Harmful Algal Blooms and Emerging Contaminants

OTCO Workshop

July 25, 2018

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Ohio Environmental Protection Agency

Outline

- Harmful Algal Blooms (HABs)
  - 2017/18 HAB Monitoring Overview
  - Cyanotoxin Treatment Update
  - Water Treatment Residuals General Permit
- Other Emerging Contaminants
  - Manganese
  - Per- and Polyfluoroalkyl Substances (PFAS)

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2017 HAB Source Water Monitoring Summary

- Microcystins Detected at 43 PWSs (Raw Water)
  - mcyE gene detected at 62 PWSs
  - Gene detections provided early warning
- Saxitoxins Detected at 12 PWSs (Raw Water)
  - sxtA gene detected at 34 PWSs
- Cylindrospermopsin Detected at 1 PWS (Raw Water)
  - cyrA gene detected at 2 PWSs

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2017 Maumee River Blooms Makes National Headlines

Photo Credit: Toledo Aerial Media

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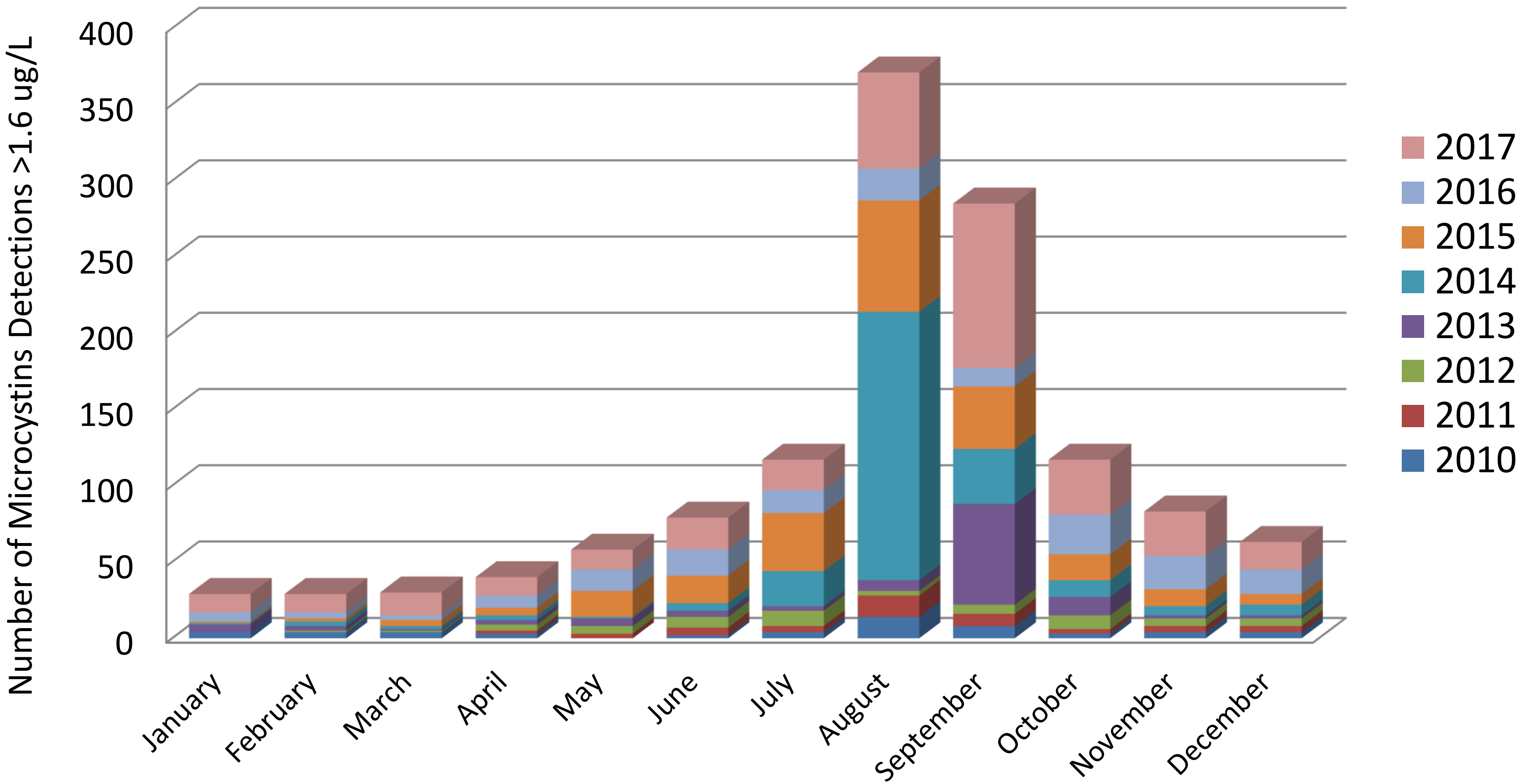
Frequency of Source Water Microcystins Detections > 1.6 ug/L in Ohio



Response Sampling (2010-2015):

- 745 samples >1.6 ug/L microcystins (21%). 44% of samples were > 0.30 ug/L microcystins.

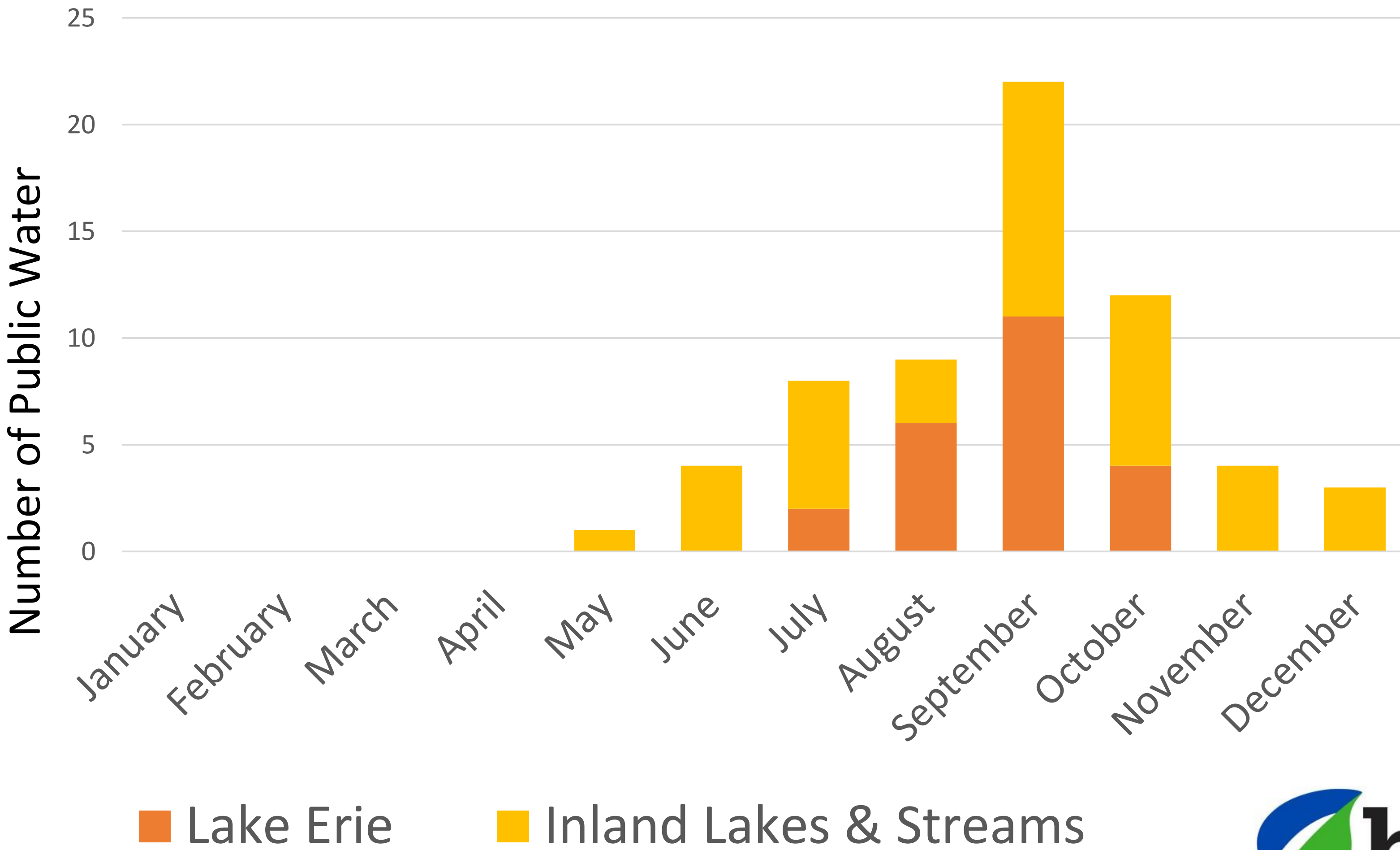
Routine Monitoring (2016):

- 164 samples >1.6 ug/L microcystins (5%). 11% of samples were > 0.30 ug/L microcystins.

Routine Monitoring (2017):

- 357 samples >1.6 ug/L microcystins (10%). 17% of samples were > 0.30 ug/L microcystins.

