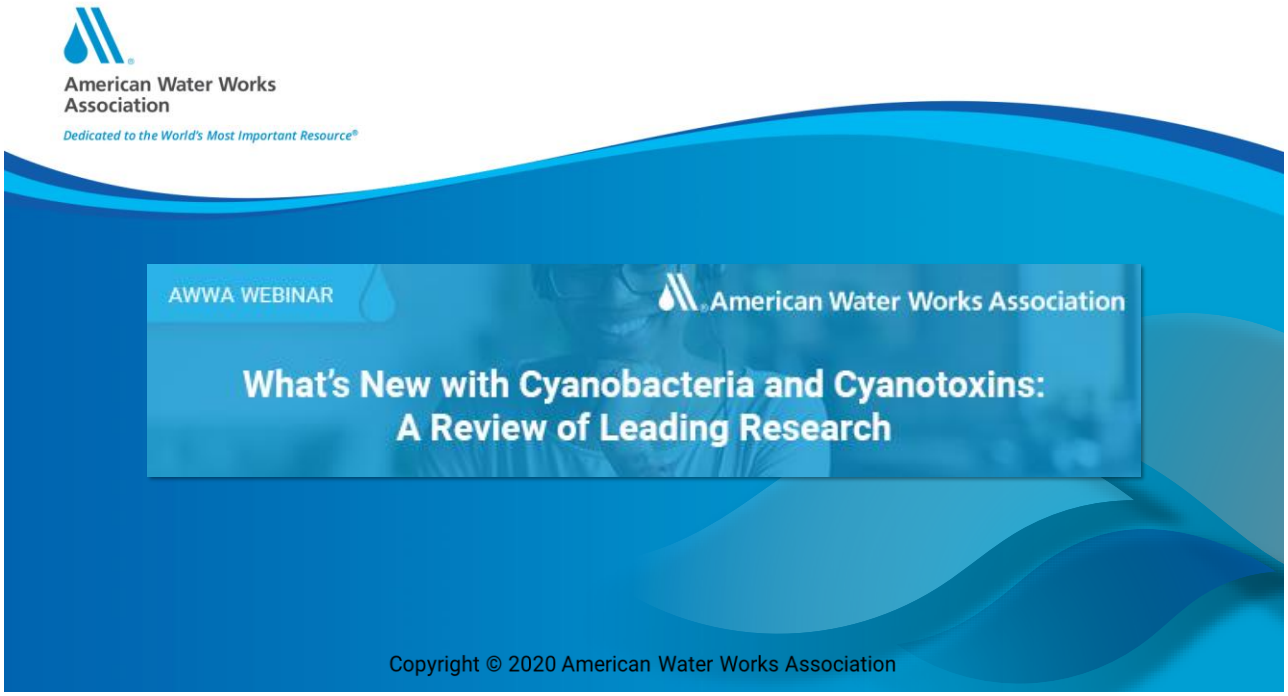

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WEBINAR MODERATOR

Chris Owen

Director of Water and Reuse Innovations

Hazen and Sawyer

Chris is the Director of Water and Reuse Innovations for Hazen and Sawyer. She has 29 years of experience in water quality, research, treatment and regulatory compliance. Her utility roles have included regulatory compliance, research, laboratory management, source water assessment and protection, and distribution system issues. Research work included investigations of UF/MF/RO membranes, online monitoring, total coliform occurrence, enhanced coagulation, biofiltration, distribution system, corrosion, biostability, ion exchange, chloramine chemistry and stability, contaminants of emerging concern, and algal toxins. She is active in regulatory issues at the state and federal levels, promoting utility concerns and science-based decisions. She served on the USEPA SAB for Drinking Water and the USEPA NACEPT.

She is an active member of the American Water Works Association (AWWA), serving as a Trustee and the current Chair of the Water Science and Research Division. She is a Trustee for WateReuse FL and the President of the Board of Directors for the American Membrane Technology Association. She has been active in the Water Research Foundation (WRF) and the WateReuse Foundation for more than 20 years.

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PANEL OF EXPERTS

Tarrah Henrie
Senior Scientist
Corona Environmental

Elizabeth Crafton-Nelson, PhD
Assistant Engineer
Hazen & Sawyer

Craig Adams, PhD, PE, F. ASCE
Oliver Parks Professor
Saint Louis University

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AGENDA

I.	Cyanotoxin Research Update	Tarrah Henrie
II.	Advancements in Algaecide Products and Approach for Harmful Algal Bloom Management	Elizabeth Crafton-Nelson
III.	Hazen-Adams CyanoTOX Tool to Assist Utilities with Complex Cyanotoxin Issues	Craig Adams

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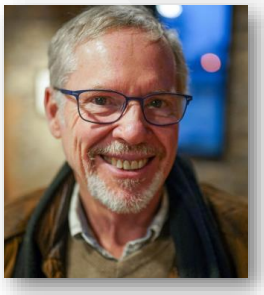
ASK THE EXPERTS

Tarrah Henrie
Corona Environmental

Elizabeth Crafton-Nelson, PhD
Hazen & Sawyer



Craig Adams, PhD, PE, F. ASCE
Saint Louis University

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CORONA ENVIRONMENTAL CONSULTING

CYANOTOXIN RESEARCH UPDATE

Tarrah Henrie
Senior Scientist
Corona Environmental Consulting

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PURPOSE

- Introduce the topic of cyanobacteria and cyanotoxins
- Show case studies of utilities managing cyanotoxins

LEARNING OBJECTIVES

As a result of this presentation you will learn about:

- Cyanobacterial blooms and cyanotoxins
- Management strategies for cyanobacteria
- Recommendations for monitoring and evaluation of treatment options

PRESENTATION OUTLINE

- Background
- Occurrence overview
  - Cyanobacteria, T&O, cyanotoxins
- Management strategies
  - Comprehensive monitoring
  - Source water control
  - Treatment plant control
- Recommendations for utilities

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CREDIT

- Many of these slides were developed by Amlan Ghosh, with Corona Environmental Consulting

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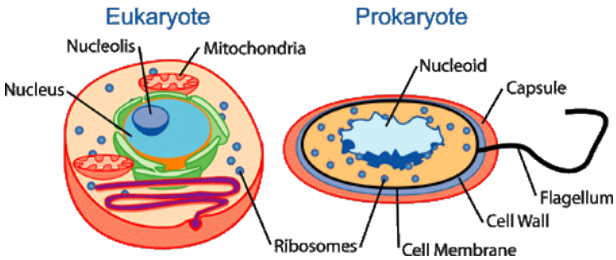
ALGAE VS. CYANOBACTERIA

	Algae	Cyanobacteria
Cell type	Eukaryotic	Bacteria (Prokaryotic)
Photosynthesis?	Yes	Yes
MIB and Geosmin?	No	Sometimes
Cyanotoxins?	No	Sometimes



http://www.daviddarling.info/encyclopedia/E/eukarycell.html

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ALGAE VS. CYANOBACTERIA

	Algae	Cyanobacteria
Colors	Green	Blue-green, yellow, brown, red or white

http://epa.ohio.gov/portals/28/Documents/HAB/BloomCharacterizationGuide-DRAFT.pdf
http://www.lovethesepics.com/2013/03/red-tide-phenomenon-in-rainbow-of-algal-bloom-colors-38-pics/
https://upload.wikimedia.org/wikipedia/commons/4/47/Maré_vermelha.JPG

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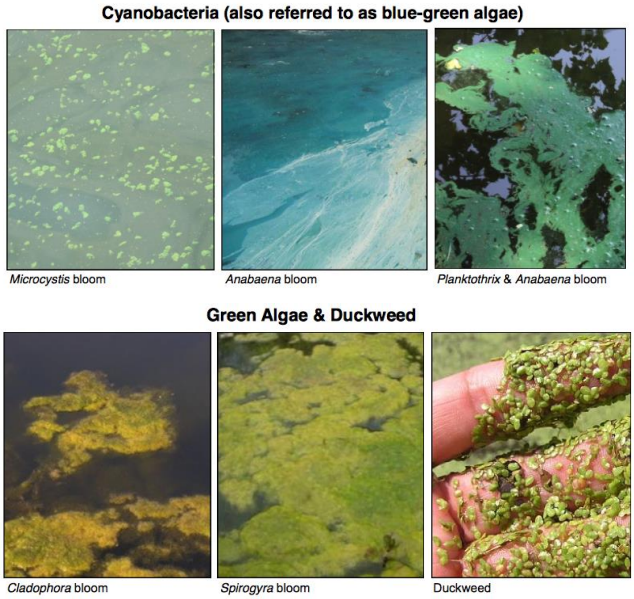
HOW DOES IT LOOK?



http://epa.ohio.gov/portals/28/Documents/HAB/BloomCharacterizationGuide-DRAFT.pdf

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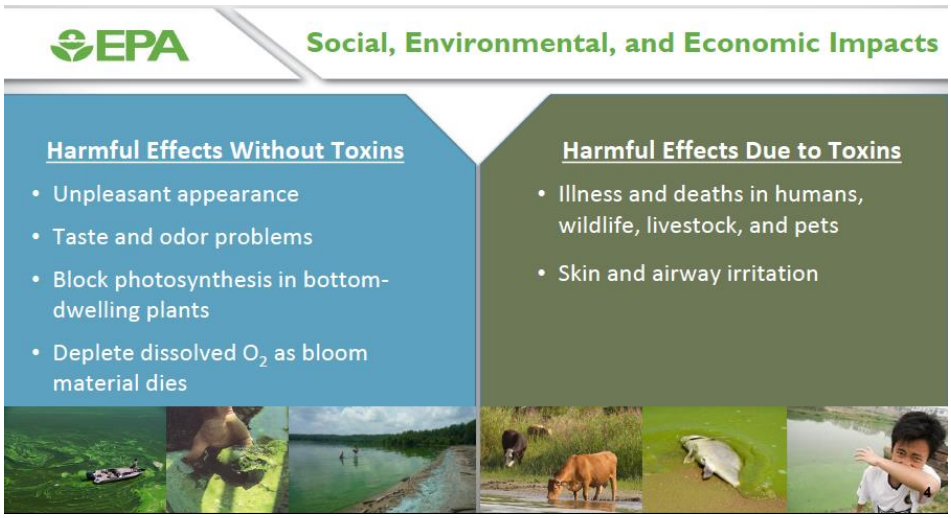

USEPA, 2018

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Cyanobacteria Strains & Associated Toxins

- Strains produce different toxins at different amounts
- Toxins can have multiple variants

Example: Over 80 known microcystin variants

Toxins analyzed by USEPA (544 and 545)

Adapted from : Paerl and Otten 2013. Harmful Cyanobacterial Blooms: Causes, Consequences, and Controls. Microbial Ecology 65:4 995-1010

Toxin	Cyanobacteria Taxa: Anabaena	Aphanizomenon	Aphanocapsa	Chroococcus	Cylindrospermopsis	Limnothrix	Merismopedia	Microcystis	Planktolyngbya	Planktothrix	Pseudanabaena	Nodularia
Aeruginosin								X		X		
Anatoxin-a/homoanatoxin-a	X	X			X				X	X		
Anatoxin-a(S)	X											
Aplysiatoxins									X			
BMAA	X	X			X			X	X	X		
Cyanopeptolin	X							X		X		
Cylindrospermopsin	X	X			X							
Jamaicamides									X			
Lyngbyatoxin									X			
Microcystin	X	X	X		X	X	X	X		X	X	
Nodularin												X
Saxitoxin	X	X			X					X		

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USEPA, 2016

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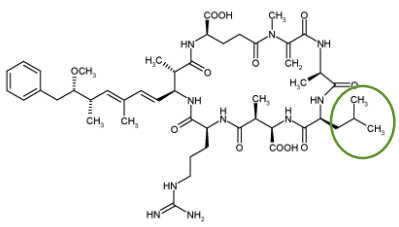
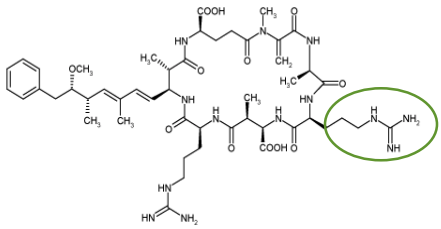
WHAT ARE CONGENERS?

