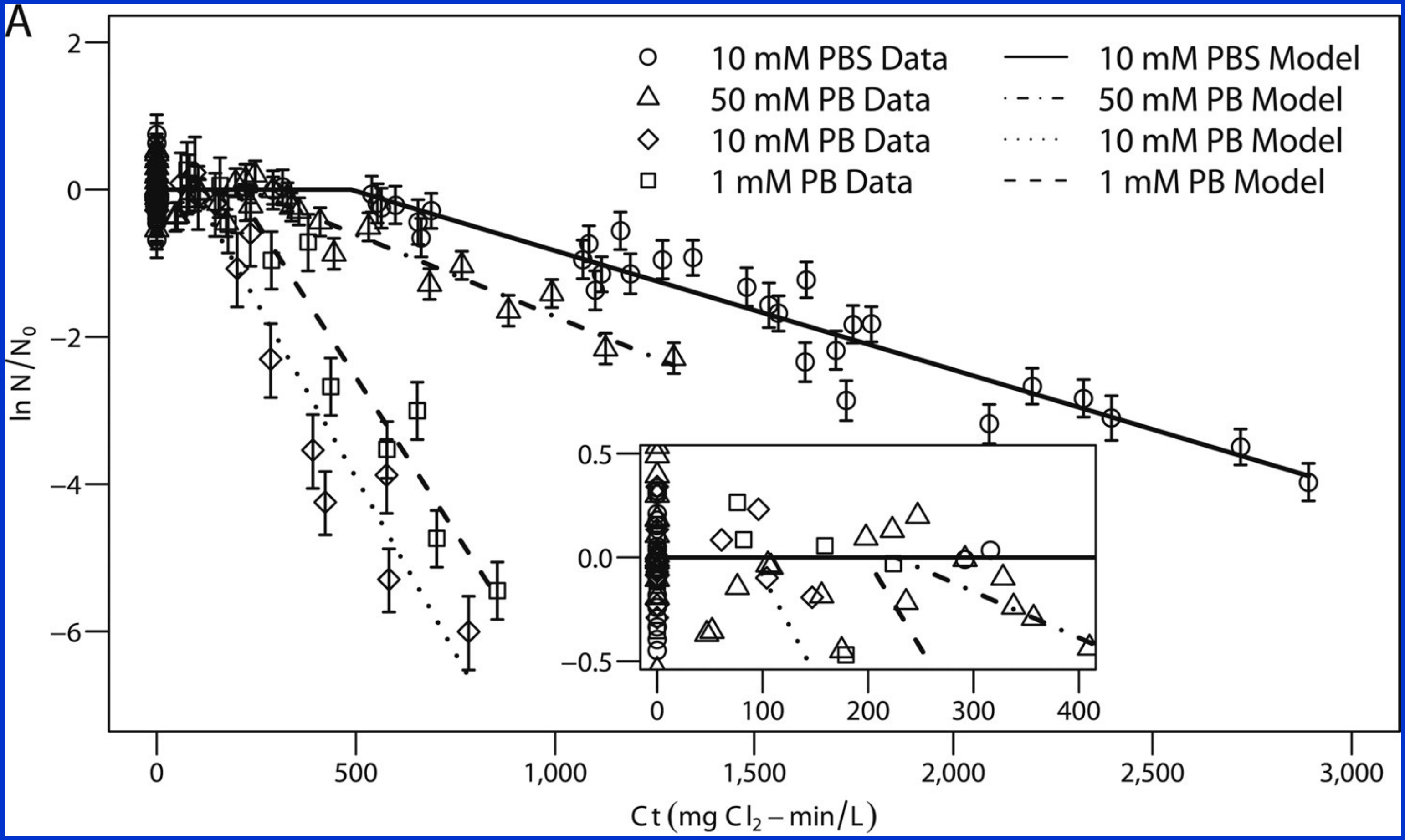
UT Research		Literature Reported Values		
Chemical	T_c (nmol/mg)	Chemical	T_c (nmol/mg)	Source
TCM	77	TCM	92-150	Ely (1996)
BDCM	45	TCE	61-99	Alvarez-Cohen and Speitel (2001)
DBCM	31	1,1-DCE	24-45	
TBM	22	1,2-DCA	>3,500	

Monochloramine Impacts



Source: Adapted from Sayavedra-Soto and Arp (2011)

Monochloramine Inactivation
N. europea Disinfection Kinetics
(Wahman et al., AEM 2010)