Maximum Microcytins Detection By Month



Based on Microcystin Detections at 62 Public Water Systems (2010 - 2016)

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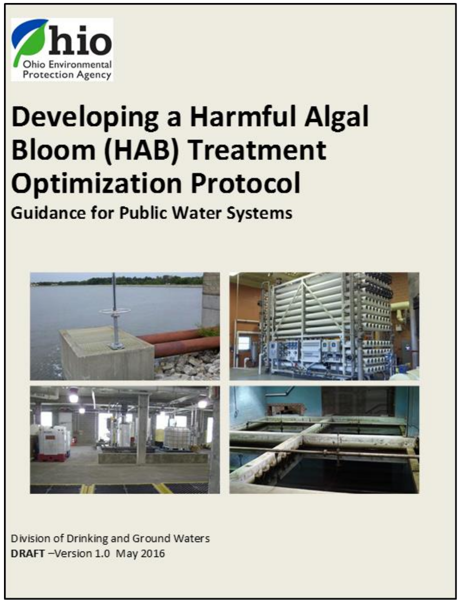
Treatment Update and Guidance

- 71 PWS triggered Treatment Optimization Protocols
  – 19 in 2017
- 19 PWS triggered Cyanotoxin General Plans
  – 13 in 2017

Guidance available: http://epa.ohio.gov/ddagw/HAB.aspx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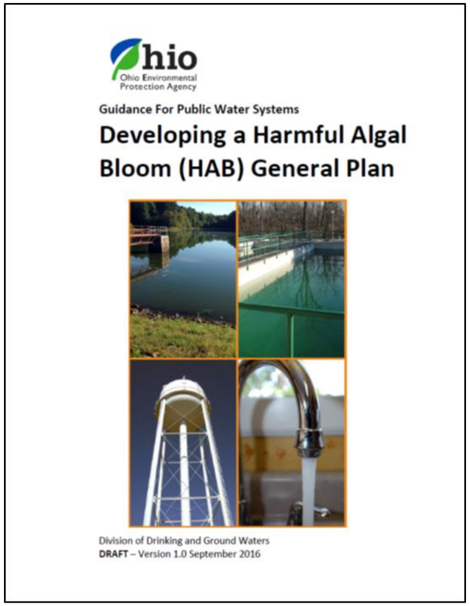
Developing a Harmful Algal Bloom (HAB) Treatment Optimization Protocol

Guidance for Public Water Systems

Division of Drinking and Ground Waters

DRAFT –Version 1.0 May 2016

May 2016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Guidance For Public Water Systems

Developing a Harmful Algal Bloom (HAB) General Plan

Division of Drinking and Ground Waters

DRAFT – Version 1.0 September 2016

September 2016

Recent Finished Water Microsystins Detections

- Finished water detections at two PWSs:
  - 3.5 ug/L (September 2017)
  - 0.48 ug/L (February 2018)
- No drinking water advisories issued!
  - Quick plant optimization resulted in resample and repeat samples below action levels.

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First Finished Water Cylindrospermopsin Detection (2018)

- Detection less than Ohio EPA threshold – USEPA Health Advisory Level
- PAC and Chlorine oxidation insufficient for complete removal
- Water system blended with alternate source water then fully transitioned to alternate source water, resulting in no additional finished water detections.
- No drinking water advisories!

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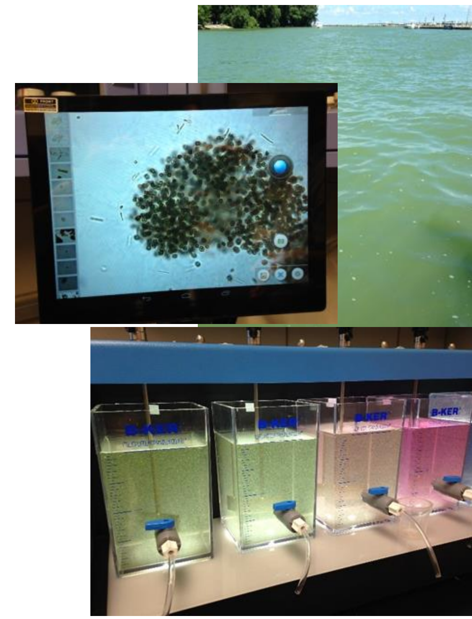
Comprehensive Performance Evaluation (CPE) Approach to Addressing HABs

- Ohio EPA partnered with USEPA & their consultant, Process Applications, Inc.
- Completed 4 pilot HAB CPEs at Ohio public water systems
- Develop protocol for conducting a HAB CPE by modifying existing microbial CPE guidance to address both cyanobacteria cell removal and extracellular cyanotoxins
  - Conduct Special Studies
- Transfer capability to conduct CPEs from USEPA and consultants to Ohio EPA staff
- Provide assistance to PWSs in HAB treatment optimization and general plan guidance



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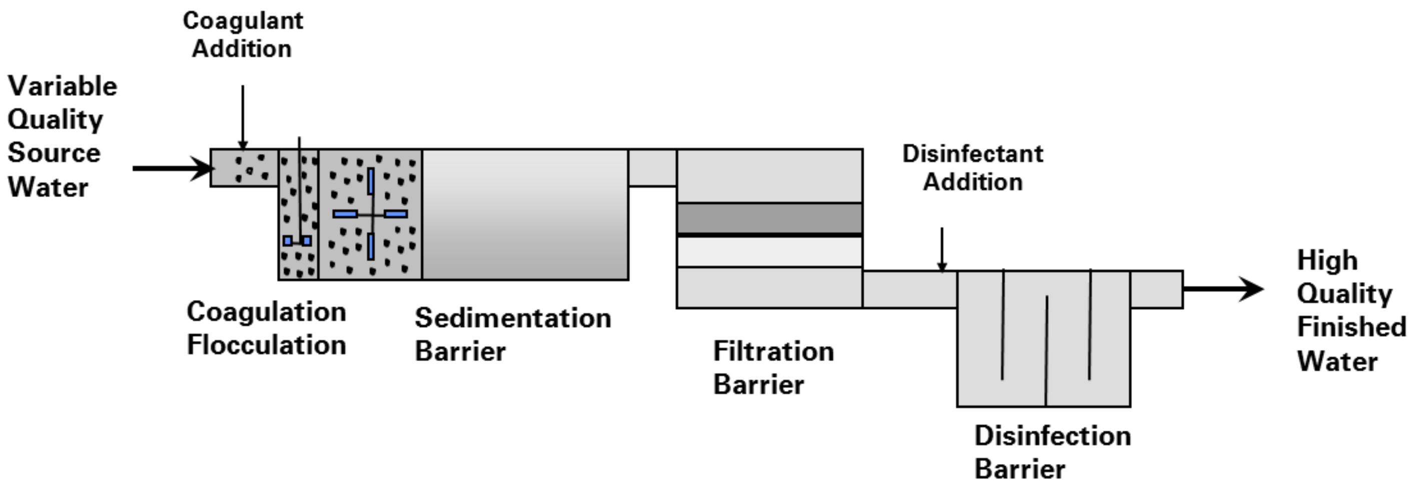
Applying the CPE to Address Cyanotoxins

- Optimize Existing Facilities for cyanobacteria cell removal
  - Majority of cyanotoxins are typically intracellular
  - Avoid/Minimize pre-oxidation and release of cyanotoxins
  - Optimize cell removal through improved coagulation, sedimentation and filtration processes and residuals handling
- Multiple Barrier Approach to achieve action levels for microcystins and thresholds for saxitoxins
  - Identify and assess strategies for extracellular microcystins removal or destruction through adsorption and oxidation processes



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Treatment Optimization: Jar Test Experiments

- Conduct experiments to assist with site-specific treatment optimization
  - 12 Jar Tests
  - 2 Hold Time Studies
- Simulate HAB conditions by concentrating cyanobacteria in raw water using phytoplankton net and spiking PWS raw water with concentrated biomass
- Compare "Real-World" data to lab data and published studies
- Inform USEPA guidance

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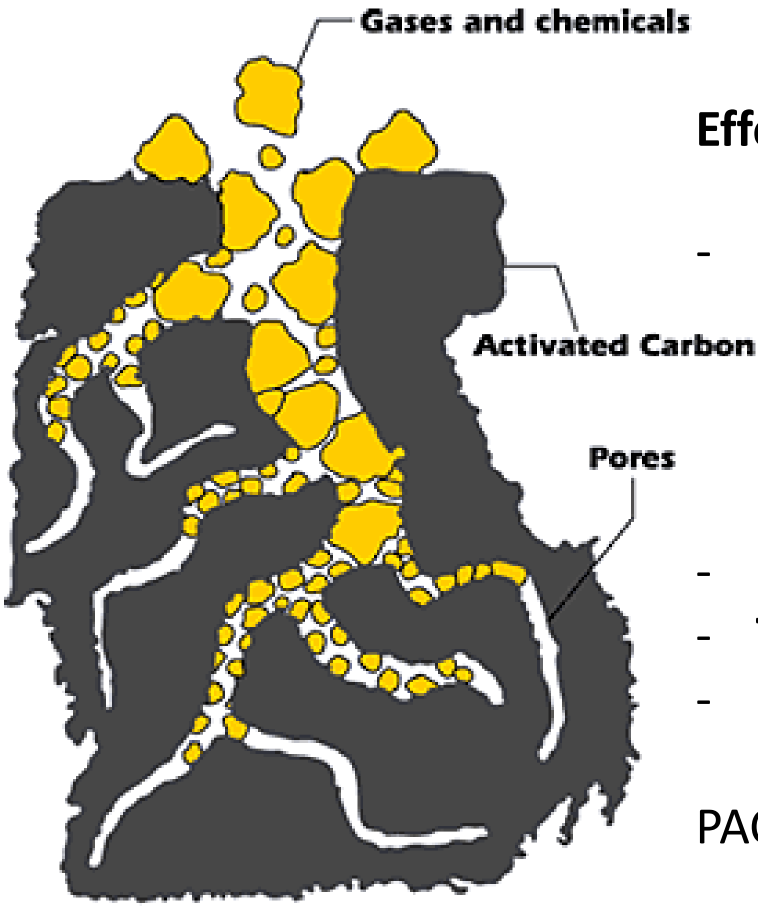
Powdered Activated Carbon (PAC)



Effectiveness varies based on:

- **Size of Pores (related to carbon source)**
  - **Mesopores** (wood based) – microcystins (variant differences)
  - **Micropores** (coconut based)- saxitoxins and taste & odor compounds
- **Dose**
- **Time**
- **Natural Organic Matter** (NOM) Interference

PAC Doses in excess of 40 mg/L often needed

Micropores: d <2.0 nm
Mesopores: 2.0 nm < d < 50.0 nm
Macropores: d > 50.0 nm

Microcystin-LR:
1.2 < d < 2.6 nm

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Estimating Dosages of PAC

TABLE II. Comparison of Freundlich isotherm parameters of *Microcystis* and *Oscillatoria* toxins adsorbed by different kinds of activated carbons

Activated Carbon	Microcystis Toxins[a]		Oscillatoria Toxins[a]	
	K_f	$1/n$	K_f	$1/n$
Wood GAC	501.2	0.36	15.5	0.99
Calgon coal GAC	512.9	0.36	83.2	0.53
Culligon coal GAC	126	0.57	2.0	1.24
Coconut GAC	331.1	0.44	12.6	1.1
Nonactivated GC	2.1	1.3	1.48	1.4
Wood PAC	6309	0.56	1259	0.9
Calgon coal PAC	3630	0.9	955	2
Coconut PAC	1259	1	1000	1

[a] K_f, adsorption capacity in $(\mu g/g)(L/\mu g)^{1/n}$; $1/n$, adsorption intensity.