- Over 90 Microcystins
- Microcystin LR, YR, RR and LA - further EPA research
- Microcystin-LR is the most common

Microcystin-LR	Microcystin-RR





https://www.enzolifesciences.com/ALX-350-012/microcystin-lr/
https://www.enzolifesciences.com/ALX-350-043/microcystin-rr/

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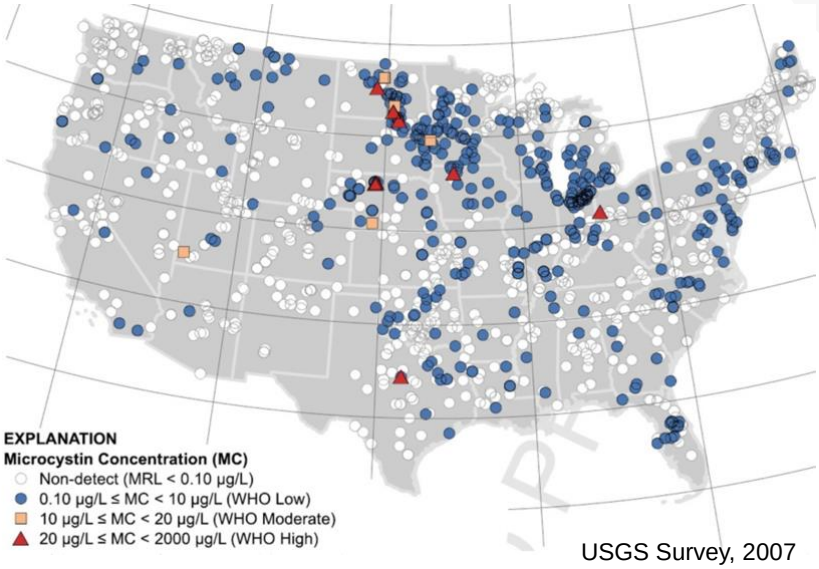
MICROCYSTIN OCCURRENCE



USGS Survey, 2007

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CYANOTOXINS TIMELINE

- August 2014 – Toledo cyanotoxin event
- 2015: USEPA released health advisories for two cyanotoxins
- 2018 – 2020: 10 cyanotoxins included as part of Unregulated Contaminant Monitoring Rule 4 (UCMR4)

Cyanotoxin	10-day Health Advisory (µg/L)	
	Bottle-fed Infants	School-age and Older
Microcystin-LR	0.3	1.6
Cylindrospermopsin	0.7	3

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NATIONWIDE RESULTS

- From UCMR4
- Data collected in 2018 and 2019

Cyanotoxin	Results	Count of samples	Range (ug/L)	Average (ug/L)	Count of samples	EPA Heath Advisory - Sensitive
Anatoxin-a	Non-detect	21,464	0.03 - 13.22	0.23	104	None
Cylindrospermopsin	Non-detect	21,567	0.09 - 0.88	0.26	11	0.7
Microcystin congeners	Non-detect	18			0	
Total Microcystin	Non-detect	21,277	0.32 - 0.79	0.43	6	0.3
Nodularin	Non-detect	3			0	
Total		**64,329**			**121**	

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MANAGEMENT STRATEGIES

Utility 1, LA

Utility 2, NJ

Utility 3, CO

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MONITORING

- Why?
  - Know your water, develop and track indicators, identify excursions, early warning
- What?
  - Algae, indicators, T&O, cyanotoxins, general water quality
- Where?
  - Source water, treatment processes, facility specific
- When?
  - Baseline monitoring, enhanced monitoring based on triggers
- How?
  - Field, laboratory, sensory
  - Continuous, online

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WATER QUALITY PARAMETERS

Water Quality Group	Parameter
General water quality	Temperature
	pH, Alkalinity
	Turbidity
	TOC, UV-254
	Dissolved Oxygen
Cyanobacteria related parameters	**Phycocyanin**
	Chlorophyll-a
	Identification
	Enumeration
	Sensory Analysis 1 (TON)
	Total Nitrogen
	Nitrogen Speciation (nitrate, nitrite, ammonia)
	Total Phosphorus
T&O, Cyanotoxins	MIB
	Geosmin
	Cyanotoxins (10 listed in UCMR 4)

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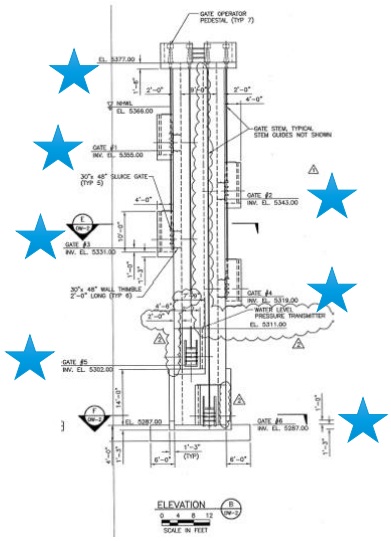
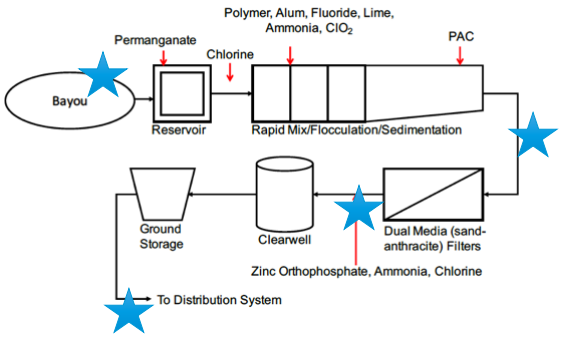
MONITORING LOCATIONS



Utility 3 Raw Water Intake



Utility 1 Process Flow Schematic

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MONITORING FREQUENCIES

Baseline

Trigger(s)	Routine Monitoring				
	Parameter	Frequency	Location 1	Location 2	Location 3
June 1 to September 30	Temperature	Daily		Reservoirs	
	pH	Daily		Reservoirs	
	Alkalinity	Daily		Reservoirs	
	Turbidity	Daily		Reservoirs	
	Phycocyanin	Daily		Reservoirs	
	Chlorophyll-a	Daily		Reservoirs	
	Dissolved Oxygen	Daily		Reservoirs	
	MIB/Geosmin	Weekly		Reservoirs	
	Algae ID/En	Monthly		Reservoirs	
	TOC	Monthly		Reservoirs	
	Total Nitrogen	Monthly		Reservoirs	
	Total Phosphorus	Monthly		Reservoirs	

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MONITORING FREQUENCIES

Alert Level

Trigger(s)	Alert Level Monitoring				
ALL must be met	Parameter	Frequency	Location 1	Location 2	Location 3
Phycocyanin > 10 µg/L	Temperature	Daily	Bayou	Reservoirs	
	pH	Daily	Bayou	Reservoirs	
	Alkalinity	Daily	Bayou	Reservoirs	
	Turbidity	Daily	Bayou	Reservoirs	
AND	Phycocyanin	2/day	Bayou	Reservoirs	
Chlorophyll-a > 2.2 µg/L	Chlorophyll-a	2/day	Bayou	Reservoirs	
AND	Dissolved Oxygen	Daily	Bayou	Reservoirs	
	MIB/Geosmin	1/week*	Bayou	Reservoirs	Filter (combined)
Visual signs of algal bloom	Algae ID/En	Weekly	Bayou	Reservoirs	
	TOC	Monthly	Bayou	Reservoirs	
For 2 days	Total Nitrogen	Monthly	Bayou	Reservoirs	
	Total Phosphorus	Monthly	Bayou	Reservoirs	

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MONITORING FREQUENCIES

Action Level

Trigger(s)	Action Level Monitoring				
ALL must be met	Parameter	Frequency	Location 1	Location 2	Location 3
Phycocyanin > 25 µg/L	Temperature	2/day	Bayou	Reservoirs	
	pH	Daily	Bayou	Reservoirs	
	Alkalinity	Daily	Bayou	Reservoirs	
	Turbidity	Daily	Bayou	Reservoirs	
AND	Phycocyanin	2/day	Bayou	Reservoirs	
Chlorophyll-a > 2.2 µg/L	Chlorophyll-a	2/day	Bayou	Reservoirs	
AND	Dissolved Oxygen	2/day	Bayou	Reservoirs	
	MIB/Geosmin	3/week	Bayou	Reservoirs	Filter
Intense signs of algal bloom	Algae ID/En	3/week	Bayou	Reservoirs	Filter
	TOC	Weekly	Bayou	Reservoirs	
For 2 days	Total Nitrogen	Weekly	Bayou	Reservoirs	
	Total Phosphorus	Weekly	Bayou	Reservoirs	

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MONITORING METHODS

Algae

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MONITORING METHODS

Indicators (Chlorophyll-a, Phycocyanin)

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MONITORING METHODS

Cyanotoxins

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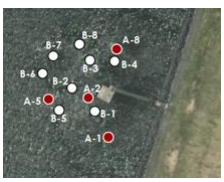
SOURCE WATER CONTROL

Utility 1 Baffle Curtains



Utility 2 Disk Aeration System

Utility 3 Solar Mixers

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SOURCE WATER CONTROL

Control Strategy	Treatment Technology
Operational optimization	Temporary use of alternate source(s)
	Screening of intake depths
Chemical application	Copper based algaecide
	Non-copper algaecide (e.g. peroxide)
	Nutrient removal chemicals (e.g. alum)
Physical control	Surface mixing/ circulation
	Hypolimnetic aeration (line diffusers, disk diffusers, layer aeration)
	Dissolved oxygen augmentation (e.g. Speece Cone)
Emerging technologies	Ultrasonication
	White amur fish (grass carp)
Watershed management	Land acquisition (forestation), wetlands
	Reduce wastewater influence to source

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SOURCE WATER CONTROL

- Consider:
  - Water quality objectives
  - Site constraints
  - Utility resources
  - Costs (life cycle)

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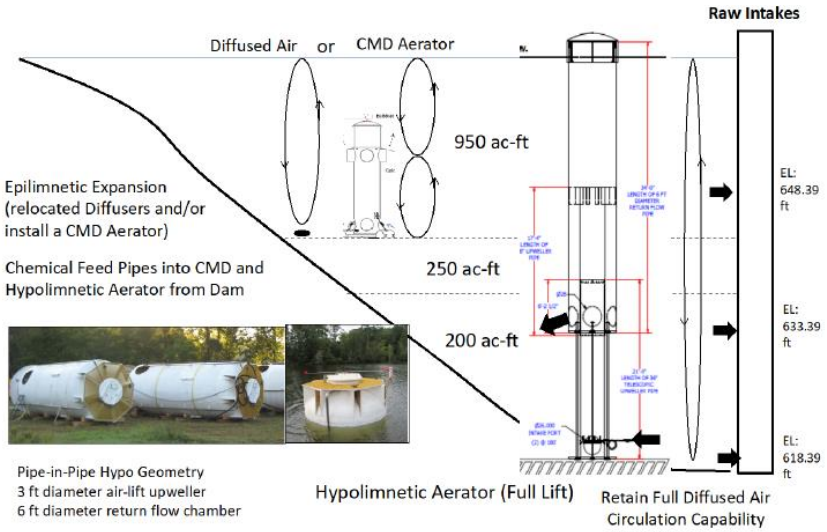
UTILITY 2 AERATION IMPROVEMENTS



