Chemistry of Cyanotoxins in Surface Waters

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OTCO Reservoir Management Webinar

July 12, 2022

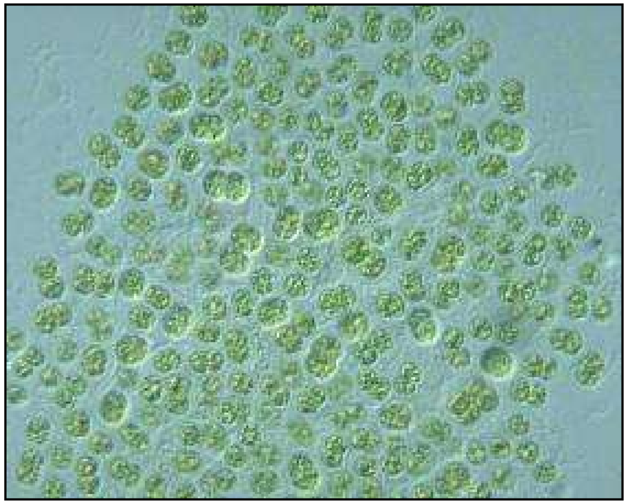
Agenda

- Cyanotoxins in water
  - Microcystins
  - Cylindrospermopsins
  - Anatoxin-a
  - Saxitoxins
  - Nodularins
- Observations from Case Studies
- AWWA CyanoTox 2.0 vs. Oxidation Studies

Microcystins

Microcystins in Water

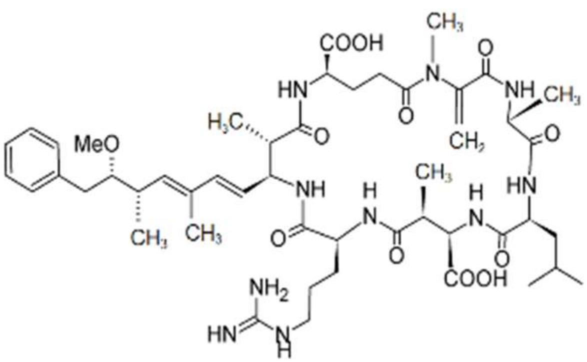
- Most common cyanotoxin
  - Presence of nitrate increases toxin concentration within cells
  - Maximum toxin concentration at 20°C to 25°C
  - Intracellular toxins released as cell lysing or mortality occurs
    - Natural life cycle or chemical means
    - UV irradiation slowly breaks down microcystins



Microcystis Aeruginosa

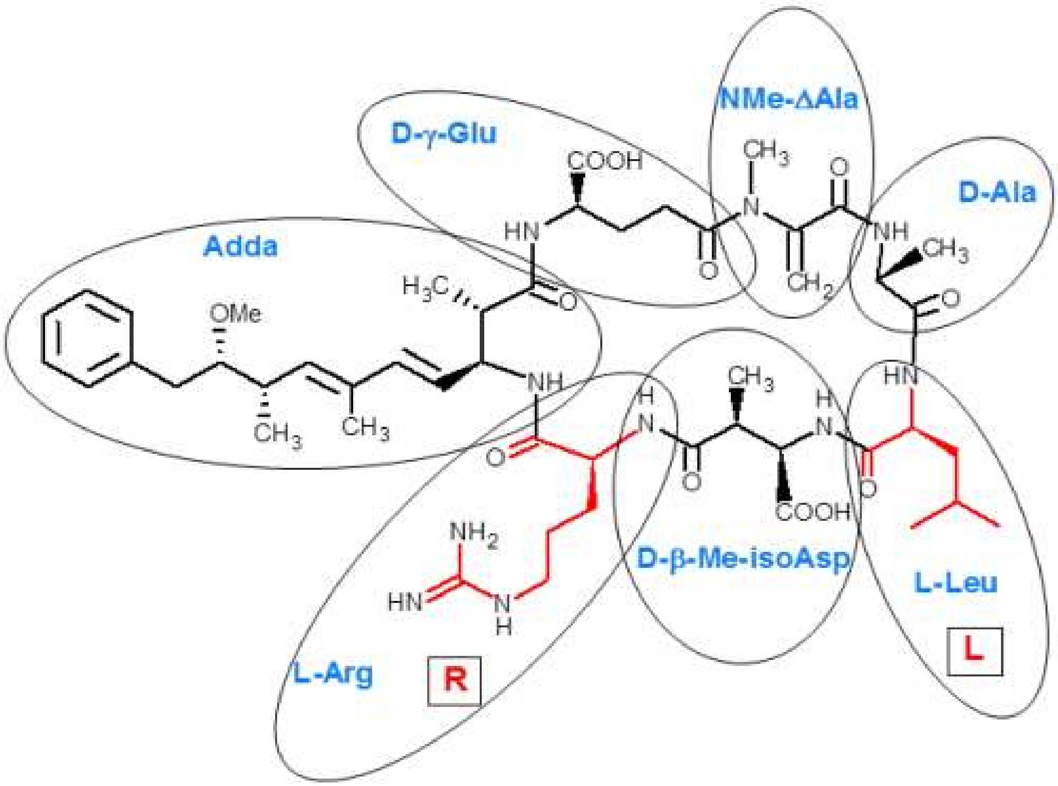
Microcystins in Water

- Made up of 7 amino acids in unique structure
  - $C_{49}H_{74}N_{10}O_{12}$ (MC-LR)
    - Similar for other variants
  - 995 g/mole to 1,040 g/mole
  - Solubility in water ~1,500 mg/L
  - Half-life in water environment is up to 10 weeks
  - Henry's Law constant
    - *Reduction by aeration not likely*
  - Toxicity from enzyme reaction stripping phosphate from proteins that leads to liver damage
  - LD50
    - 5 mg/kg



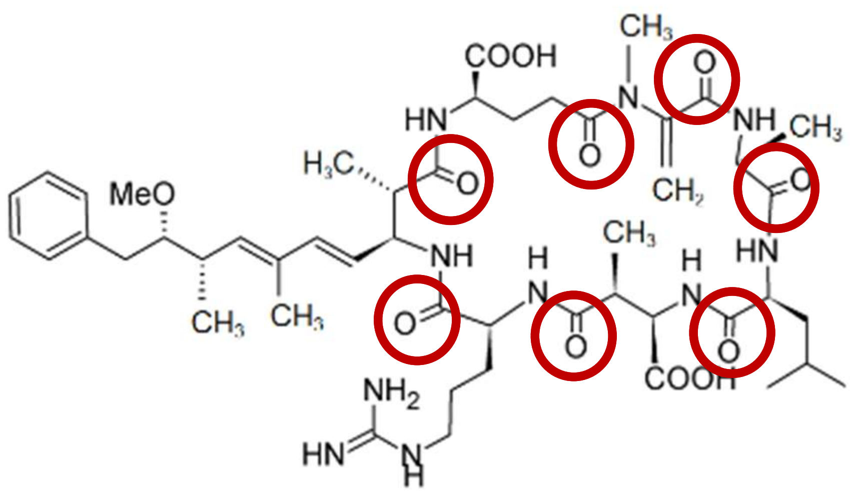
Microcystin-LR

Microcystins in Water



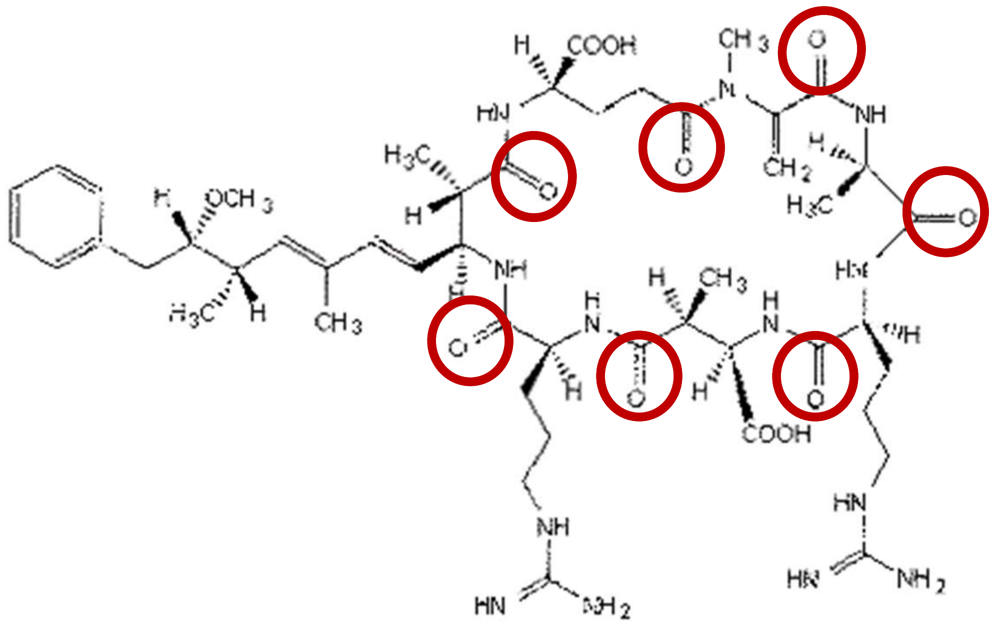
Microcystin-LR (7) amino acids

Microcystin-LR

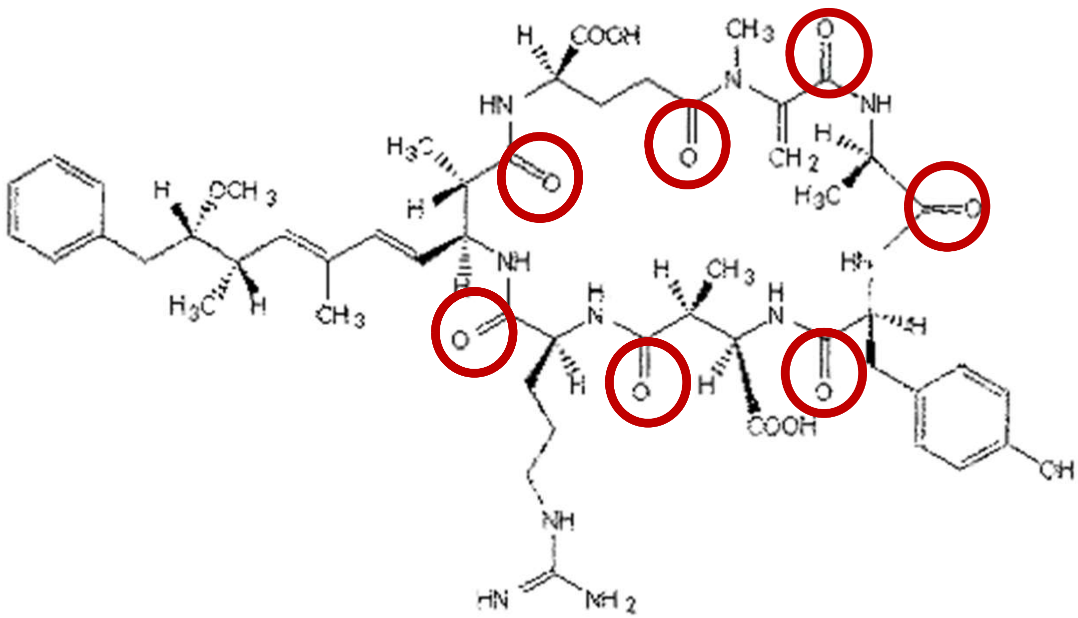


Oxidation at double bonds degrades structure
to amino acids groups

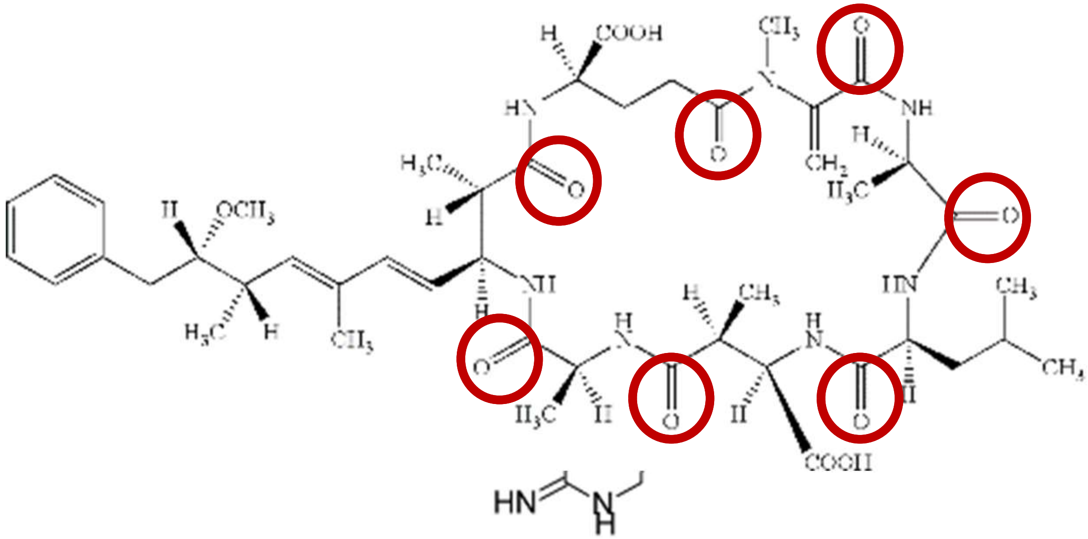
Microcystin-RR



Microcystin-YR



Microcystin-LA

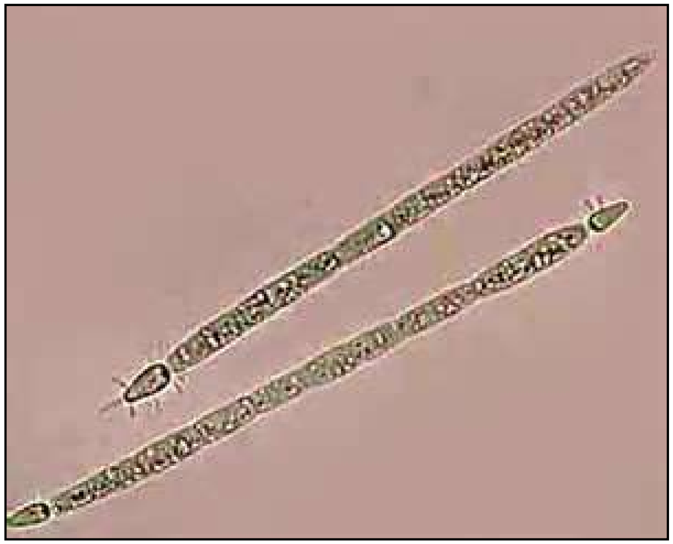


Other congeners include MC-H4YR, MC-WR, MC-FR

Cylindrospermopsins

Cylindrospermopsins in Water

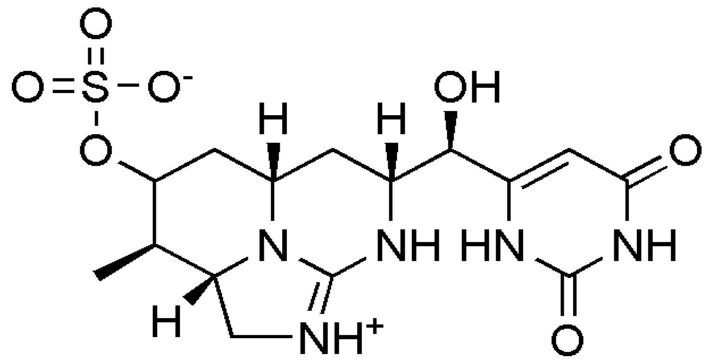
- Common cyanotoxin
  - Presence of nitrate increases toxin concentration within cells
  - Maximum toxin concentration at 20°C to 25°C
  - Intracellular toxins released as cell lysing or mortality occurs
    - Natural life cycle or chemical means
    - More toxic than microcystins
    - UV irradiation breaks down cylindrospermopsins