Mohamed et al., "Activated Carbon Removal Efficiency of Microcystins in an Aqueous Cell Extract of Microcystis aeruginosa and Oscillatoria tenuis Strains Isolated from Egyptian Freshwaters," Env. Tox., 15(5), 197-201, 1999.

EXAMPLE: Estimating Dosages of PAC Using Isotherm Equations

Example 1

Assume:
-Wood PAC
-Initial MC-LR conc. = 50 μg/L
-Final MC-LR conc. = 1 μg/L
-No NOM competition

$q = 6309\ Cf^{0.56} = 6309(1)^{0.56}$
$q = 6309$ μg/g
Dose = (50 μg/L – 1μg/L)/6309
Dose = 0.0077 g/L = 7.7 mg/L

Example 2

Assume:
-Coconut PAC
-Initial MC-LR conc. = 50 μg/L
-Final MC-LR conc. = 1 μg/L
-No NOM competition

$q = 1259\ Cf^{1.0} = 1259(1)^{1.0}$
$q = 1259$ μg/g
Dose = (50 μg/L – 1μg/L)/1259
Dose = 0.0389 g/L = 38.9 mg/L

q determined using published isotherm data on adsorption capacity and adsorption intensity

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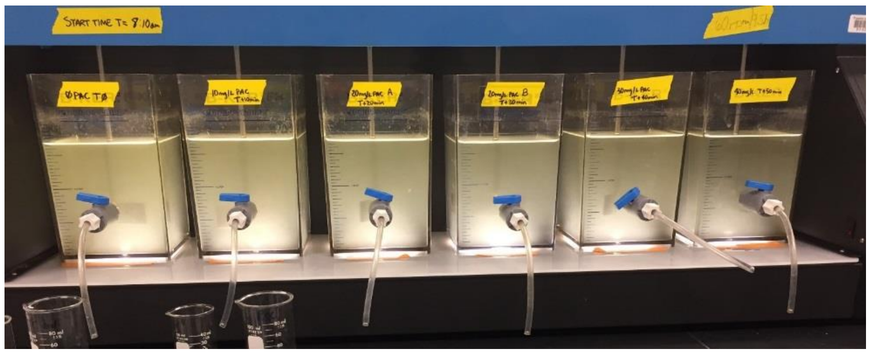
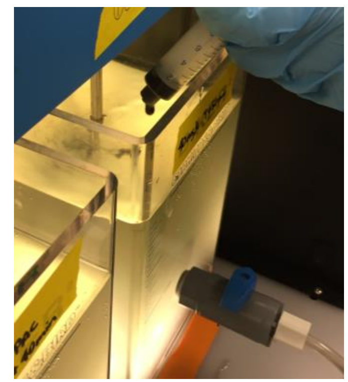
Carbon Dose and Contact Time Impact on Microcystins Adsorption

4 PAC Doses (plus control and duplicate), 5 Time Steps



Control No PAC → Increasing PAC Dose → **40 mg/L PAC**



Challenge Water: Simulated bloom by concentrating cyanobacteria in raw water using phytoplankton net, lysing concentrate using freeze/thaw, and adding concentrate to raw water

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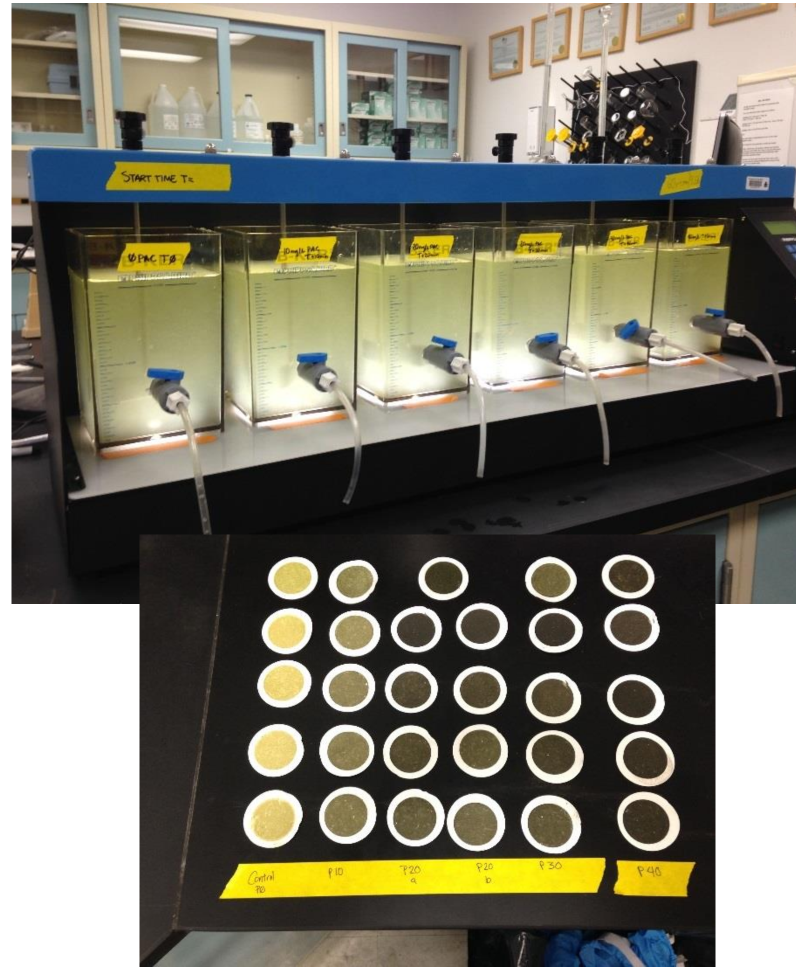
PAC Jar Testing

- Coal-based PAC added at raw water pump station
- 9.5 hour travel time to WTP
- Determine adsorption capacity at various PAC doses
- Plant dose ~ 17 mg/L of PAC
- Microcystins Dose:

  Total 23 ug/L

  Extracellular 11 ug/L



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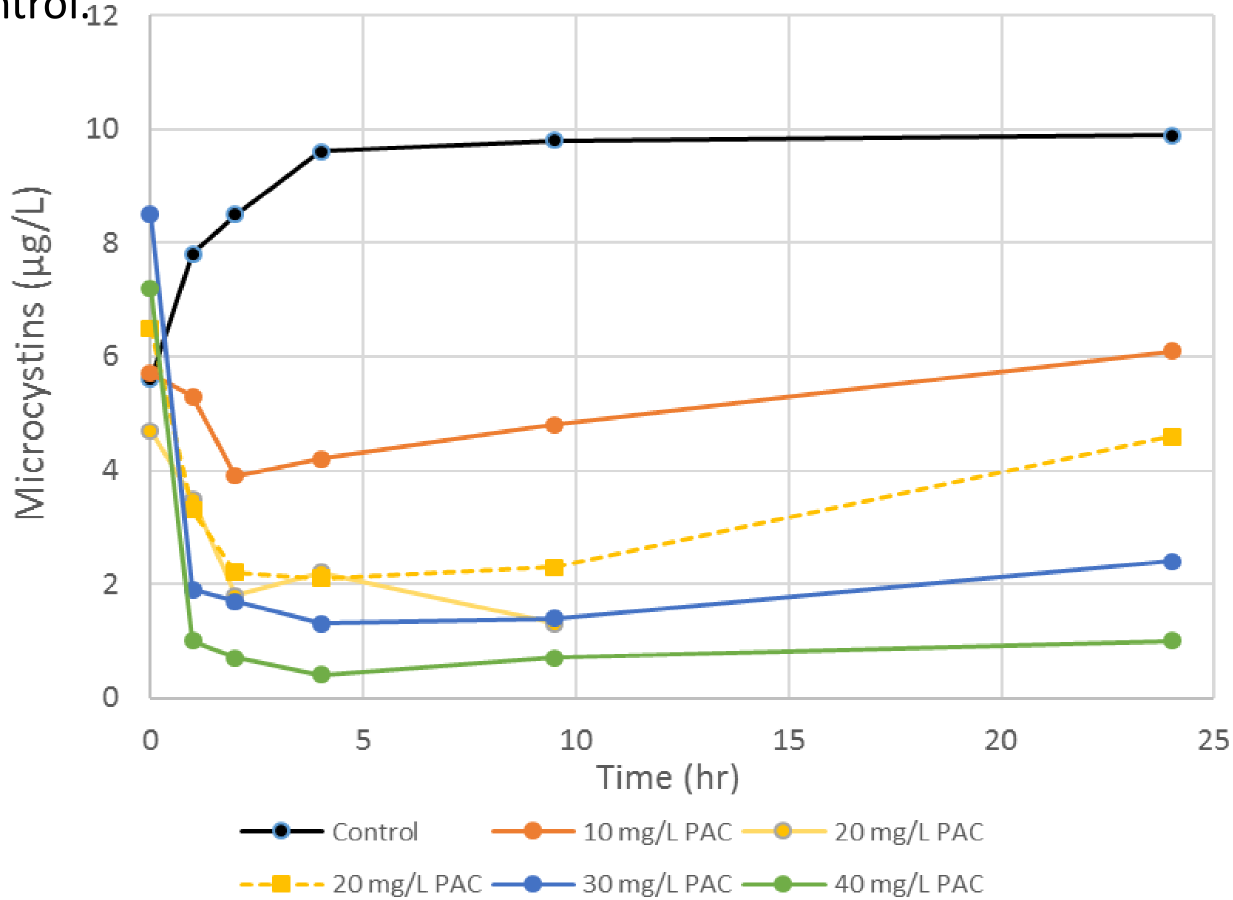
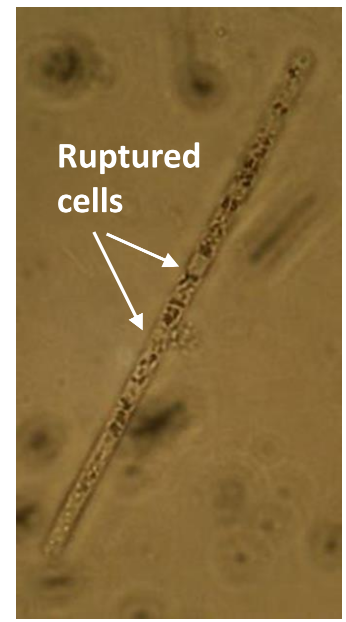
PAC Dose Study Results

- Increasing PAC dose improved microcystins removal, but even highest dose did not achieve total removal. <u>Isotherm equation estimated only 2.5 – 9.4 mg/L PAC needed to reduce 10 ug/L to 1 ug/L microcystins.</u>
- Most removal occurs during first four hours of contact time.
- Unexpected high variability between jars and increase in extracellular microcystins in control.