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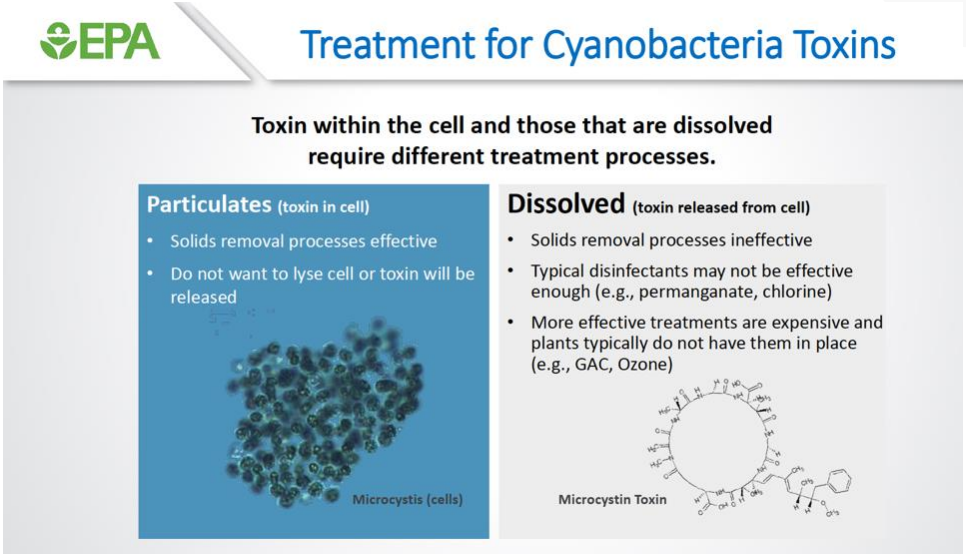
INSIDE THE WATER TREATMENT PLANT



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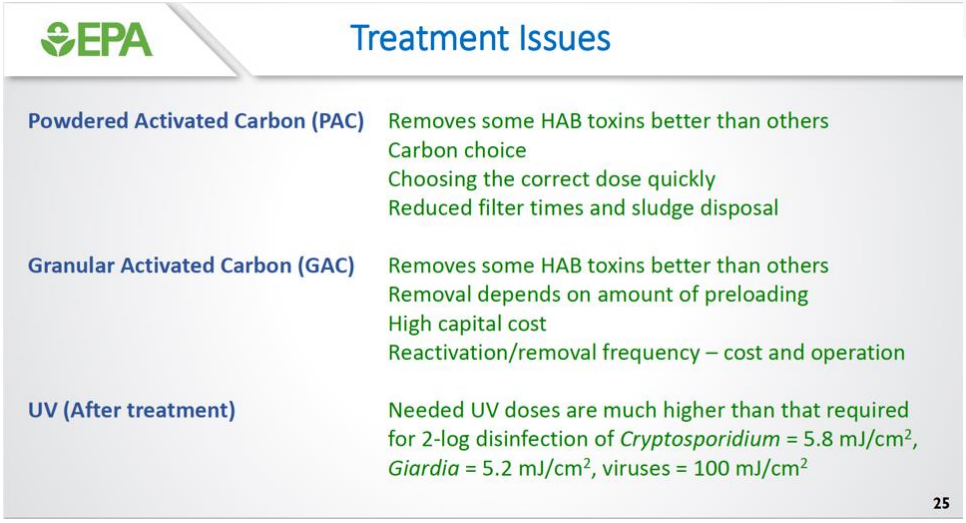
INSIDE THE WATER TREATMENT PLANT



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UTILITY 1: CYANOTOXINS EVALUATION

- Test removal of all 10 UCMR4 cyanotoxins
- Test simultaneously in presence of T&O compounds (MIB)
- Five pre-approved PACs tested
- Simulate all other WTP processes for routine operations

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PACS USED IN JAR TESTS

PAC Product	PAC A	PAC B	PAC C	PAC D	PAC E
Size Distribution	Less than 150 µm: 99%	Less than 45 µm: 65%	Less than 150 µm: 99%	Less than 150 µm: 99%	Less than 45 µm: 90%
	Less than 75 µm: 95%		Less than 75 µm: 95%	Less than 75 µm: 95%	
	Less than 45 µm: 90%		Less than 45 µm: 90%	Less than 45 µm: 90%	
Density	0.51 g/mL; 32 lb/ft^3	0.51 g/mL; 32 lb/ft^3	0.51 g/mL; 32 lb/ft^3	0.4 - 0.7 g/mL	0.4 - 0.7 g/mL
Iodine Number	500 mg/g	500 mg/g	800 mg/g	1000 mg/g	1000 mg/g

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CYANOTOXINS & MIB CONCENTRATIONS

Cyanotoxin	Target Initial Concentration (µg/L)
MC-LR	3.1
MC-RR	3.1
MC-YR	3.1
MC-LA	3.1
MC-LF	3.1
MC-LY	3.1
Total Microcystin	18.6
Anatoxin	10
Nodularin	6.2
Cylindrospermopsin	6.2
2-MIB	0.1

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JAR TEST RESULTS

Product ID	PAC A	PAC C	PAC D	PAC E
Microcystin-RR	27%	80%	65%	82%
Microcystin-YR	26%	78%	45%	80%
Microcystin-LR	35%	80%	51%	68%
Microcystin-LA	33%	82%	44%	82%
Microcystin-LY	31%	84%	60%	81%
Microcystin-LF	39%	79%	56%	85%
Total Microcystin	31%	81%	54%	80%
Nodularin	18%	80%	51%	81%
Anatoxin	24%	35%	44%	55%
Cylindrospermopsin	60%	85%	75%	91%
Average	32%	76%	54%	79%

PAC dose is 50 mg/L

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JAR TEST RESULTS

Product ID	PAC A	PAC C	PAC D	PAC E
Microcystin-RR	27%	80%	65%	82%
Microcystin-YR	26%	78%	45%	80%
Microcystin-LR	35%	80%	51%	68%
Microcystin-LA	33%	82%	44%	82%
Microcystin-LY	31%	84%	60%	81%
Microcystin-LF	39%	79%	56%	85%
Total Microcystin	31%	81%	54%	80%

PAC dose is 50 mg/L

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JAR TEST RESULTS

Product ID	PAC A	PAC C	PAC D	PAC E
Nodularin	18%	80%	51%	81%
Anatoxin	24%	35%	44%	55%
Cylindrospermopsin	60%	85%	75%	91%

PAC dose is 50 mg/L

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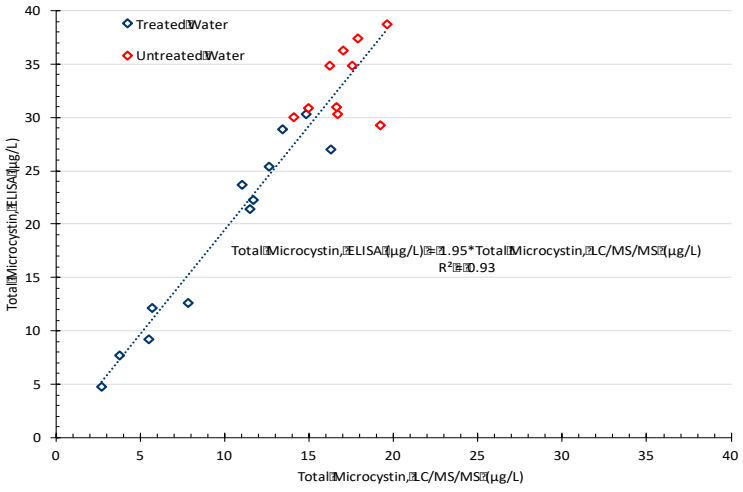
COMPARISON OF ELISA VS LC/MS/MS



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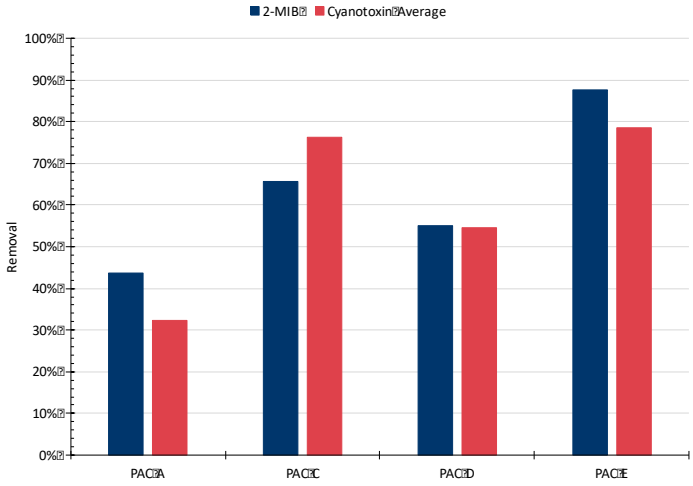
REMOVAL OF T&O VS. CYANOTOXINS



PAC dose is 50 mg/L

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SUMMARY

- Monitor:
  - Know your water, develop and track indicators, identify excursions, early warning
- Source water control:
  - Numerous strategies available
  - Site specific, driven by water quality objectives

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SUMMARY

- In plant treatment:
  - Consider both intracellular and extracellular cyanotoxins
  - Oxidants: risk of cell lysis and release of toxins
  - PAC/ GAC: effectiveness varies between toxins
  - Relative performance of PACs for toxin removal similar to relative performance for T&O removal

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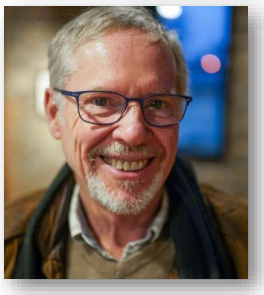
ASK THE EXPERTS

Tarrah Henrie
Corona Environmental

Elizabeth Crafton-Nelson, PhD
Hazen & Sawyer



Craig Adams, PhD, PE, F. ASCE
Saint Louis University

Enter your **question** into the **question pane** at the lower right-hand side of the screen.

Please specify to whom you are addressing the question.

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ADVANCEMENTS IN ALGAECIDE PRODUCTS AND APPROACH FOR HARMFUL ALGAL BLOOM MANAGEMENT

Elizabeth Crafton-Nelson, PhD
Assistant Engineer
Hazen and Sawyer

Hazen

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PURPOSE

- More frequent harmful algal blooms (HABs)
- Requires short- and long-term management
- Immediate action is needed to maintain conditions
- Optimize short-term management plan

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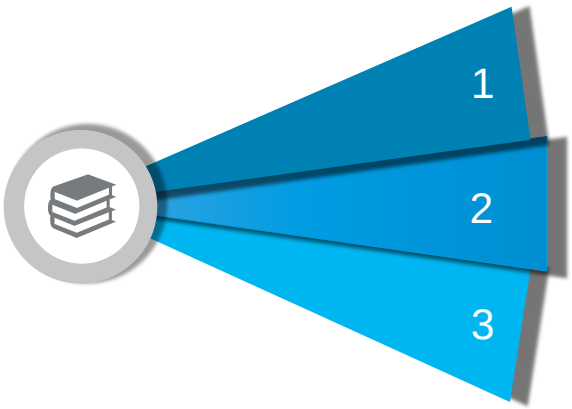
LEARNING OBJECTIVES



Review advances in algaecide products and approach

Review bench-scale testing

Recognize opportunities to apply advances

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AGENDA

1. Summarize advancements
2. Review Hydrogen Peroxide Products
3. Review bench-scale testing of products
4. Apply to full season management plan

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AGENDA

1. Summarize advancements
2. Review Hydrogen Peroxide Products
3. Review bench-scale testing of products
4. Apply to full season management plan

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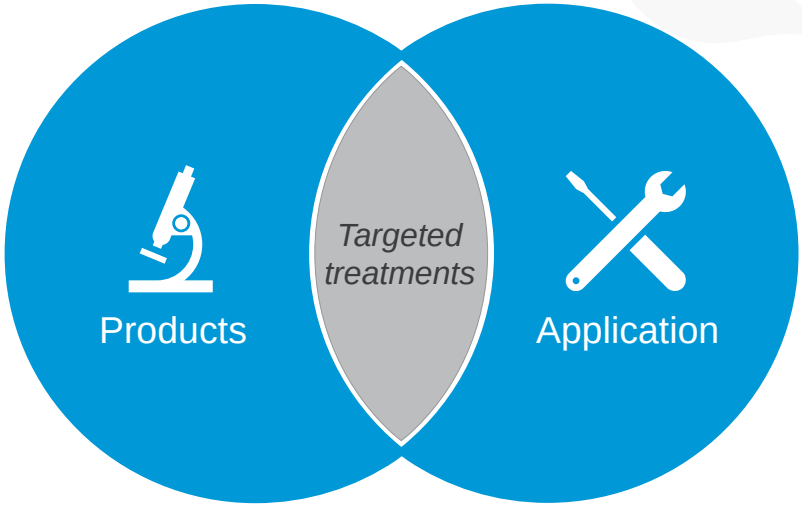
OVERVIEW

More options for in-situ control

Minimize impact to non-target organisms

Eco-friendly approach



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OVERVIEW

Products

Additional products developed

Reduce copper added

Alternative products

Selective treatment

Target bloom-forming organism

&

Application Approach

Injection at sediment-water interface

Partial water column treatments

Targeted sport treatments

High-yield and accumulation areas

Shifting dominance

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AGENDA

1. Summarize advancements
2. Review Hydrogen Peroxide Products
3. Review bench-scale testing of products
4. Apply to full season management plan

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HYDROGEN PEROXIDE PRODUCTS

- PAK27 & GreenClean Pro
  - Granular
  - Active ingredient sodium carbonate peroxyhydrate (85%)
  - 27% Hydrogen peroxide
- GreenClean Liquid 5.0
  - Liquid
  - 23% Hydrogen peroxide
  - 5.3% Peroxyacetic acid

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HYDROGEN PEROXIDE PRODUCTS

- Alternative to copper products
- Selectively target cyanobacteria
  - Toxic HABs
  - Geosmin/MIB
- Intent differs from copper-based products
  - Prevent
  - 'Injury' not 'kill'

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WHY USE HYDROGEN PEROXIDE?