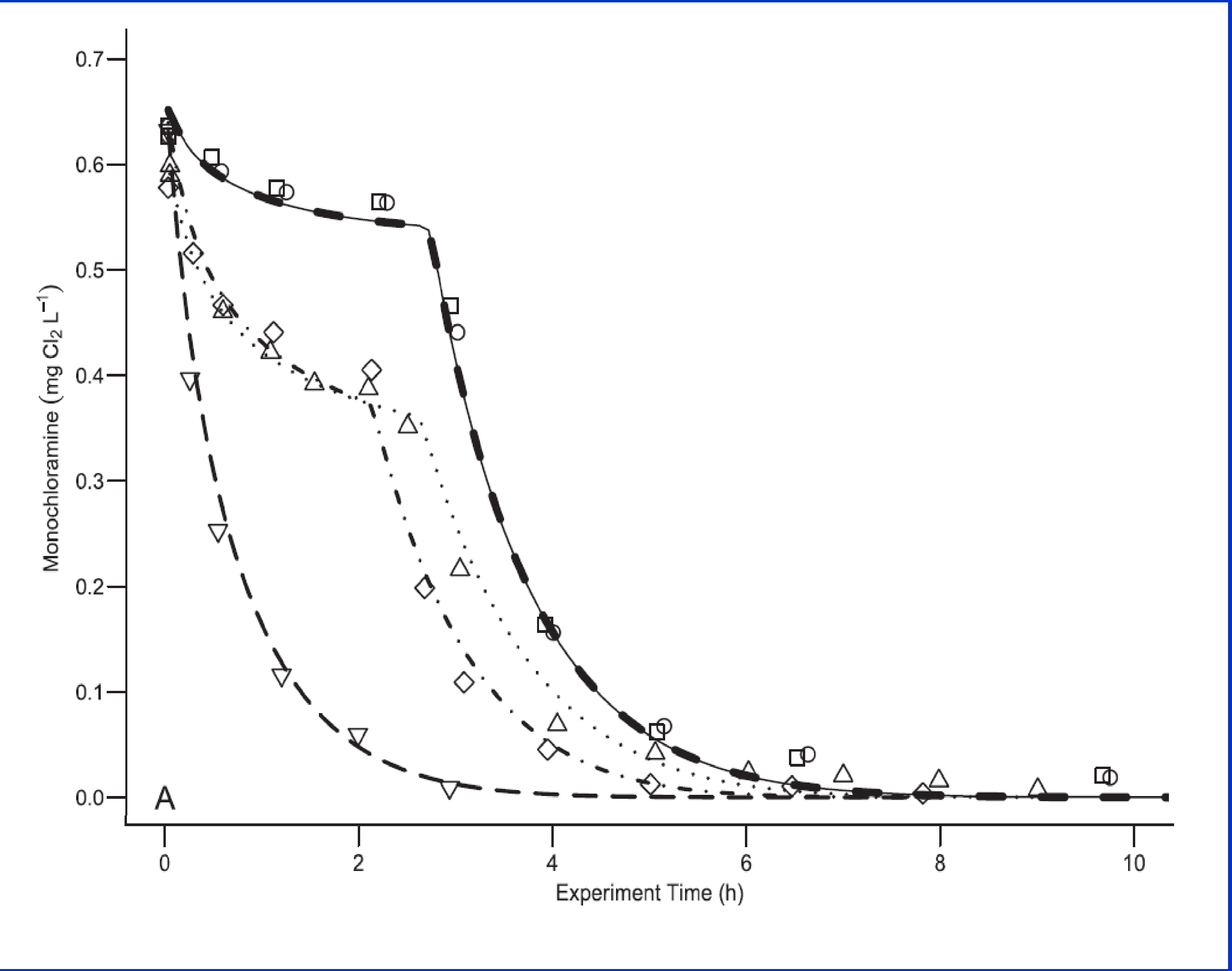


Delayed Chick Watson Model used to describe disinfection kinetics

Ionic strength and buffer concentration effects on disinfection kinetics

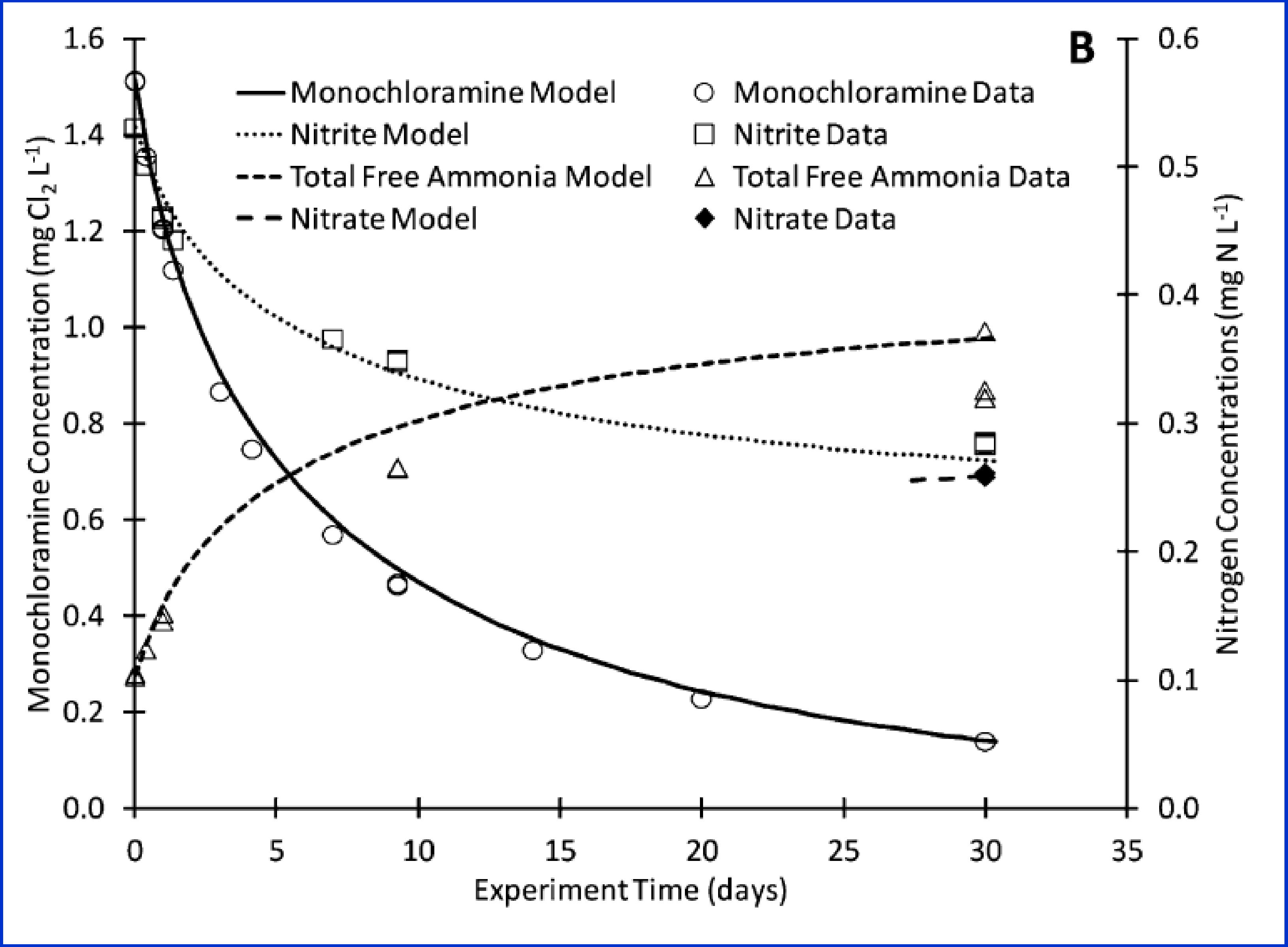
Monochloramine & Hydroxylamine Reaction

(Wahman & Speitel, *Water Research* 2015)