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Carbon Type (Coal vs. Wood), Dose, and Treatment Chemical (alum & lime) Impact on Microcystins Adsorption

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Jar Test Setup

Jar Set	PAC Dose	Alum	Lime
	mg/L	mg/L	mg/L
Control	0	0	0
	0	20	120
Low Carbon	10	0	0
	10	20	120
High Carbon	40	0	0
	40	20	120

Evaluated both wood and coal-based PAC

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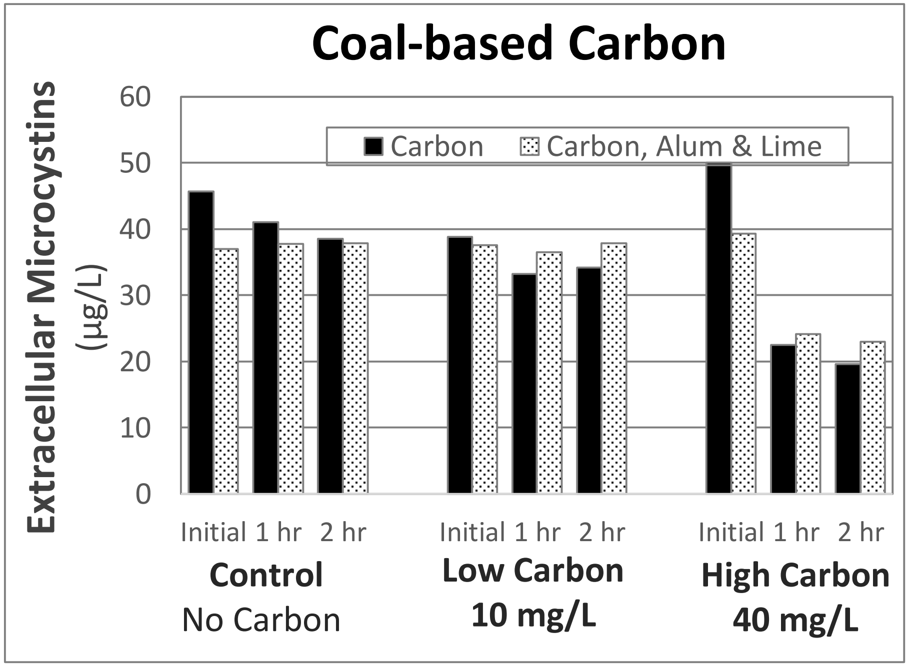
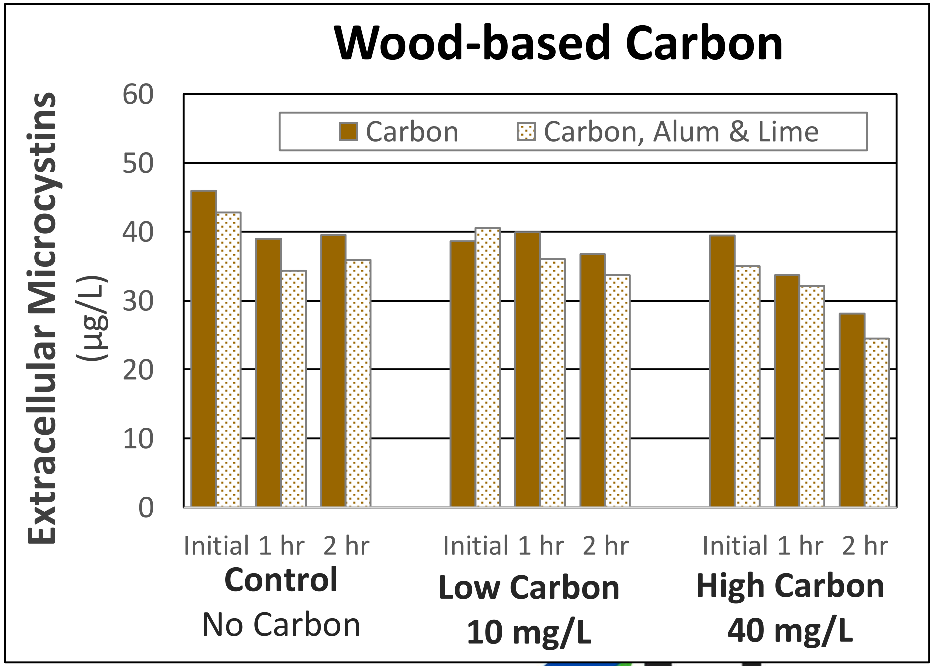
PAC Type, Dose, and Treatment Chemical Study Results

- PAC Dose Impacted Microcystins Reduction:
  - No appreciable microcystins reduction at 10 mg/L
  - Highest reduction at 40 mg/L
    - Coal PAC had higher adsorption than wood in this study
- No appreciable difference between PAC only and PAC + Alum & Lime





<u>Isotherm equation estimates (40 ug/L to 1 ug/L):</u>

Coal PAC: 11 mg/L; Wood PAC: 6 mg/L

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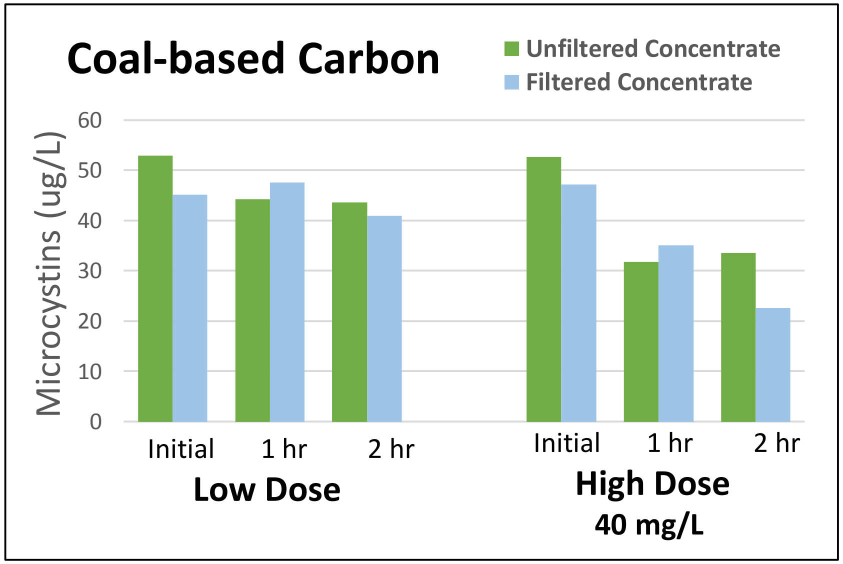
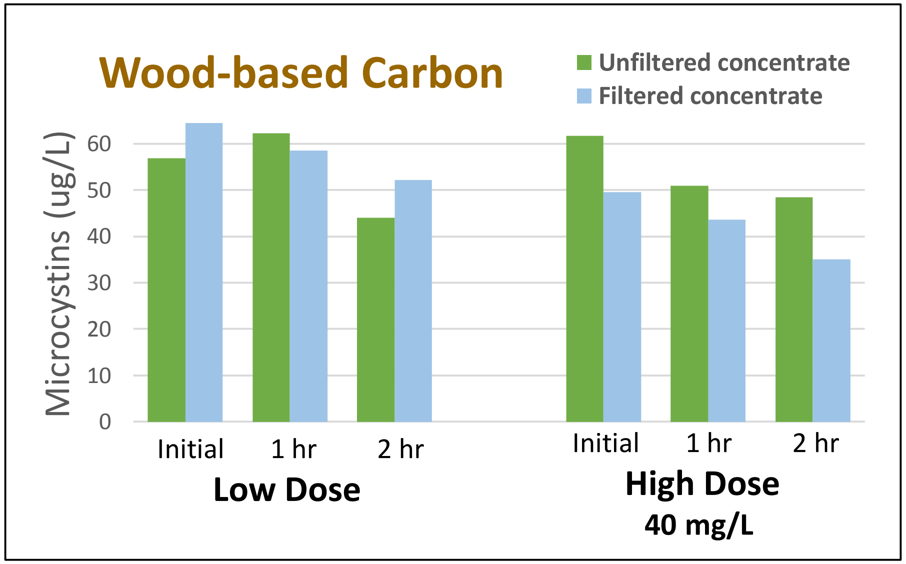
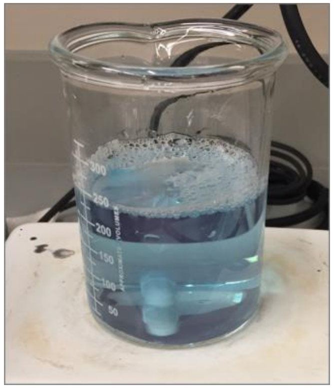
Evaluate Filtered vs Unfiltered Concentrate Spike, Carbon Types (Coal & Wood), and Dose (10 & 40 mg/L)