- Target cyanobacteria with hydrogen peroxide
- HABs in surface water are characteristically cyanobacteria-dominated
- Cyanobacteria are the only known source of cyanotoxins
- Typically the source of MIB/geosmin
  - Fungi, actinomycetes

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WHY USE HYDROGEN PEROXIDE?

- Cyanobacteria are prokaryotic
- Mehler reaction
- ROS-eliminating enzymes
- Ascorbate peroxidase (APX)

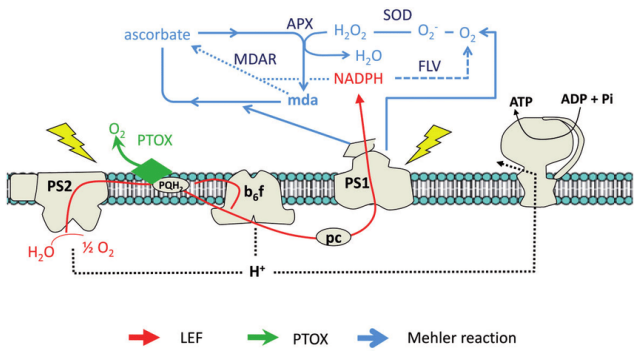

Image: Curien et al. 2016

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WHY USE HYDROGEN PEROXIDE?

- Changes in circadian gene expression pattern
- Impacts both metabolic and physiological function
  - Controls cell division
  - Nitrogen fixation
  - Carbon uptake
  - Biosynthesis of secondary metabolites
    - T&O
    - Cyanotoxins
  - Photosynthesis (reduced photosynthetic viability)

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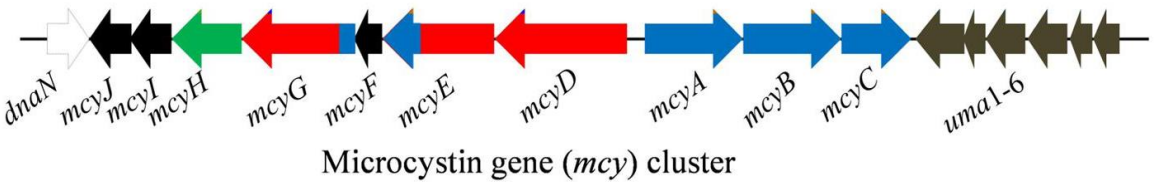
WHY USE HYDROGEN PEROXIDE?

- Downregulates microcystin synthesis
- Reduced transcription of *mcyA, mcyD*, *mcyH* gene clusters



Microcystin gene (*mcy*) cluster

Image: Rastogi et al. 2015

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WHY USE HYDROGEN PEROXIDE?

- Induces the least amount of cell lysis
  - Copper products
- Intended to reduce photosynthetic viability of the cells
- Impairs the cyanobacteria community, allowing eukaryotic algae and other bacteria to compete

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WHY USE HYDROGEN PEROXIDE?

- No residual or accumulation
- Terminal end products are oxygen and water
- No toxicity induced mutation
- Better protect non-target organisms

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AGENDA

1. Summarize advancements
2. Review Hydrogen Peroxide Products
3. Review bench-scale testing of products
4. Apply to full season management plan

EXPERIMENTAL CONDITIONS

- Initial cyanobacteria population: 40,000 cells/mL
- Time intervals: baseline, 1.5 hours, 2, 7, and 14 days after treatment
  - Treatment impact vs. rebound
- Three doses of PAK27®
  - Full Dose: 12.4 mg/L H_2O_2
  - Half Dose: 6.2 mg/L H_2O_2
  - Quarter Dose: 3.1 mg/L H_2O_2
- Negative controls
- Each condition assessed in triplicates

EXPERIMENTAL METHODS

- Water Quality Sonde (YSI 6600 V2)
  - Temp (°C), DO (mg/L), TDS (g/L), Chl-a (µg/L), cyanobacteria (cells/mL)
- Genera-based population composition
  - Palmer-Maloney counting chamber (400x)
- Total microcystin concentration (ELISA)
- qPCR – Multiplex assay (16s rRNA, mcyE, sxtA, cyrA)

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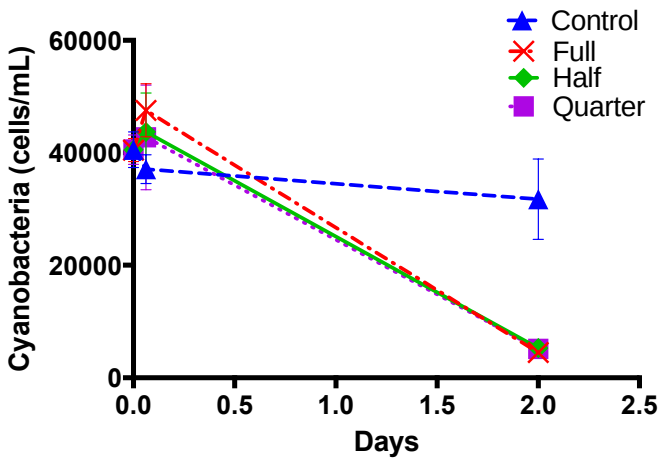
PAK27®

- Cyanobacteria
- Baseline to 2-days
- Dose trend

Percent Change in Cyanobacteria	
Dose	Baseline to 2 days
Full	-89% ★
Half	-87% ★
Quarter	-87% ★
Control	-21%



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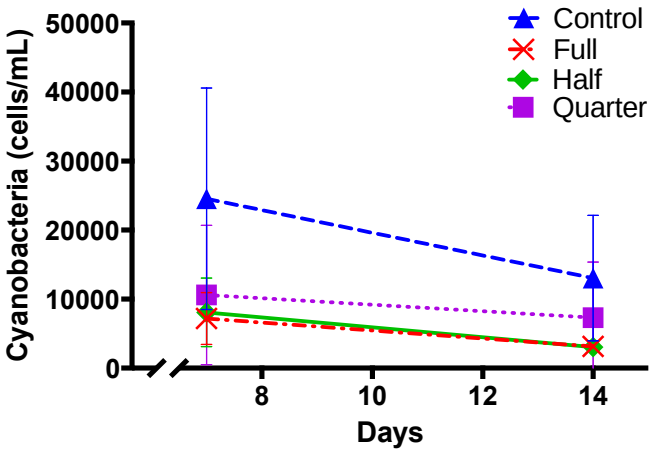
PAK27®

- Cyanobacteria
- Rebound
- 7 to 14 days after treatment

Percent Change in Cyanobacteria	
Dose	7 to 14 days
Full	-44%
Half	-49%
Quarter	-34%
Control	-47%



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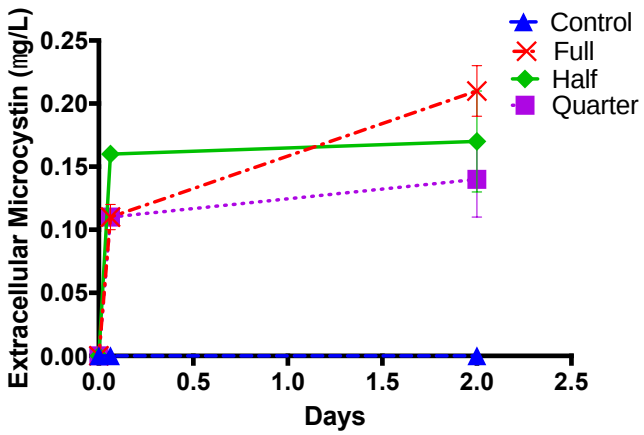
PAK27®

- Extracellular microcystin
- Baseline to 2 days

Percent Change in Extracellular Microcystin	
Dose	Baseline to 2 days
Full	<0.10 (MDL) to 0.21 ± 0.02
Half	<0.10 (MDL) to 0.17 ± 0.04
Quarter	<0.10 (MDL) to 0.14 ± 0.03
Control	<0.10 (MDL)

MDL: 0.1 µg/L
PQL: 0.3 µg/L



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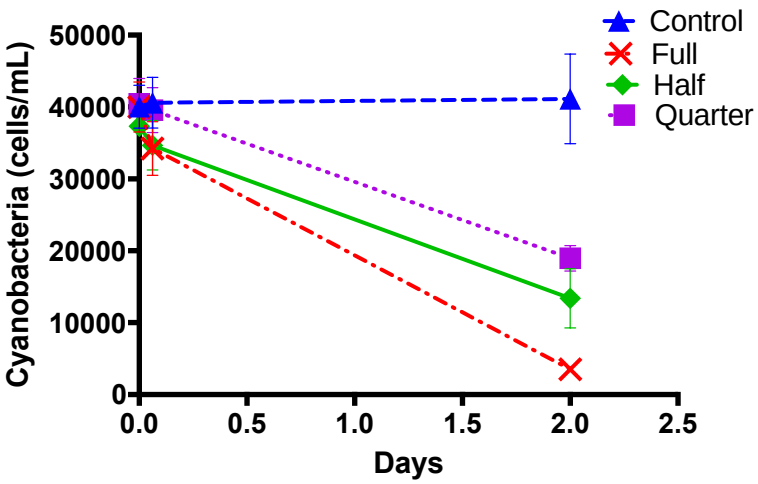
CUTRINE ULTRA

- Cyanobacteria
- Baseline to 2 days

Percent Change in Cyanobacteria	
Dose	Baseline to 2 days
Full	-91% ★
Half	-64% ★
Quarter	-53% ★
Control	+2%



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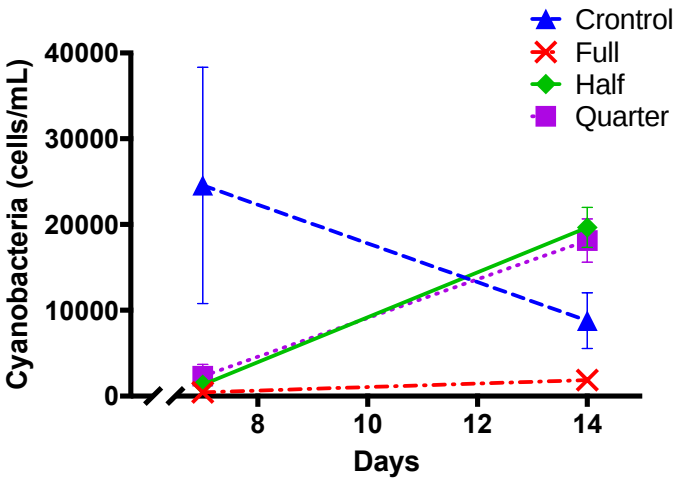
CUTRINE ULTRA