Cylindropspermopsis Raciborskii

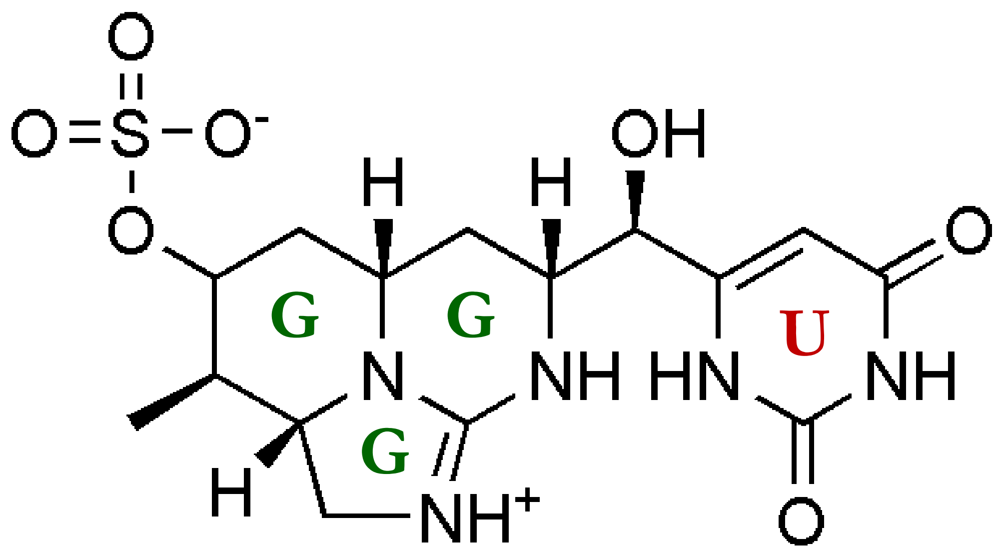
Cylindrospermopsins in Water

- Polycyclic uracil derivative in unique structure
  - $C_{15}H_{21}N_5O_7S$
  - 415 g/mole
  - Solubility in water very high
    - Stable over wide pH range
  - Half-life in water environment is about 8 weeks
  - Toxicity from inhibited protein synthesis leading to cell mortality
  - LD50
    - 4.4 mg/kg to 6.9 mg/kg



Cylindrospermopsin

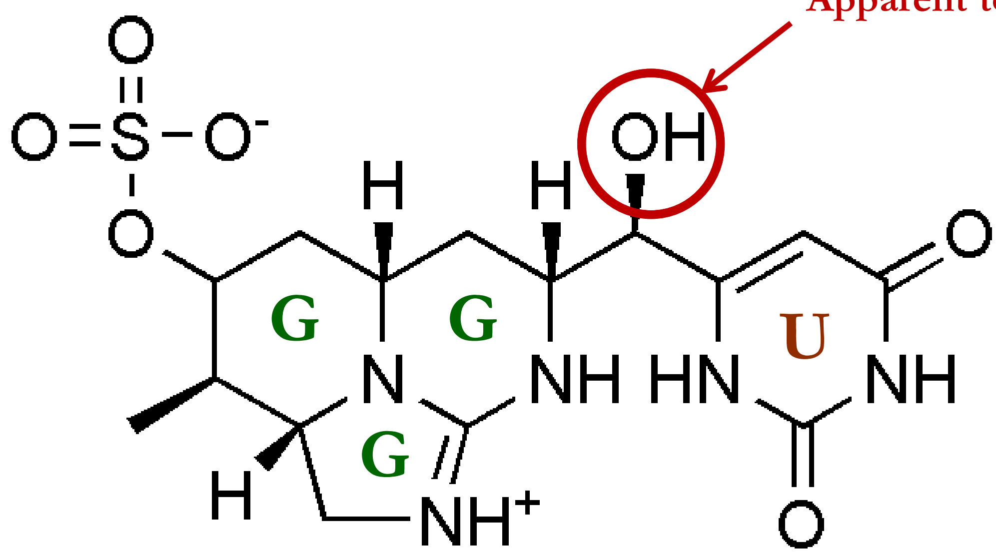
Cylindrospermopsins in Water



Guanidine and **Uracil** rings

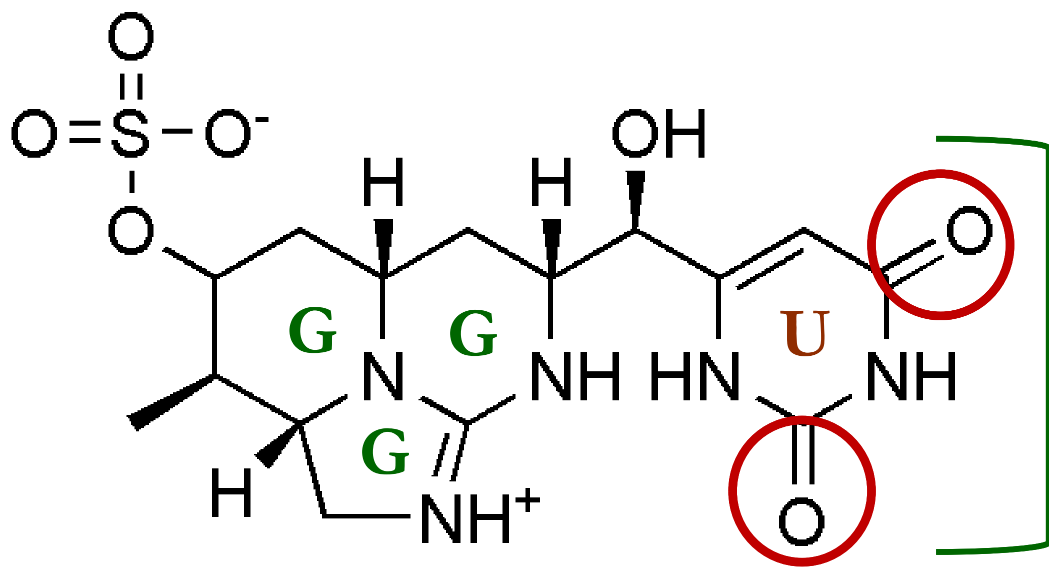
Cylindrospermopsins in Water

Apparent toxicity from -OH



Guanidine and **Uracil** rings

Cylindrospermopsins in Water

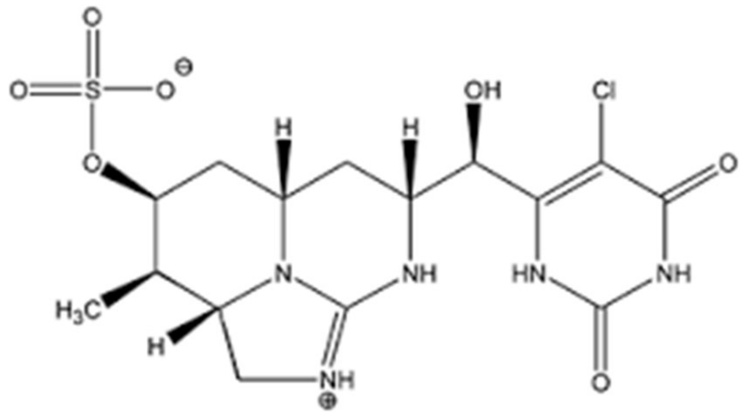


Oxidation or substitution at uracil group alters structure

Guanidine and **Uracil** rings

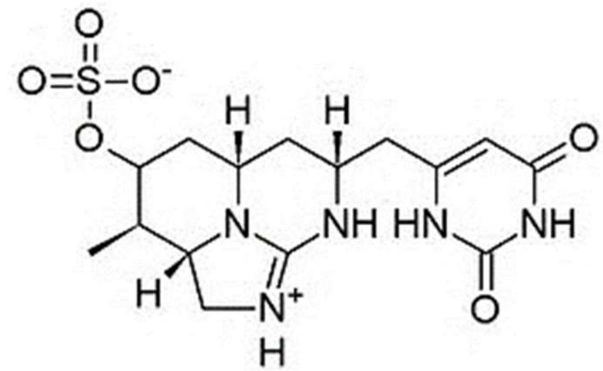
Cylindrospermopsins in Water

Non-toxic metabolites



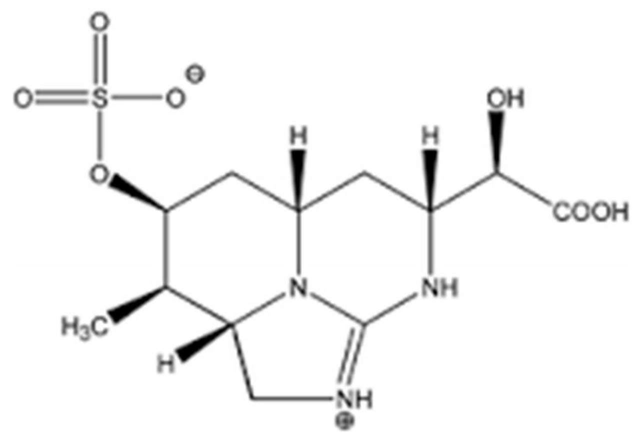
5-chloro-cylindrospermopsin

uracil ring altered with Cl



Deoxycylindrospermopsin

no toxicity - OH stripped

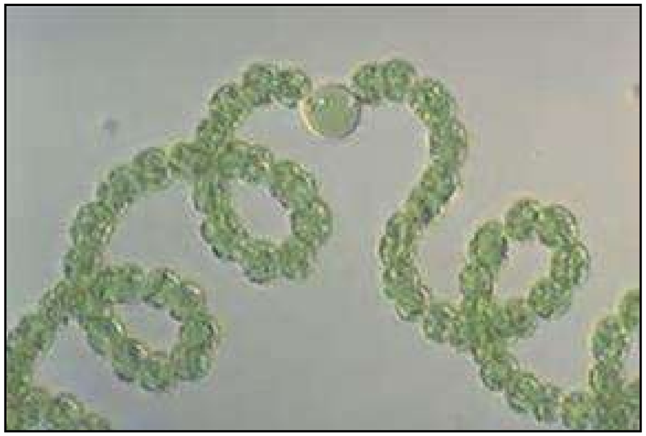


Cylindrospermopsic acid

no uracil ring

Anatoxin-a

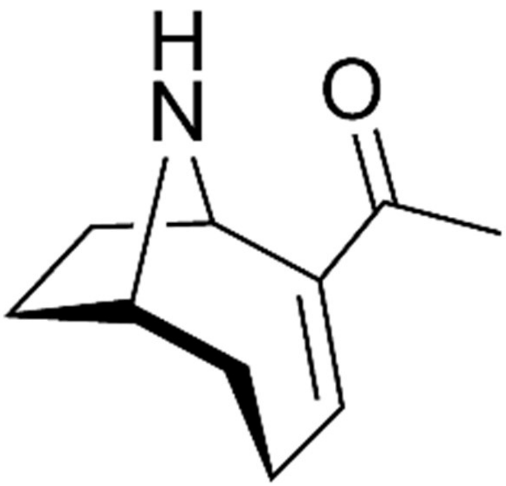
Anatoxin-a in Water



Anabeana Aequalis

- Less common cyanotoxin
  - Maximum toxin concentration at 20°C to 25°C
  - Intracellular toxins released as cell lysing or mortality occurs
    - Natural life cycle or chemical means
  - Strong neurotoxin with acute toxicity
    - Named very fast death factor (VFDF) aquatic toxin
    - LD50 - 0.25 mg/kg
    - Toxicity from attack of neuromuscular receptors resulting in paralysis
  - Half-life in water environment
    - <24 hours, degrades within hours at pH greater than 8

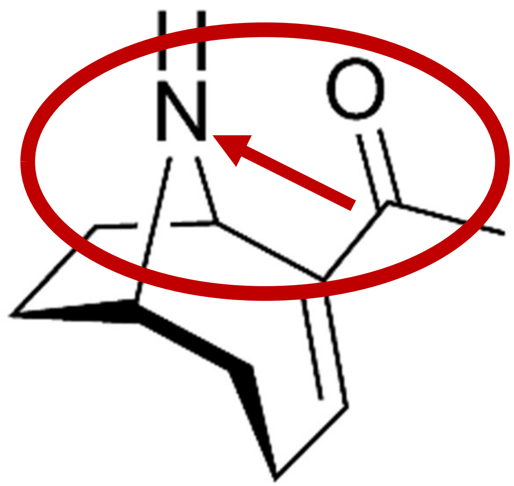
Anatoxin-a in Water



Anatoxin-a

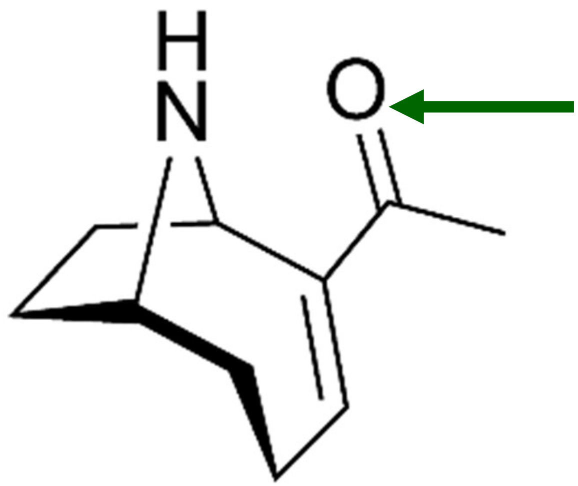
- Bicyclic amine alkaloid in unique structure
  - $C_{10}H_{15}NO$
  - 165 g/mole
  - Solubility in water very low
    - <50 mM/L
  - Unstable in water, UV irradiation leads to degradation into non-toxic forms
    - Dihydroanatoxin-a
    - Epoxyanatoxin-a

Anatoxin-a in Water



Carbonyl (C=O) near nitrogen responsible for toxicity

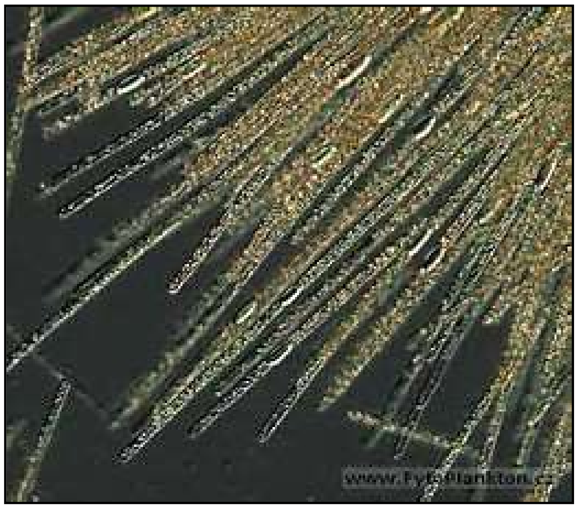
Anatoxin-a in Water



Possible substitution at C=O may alter toxicity, Adsorption also likely treatment option

Saxatoxins

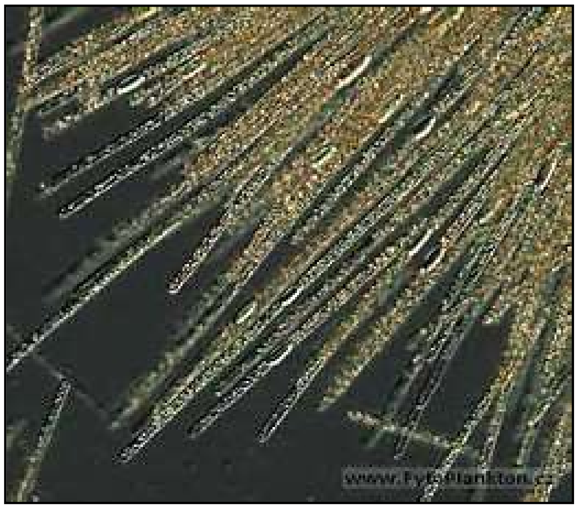
Saxitoxins in Water



Aphanizomenon flos-aquae

- Less common cyanotoxin
  - Maximum toxin concentration at 20°C to 25°C
  - Intracellular toxins released as cell lysing or mortality occurs
    - Natural life cycle or chemical means
  - Strong neurotoxin with acute toxicity
    - Named paralytic shellfish toxin (PST)
    - $LD50 \approx 0.26$ mg/kg
    - Toxicity from attack of neuromuscular receptors resulting in paralysis
  - Half-life in water environment
    - Up to 10 weeks