Coal test DOC range: 11.4—13.1 mg/L





Unfiltered Concentrated Spike Solution



Filtered Concentrated Spike Solution

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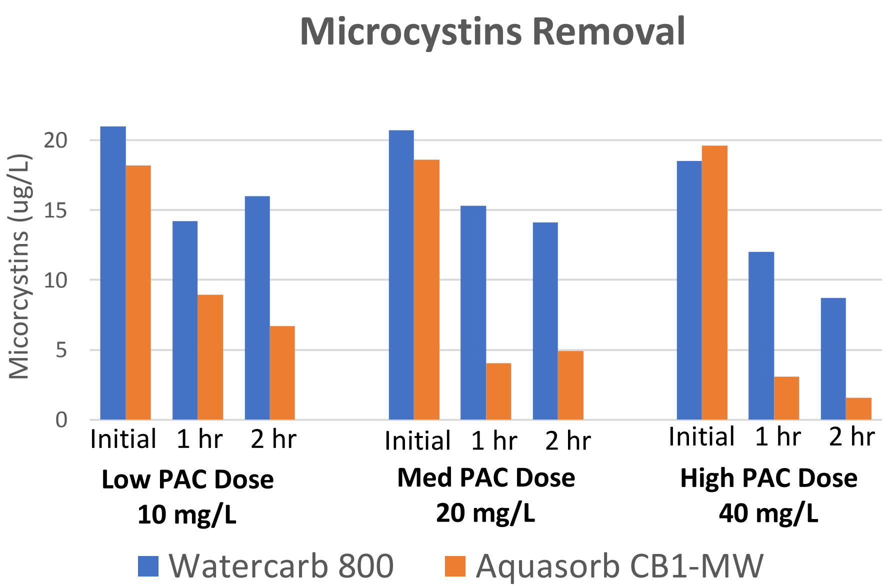
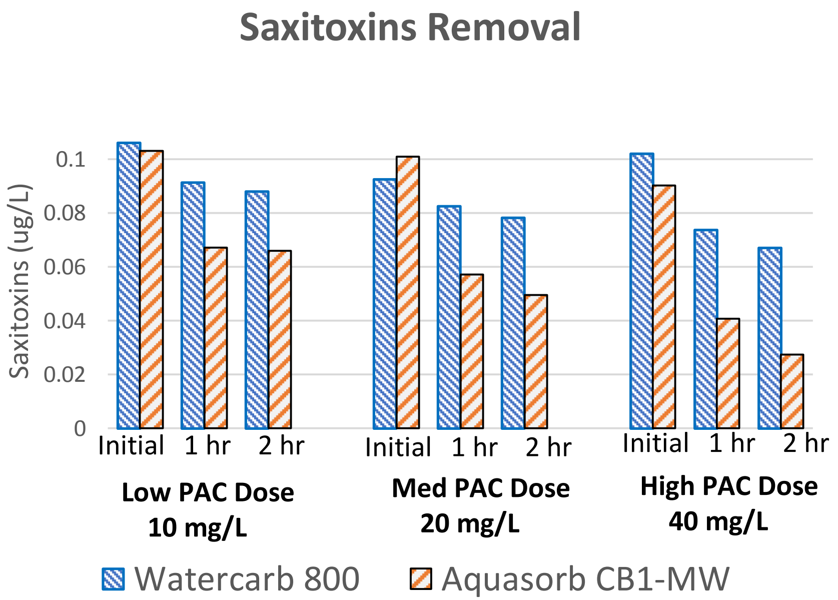
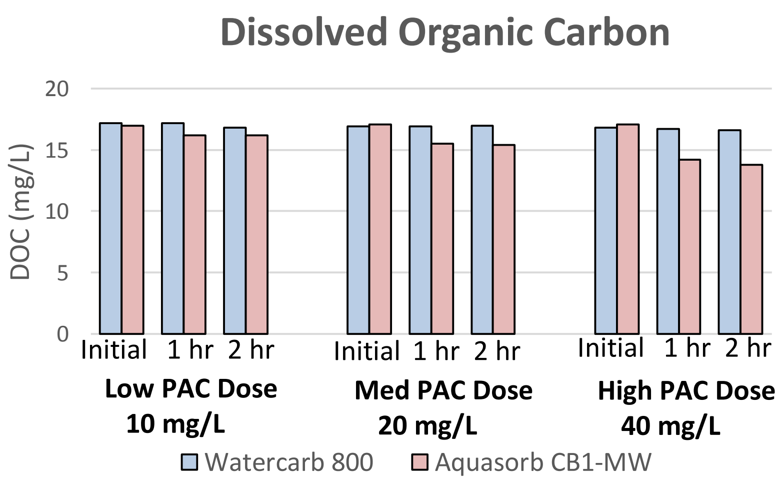
Evaluate Impact of PAC Type and Contact Time on Removal of Microcystins, Saxitoxins, and DOC





WaterCarb 800:
Coal Blend

Aquasorb:
Wood/Coal/Coconut Blend



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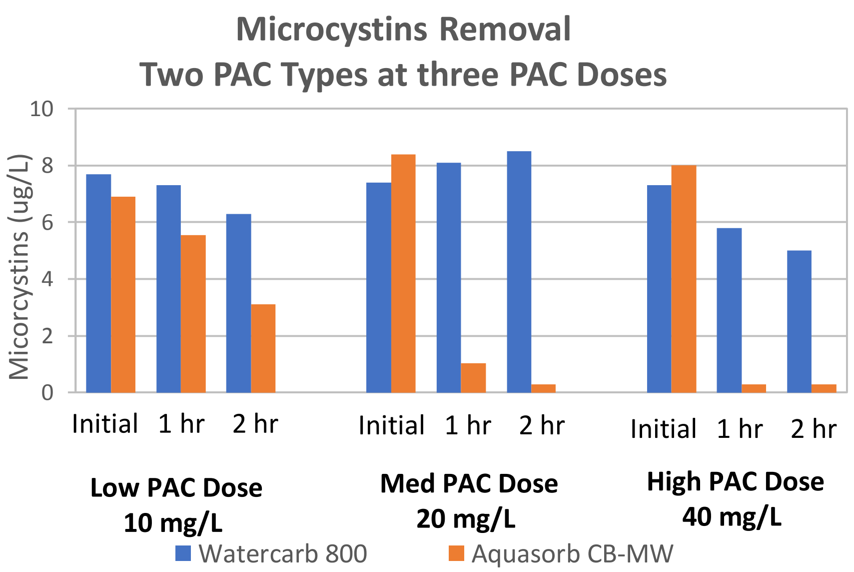
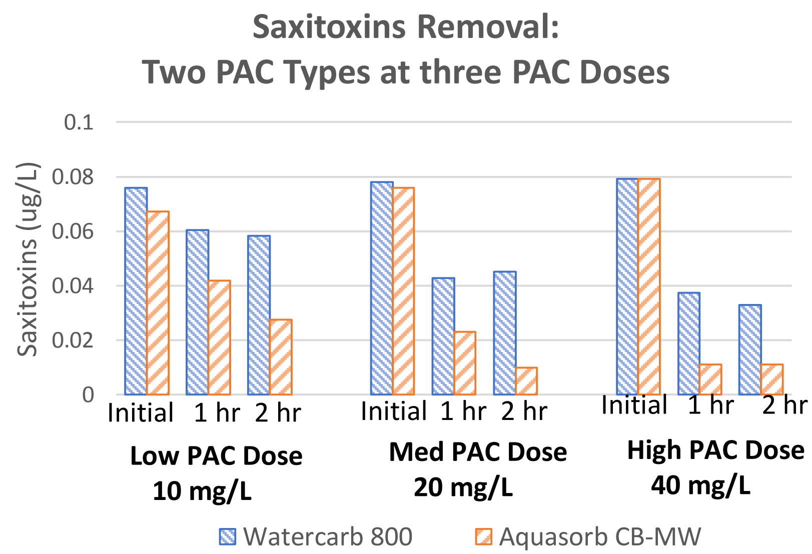
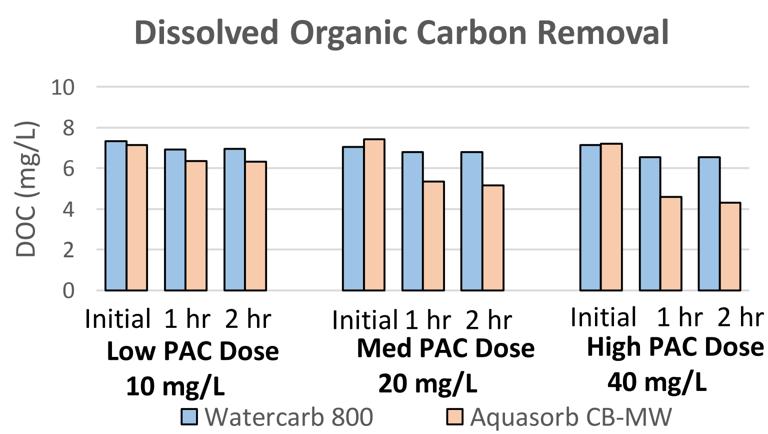
Evaluate Impact of PAC Type and Contact Time on Removal of Microcystins, Saxitoxins, and DOC (Raw Water, No Spike)