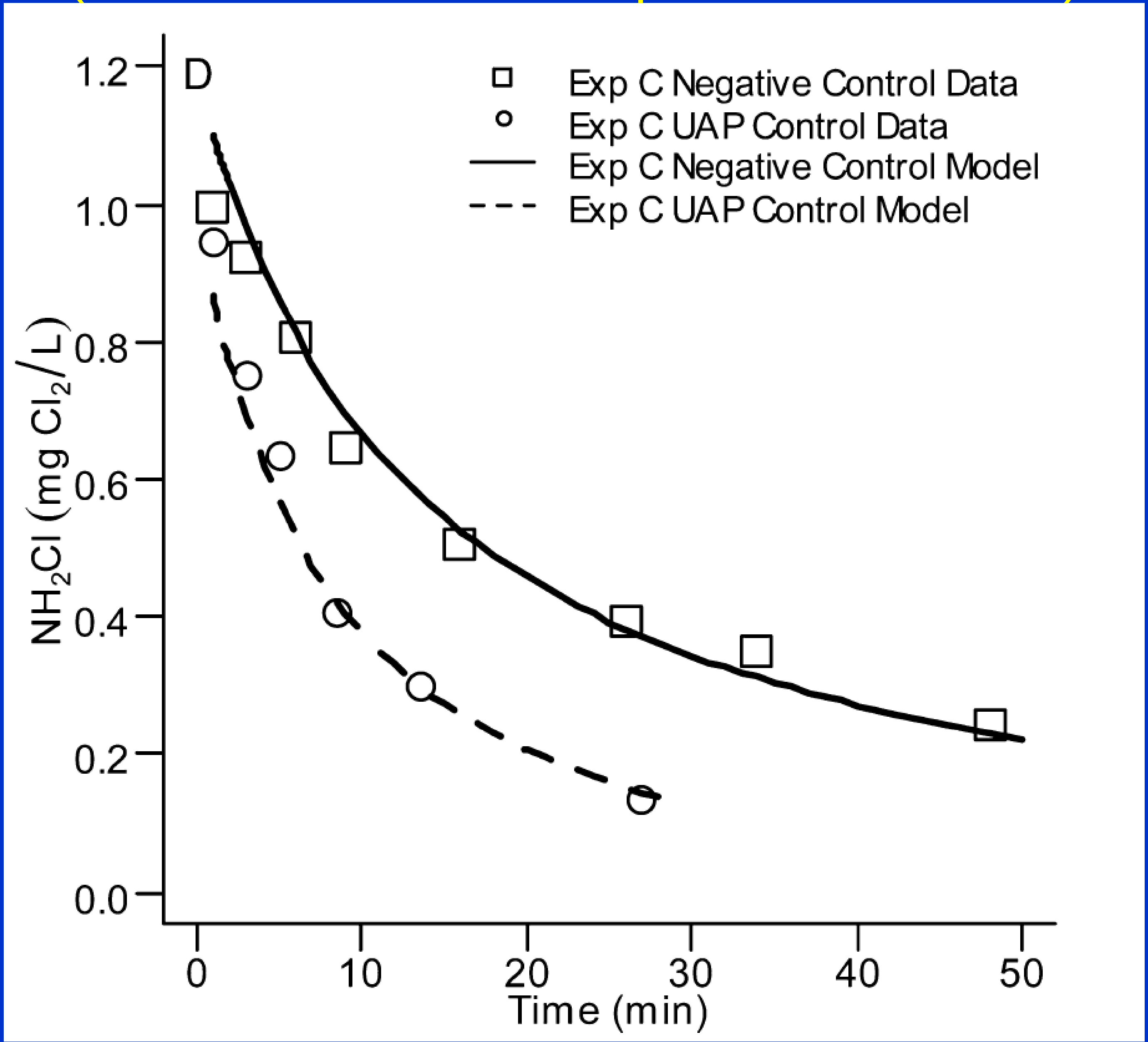
Monochloramine & Nitrite Reaction

(Wahman & Speitel, *ES&T* 2012)