- Cyanobacteria
- 7 to 14 days after treatment

Percent Change in Cyanobacteria	
Dose	7 to 14 days
Full	315%
Half	1,414% ★
Quarter	827% ★
Control	-61%



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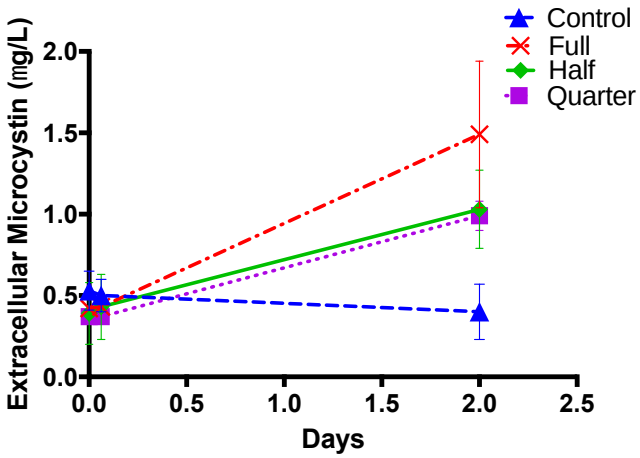
CUTRINE ULTRA

- Extracellular microcystin
- Baseline to 2 days

Percent Change in Extracellular Microcystin	
Dose	Baseline to 2 days
Full	254% ★
Half	177% ★
Quarter	171% ★
Control	-27% ★



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AGENDA

1. Summarize advancements
2. Review Hydrogen Peroxide Products
3. Review bench-scale testing of products
4. Apply to full season management plan

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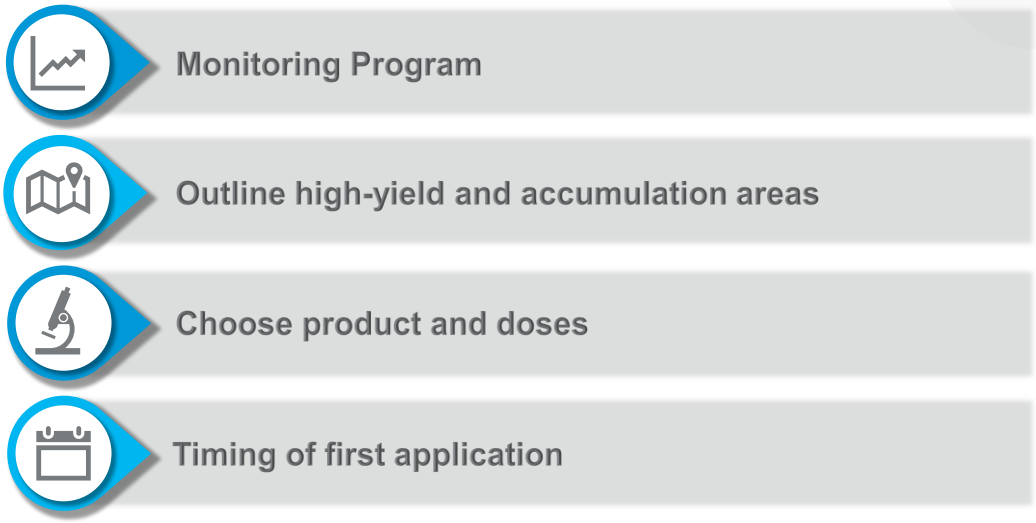
FULL SEASON MANAGEMENT



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SUMMARY

- Advances provide more options for short-term management
- Successful short-term management provides time and relief
- Long-term management techniques need to be implemented for prevention

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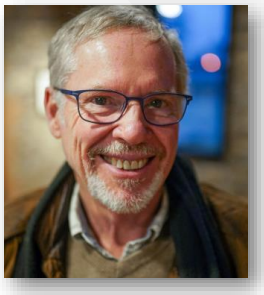
ASK THE EXPERTS

Tarrah Henrie
Corona Environmental

Elizabeth Crafton-Nelson, PhD
Hazen & Sawyer



Craig Adams, PhD, PE, F. ASCE
Saint Louis University

Enter your **question** into the **question pane** at the lower right-hand side of the screen.

Please specify to whom you are addressing the question.

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SAINT LOUIS UNIVERSITY

HAZEN-ADAMS CYANOTOX TOOL TO ASSIST UTILITIES WITH COMPLEX CYANOTOXIN ISSUES

Speaker: Craig Adams, Ph.D., P.E., F. ASCE

Oliver Parks Professor

Saint Louis University

Co-Developer: Ben Stanford, Ph.D., P.E.

Associate Vice President

Hazen and Sawyer

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ACKNOWLEDGEMENTS

- CyanoTOX was **conceived and developed** by Craig Adams (SLU) and Ben Stanford (Hazen and Sawyer) with significant **contributions** from Elisa Arevalo, Erik Rosenfeldt, Elizabeth Crafton and others
- The development of Hazen-Adams CyanoTox program was **funded** by the American Water Works Association and Water Research Foundation
- Special thanks for **reviews** and input to:
  - AWWA Cyanotoxin workgroup
  - Bob Raczko (United Water), Keith Cartnick (United Water), and Erik Rosenfeldt (Hazen and Sawyer), Steve Via (AWWA), Alan Roberson (AWWA), Adam Carpenter (AWWA), Djanette Khiari (WaterRF)

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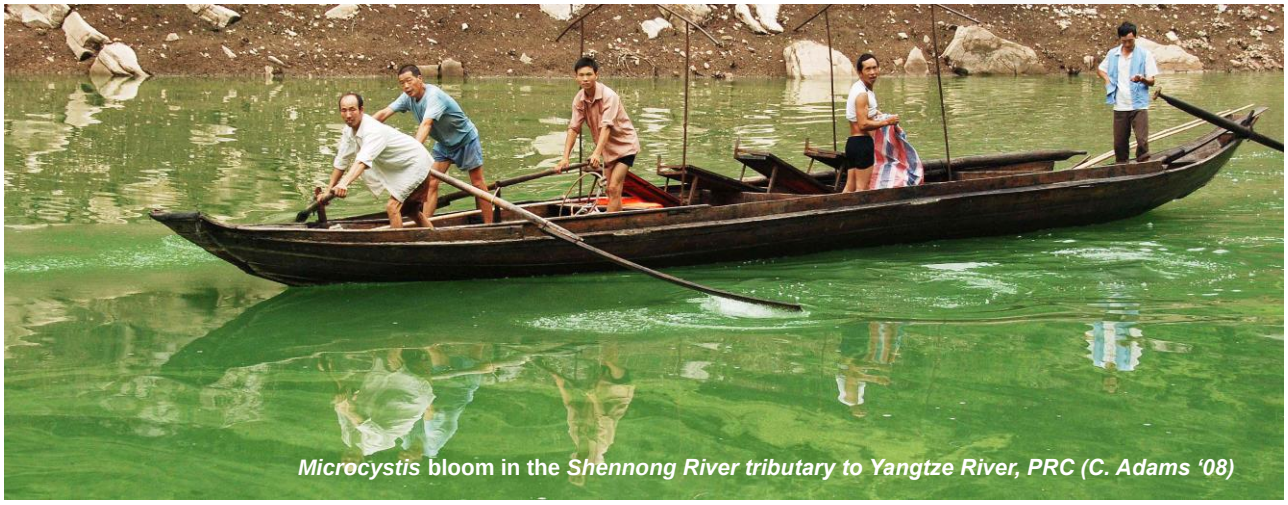

Microcystis* bloom in the *Shennong River tributary to Yangtze River, PRC (C. Adams '08)

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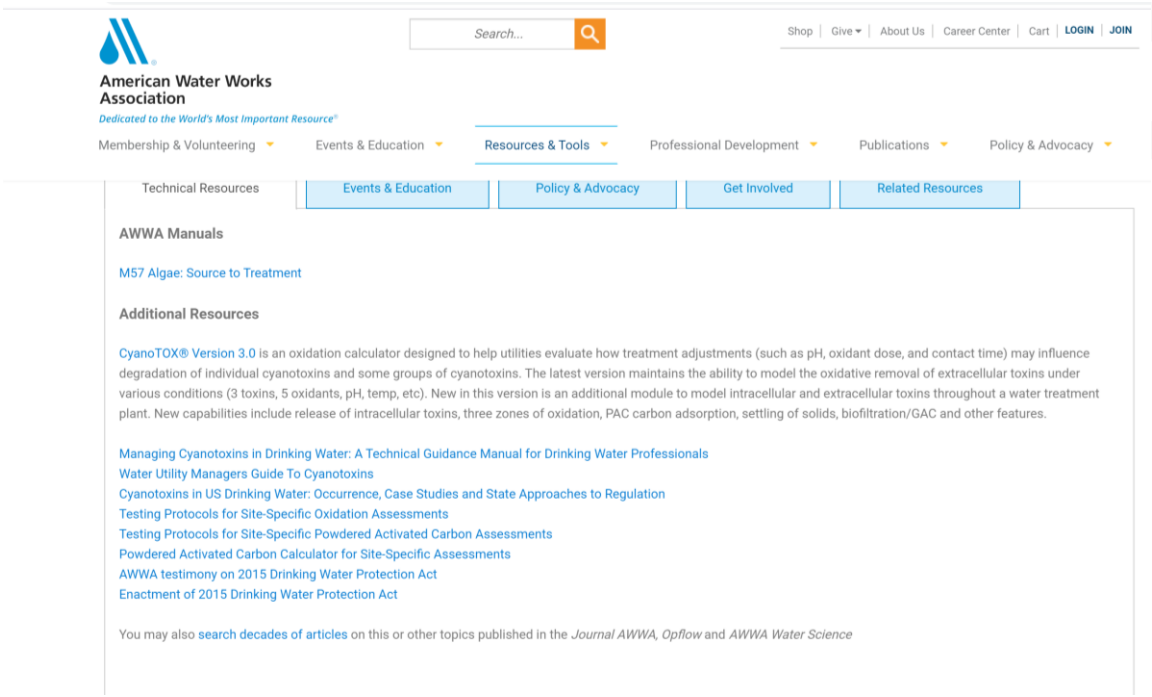

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USES FOR HAZEN-ADAMS CYANOTOX (VER. 3.0) TOOL

- Protocol development for Hazardous Algal Blooms (HAB)
- Sensitivity analysis (for design, operational and water quality parameters)
- Plant design, upgrade and operations analysis
- Creation of graphs and tables for reports
- Real-time response to HAB/cyanotoxin events

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CYANOTOX® VERSION 3.0

- An oxidation calculator designed to help utilities evaluate how treatment adjustments (such as pH, oxidant dose, and contact time) may influence degradation of individual cyanotoxins and some groups of cyanotoxins.
- The latest version (3.0)
  - Maintains the ability to model the oxidative removal of extracellular toxins under various conditions (3 toxins, 5 oxidants, pH, temp, etc).
  - Includes an additional module to model intracellular and extracellular toxins throughout a water treatment plant.
    - New capabilities include release of intracellular toxins, three zones of oxidation, PAC carbon adsorption, settling of solids, biofiltration/GAC and other features.
- Downloadable for free from
- https://www.awwa.org/Resources-Tools/Resource-Topics/Source-Water-Protection/Cyanobacteria-Cyanotoxins

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CYANOTOX MODEL ORIGINALLY FOCUSED ON REMOVAL BY DISINFECTION AND/OR OXIDATION PROCESSES

	Extracellular Cyanotoxins			
Process	Microcystin	Cylindro-spermopsin	Anatoxin A	Saxitoxin
Free chlorine	Moderate (f(pH))	Effective	No, slow	Effective
Permanganate	Effective	No	Moderate	No
Monochloramine	Slow/no oxidation	No	No	??
Ozone	Effective	Effective	Effective	No
Chlorine dioxide	Slow/no oxidation	No	No	??
AOP	Effective	Effective	Effective	??
UV	No	No	??	??