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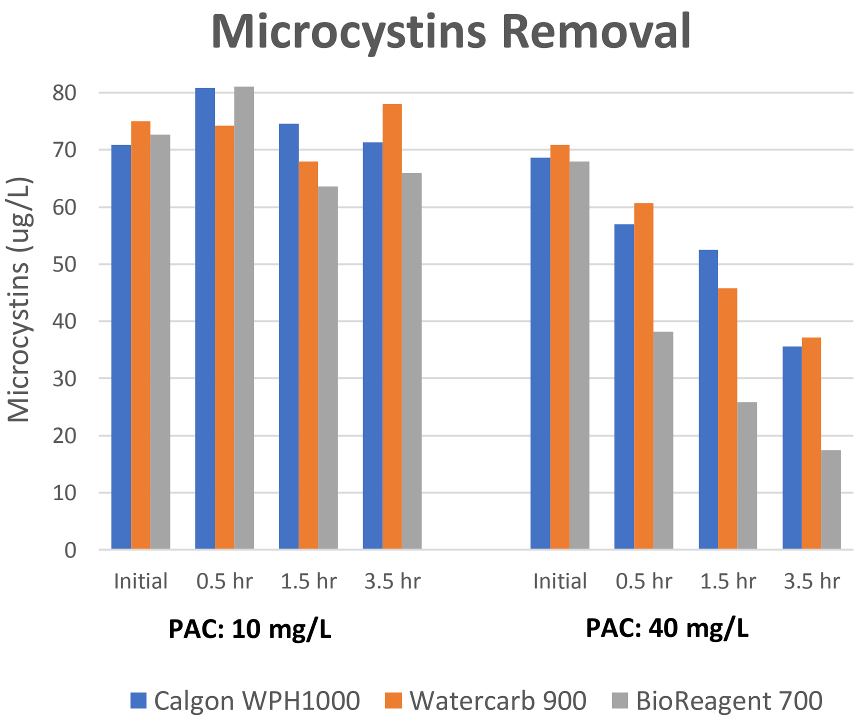
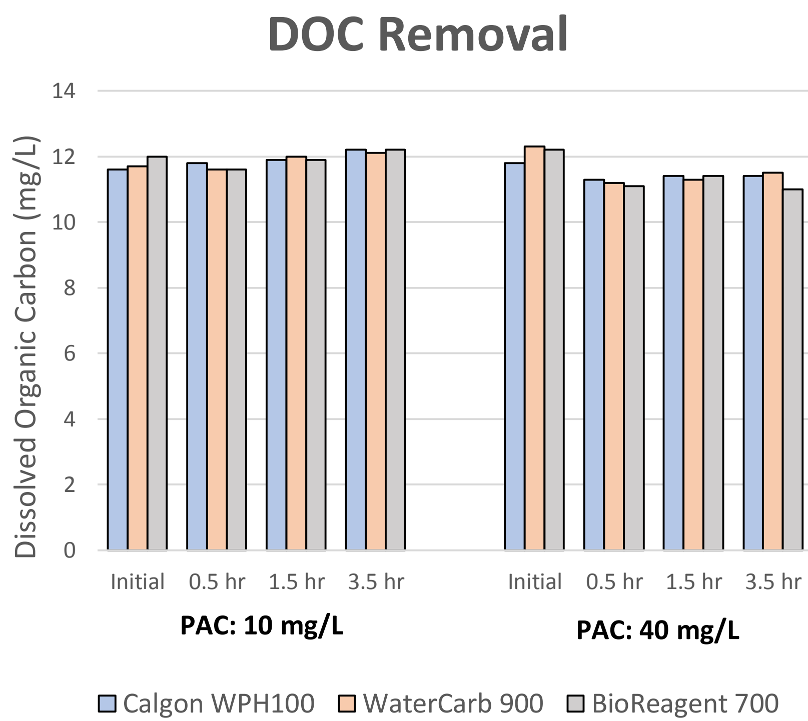
High Microcystins Challenge
Evaluate Removal of Microcystins and DOC from Lake Erie 2017 Harmful Algal Bloom





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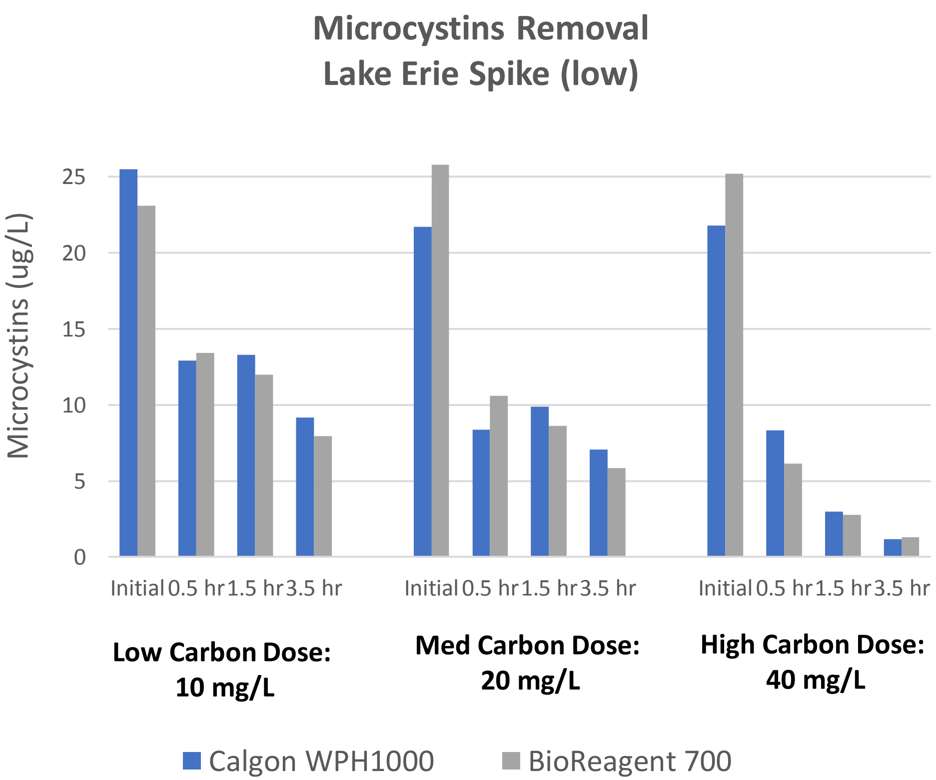
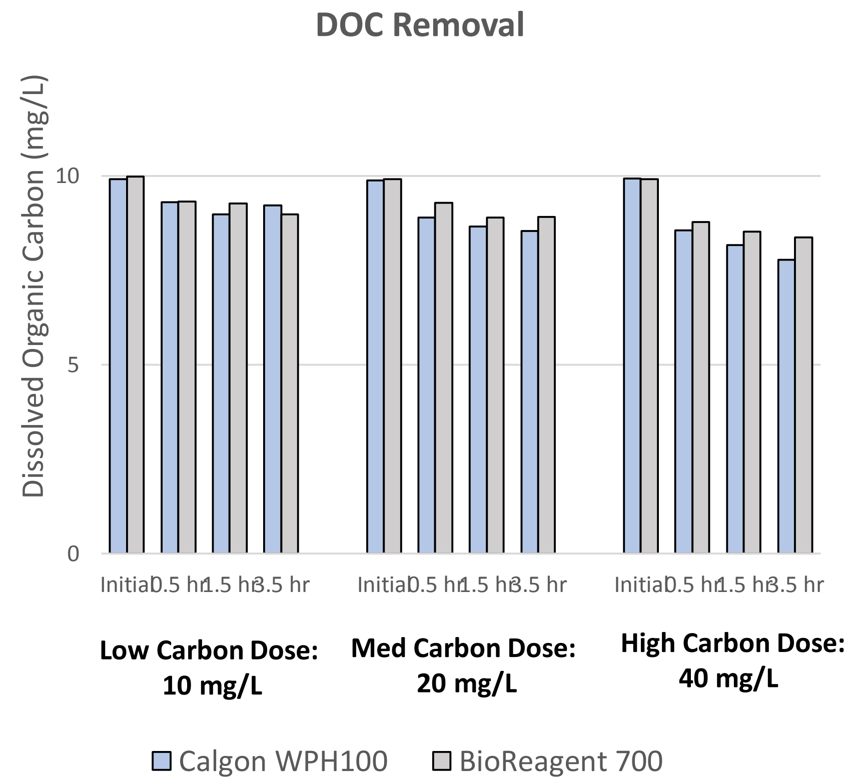
Moderate Microcystins Challenge

Evaluate Removal of Microcystins and DOC from Lake Erie 2017 Harmful Algal Bloom





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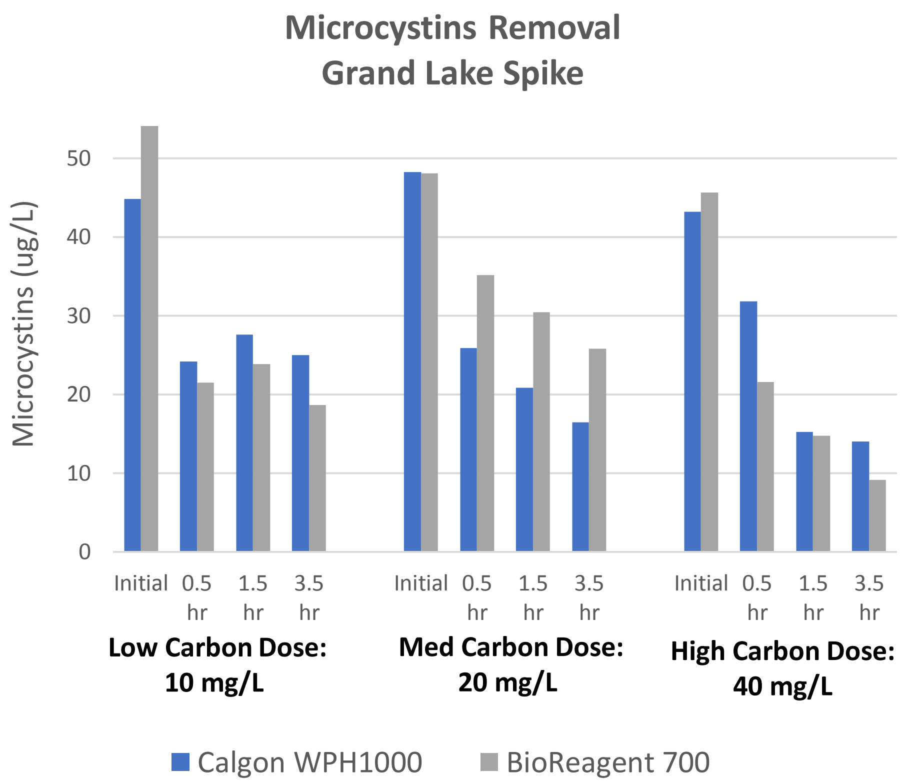
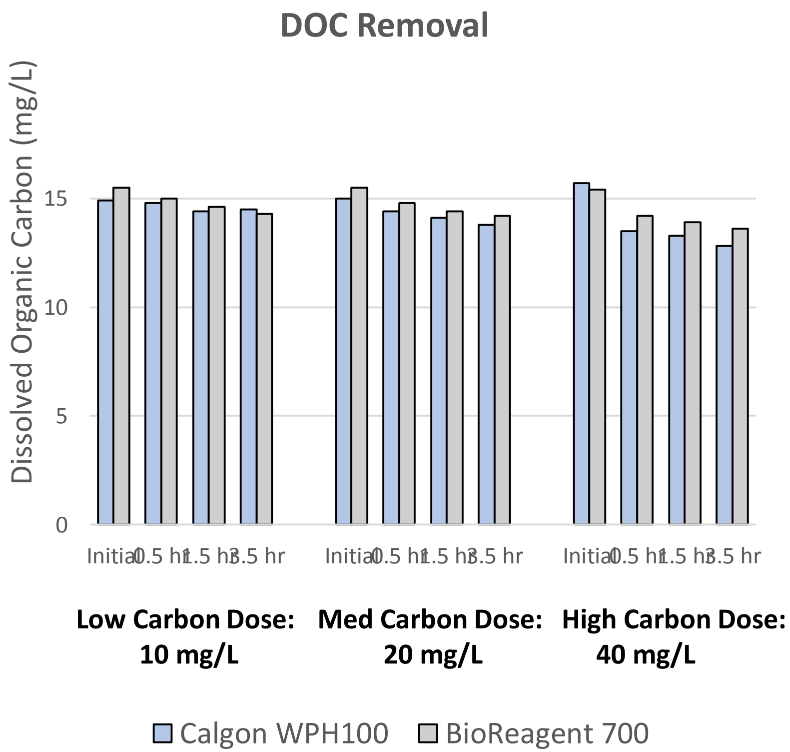
High Microcystins Challenge
Evaluate Removal of Microcystins and DOC from Grand Lake 2017 Harmful Algal Bloom