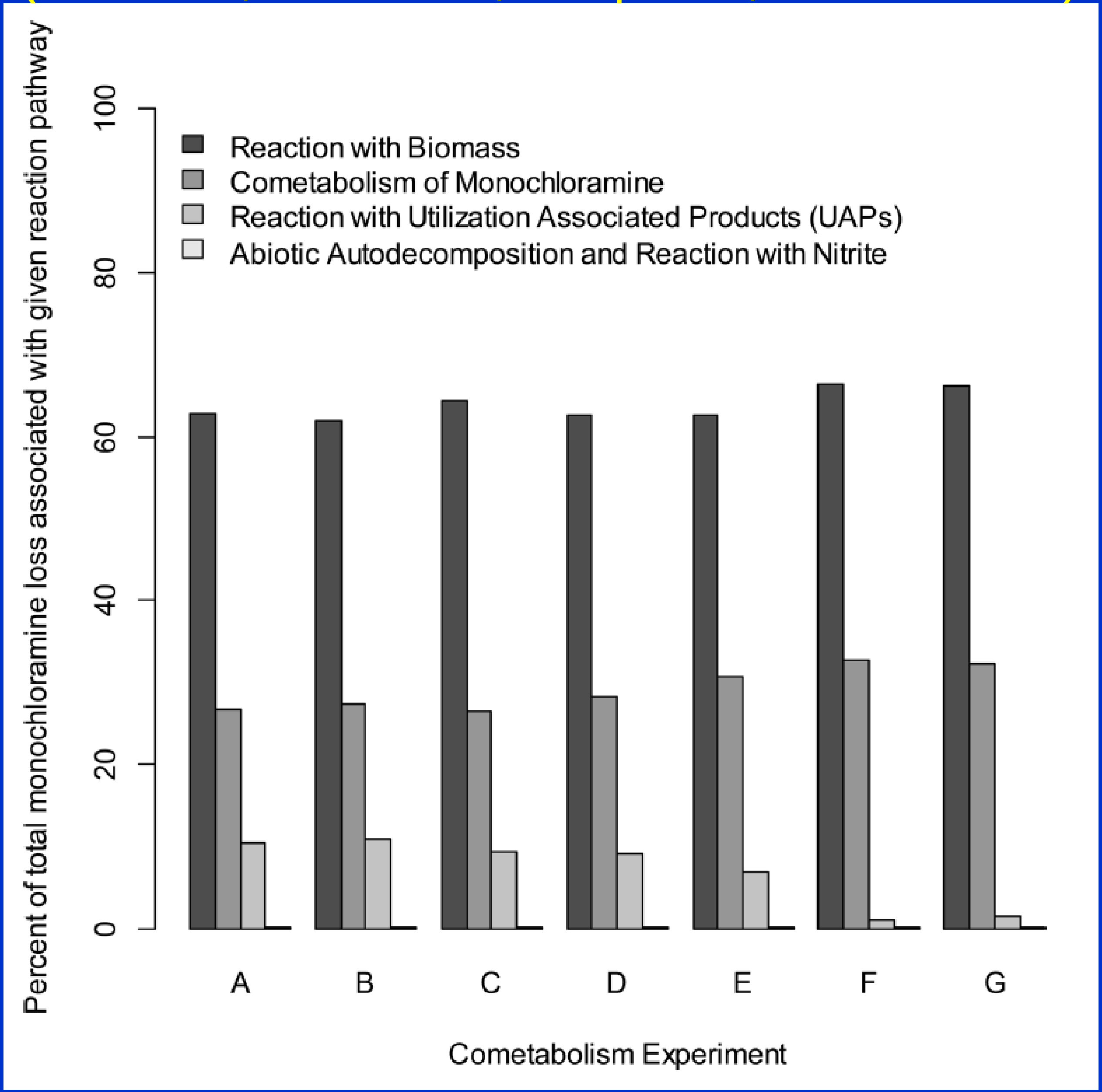


Cellular & UAP Reactions with Monochloramine

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



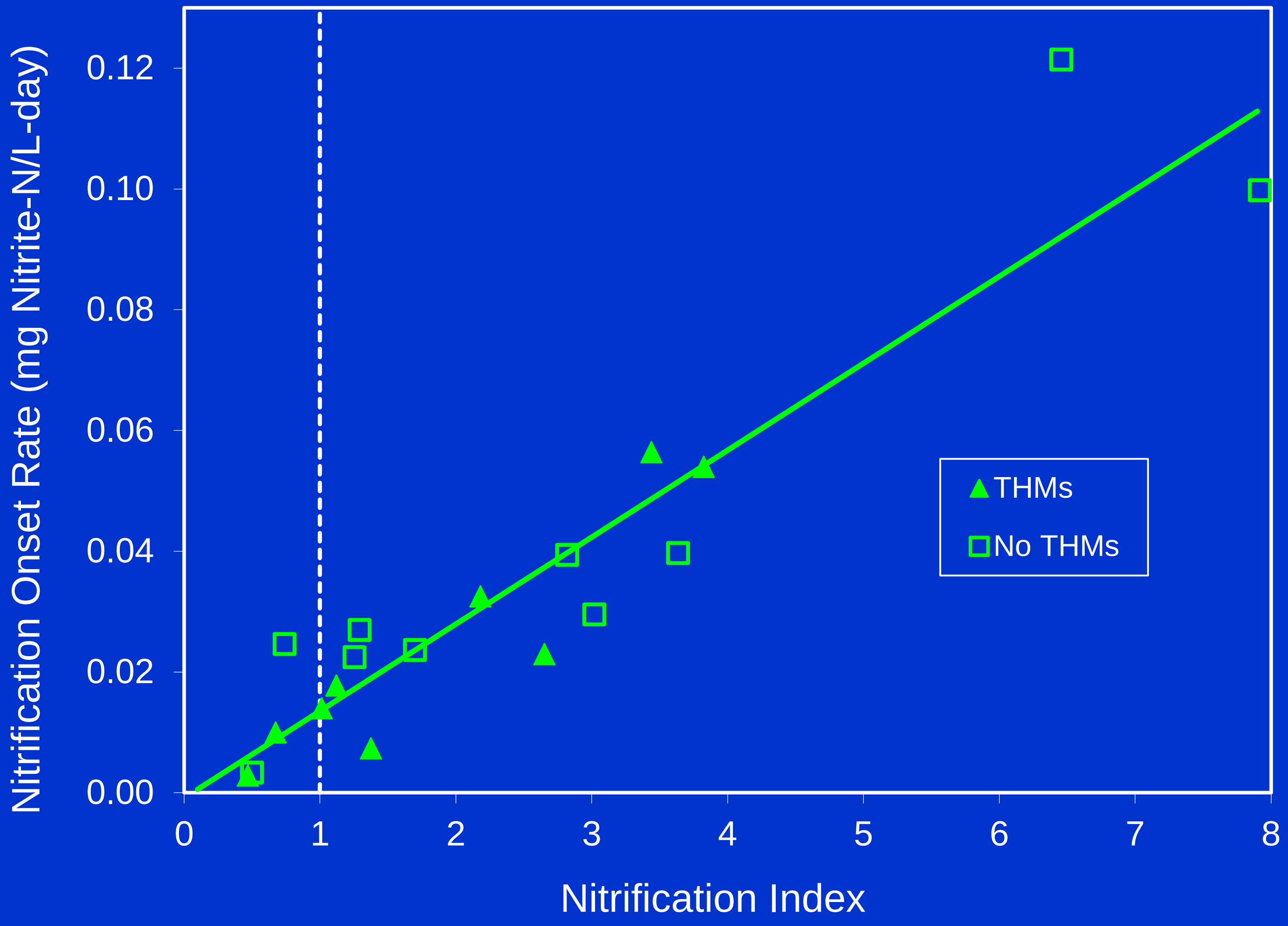
Monochloramine Cometabolism
(Maestre, Wahman, & Speitel, *ES&T* 2016)