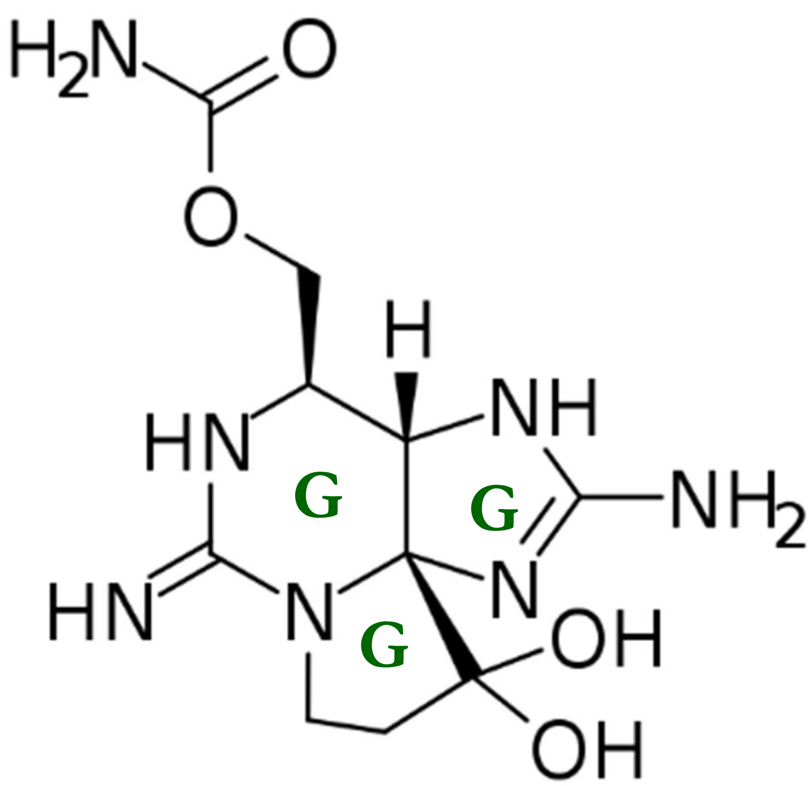
Saxitoxins in Water



Aphanizomenon flos-aquae

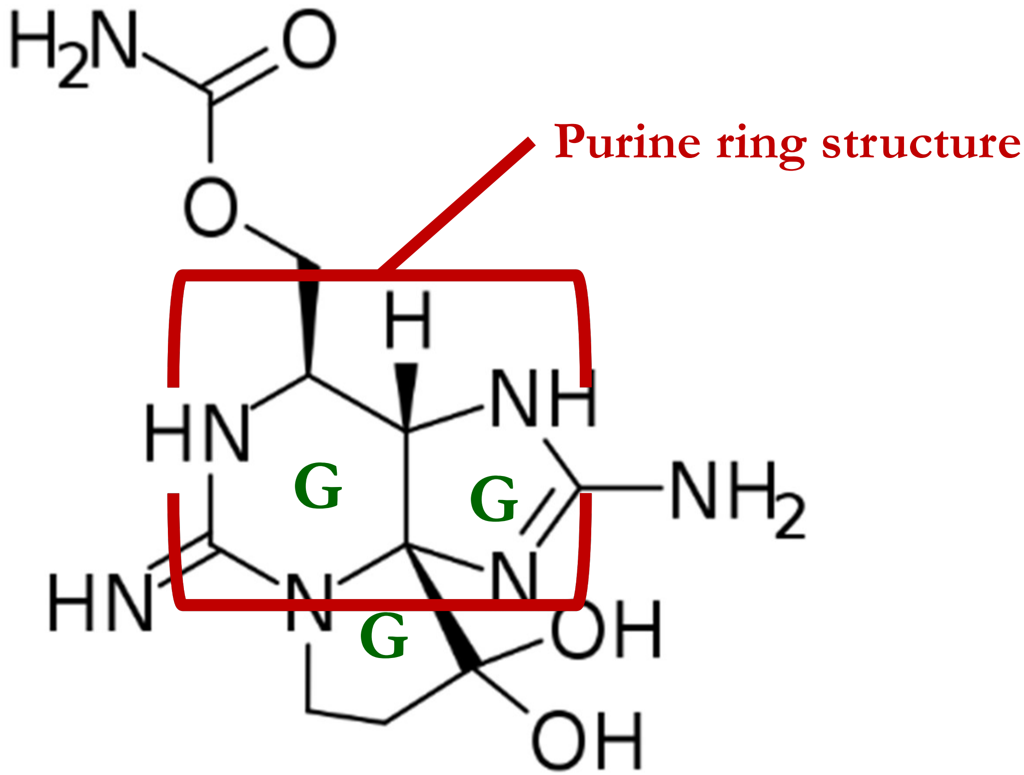
- Reduced purine and guanidine rings in unique structure
  - $C_{10}H_{17}N_7O_4$
  - 299 g/mole
  - Solubility in water lower than other toxins
    - <0.14 moles/L
    - 193 µg/L found in one surface source (WHO)
  - More research needed related to saxitoxins

Saxitoxins in Water

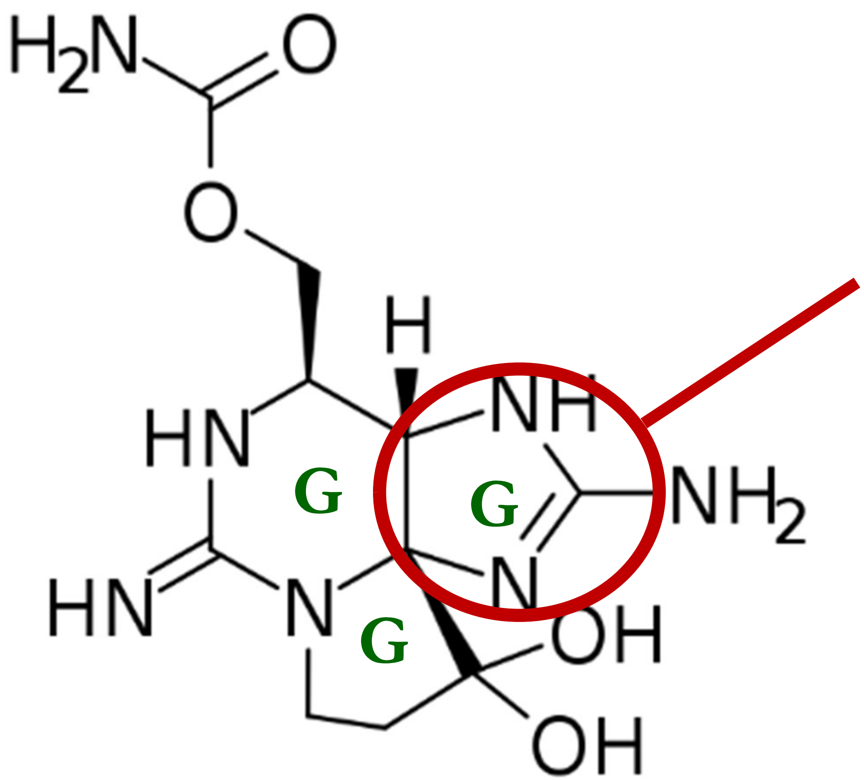


Guanidine ring structures

Saxitoxins in Water



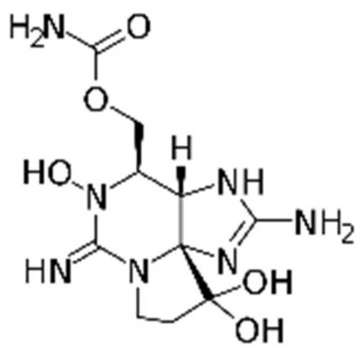
Saxitoxins in Water



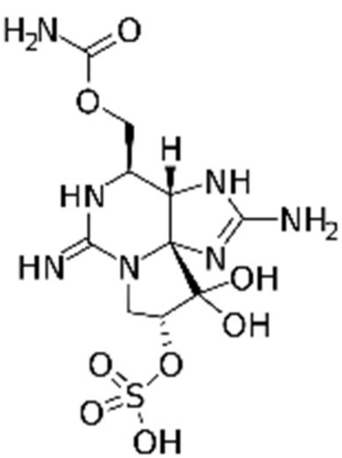
7,8,9-Guanadine ring responsible for toxic bonding at neurons - Possible substitution may alter toxicity, Oxidation possible for substitution?

Saxitoxins in Water

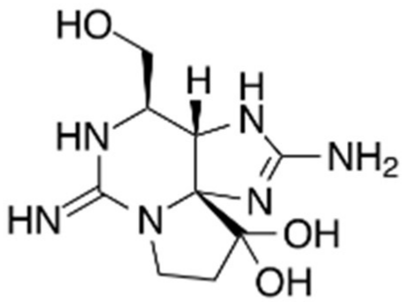
- Other metabolites
  - Neosaxitoxin
  - Gonyautoxins
  - Decarbamoylsaxitoxin
- More than 57 metabolites known



Neosaxitoxin



Gonyautoxin

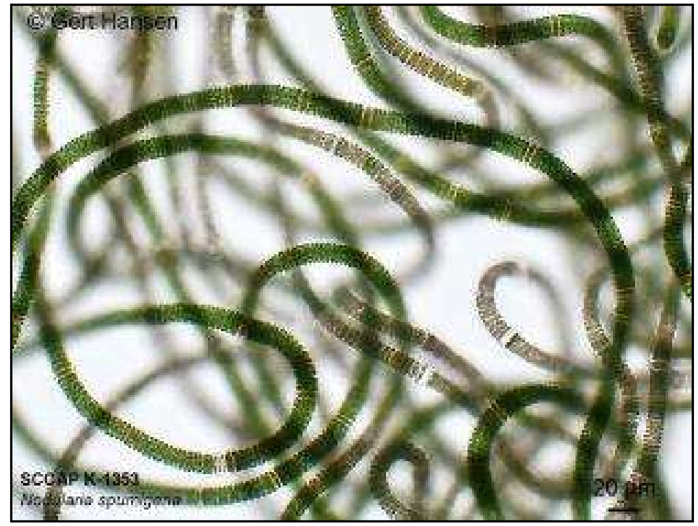


Dicarboamoylsaxitoxin

Nodularins

Nodularins in Water

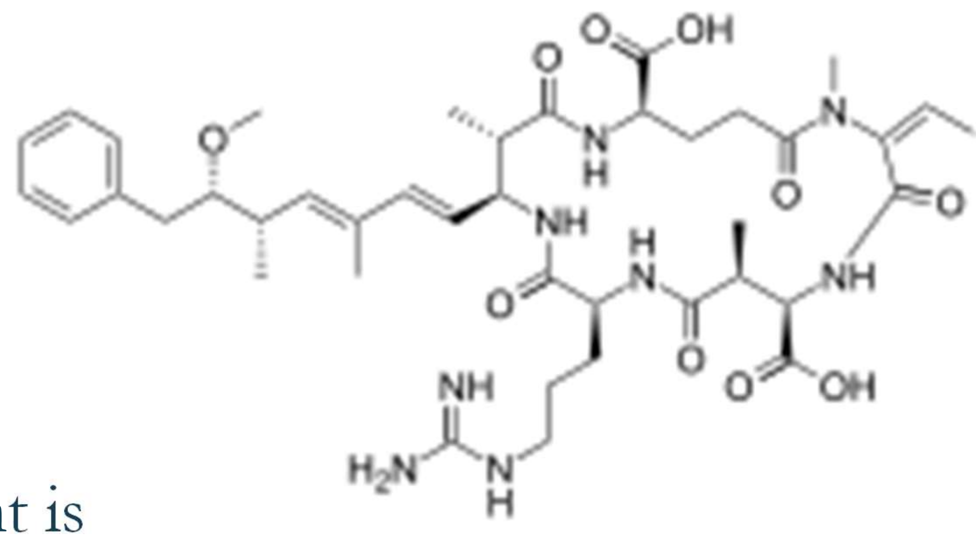
- Uncommon cyanotoxin
  - Microcystin-like structure
  - Maximum toxin concentration at 20°C to 25°C
  - Intracellular toxins released as cell lysing or mortality occurs
    - Natural life cycle or chemical means
    - UV irradiation breaks down nodularins
    - Toxicity like microcystins



Nodularia spumigena

Nodularins in Water

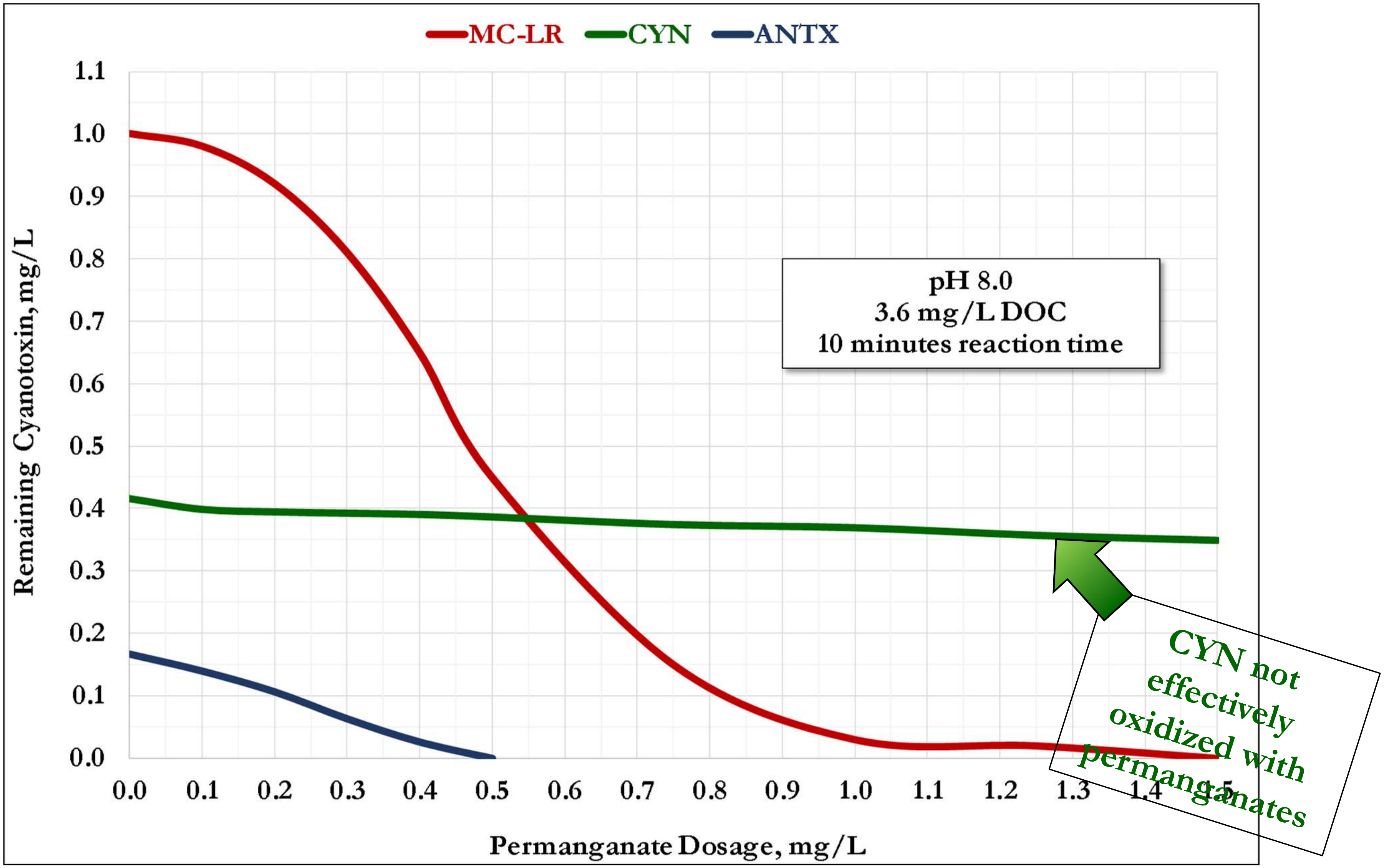
- Made up of 5 amino acids in unique structure
  - $C_{41}H_{60}N_8O_7$
    - Similar for other variants
  - 825 g/mole
  - Solubility in water unknown
  - Half-life in water environment is up to 18 days
  - Toxicity from enzyme attack of proteins resulting in liver damage
  - LD50
    - 5 mg/kg