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Preliminary Natural Organic Matter (NOM) Effect Data

Slides courtesy:
Asnika Bajracharya

The Ohio State University
Environmental Engineering Graduate Research Assistant

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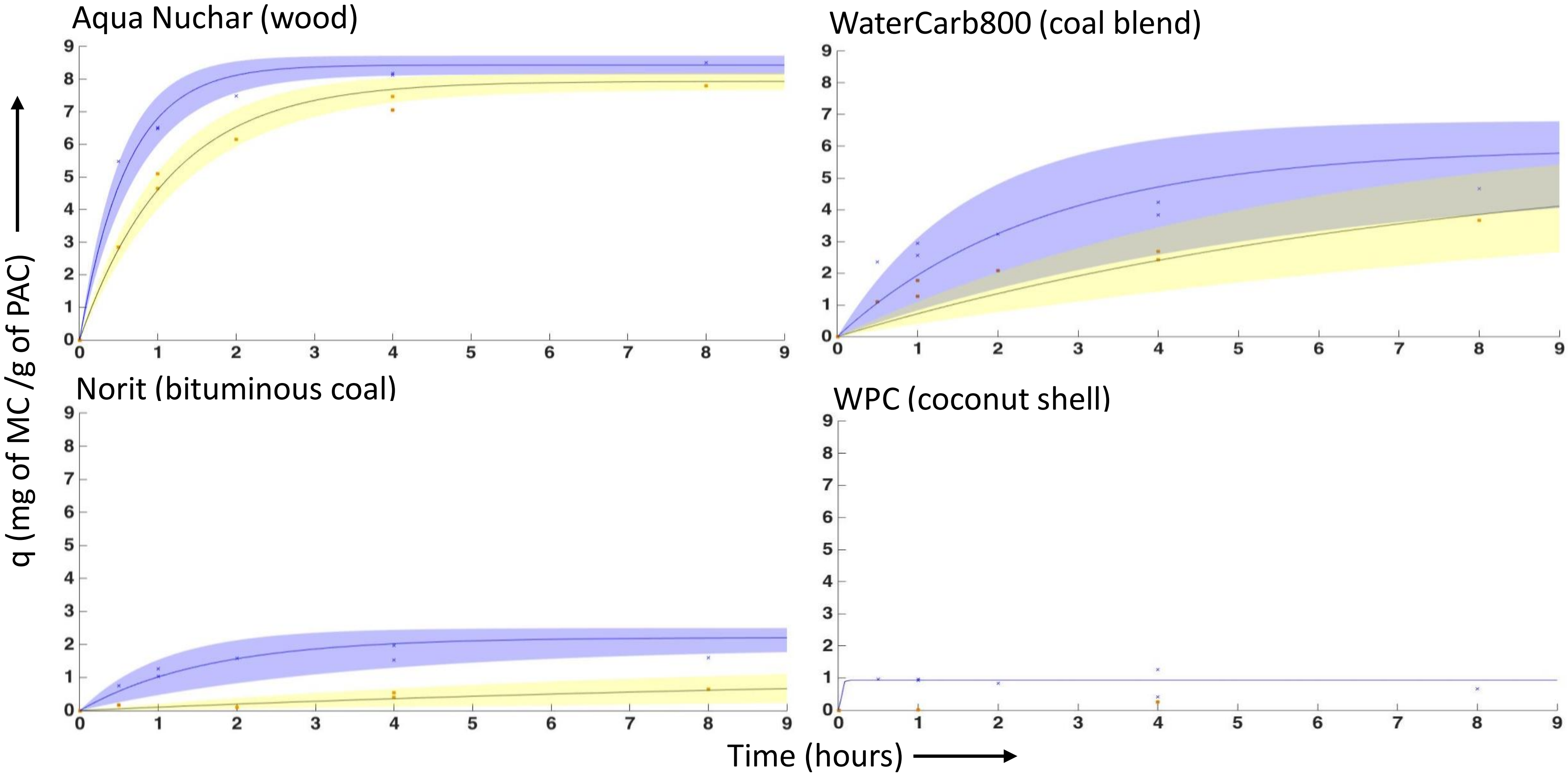
NOM Type Effect (vs. ≅ 5ppm)



Slide courtesy:

Asnika Bajracharya, OSU

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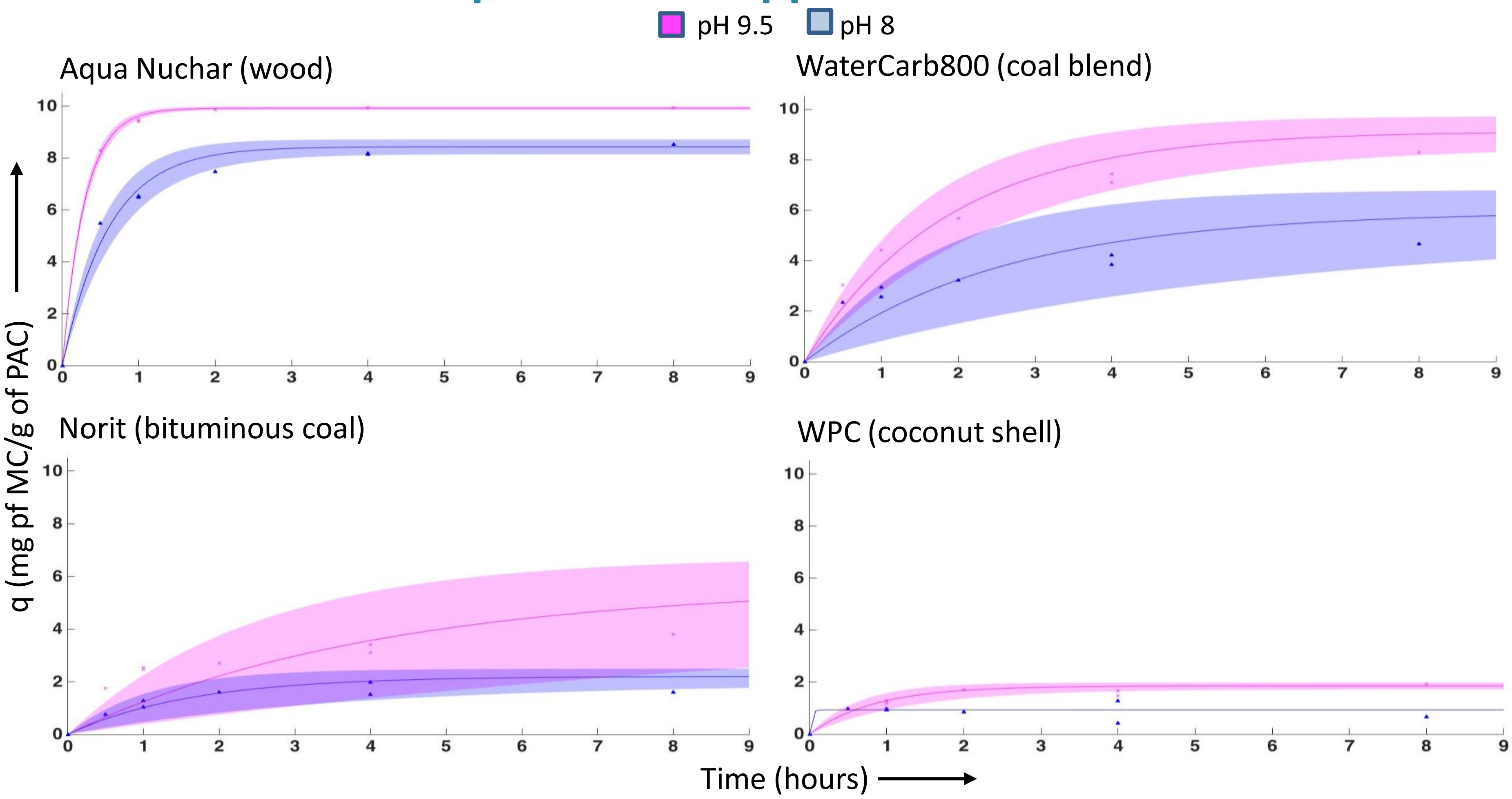
pH Effect at 5ppm of NOM