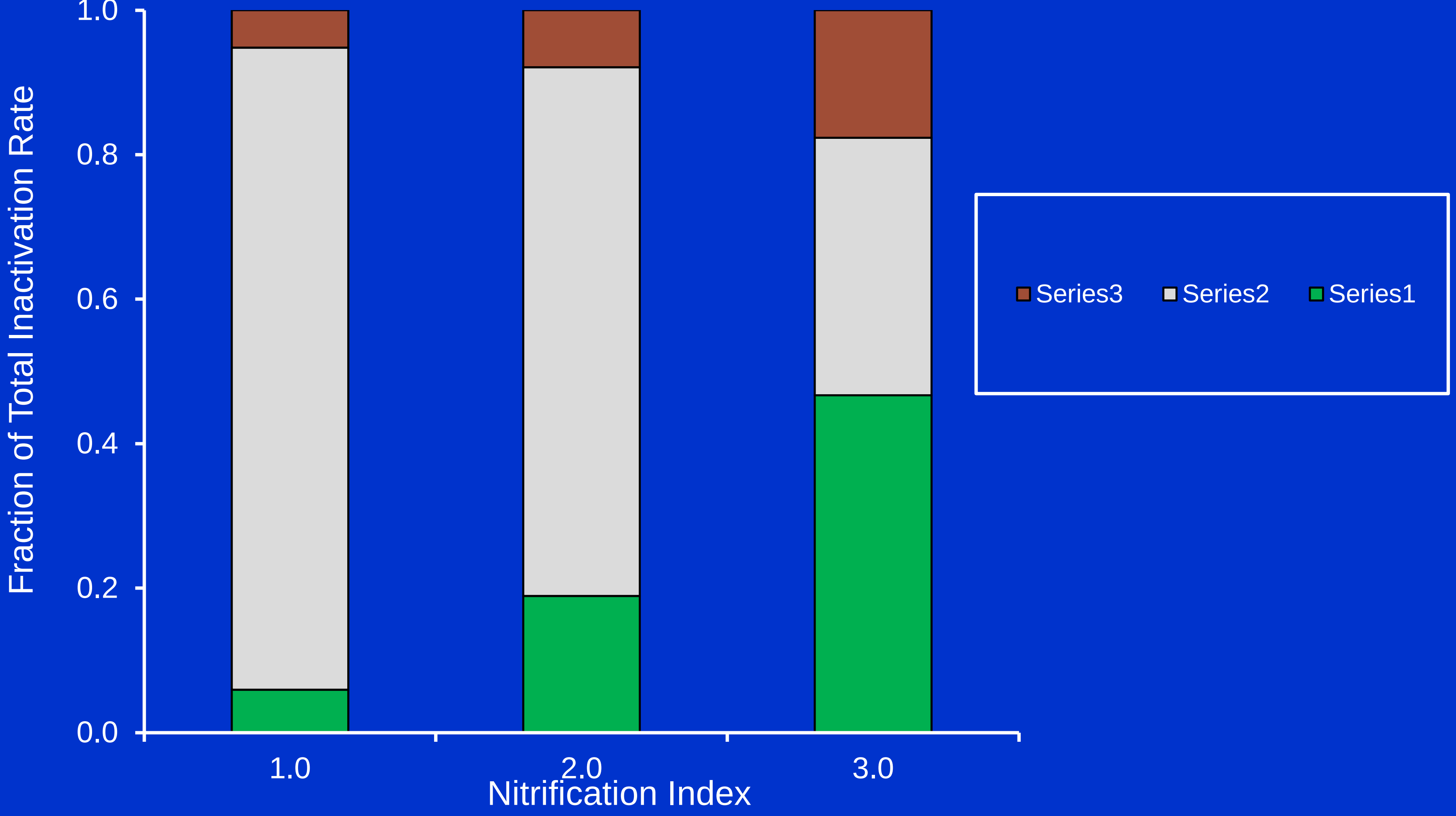
Experimental Approach

- Four annular reactors simulate distribution system - inner cylinder rotates to create hydraulic shearing force
- Parameters
  - Lake Austin (tap) water culture
  - Typical drinking water conditions
    - pH 7-9
    - Ammonia - 0.5 to 1 mg/L NH_3-N
    - Chlorine - 1 to 3 mg/L as Cl_2
  - Varied THM concentrations and bromine incorporation ratio