Adams, C. (2013) "Tailored Treatment of Cyanotoxins and Cyanobacteria: Oxidation, Adsorption and Other Technologies," Water Quality Technology Conference Workshop, Long Beach, CA, USA. (November 19, 2013)

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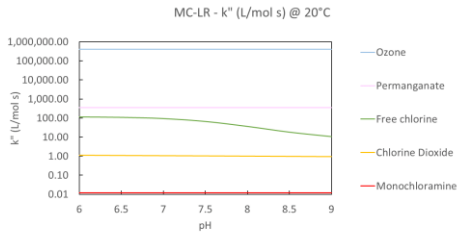
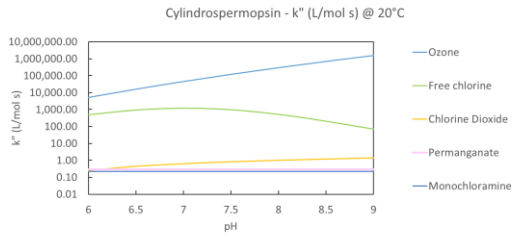
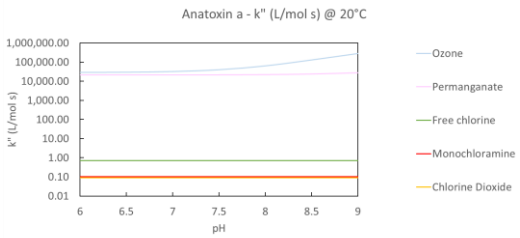
MC-LR KINETICS USED IN MODEL







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HOW THE MODEL WORKS

1. Select Cyanotoxin of interest from drop down list:
   - Anatoxin-A, Microcystin-LR, Cylindrospermopsin, Microcystin-Mix
2. Input system parameters
3. Input initial cyanotoxin concentration
4. Select final target concentration
5. Select oxidant of use
   - Free chlorine, ozone, permanganate, monochloramine, chlorine dioxide
6. Select model type

STEP 1. Select the cyanotoxin of interest from the dropdown list

Cyanotoxin Type	Microcystin-LR (MC-LR)

STEP 2. Input the following system parameters

pH (between 6-9)	6
Temperature (between 10-30°C)	19

STEP 3. Input the initial cyanotoxin concentration

Cyanotoxin Initial Concentration (µg/L)	5

(If not known, enter an assumed value for the scenario)

STEP 4. Select your target option from the dropdown list

Target. Options:	1) Input target cyanotoxin conc.
Target cyanotoxin concentration (µg/L)	0.3

STEP 5. Select the oxidant of interest from the dropdown list

Oxidant Type	Free Chlorine

STEP 6. Go to your chosen calculator version: CT based or Dose-decay based (tabs in blue)

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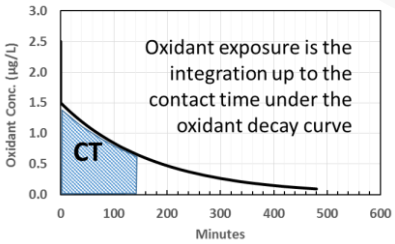
CT OR OXIDANT EXPOSURE

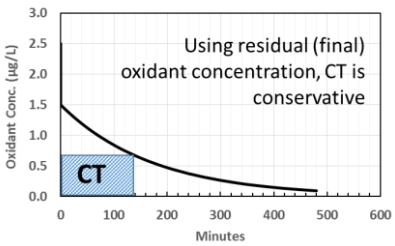
In CyanoTOX, CT can be determined:

1. By entering
   - Oxidant dose
   - Instantaneous oxidant demand (immediately subtracted from dose)
   - Oxidant decay rate (entered as a half-life (min))
   - Contact time

2. (Conservatively) by entering the residual oxidant concentration at the end of contact time;
   i.e. $CT = C_{residual} \cdot t_{contact}$

3. By directly entering the plant CT





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EXAMPLE 1. POST-FILTER OXIDATION OF MC-LR W/CHLORINE

- MC-LR post filter is 14 µg/L. (No cells left; all extracellular)
- pH = 8.2; Temp = 15°C
- Oxidant
  - Chlorine dosage = 3.0 mg/L;
  - Instantaneous demand = 0.7 mg/L;
  - Contact time = 120 min
  - Half-life (for decay) = 340 min
- Baffle factor = 0.3 (poor, no intrabasin baffles)
- Target MC-LR = 0.3 µg/L (Health Advisory)

	Ideal PFR	Adjusted for baffle factor
Final MC-LR Concentration (µg/L)	0.1	2.7
MC-LR Remaining (%)	0.4 %	19.5 %
MC-LR Removal (%)	99.6 %	80.5 %
CT for your scenario (mg-min/L)	244.8	73.4
Max influent toxin conc. to achieve target (µg/L)	69.7	1.5
CT needed to achieve target (mg-min/L)	N/A	172.7
Time needed to achieve target at current conditions (min)	0.0	0.0

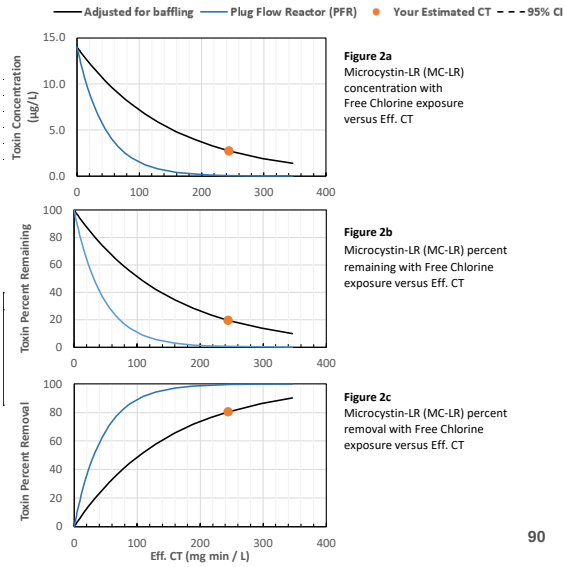

Figure 2a Microcystin-LR (MC-LR) concentration with Free Chlorine exposure versus Eff. CT

Figure 2b Microcystin-LR (MC-LR) percent remaining with Free Chlorine exposure versus Eff. CT

Figure 2c Microcystin-LR (MC-LR) percent removal with Free Chlorine exposure versus Eff. CT

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EXAMPLE 2. POST-FILTER OXIDATION OF CYN W/CHLORINE

- CYN post filter is 14 µg/L. (No cells left; all extracellular)
- pH = 8.2; Temp = 15˚C
- Oxidant
  - Chlorine dosage = 3.0 mg/L;
  - Instantaneous demand = 0.7 mg/L;
  - Contact time = 120 min
  - Half-life (for decay) = 340 min
- Baffle factor = 0.3 (poor, no intrabasin baffles)
- Target CYN = 0.7 µg/L (Health Advisory)

	Ideal PFR	Adjusted for baffle factor
Final CYN Concentration (µg/L)	0.0	0.0
CYN Remaining (%)	0.0 %	0.0 %
CYN Removal (%)	100.0 %	100.0 %
CT for your scenario (mg-min/L)	244.8	73.4
Max influent toxin conc. to achieve target (µg/L)	>1000	>1000
CT needed to achieve target (mg-min/L)	N/A	10.8
Time needed to achieve target at current conditions (min)	0.0	0.0

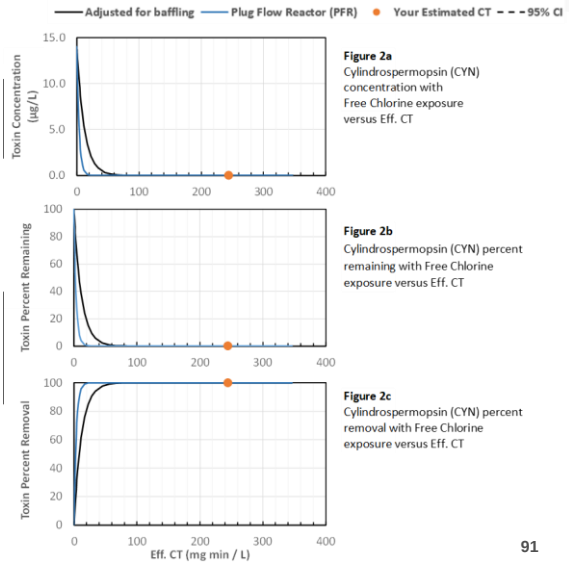

Figure 2a Cylindrospermopsin (CYN) concentration with Free Chlorine exposure versus Eff. CT

Figure 2b Cylindrospermopsin (CYN) percent remaining with Free Chlorine exposure versus Eff. CT

Figure 2c Cylindrospermopsin (CYN) percent removal with Free Chlorine exposure versus Eff. CT

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EXAMPLE 3. PRE-FILTER OXIDATION OF MC-LR W/$KMNO_4$

- Extracellular MC-LR in intake is 14 µg/L
- pH = 8.2; Temp = 15˚C
- Oxidant
  - Effective CT prior to filter = 150 mg-min/L
- Target MC-LR = 0.3 µg/L (Health Advisory)

Final MC-LR Concentration (µg/L)	0.0
MC-LR Remaining (%)	0.0
MC-LR Removal (%)	100.0
CT value of your system (mg-min/L)	150.0
Max influent toxin conc. to achieve target (µg/L)	>1000
Effective CT to achieve target (mg-min/L)	34.8

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

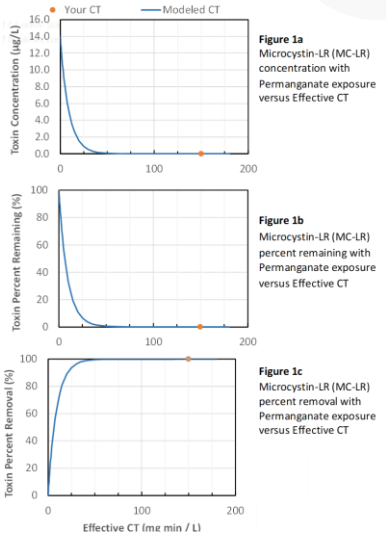

Figure 1a Microcystin-LR (MC-LR) concentration with Permanganate exposure versus Effective CT

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

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

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EXAMPLE 4. PRE-FILTER OXIDATION OF CYN W/KMNO$_4$

- Extracellular CYN in intake is 14 µg/L
- pH = 8.2; Temp = 15°C
- Oxidant
  - Effective CT prior to filter = 150 mg-min/L
- Target CYN = 0.7 µg/L (Health Advisory)

Final CYN Concentration (µg/L)	13.8
CYN Remaining (%)	98.7
CYN Removal (%)	1.3
CT value of your system (mg-min/L)	150.0
Max influent toxin conc. to achieve target (µg/L)	0.3
Effective CT to achieve target (mg-min/L)	43108.9

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

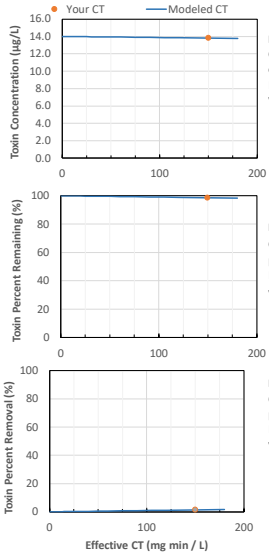

Figure 1a Cylindrospermopsin (CYN) concentration with Permanganate exposure versus Effective CT

Figure 1b Cylindrospermopsin (CYN) percent remaining with Permanganate exposure versus Effective CT

Figure 1c Cylindrospermopsin (CYN) percent removal with Permanganate exposure versus Effective CT

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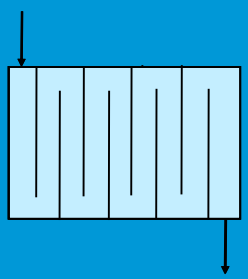
CONTACTOR NON-IDEALITIES