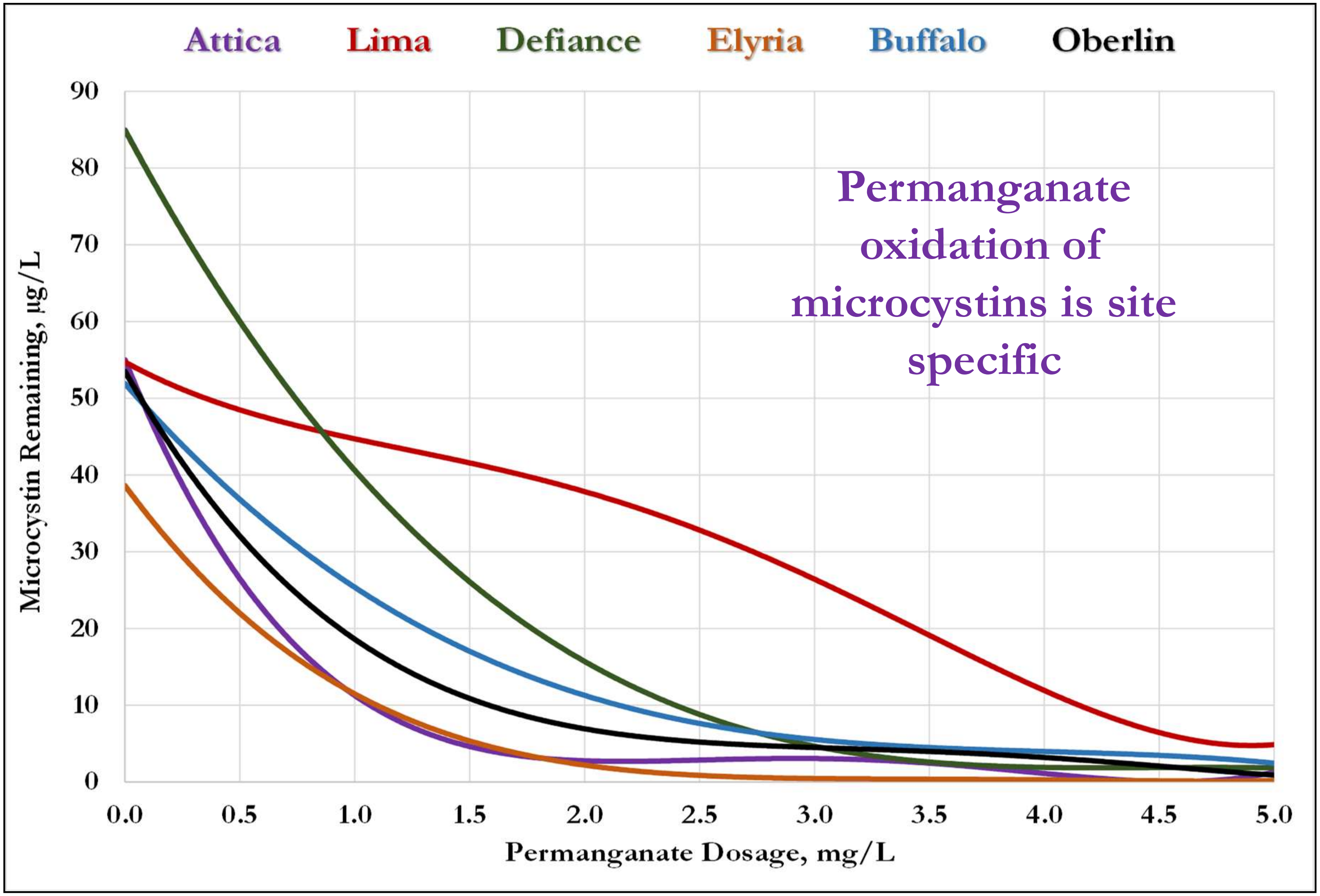
Nodularin-R

Oxidative Treatments

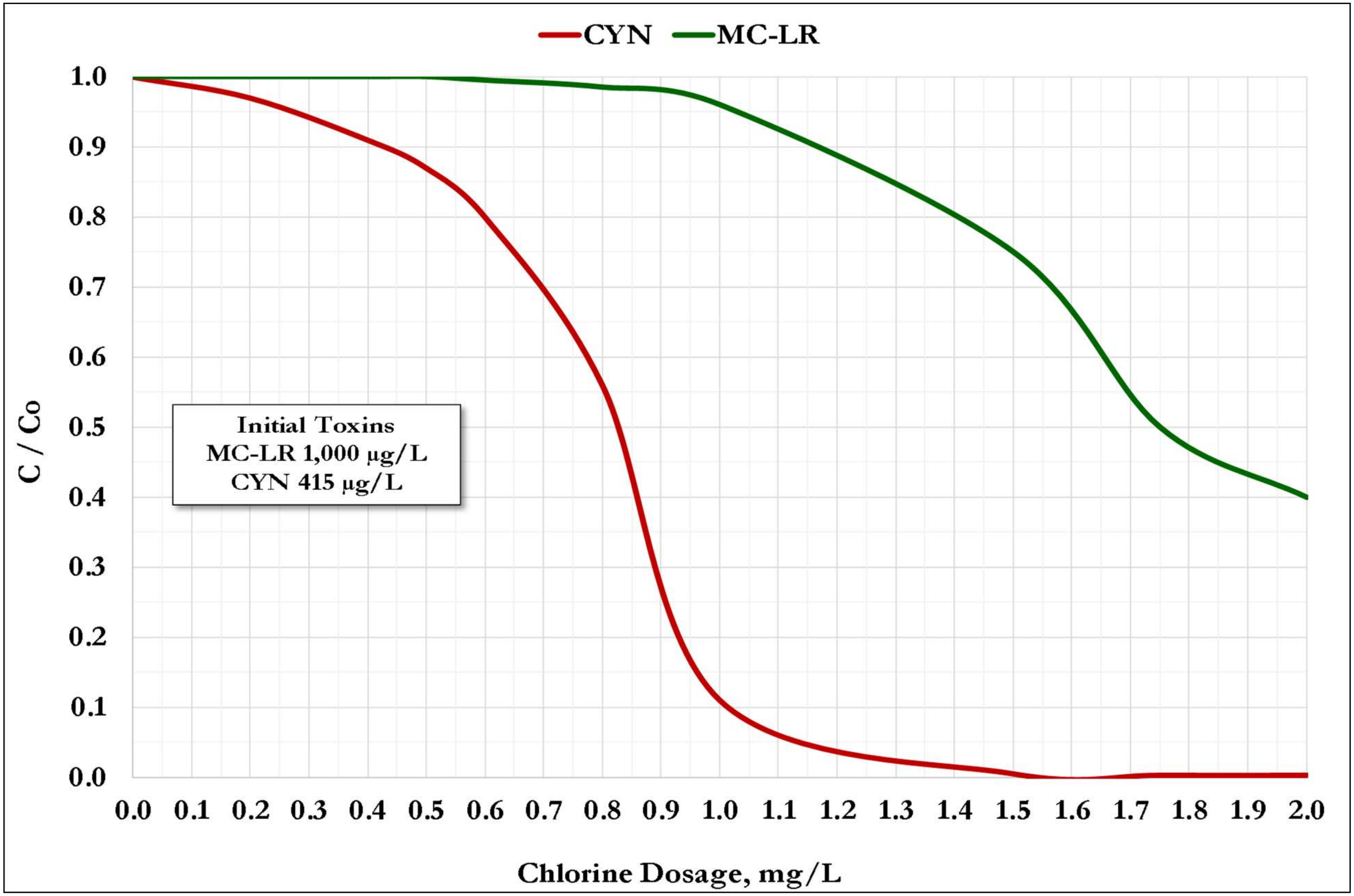
Permanganate Treatment



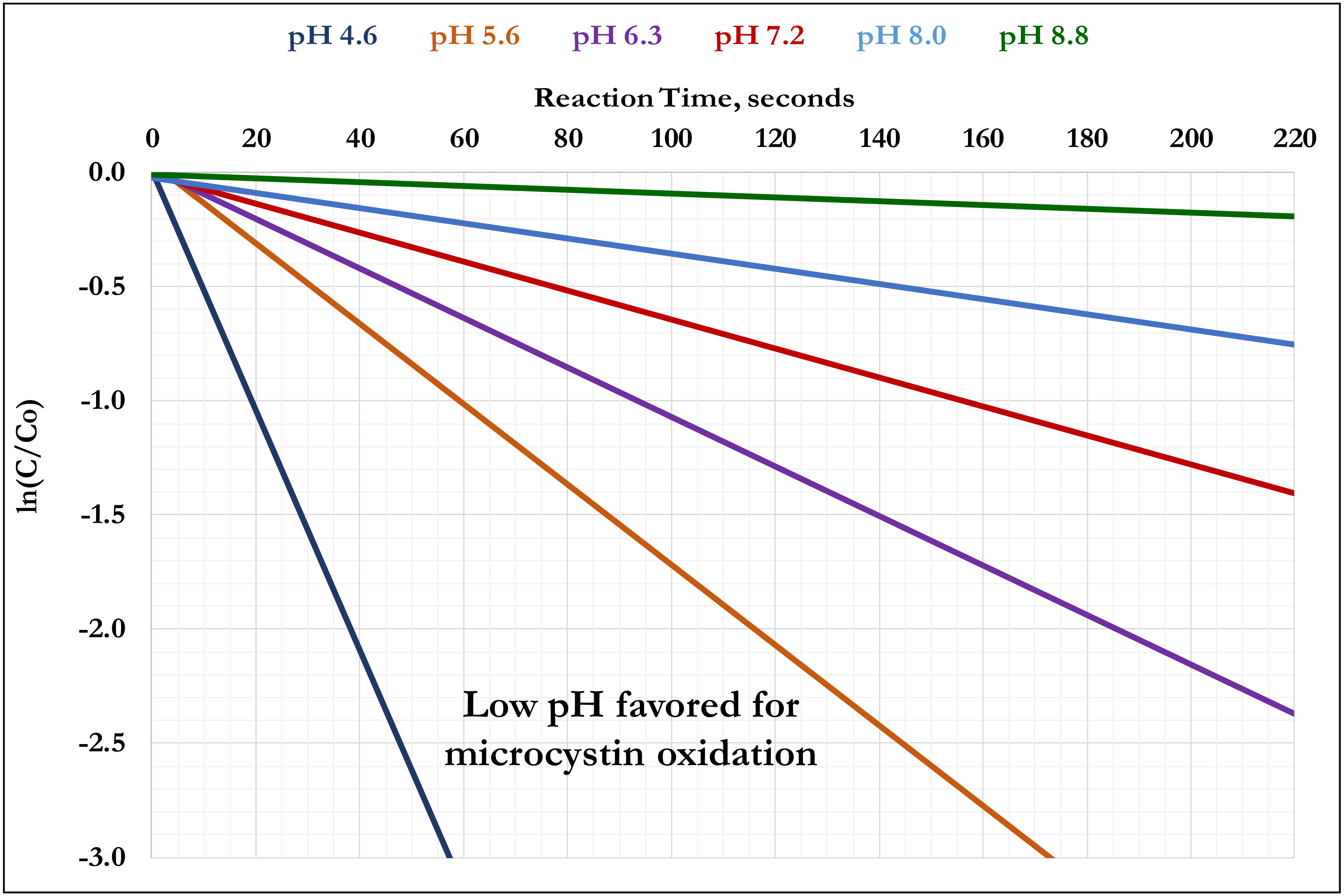
Permanganate Treatment



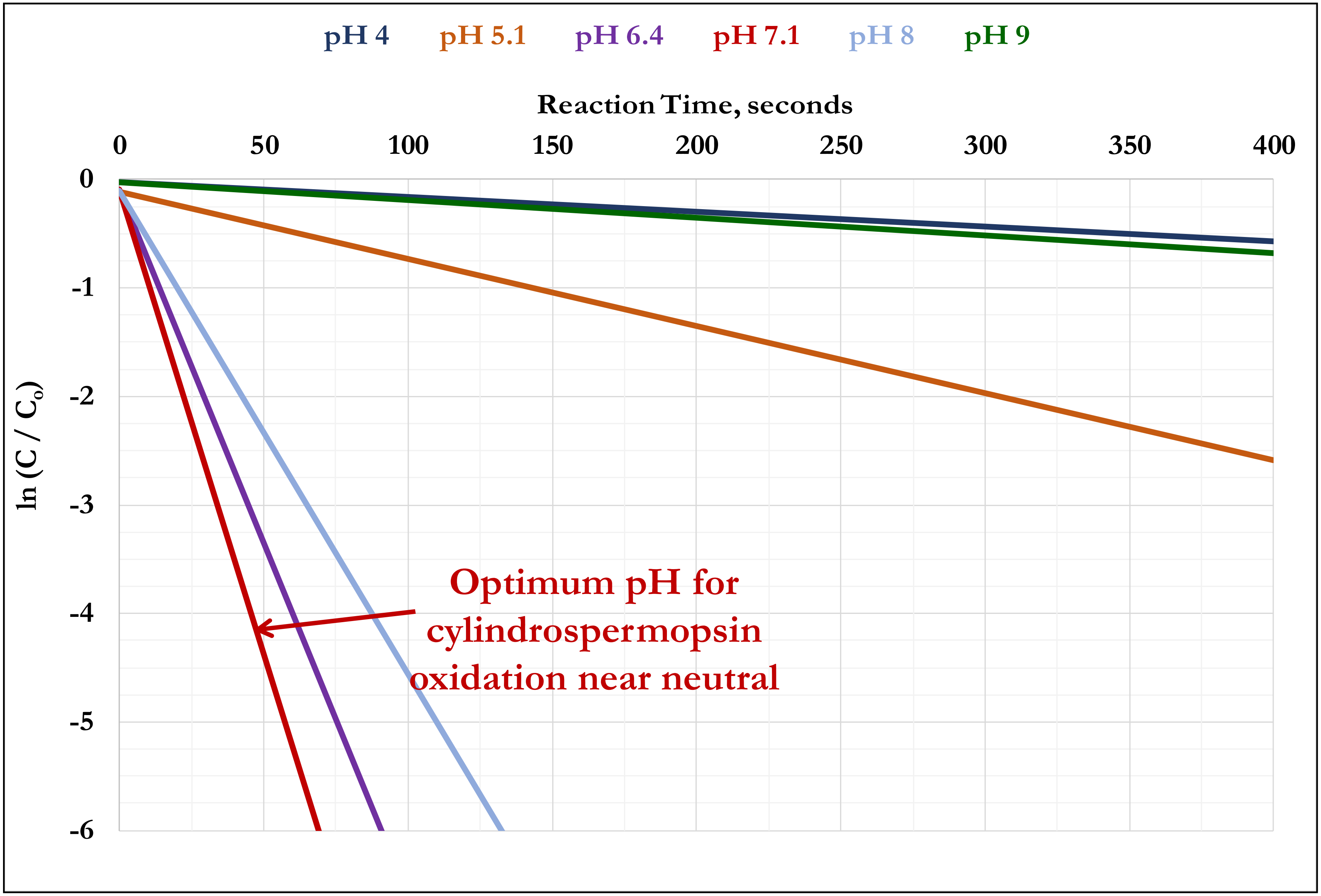
Chlorine Treatment



Chlorine Treatment



Chlorine Treatment



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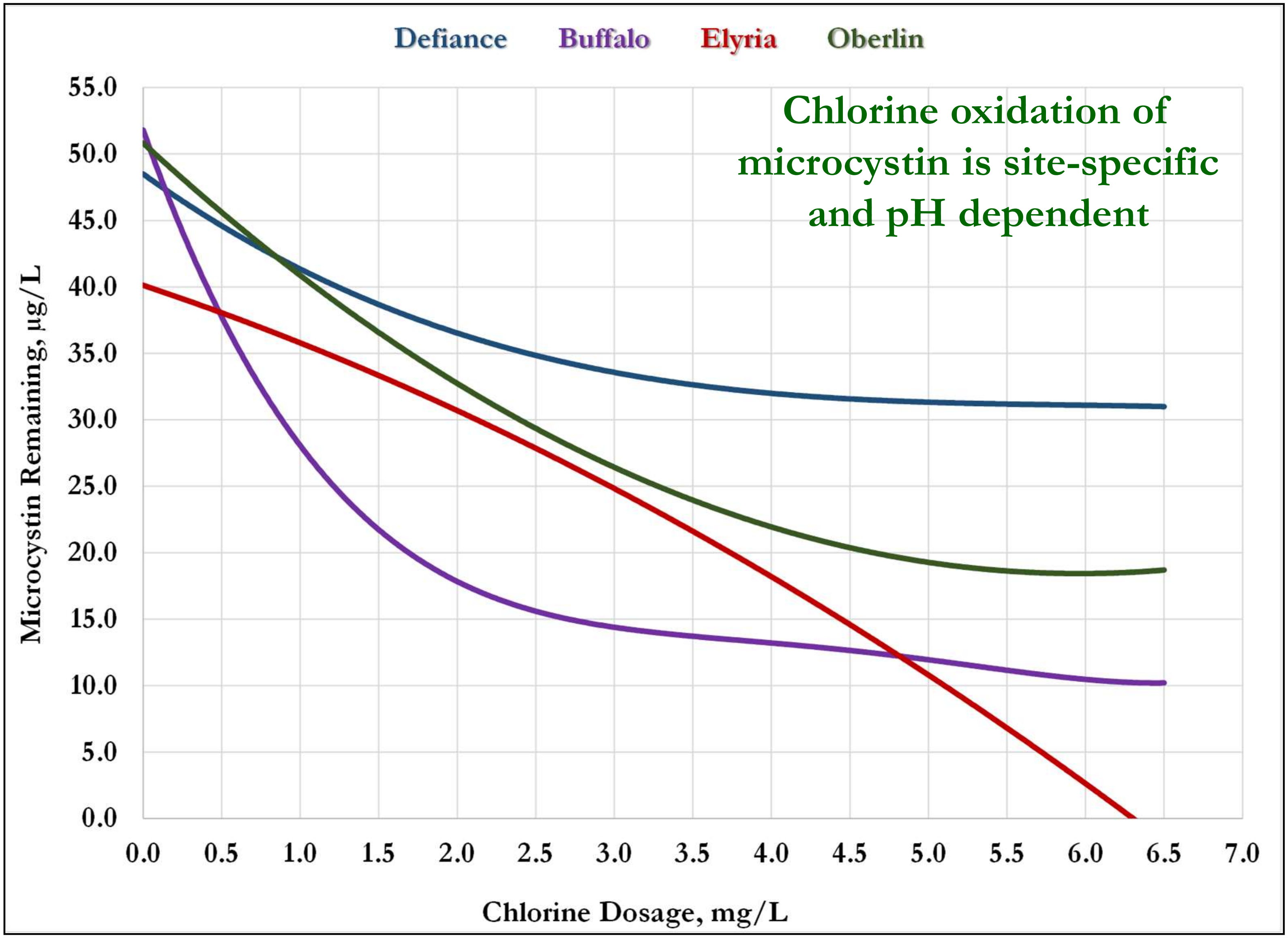