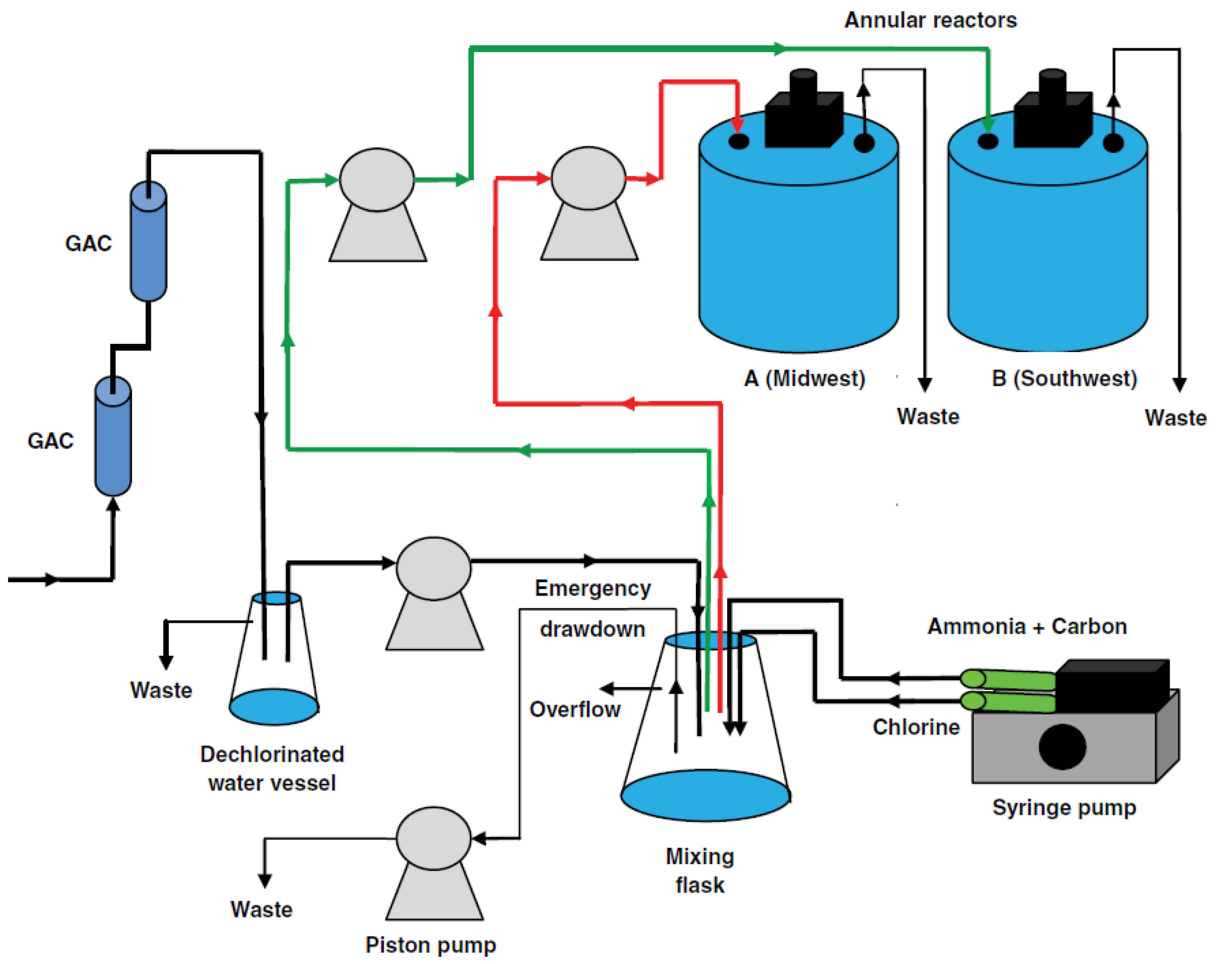
Results – Onset Rate vs. NI



Inactivation Mechanisms in NI Model



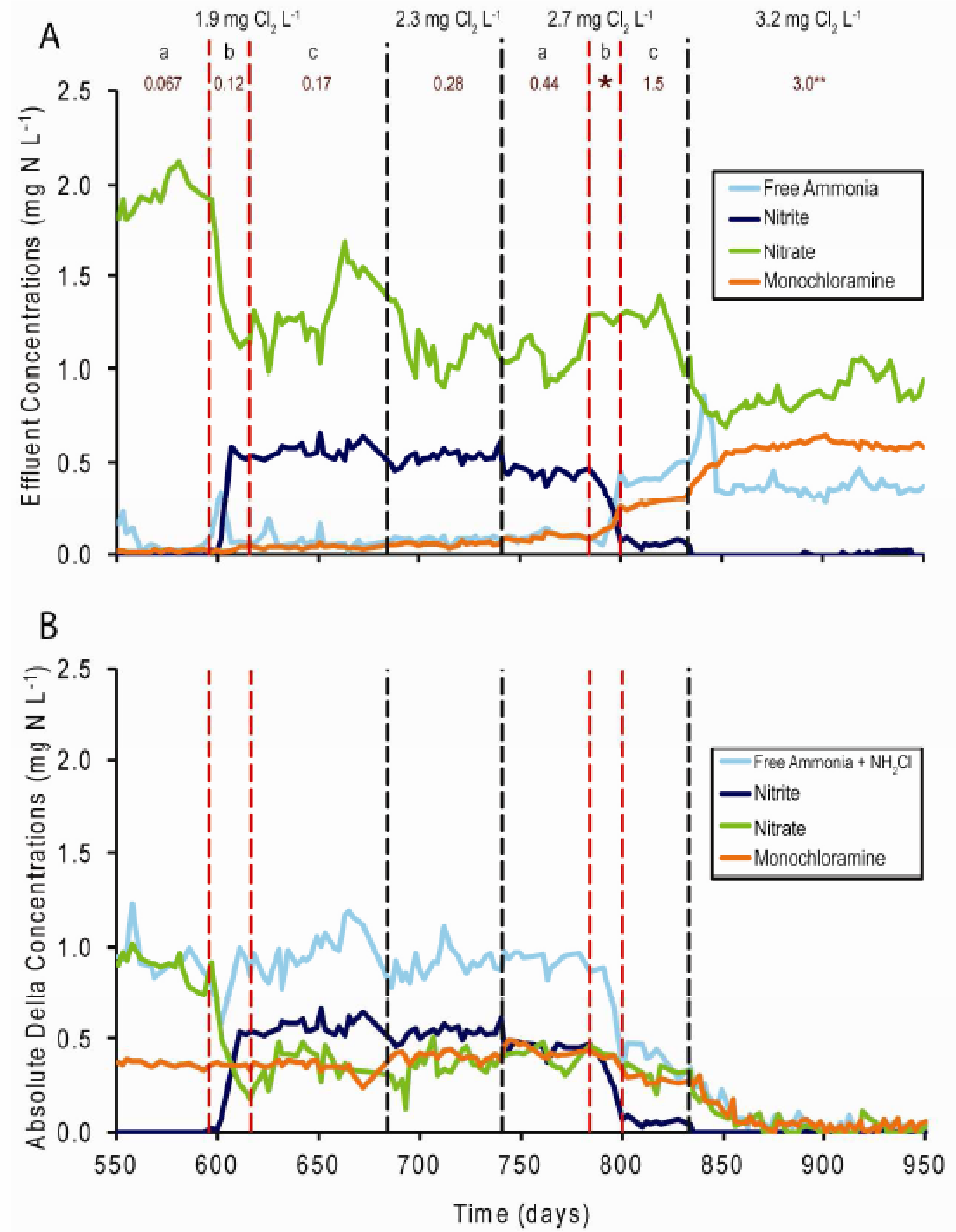
Long-Term Evaluation of NI



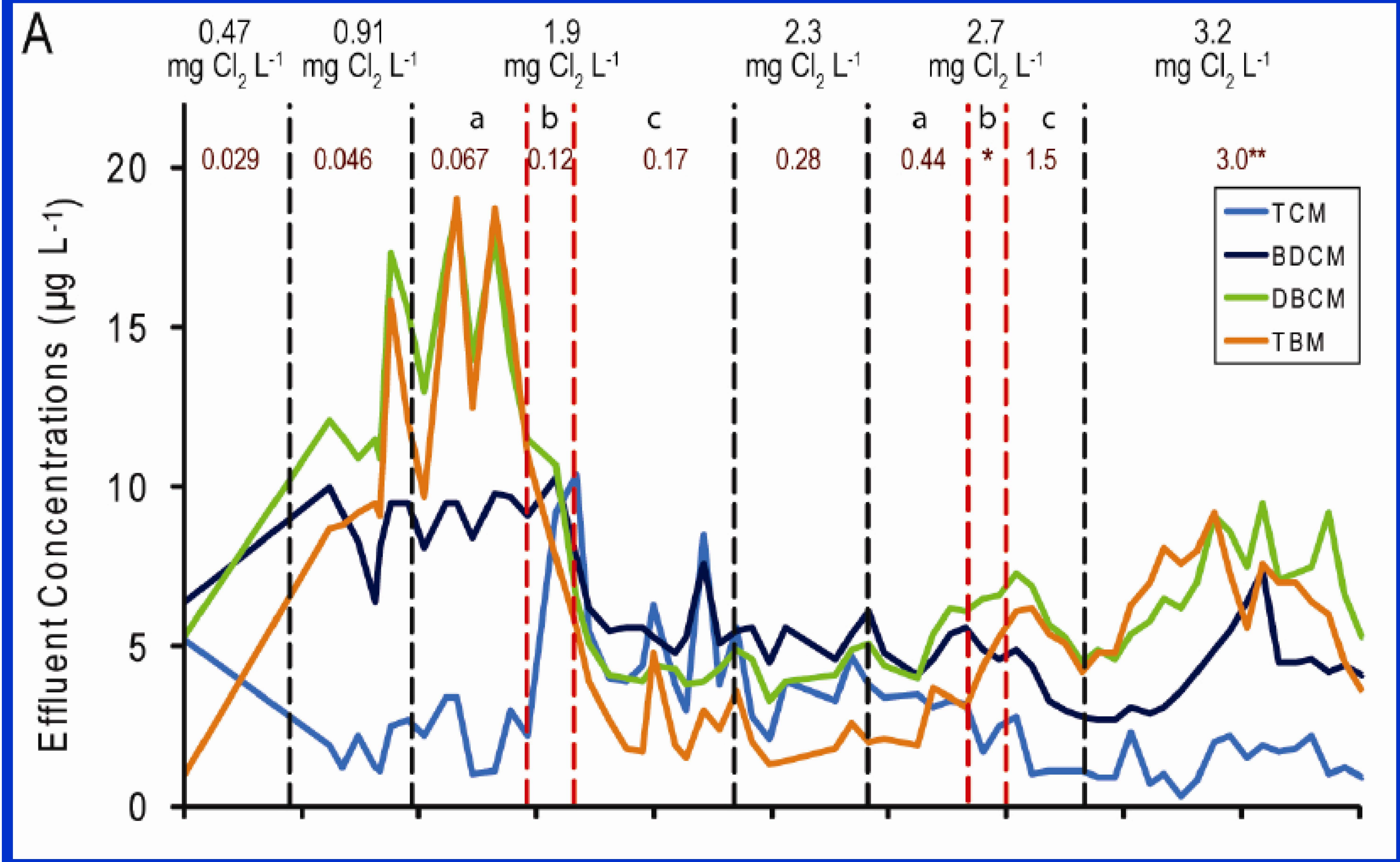
GAC—granular activated carbon

Source: Schrantz, Pressman, & Wahman (JAWWA, 2013)