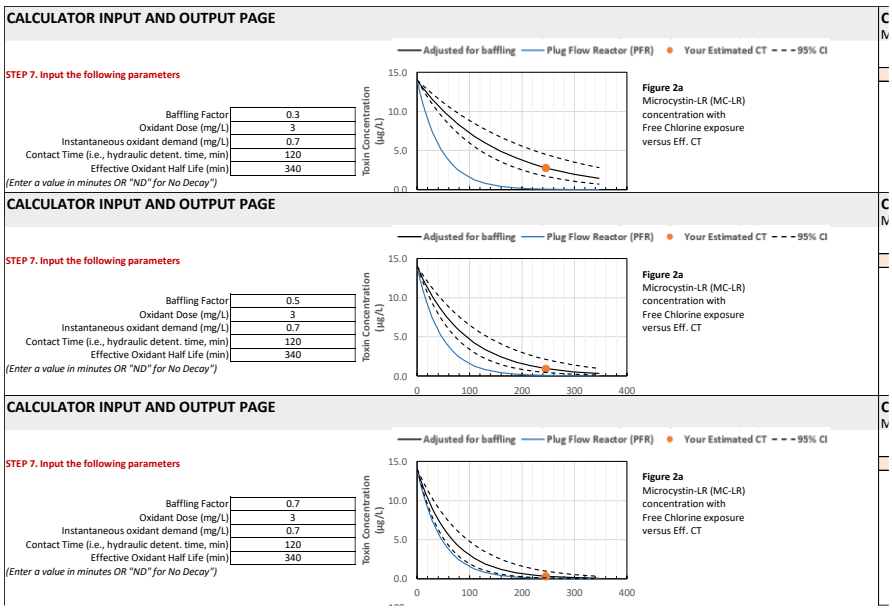


Figure 2a Microcystin-LR (MC-LR) concentration with Free Chlorine exposure versus Eff. CT

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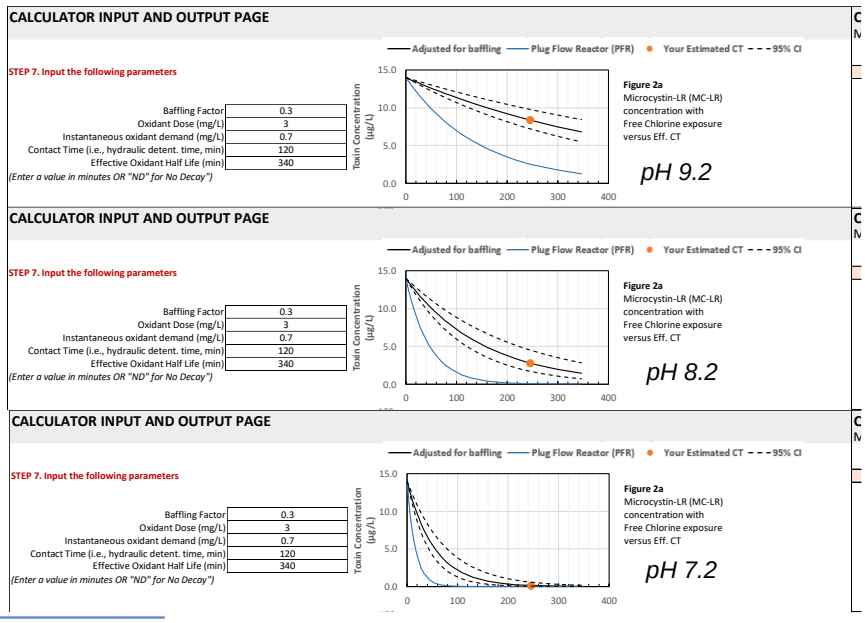
PH EFFECTS (HOCL/OCL$^-$ + MC-LR)



Hazen-Adams CyanoTOX Tool (Ver. 3.0)

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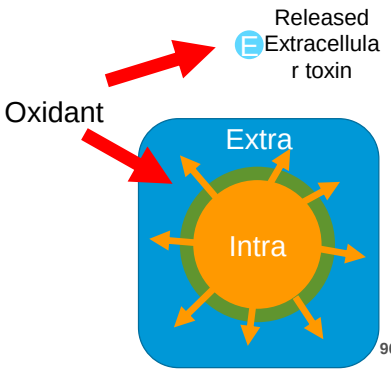
INTRACELLULAR VS. EXTRACELLULAR TOXINS

- Cyanotoxins entering a treatment plant may be:
  - Extracellular – Outside the cyanobacterial cells in solution
  - Intracellular – Within cyanobacterial cells
- Analysis
  - Total toxin
    - Lyse cell with freeze thaw
  - Extracellular
    - Prefiliter cells
  - Intracellular
    - ICT = TT – ECT
- Oxidation can cause cells to lyse and release toxins slowly or rapidly



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Hazen | American Water Works Association | **Hazen-Adams CyanoTOX Tool (Ver. 3.0)** | The Water Research Foundation | Saint Louis University

Zone 1 (intake to rapid mix)

The model allows release of intracellar toxin (IT) based on the assumed release rate.
Oxidation of the extracellular toxins (ET) occurs concurrently.

Zone 2 (rapid mix to filter intake)

The model allows release of intracellar toxin (IT) based on the assumed release rate.
Oxidation of the extracellular toxins (ET) occurs concurrently.
Removal of intracellular toxin (intact cells) occurs by coagulation/flocculation/sedimentation throughout the sedimentation basin based on a percentage removal input by the user.
Removal of extracellular toxin (ET) occurs by powdered activated carbon (PAC) sorption throughout the flocculation and sedimentation basins based on a percentage removal input by the user.

Rapid gravity filter

Extracellular toxin (ET) release is allowed for on the filter based on a percentage release entered by the user.
Adsorption/biodegradation of extracellular toxin (ET) (including all of the released toxin) is allowed for on the filter based on a percentage release entered by the user.

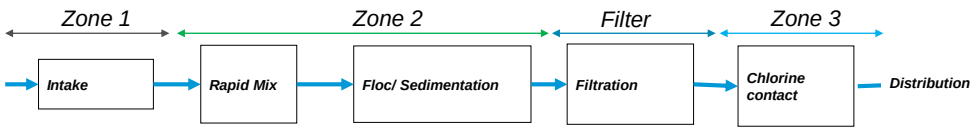
Zone 3 (post filtration contactor)

All cells are assumed removed on the filter such that the post filter intracellular toxin (IT) is zero.
Oxidation of the extracellular toxins occurs within the contactor based on user input parameters.

Hydraulic retention times (HRT) for each zone are entered by the user, specifically as: intake pipe, flocculation basin, sedimentation basin, and post filtration contactor
Flocculation and sedimentation HRTs are separated as the program allows for PAC removal throughout both basins, but sedimentation only in the sedimentation basin.

OUTPUT

Graphical output is presented showing total, intracellular (IT) and extracellular toxin (ET) concentrations throughout the plant as a function of time from the intake
Tabular results are also provided at the key locations throughout the plant.



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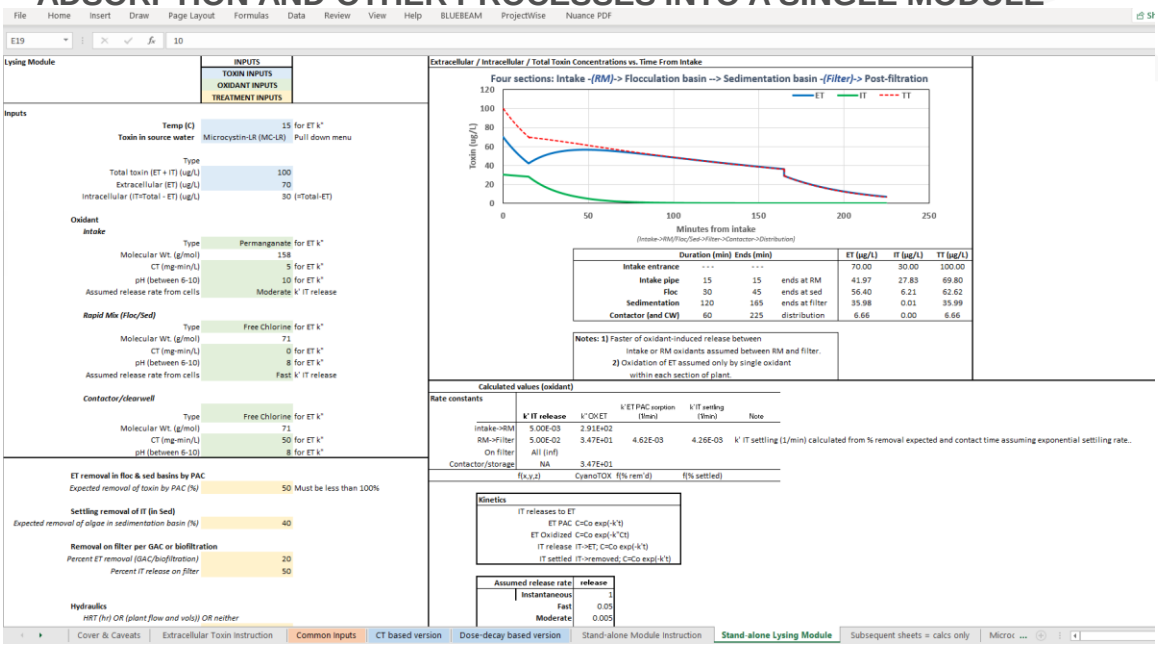
CYANOTOX 3.0 COMBINES TREATMENT, LYSING/LEAKING, ADSORPTION AND OTHER PROCESSES INTO A SINGLE MODULE



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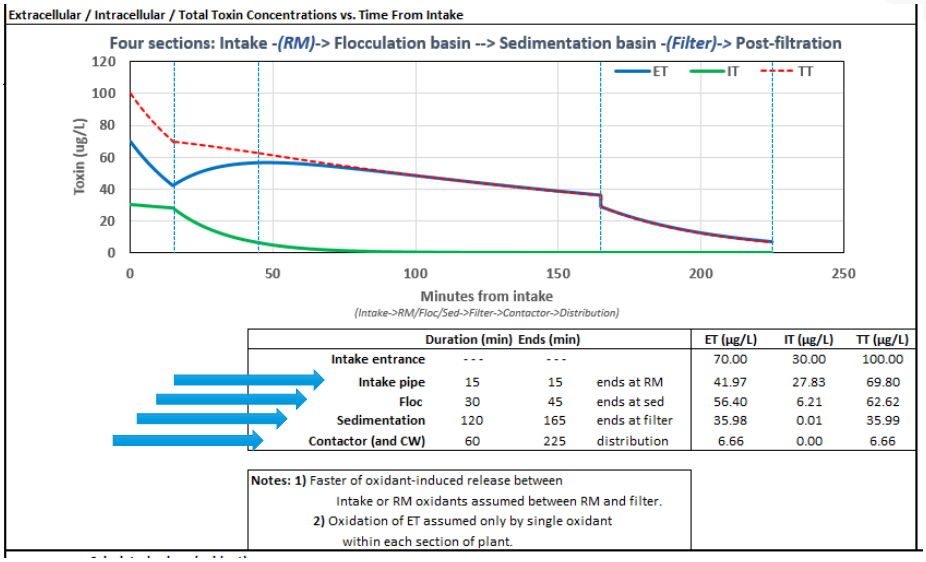
RESULTS ARE DISPLAYED GRAPHICALLY WITH DATA TABLES



	Duration (min)	Ends (min)		ET (µg/L)	IT (µg/L)	TT (µg/L)
Intake entrance	---	---		70.00	30.00	100.00
Intake pipe	15	15	ends at RM	41.97	27.83	69.80
Floc	30	45	ends at sed	56.40	6.21	62.62
Sedimentation	120	165	ends at filter	35.98	0.01	35.99
Contactor (and CW)	60	225	distribution	6.66	0.00	6.66

Notes: 1) Faster of oxidant-induced release between Intake or RM oxidants assumed between RM and filter.
2) Oxidation of ET assumed only by single oxidant within each section of plant.