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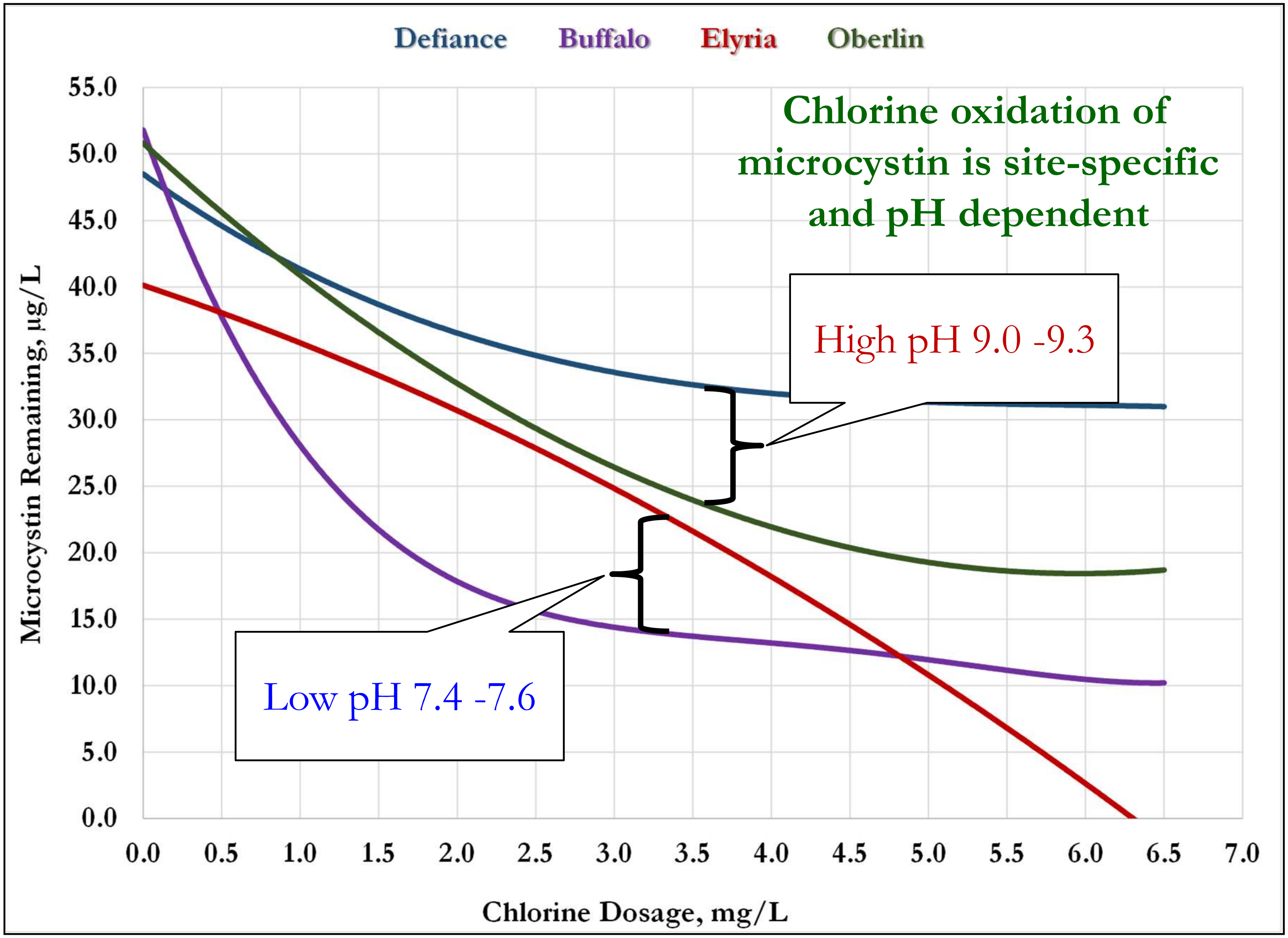
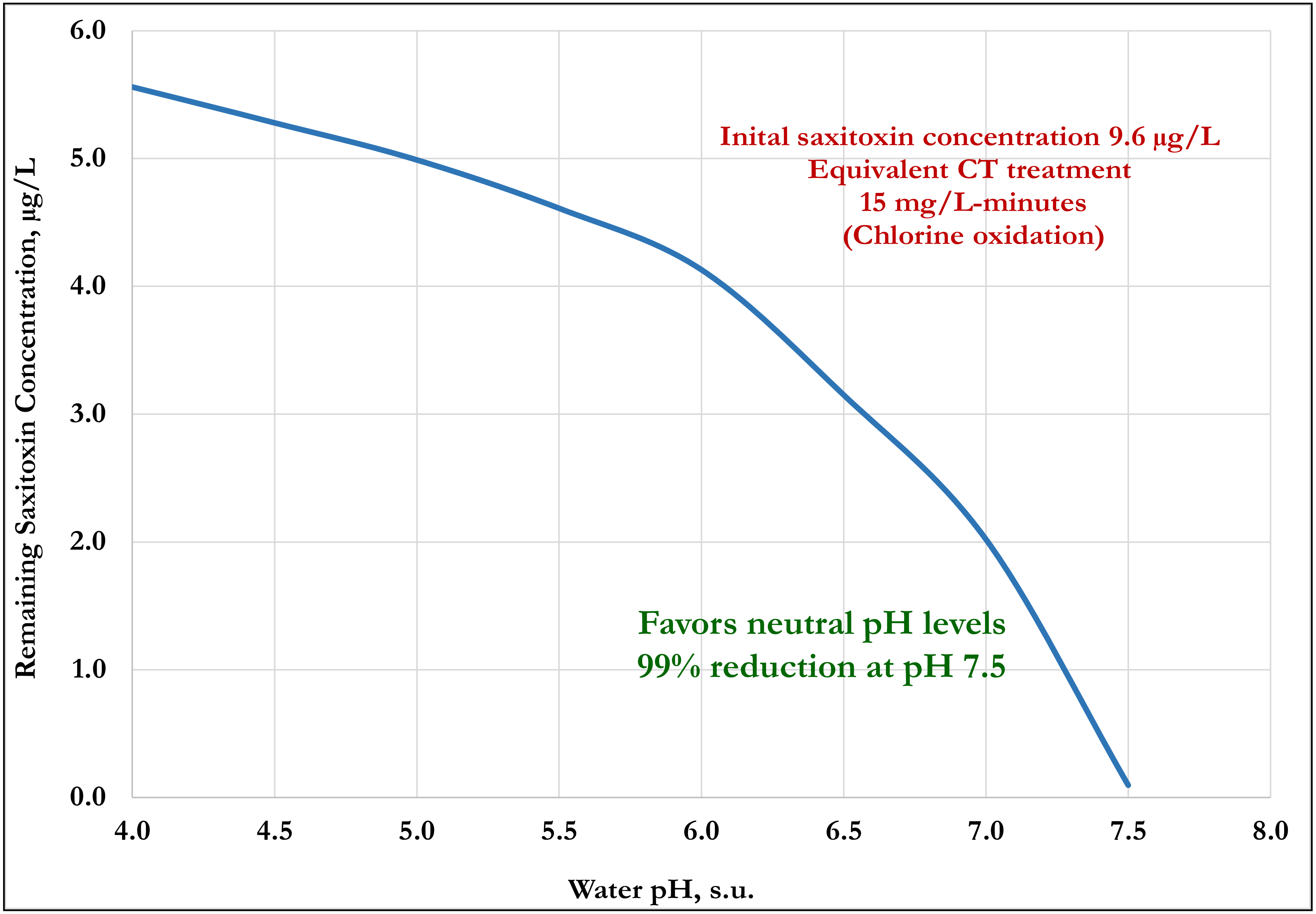
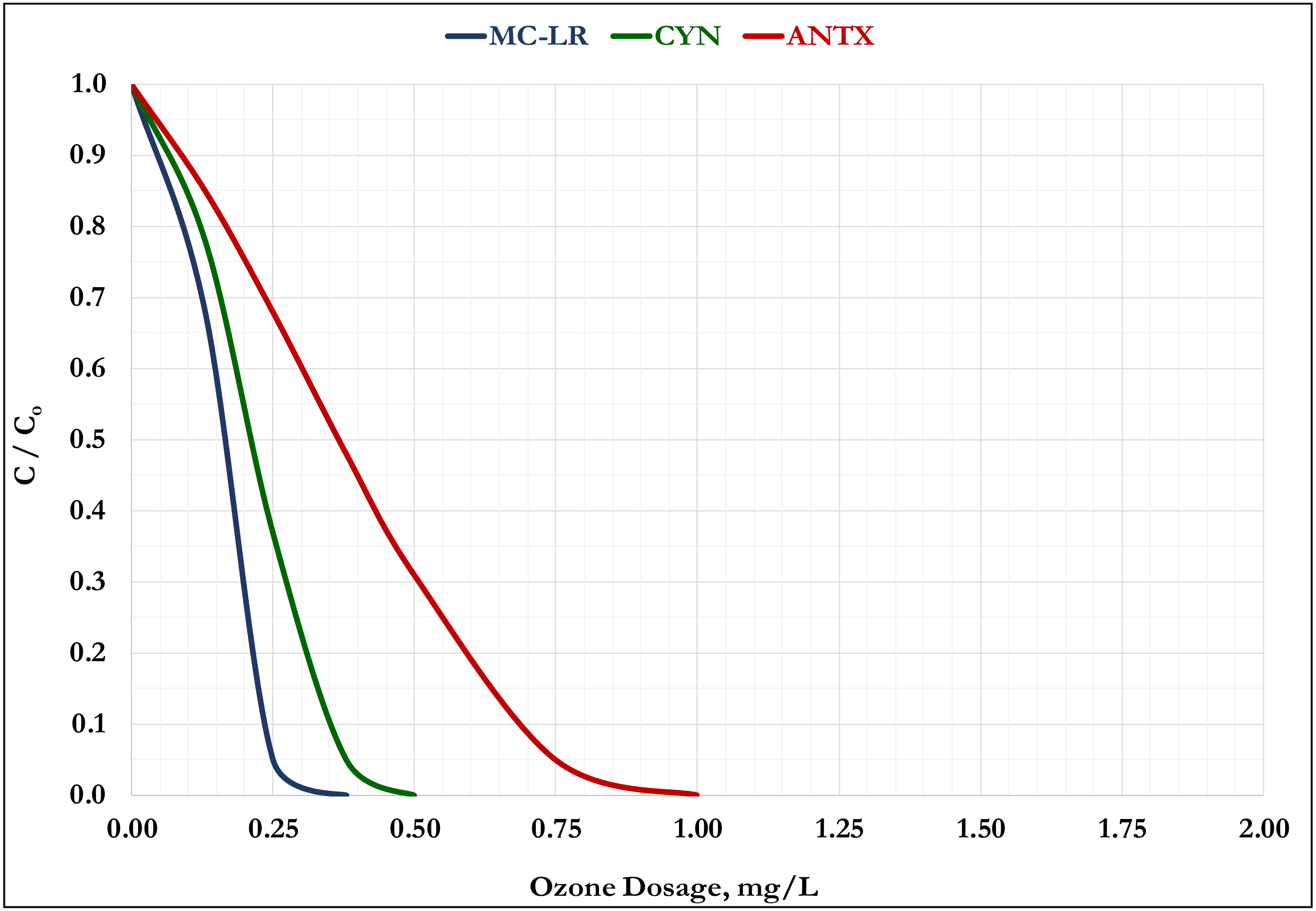