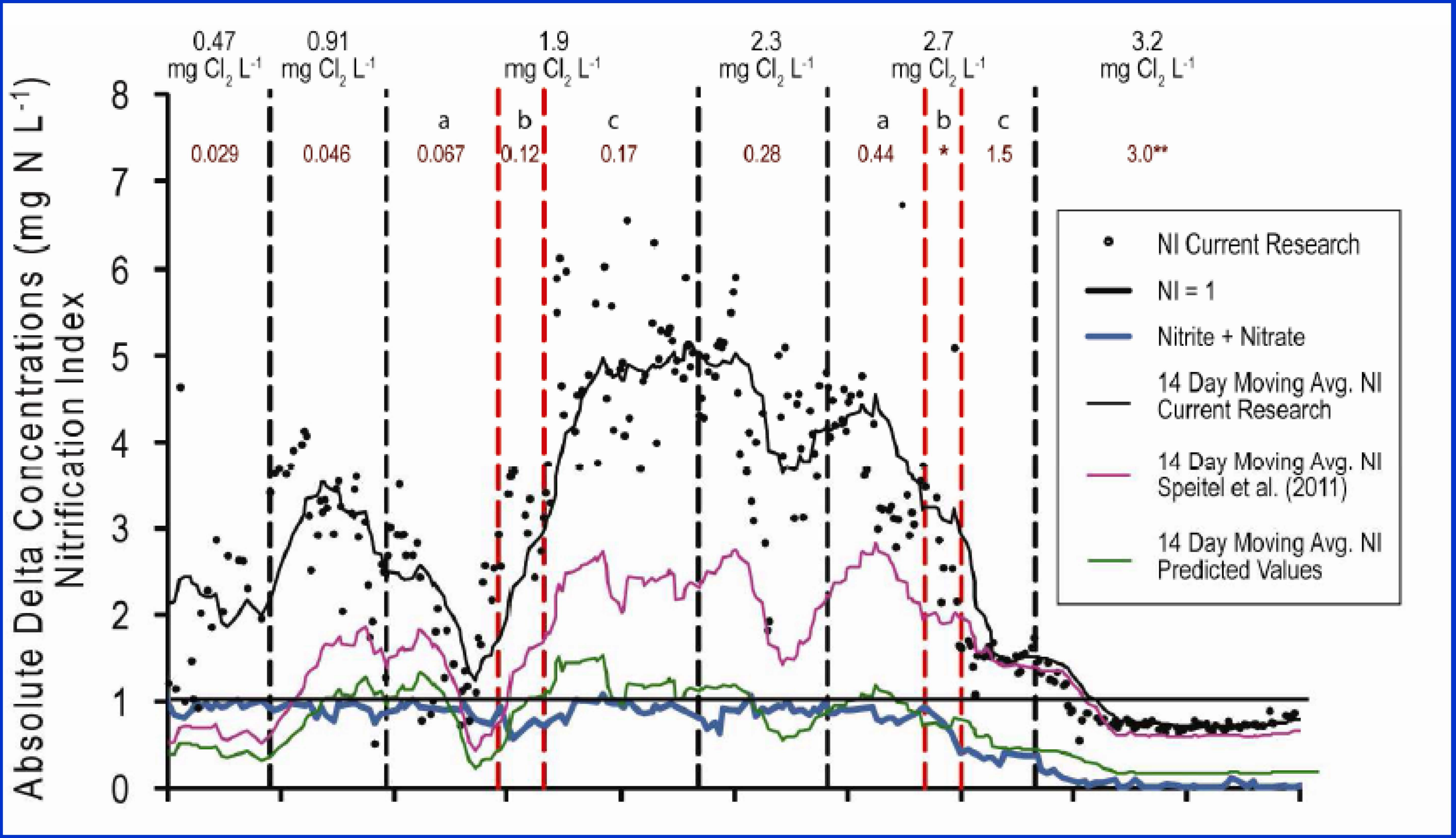
Concentrations in "Midwest" Annular Reactor