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EXAMPLE: LATE FALL BLOOM

15 Degrees C, pH is 8.2 intake to filter
Minimum chlorine CT of 80 mg-min/L at pH 7.5 in clearwell (Finished Water)

- Develop a solution to bring MC-LR concentration to below 0.3 ug/L for a facility that is experiencing a bloom that creates an intake of water with 100 ug/L of total toxins but 70 ug/L as extracellular.
- The facility has the following capabilities and assumptions:
  - Permanganate can be added up to 10 mg-min/L CT at intake causing moderate release rate of intracellular toxin
  - PAC can be added with up to 50% removal
  - Free chlorine can be added in Rapid Mix (will assume 20 mg-min/L CT to prior to filter) causing slow release rate of intracellular toxin
  - Facility has no GAC capacity nor intentional biofiltration
  - Assume 20% of intracellular toxin is released from cells while sitting on filter bed
  - Assume 40% of cells settle out in clarifier

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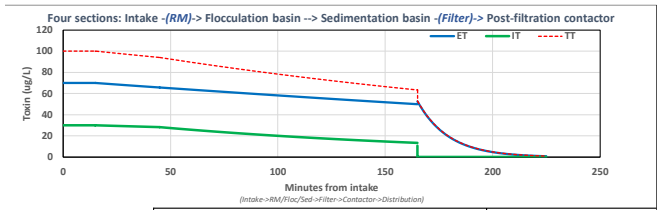
NO $KMNO_4$ IN INTAKE, NO PAC ADDED

Inputs		
Temp (C)	15	for ET k"
Toxin in source water	Microcystin-LR (MC-LR)	Pull down menu
Type		
Total toxin (ET + IT) (ug/L)	100	
Extracellular (ET) (ug/L)	70	
Intracellular (IT=Total - ET) (ug/L)	30	(=Total-ET)
Oxidant		
Intake		
Type	Permanganate	for ET k"
Molecular Wt. (g/mol)	158	
CT (mg-min/L)	0	for ET k"
pH (between 6-10)	8.2	for ET k"
Assumed release rate from cells	None	k' IT release
Rapid Mix (Floc/Sed)		
Type	Free Chlorine	for ET k"
Molecular Wt. (g/mol)	71	
CT (mg-min/L)	20	for ET k"
pH (between 6-10)	8.2	for ET k"
Assumed release rate from cells	Slow	k' IT release
Contactor/clearwell		
Type	Free Chlorine	for ET k"
Molecular Wt. (g/mol)	71	
CT (mg-min/L)	80	for ET k"
pH (between 6-10)	7.5	for ET k"
ET removal in floc & sed basins by PAC		
Expected removal of toxin by PAC (%)	0	Must be less than 100%
Settling removal of IT (in Sed)		
Expected removal of algae in sedimentation basin (%)	40	
Removal on filter per GAC or biofiltration		
Percent ET removal (GAC/biofiltration)	0	
Percent IT release on filter	20	



	Duration (min)	Ends (min)		ET (µg/L)	IT (µg/L)	TT (µg/L)
Intake entrance	- - -	- - -		70.00	30.00	100.00
Intake pipe	15	15	ends at RM	70.00	30.00	100.00
Floc	30	45	ends at sed	65.71	28.25	93.96
Sedimentation	120	165	ends at filter	49.96	13.32	63.28
Contactor (and CW)	60	225	distribution	0.86	0.00	0.86

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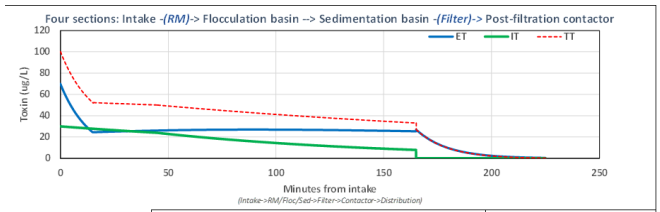
10 MG-MIN/L $KMNO_4$ IN INTAKE, NO PAC ADDED

Inputs		
Temp (C)	15	for ET k"
Toxin in source water	Microcystin-LR (MC-LR)	Pull down menu
Type		
Total toxin (ET + IT) (ug/L)	100	
Extracellular (ET) (ug/L)	70	
Intracellular (IT=Total - ET) (ug/L)	30	(=Total-ET)
Oxidant		
Intake		
Type	Permanganate	for ET k"
Molecular Wt. (g/mol)	158	
CT (mg-min/L)	10	for ET k"
pH (between 6-10)	8.2	for ET k"
Assumed release rate from cells	Moderate	k' IT release
Rapid Mix (Floc/Sed)		
Type	Free Chlorine	for ET k"
Molecular Wt. (g/mol)	71	
CT (mg-min/L)	20	for ET k"
pH (between 6-10)	8.2	for ET k"
Assumed release rate from cells	Moderate	k' IT release
Contactor/clearwell		
Type	Free Chlorine	for ET k"
Molecular Wt. (g/mol)	71	
CT (mg-min/L)	80	for ET k"
pH (between 6-10)	7.5	for ET k"
ET removal in floc & sed basins by PAC		
Expected removal of toxin by PAC (%)	0	Must be less than 100%
Settling removal of IT (in Sed)		
Expected removal of algae in sedimentation basin (%)	40	
Removal on filter per GAC or biofiltration		
Percent ET removal (GAC/biofiltration)	0	
Percent IT release on filter	20	



	Duration (min)	Ends (min)		ET (µg/L)	IT (µg/L)	TT (µg/L)
Intake entrance	- - -	- - -		70.00	30.00	100.00
Intake pipe	15	15	ends at RM	24.52	27.83	52.35
Floc	30	45	ends at sed	26.14	23.96	50.09
Sedimentation	120	165	ends at filter	25.40	7.86	33.26
Contactor (and CW)	60	225	distribution	0.44	0.00	0.44

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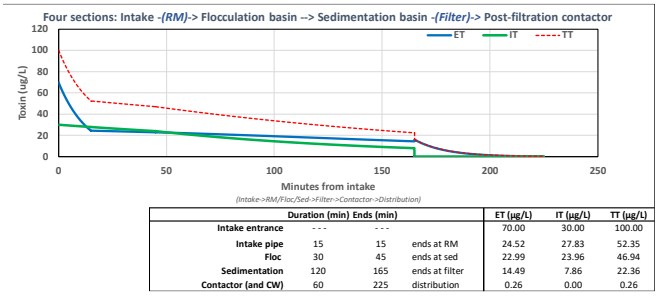
10 MG-MIN/L $KMNO_4$ IN INTAKE, PAC ADDED (W/ 50% TOXIN REMOVAL)

Inputs		
Temp (C)	15	for ET k"
Toxin in source water	Microcystin-LR (MC-LR)	Pull down menu
Type		
Total toxin (ET + IT) (ug/L)	100	
Extracellular (ET) (ug/L)	70	
Intracellular (IT=Total - ET) (ug/L)	30	(=Total-ET)
Oxidant		
Intake		
Type	Permanganate	for ET k"
Molecular Wt. (g/mol)	158	
CT (mg-min/L)	10	for ET k"
pH (between 6-10)	8.2	for ET k"
Assumed release rate from cells	Moderate	k' IT release
Rapid Mix (Floc/Sed)		
Type	Free Chlorine	for ET k"
Molecular Wt. (g/mol)	71	
CT (mg-min/L)	20	for ET k"
pH (between 6-10)	8.2	for ET k"
Assumed release rate from cells	Moderate	k' IT release
Contactor/clearwell		
Type	Free Chlorine	for ET k"
Molecular Wt. (g/mol)	71	
CT (mg-min/L)	80	for ET k"
pH (between 6-10)	7.5	for ET k"
ET removal in floc & sed basins by PAC		
Expected removal of toxin by PAC (%)	50	Must be less than 100%
Settling removal of IT (in Sed)		
Expected removal of algae in sedimentation basin (%)	40	
Removal on filter per GAC or biofiltration		
Percent ET removal (GAC/biofiltration)	0	
Percent IT release on filter	20	



	Duration (min)	Ends (min)		ET (µg/L)	IT (µg/L)	TT (µg/L)
Intake entrance	---	---		70.00	30.00	100.00
Intake pipe	15	15	ends at RM	24.52	27.83	52.35
Floc	30	45	ends at sed	22.99	23.96	46.94
Sedimentation	120	165	ends at filter	14.49	7.86	22.36
Contactor (and CW)	60	225	distribution	0.26	0.00	0.26

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SAINT LOUIS UNIVERSITY

HAZEN-ADAMS CYANOTOX (VER. 3.0) TOOL TO ASSIST UTILITIES WITH COMPLEX CYANOTOXIN ISSUES

- HAB EVENT RESPONSE SOP DEVELOPMENT
- SENSITIVITY ANALYSIS
- PLANT DESIGN, UPGRADE AND OPERATIONS ANALYSIS
- CREATION OF GRAPHS AND TABLES FOR REPORTS
- REAL-TIME RESPONSE TO HAB/CYANOTOXIN EVENTS

Dr. Craig D. Adams
Saint Louis University
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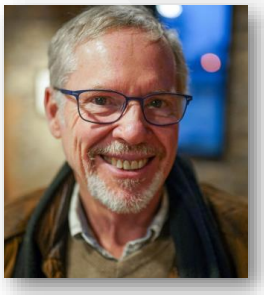
ASK THE EXPERTS

Tarrah Henrie
Corona Environmental

Elizabeth Crafton-Nelson, PhD
Hazen & Sawyer



Craig Adams, PhD, PE, F. ASCE
Saint Louis University

Enter your **question** into the **question pane** at the lower right-hand side of the screen.

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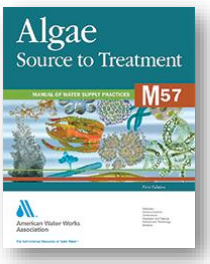
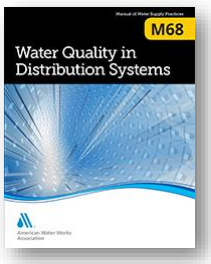
ADDITIONAL RESOURCES

- 2020 Water Quality Conference and Exposition: November 15 – 19, 2020
- M57 Algae: Source to Treatment
  - AWWA catalog no: 30057
- M68 Water Quality in Distribution Systems
  - AWWA catalog no: 30068
- AWWA Water Quality Resource Community
- AWWA Cyanobacteria/Cyanotoxins Resource Community





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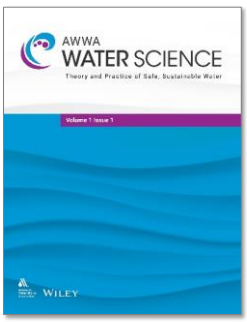

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PRESENTER BIOGRAPHY INFORMATION

Tarrah Henrie is a Senior Scientist, with Corona Environmental Consulting. She has over 16 years of experience solving inorganic and organic drinking water contaminant and regulatory compliance challenges for utilities. For the past several years Tarrah has been leading national and local cyanotoxin related projects.

Elizabeth Crafton is a Source Water Quality Engineer with Hazen and Sawyer. Elizabeth assists utilities across the country by working to increase their source water quality and treatability. Her source water management approach encompasses both short- and long-term practices for a wide variety of issues and risk assessment. Elizabeth received her PhD from the University of Akron where she studied cyanobacteria and cyanobacteria-dominated harmful algal blooms. Her PhD research was funded by the Harmful Algal Bloom Research Initiative through the Ohio Sea Grant. During her PhD research, Elizabeth worked alongside a phycologist and botanist with over 40 years of experience who was also a contributing author for the commonly referenced Freshwater Algae of North America textbook. The duel advisement from both the civil engineering and biology departments provided Elizabeth with an interdisciplinary training and education, which makes her a unique asset for assisting with source water management.

Dr. Adams is the Oliver Parks Professor of Environmental Engineering at Saint Louis University. His group conducts research with the aim to provide guidance on oxidation and sorption processes for drinking water contaminants including cyanotoxins, pharmaceuticals, taste-and-odor compounds, disinfection byproducts, and others. He also works teachs and works in developing nations on water, sanitation and hygiene (WASH) projects.

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