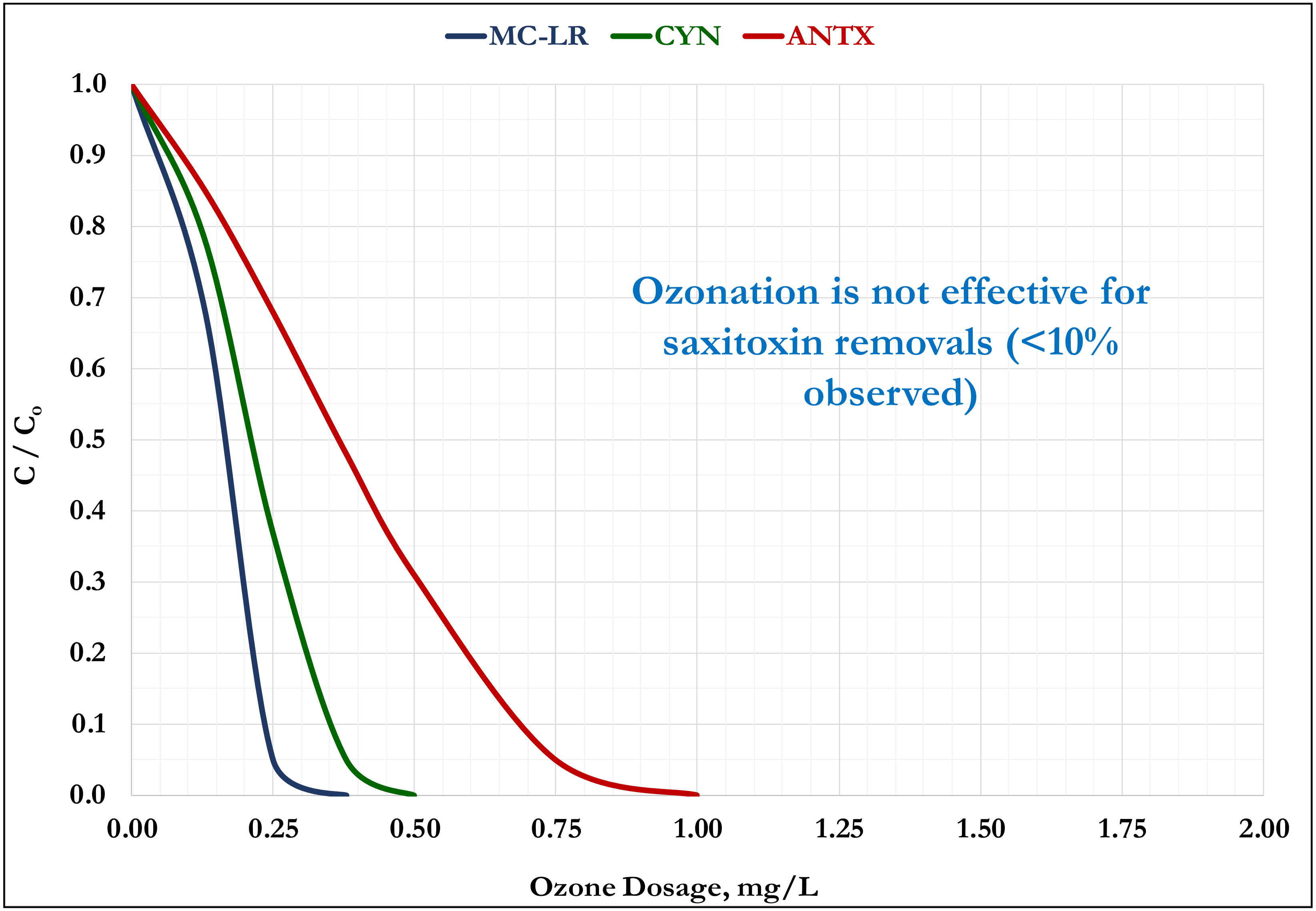
Chlorine Treatment



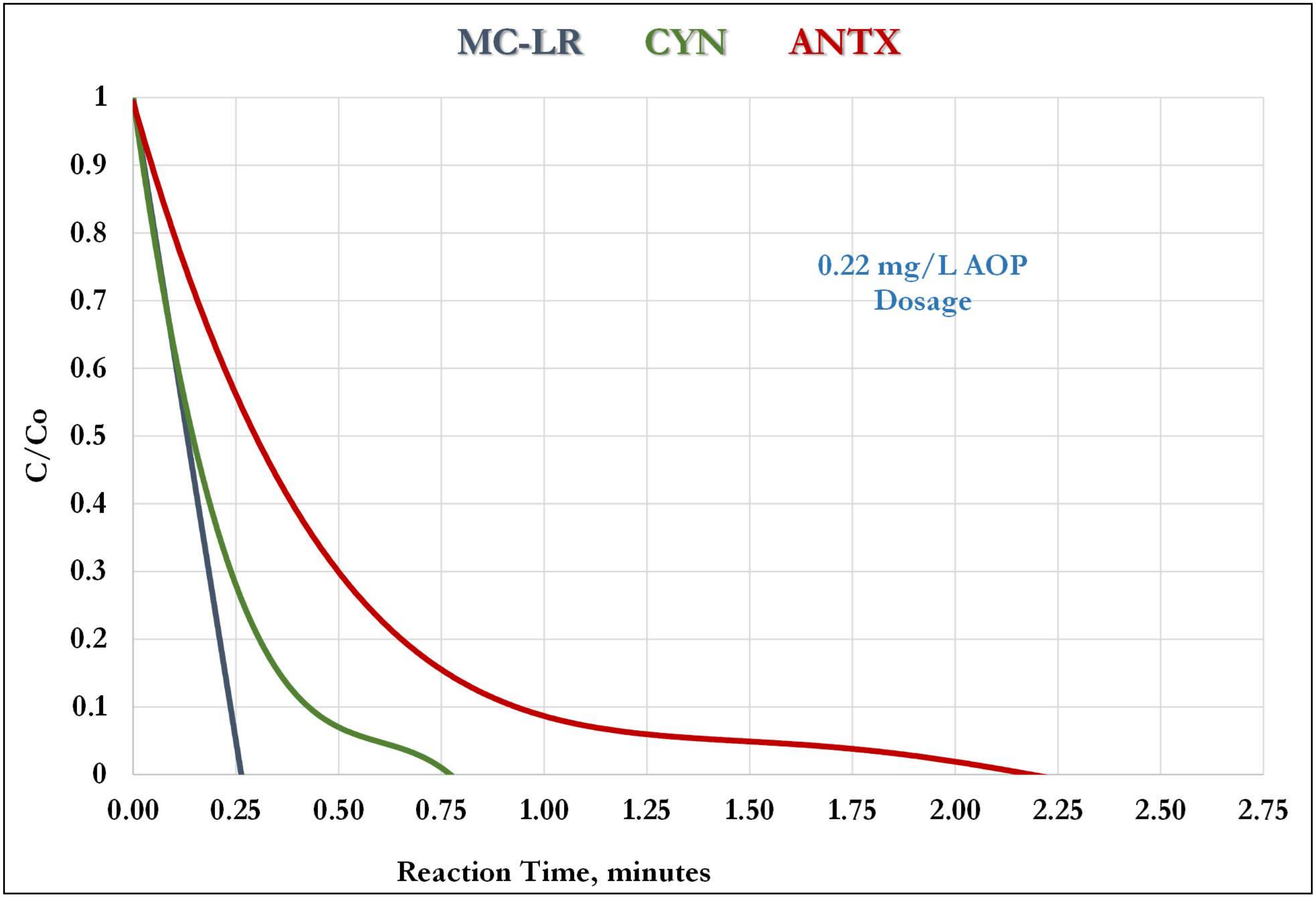
Ozone Treatment



Ozone Treatment

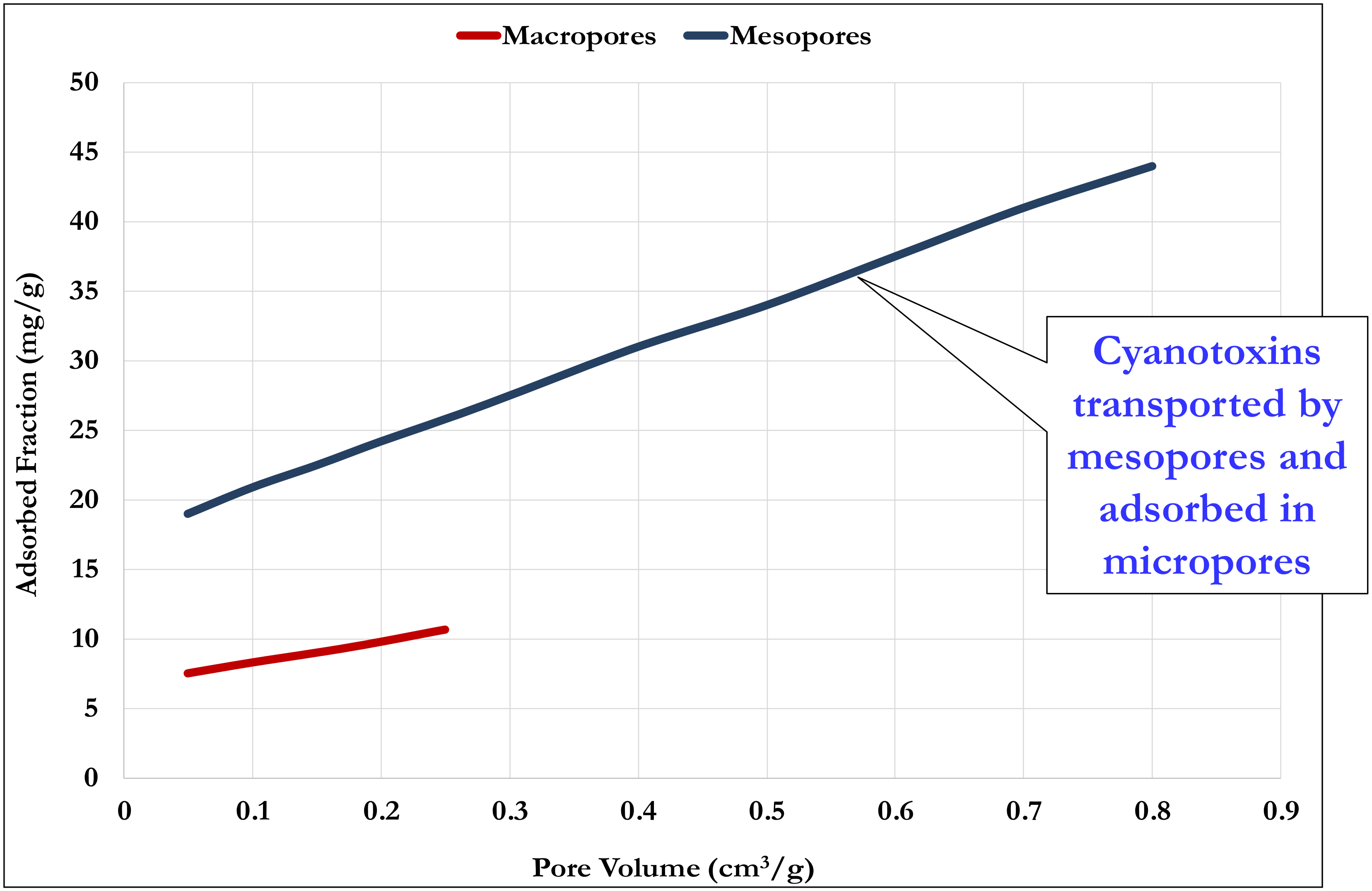


AOP Treatment

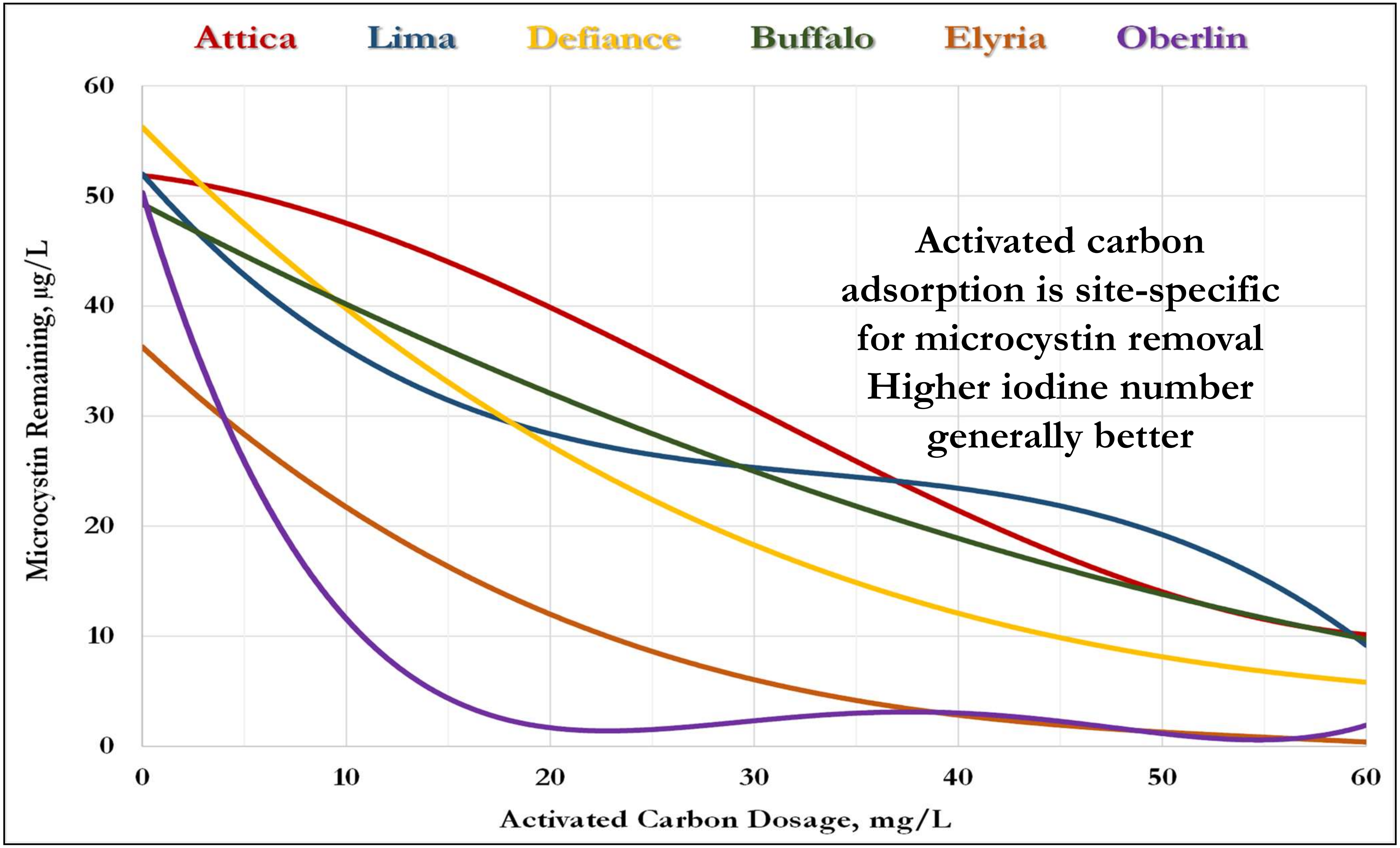


Adsorptive Treatments

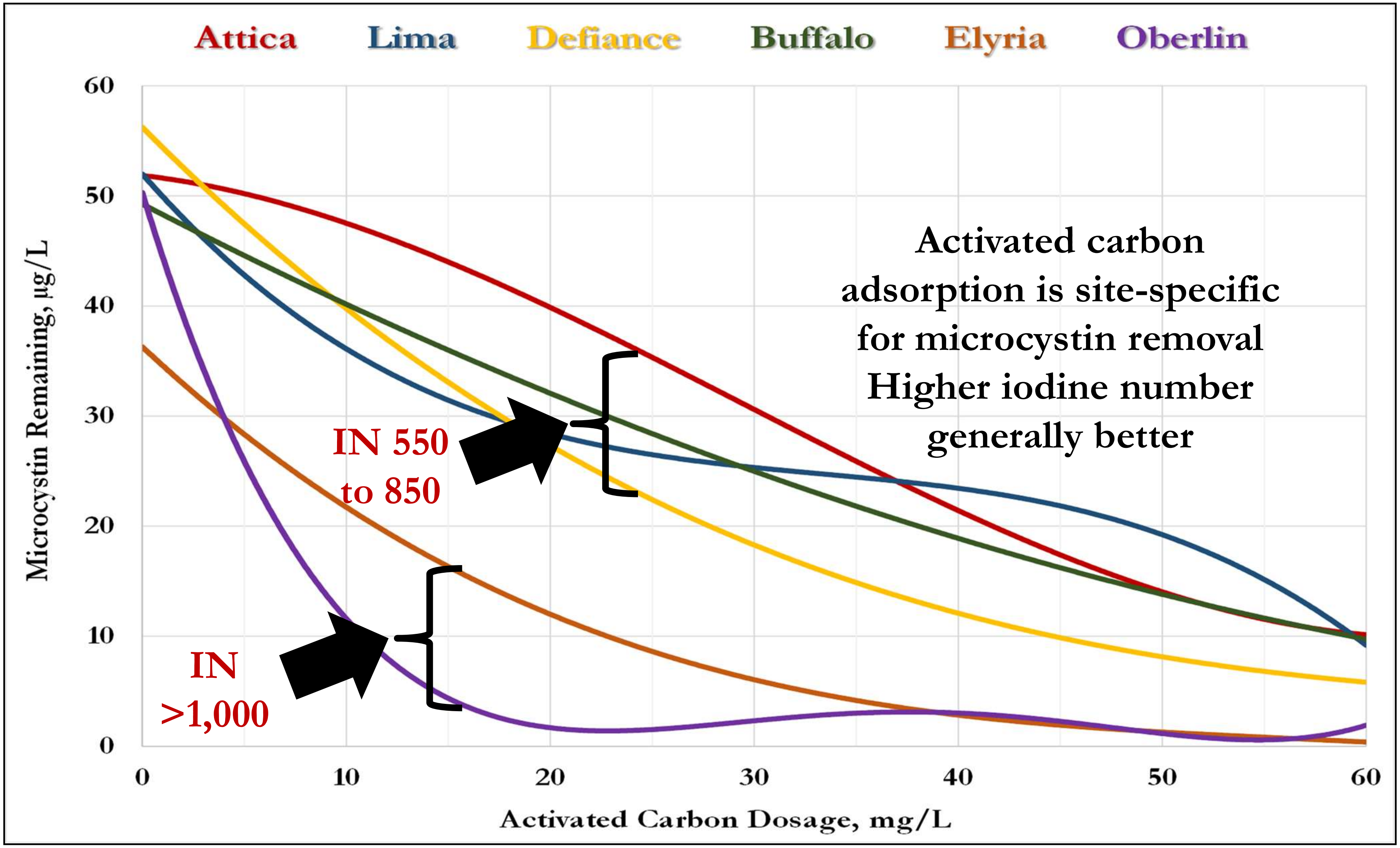
Activated Carbon Treatment



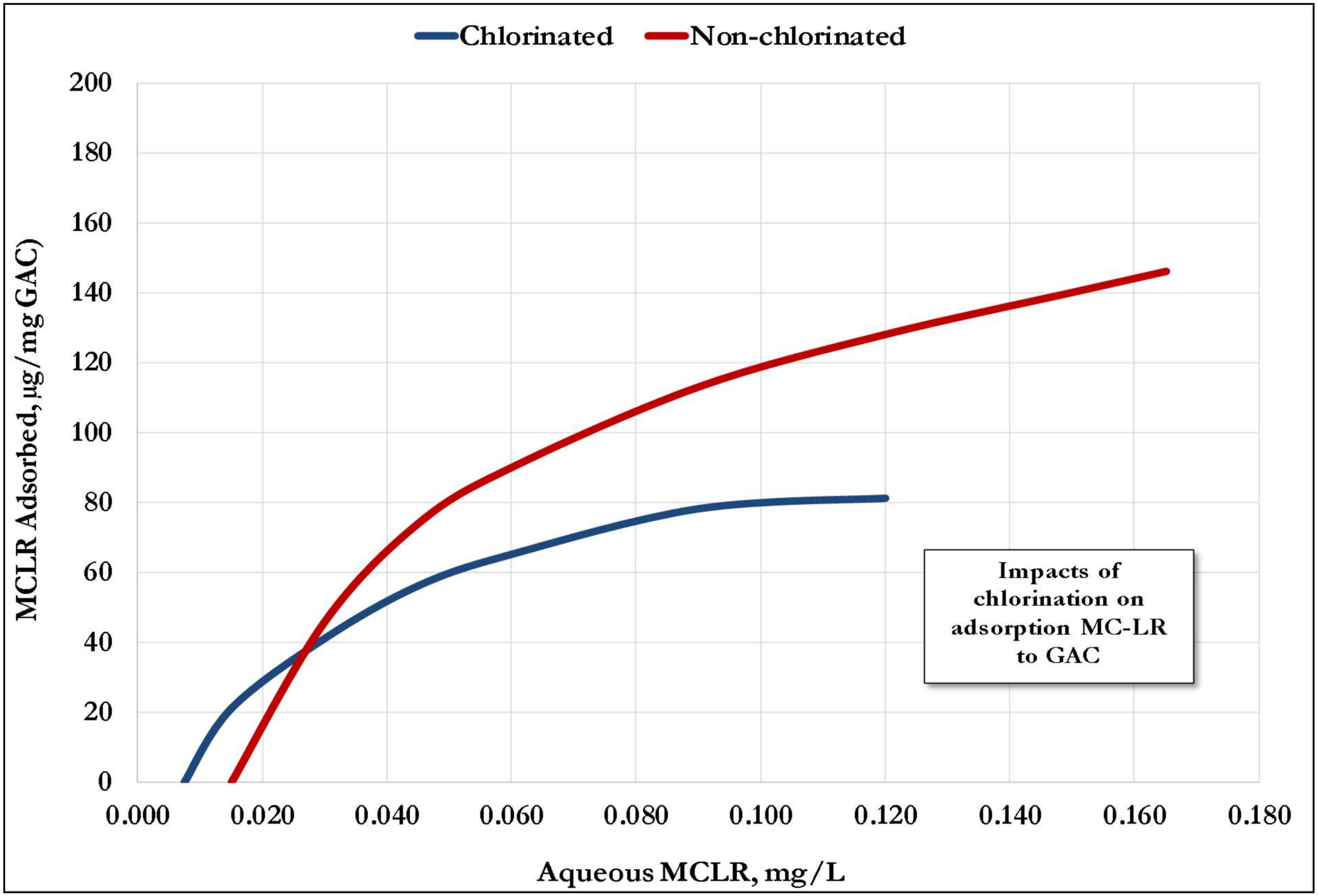
PAC Treatment



PAC Treatment



GAC Treatment



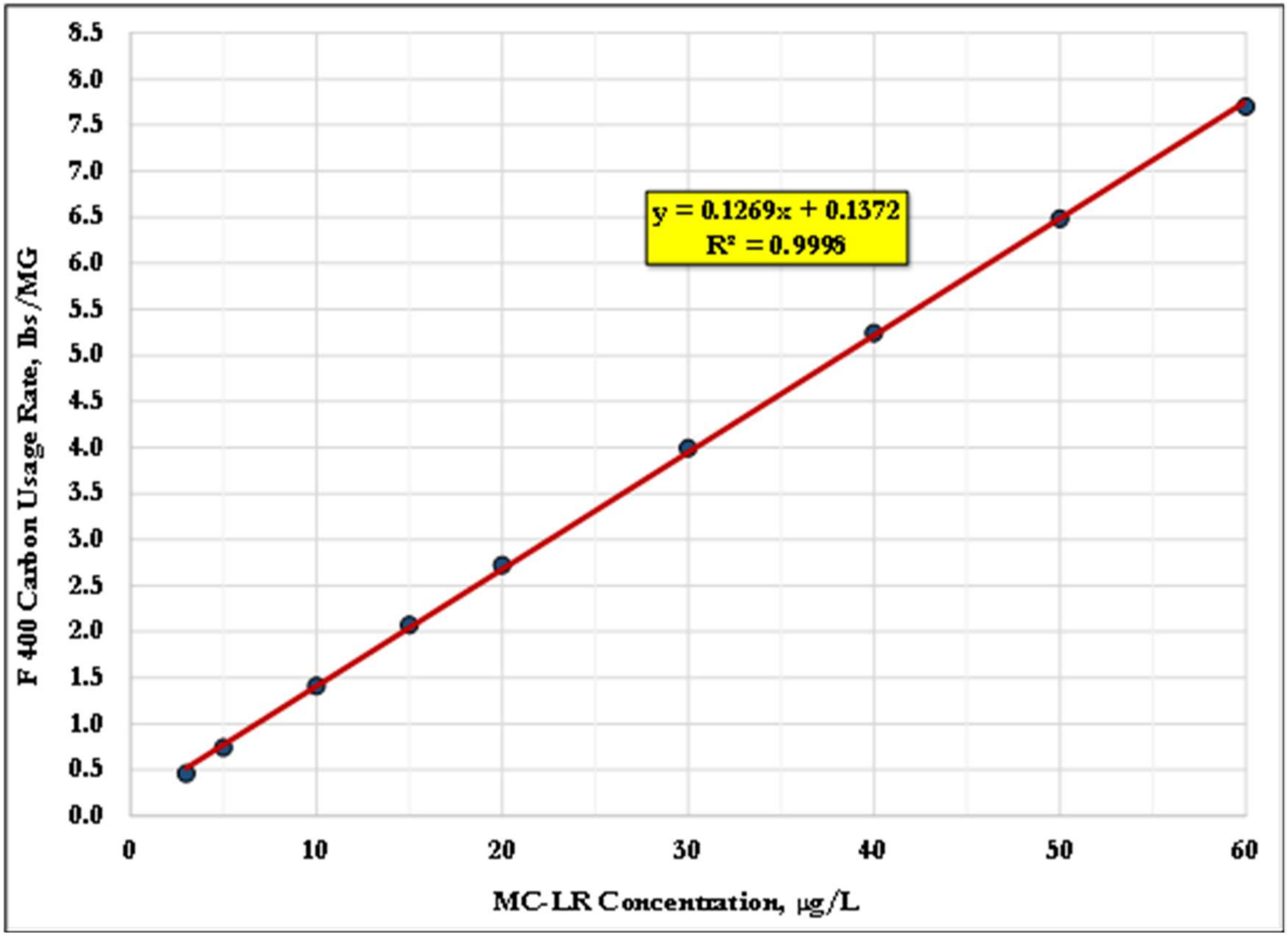
GAC Treatment

$$CUR, lbs/1{,}000 gallons = \frac{EBCT * \rho GAC * 10^3}{T * 7.48 * 1{,}440}$$

Where CUR = Carbon Usage Rate, pounds per 1,000 gallons
EBCT= empty bed contact time, minutes
ϱGAC = carbon density, pounds/cubic foot
7.48 = 7.48 gallons per cubic foot
1,440 = 1,440 minutes per day

1998 WRF report - *"Removal of DBP Precursors by GAC Adsorption"*

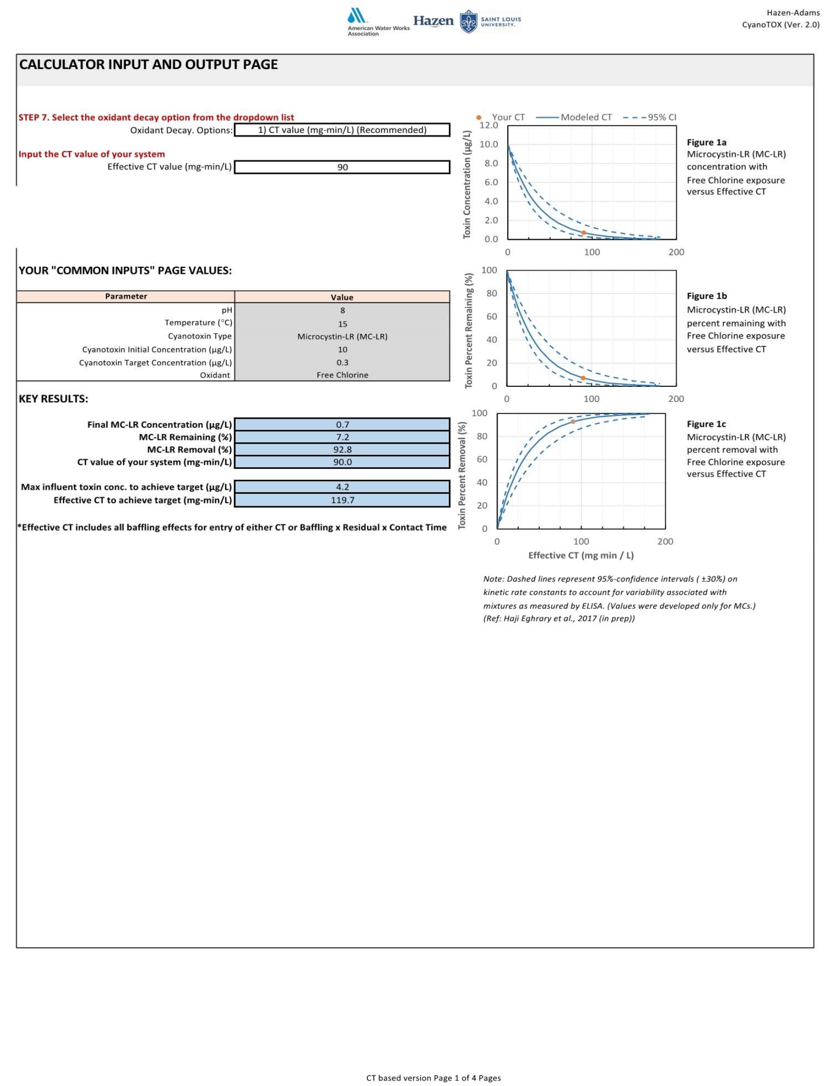
GAC Treatment



AWWA CyanoTox 2.0

AWWA CyanoTox Model (2.0)

- Oxidation model works for some water systems, not others
  - $KMnO_4$ trials
  - Chlorine trials
- Input variables and run model
- Output gives remaining cyanotoxin based on research data in lab water