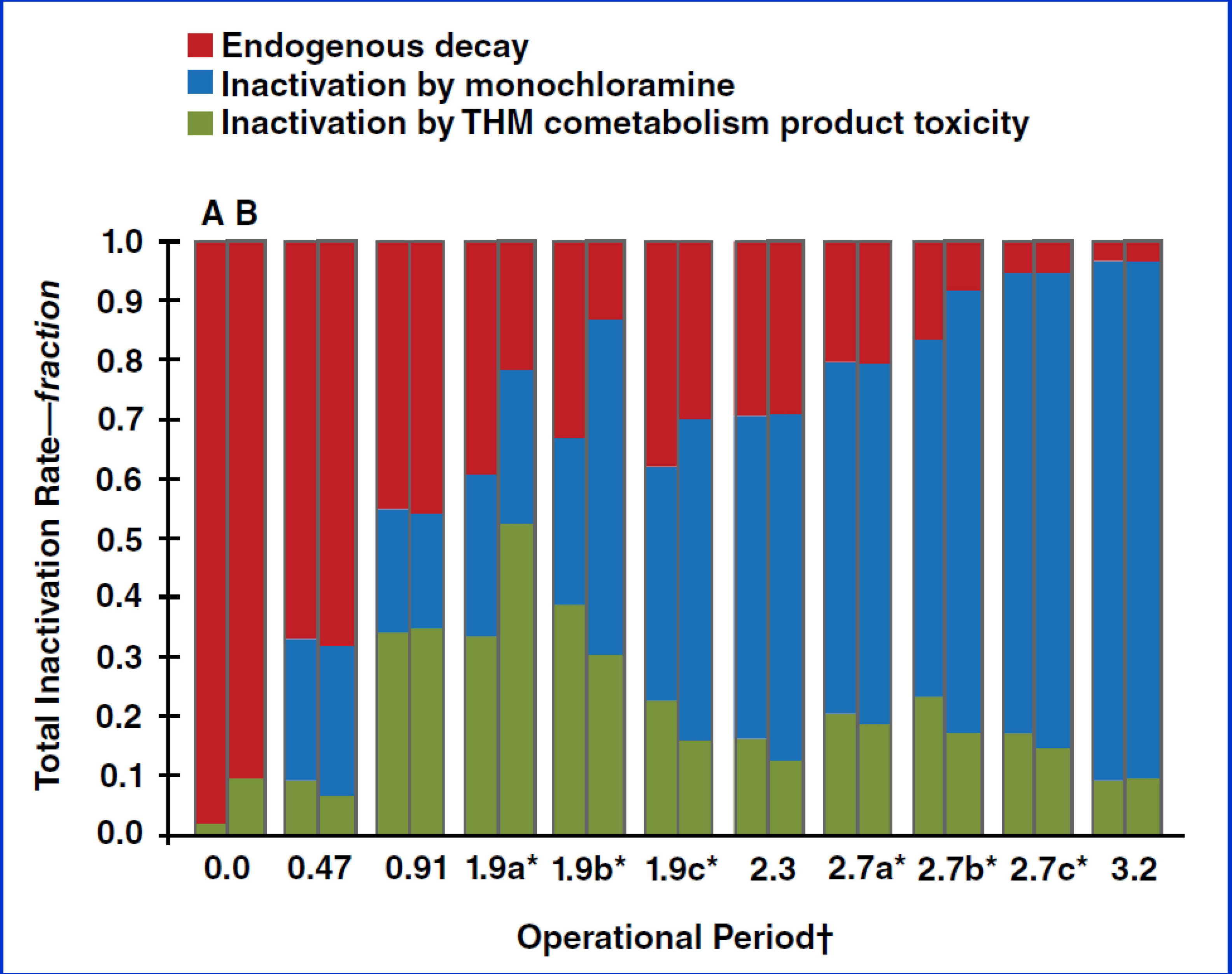
"Midwest Annular" Reactor - THMs



NI for "Midwest" Annular Reactor



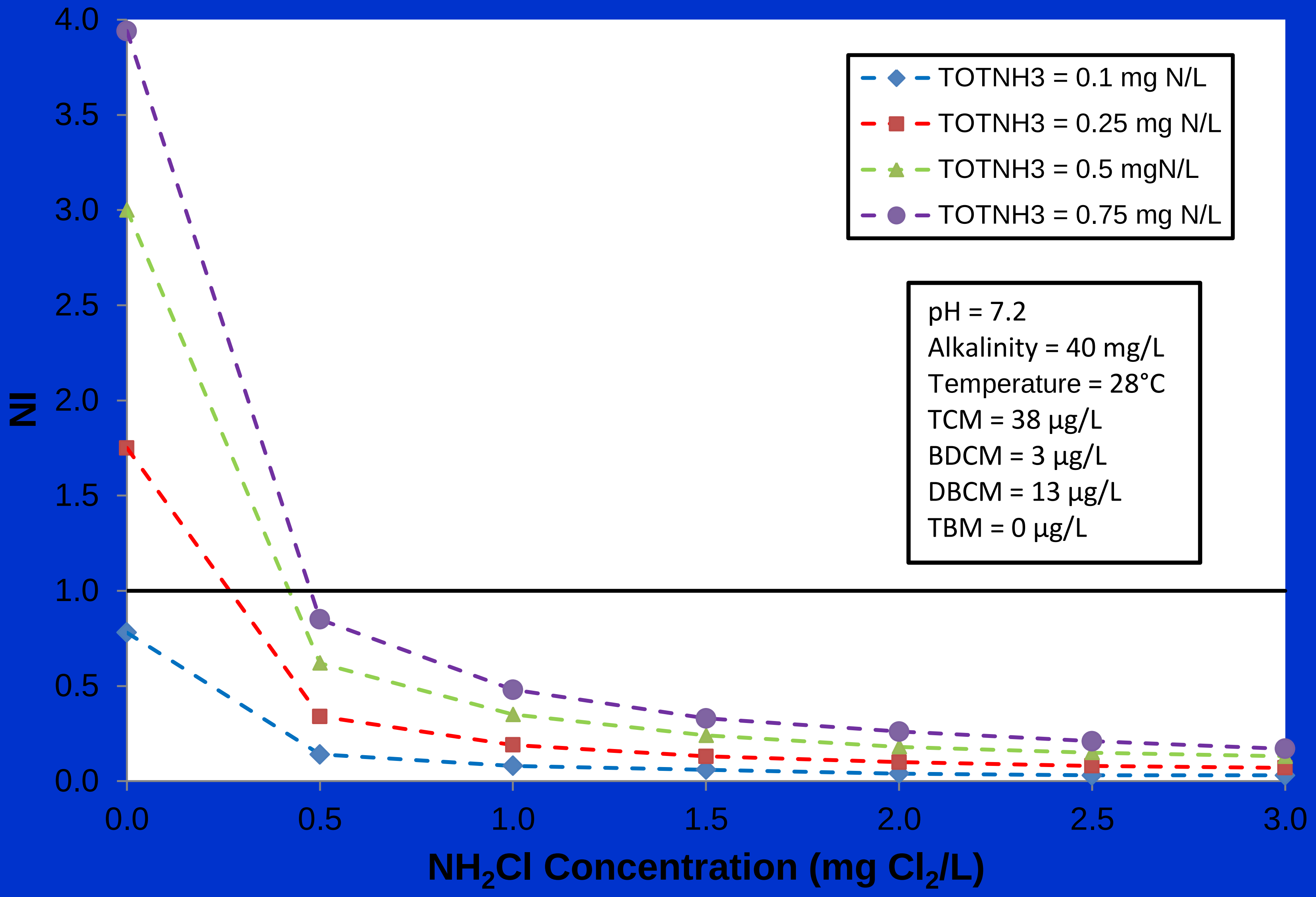
Inactivation Mechanisms vs. NH_2Cl Conc.



Implementation of NI Framework

- Calculate NI over time at locations of interest in the distribution system
  - Measure pH, ammonia, and monochloramine (Monochlor F method preferred; total chlorine okay)
  - Use THM concentrations from most appropriate regular sampling points and times
  - Measure temperature and nitrite as related data to help with interpretation
- Compare NI values to indicators of nitrification (e.g., what was NI right before onset of nitrification episodes?)
- If a correlation can be established, NI might be useful as an early warning of nitrification risk

NI Calculations for Plant in PA



Closing Thoughts

- Even though the system is complicated, the biokinetics of growth, cometabolism, decay, and inactivation, as described by the **Nitrification Index**, should improve our ability to understand and predict nitrification episodes
  - NH_2Cl and ammonia concentrations are of primary importance
  - THM concentrations and pH are of secondary importance to NI
- NH_2Cl cometabolism (NH_2Cl loss - bad) is likely to play a more important role than THM cometabolism (toxicity to nitrifiers - good)
- Easy to see how the onset of nitrification can lead to rapid loss of residual disinfectant:
  - NH_2Cl cometabolism occurs with rapid kinetics; THM cometabolism slower
  - Growing AOB biomass increases disinfectant demand
  - Nitrification product (nitrite) reacts with both HOCl and NH_2Cl
  - Decreased ammonia concentration accelerates NH_2Cl autodecomposition
  - Decreased pH (low alkalinity waters) accelerates NH_2Cl autodecomposition
- Distribution systems are complex biological & chemical reactors

Acknowledgements

Collaborators

Andrea Henry

Ben Bayer

Ram Kannappan

Juan Pedro Maestre

Lynn Katz

Funding Agencies

Water Research Foundation

Texas Advanced Technology Research Program

USEPA

Questions?