  - Does not account for natural water conditions



American Water Works Association | Hazen | Saint Louis University

Hazen-Adams
CyanoTOX (Ver. 2.0)

CALCULATOR INPUT AND OUTPUT PAGE

STEP 7. Select the oxidant decay option from the dropdown list
Oxidant Decay. Options: 1) CT value (mg-min/L) (Recommended)

Input the CT value of your system
Effective CT value (mg-min/L) 90

YOUR "COMMON INPUTS" PAGE VALUES:

Parameter	Value
pH	8
Temperature (°C)	15
Cyanotoxin Type	Microcystin-LR (MC-LR)
Cyanotoxin Initial Concentration (µg/L)	10
Cyanotoxin Target Concentration (µg/L)	0.3
Oxidant	Free Chlorine

KEY RESULTS:

Final MC-LR Concentration (µg/L)	0.7
MC-LR Remaining (%)	7.2
MC-LR Removal (%)	92.8
CT value of your system (mg-min/L)	90.0
Max influent toxin conc. to achieve target (µg/L)	4.2
Effective CT to achieve target (mg-min/L)	119.7

*Effective CT includes all baffling effects for entry of either CT or Baffling x Residual x Contact Time

Figure 1a Microcystin-LR (MC-LR) concentration with Free Chlorine exposure versus Effective CT

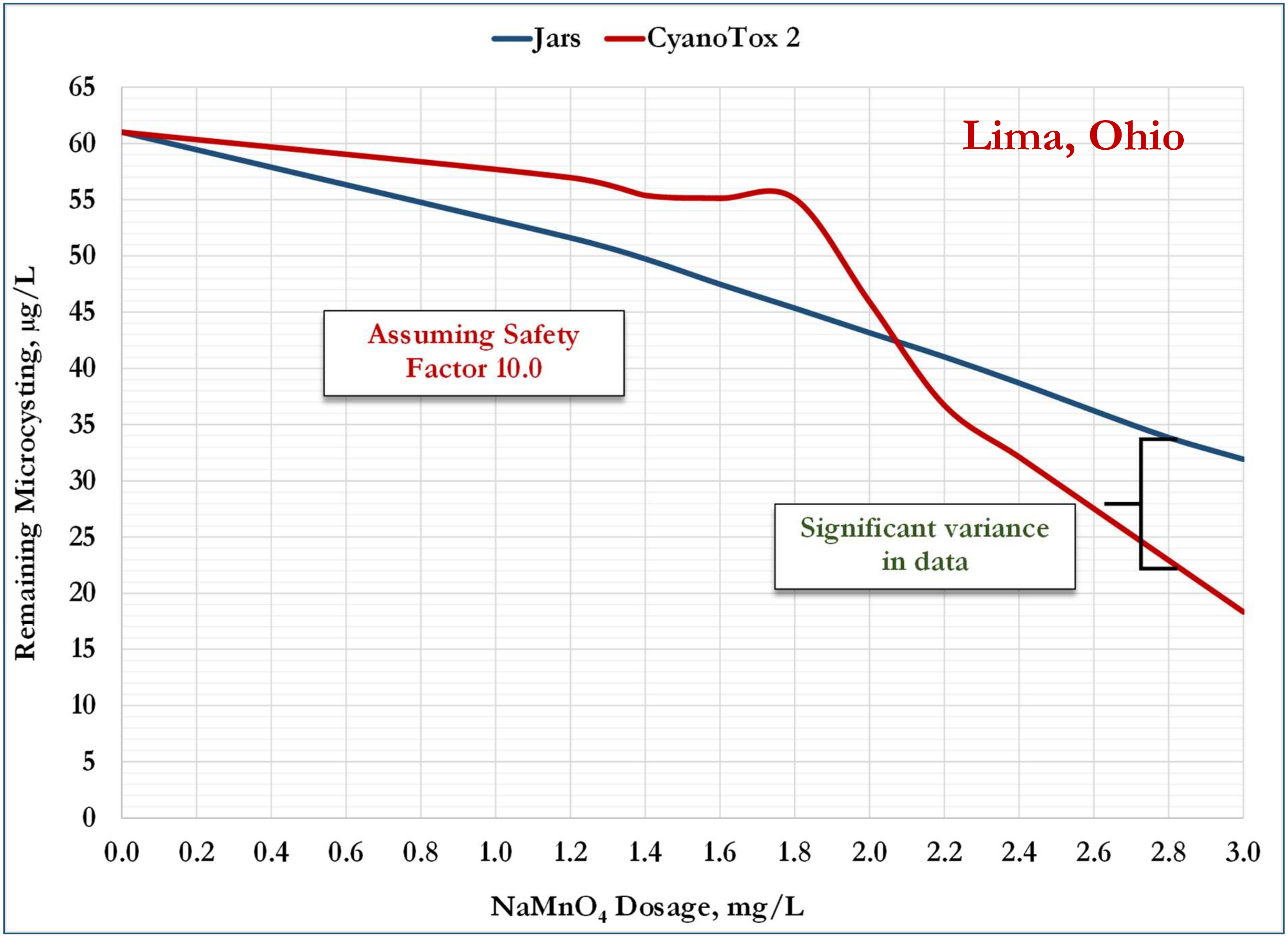
Figure 1b Microcystin-LR (MC-LR) percent remaining with Free Chlorine exposure versus Effective CT

Figure 1c Microcystin-LR (MC-LR) percent removal with Free Chlorine exposure versus Effective CT

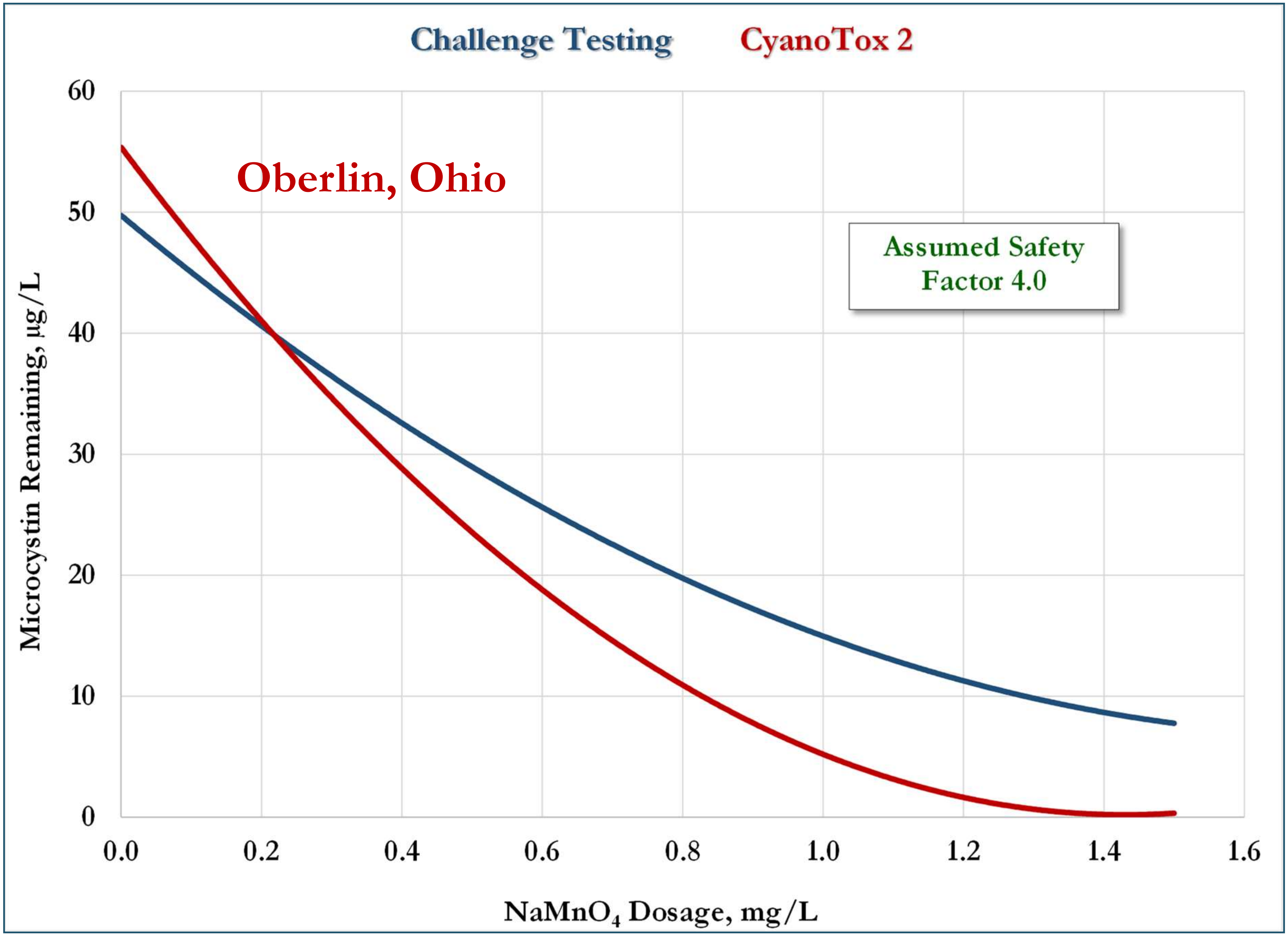
Note: Dashed lines represent 95%-confidence intervals (±30%) on kinetic rate constants to account for variability associated with mixtures as measured by ELISA. (Values were developed only for MCs.) (Ref: Haji Eghrary et al., 2017 (in prep))

CT based version Page 1 of 4 Pages

AWWA CyanoTox Model (2.0)



AWWA CyanoTox Model (2.0)



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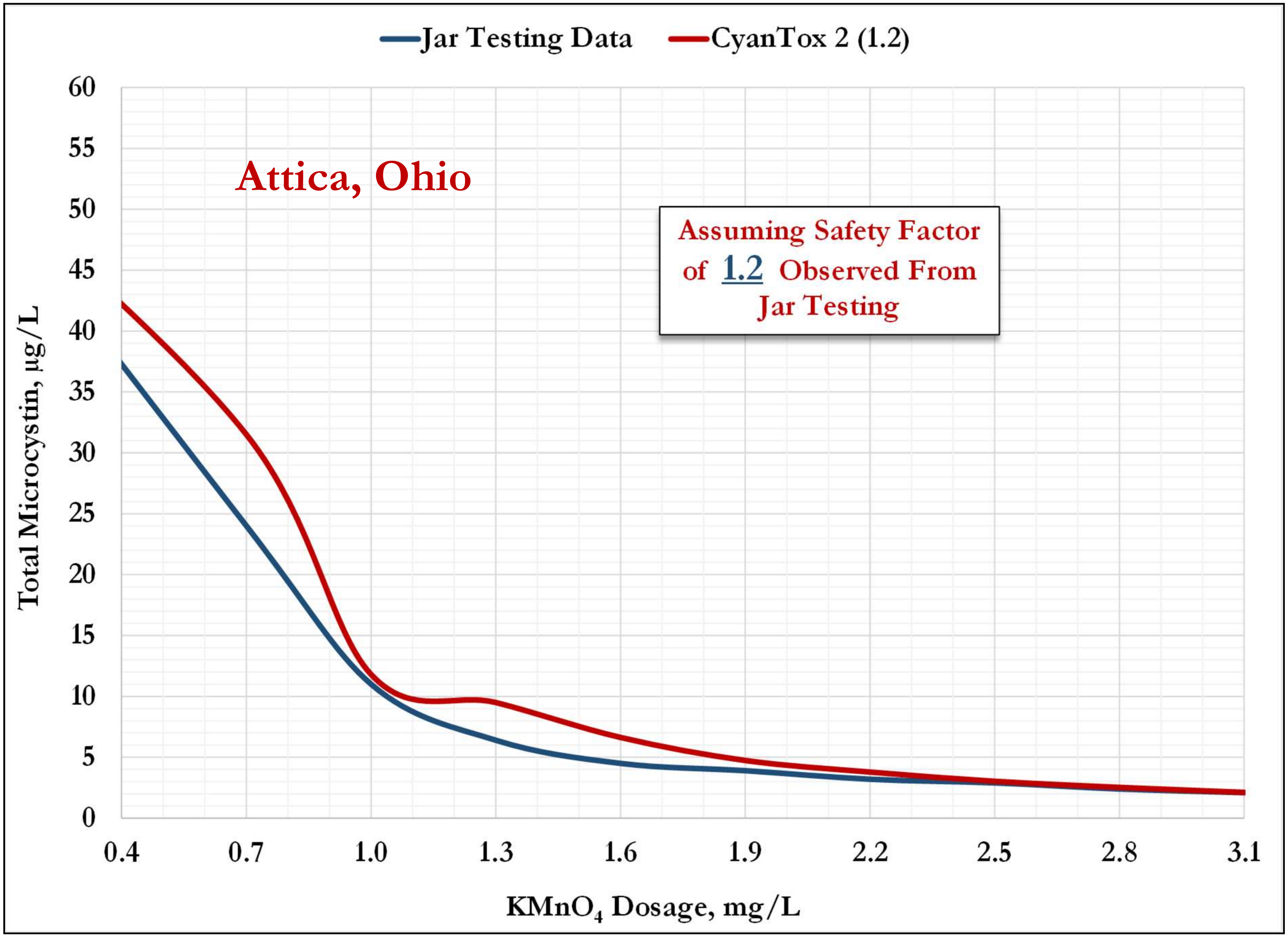

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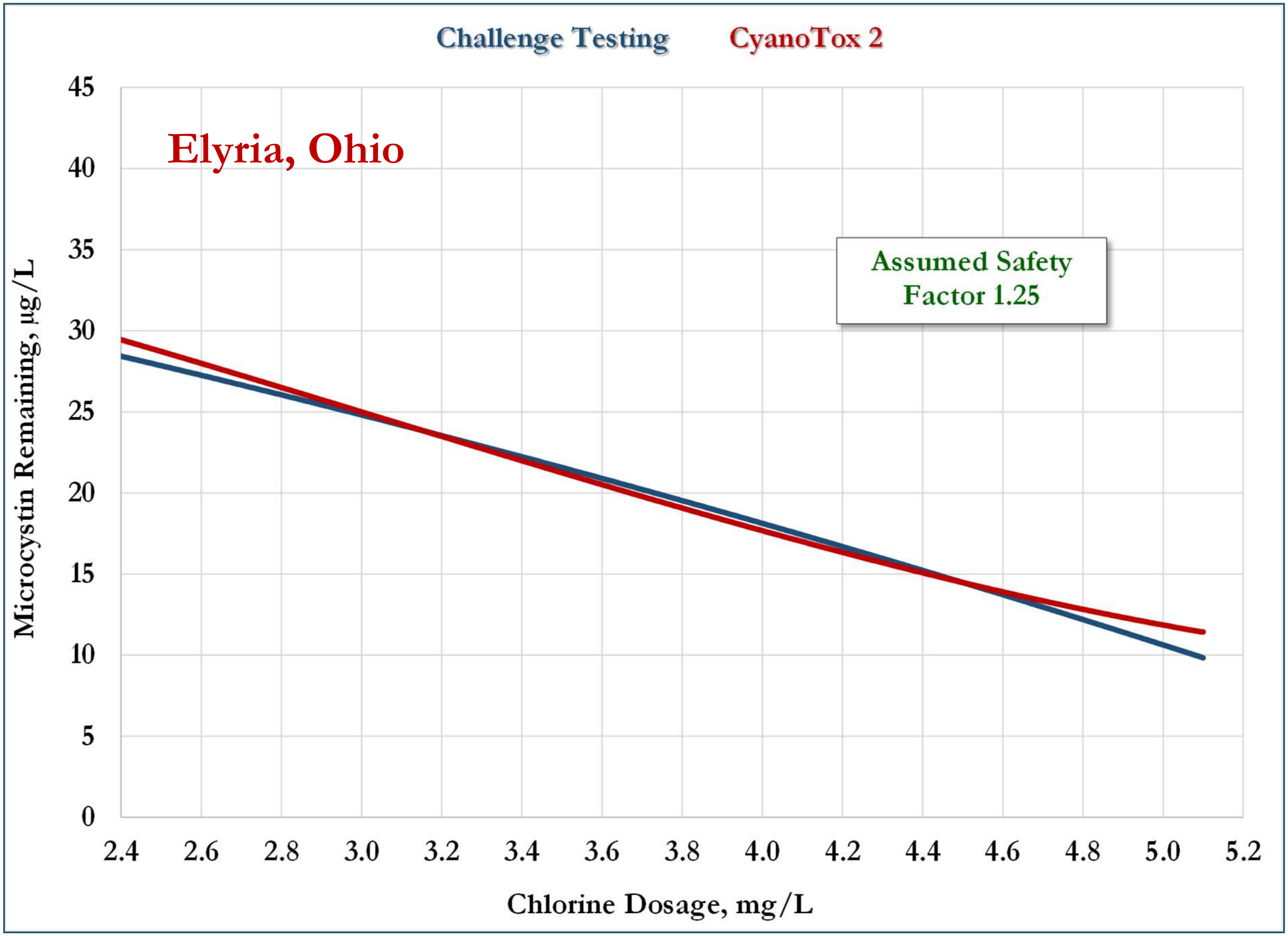

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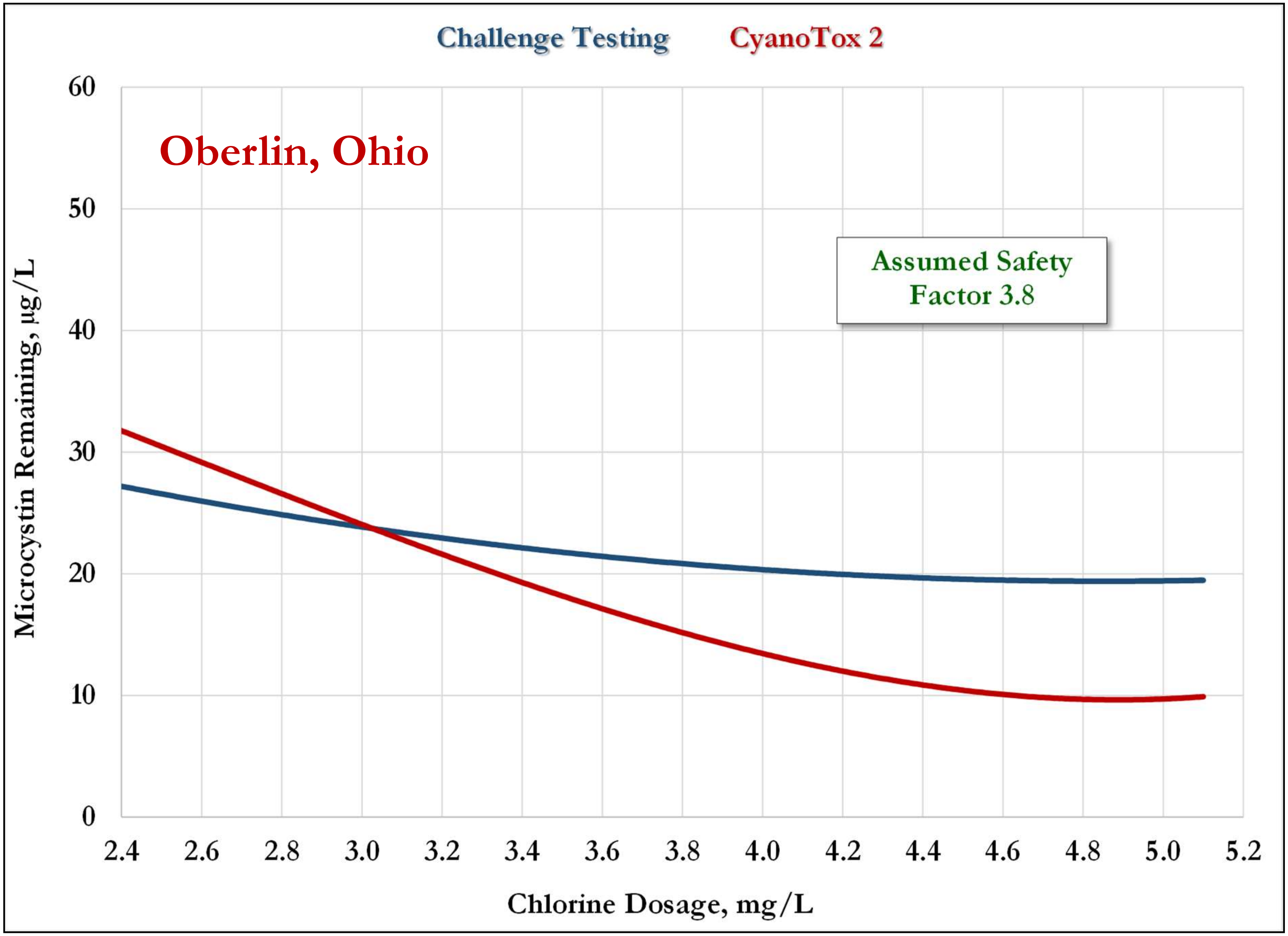

Questions

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