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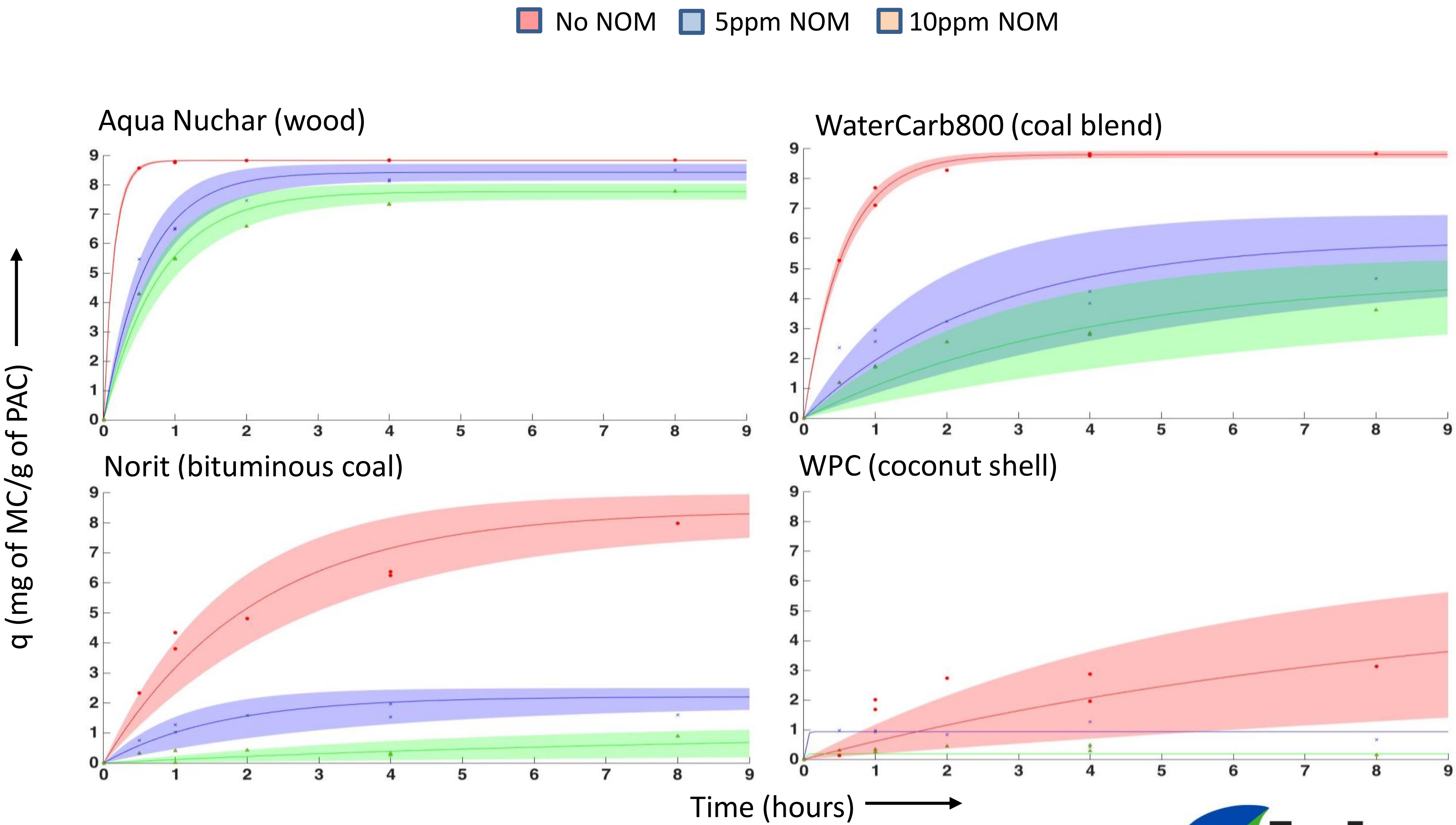
Asnika Bajracharya, OSU

NOM Concentration Effect



Slide courtesy:

Asnika Bajracharya, OSU

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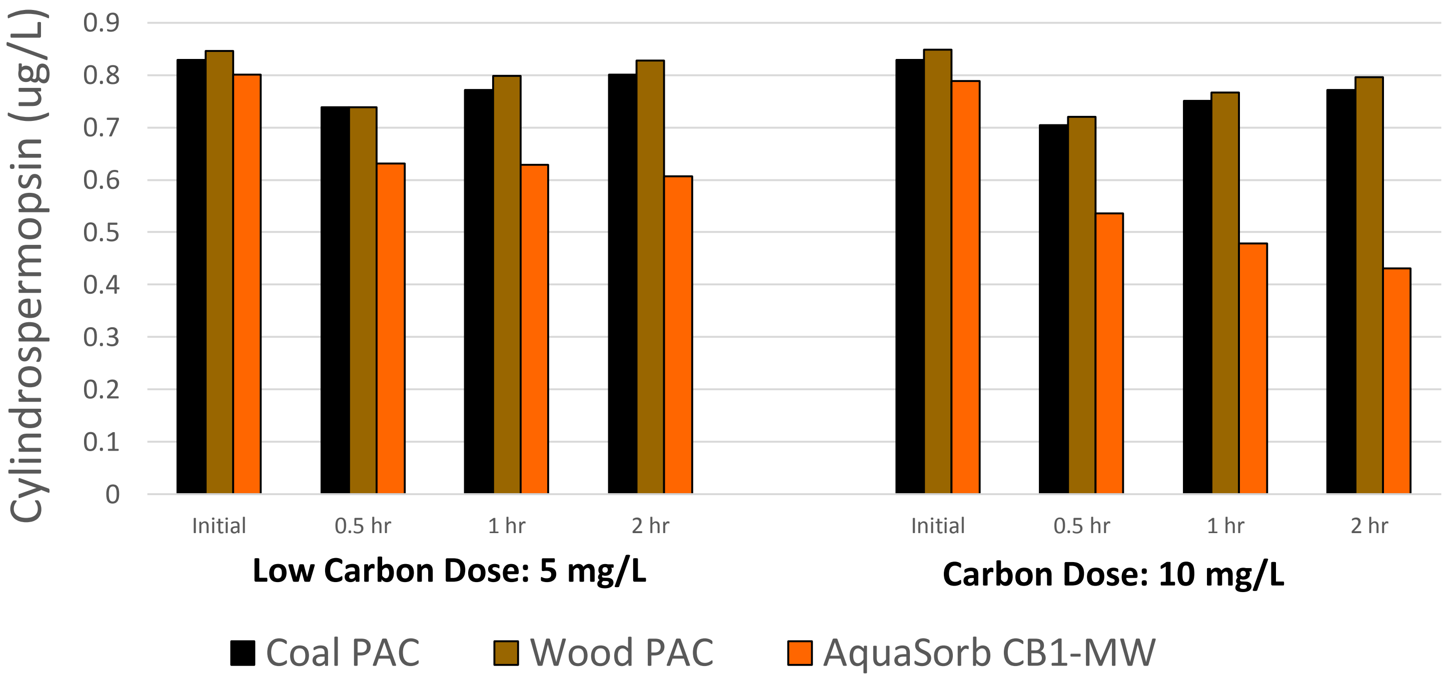
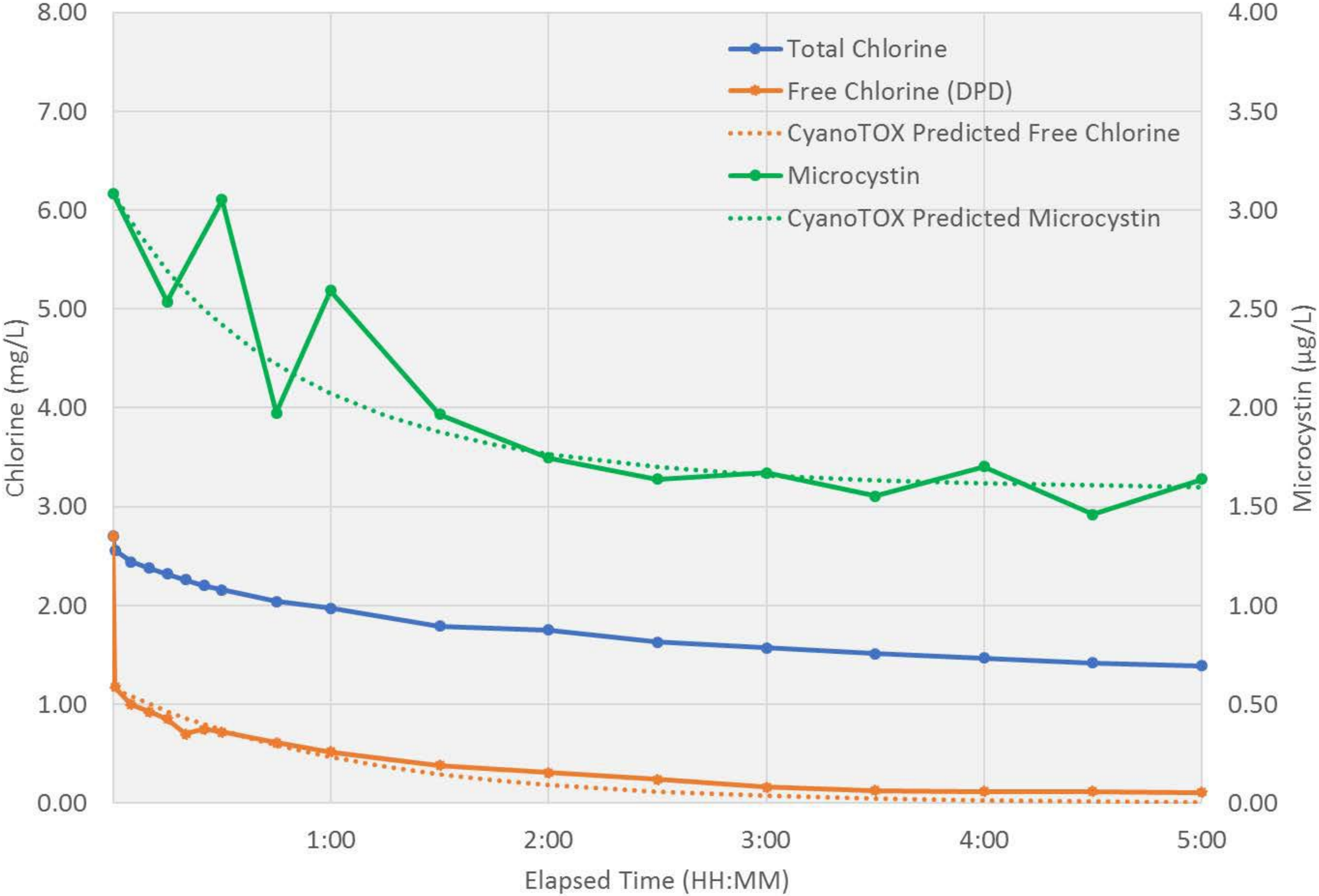
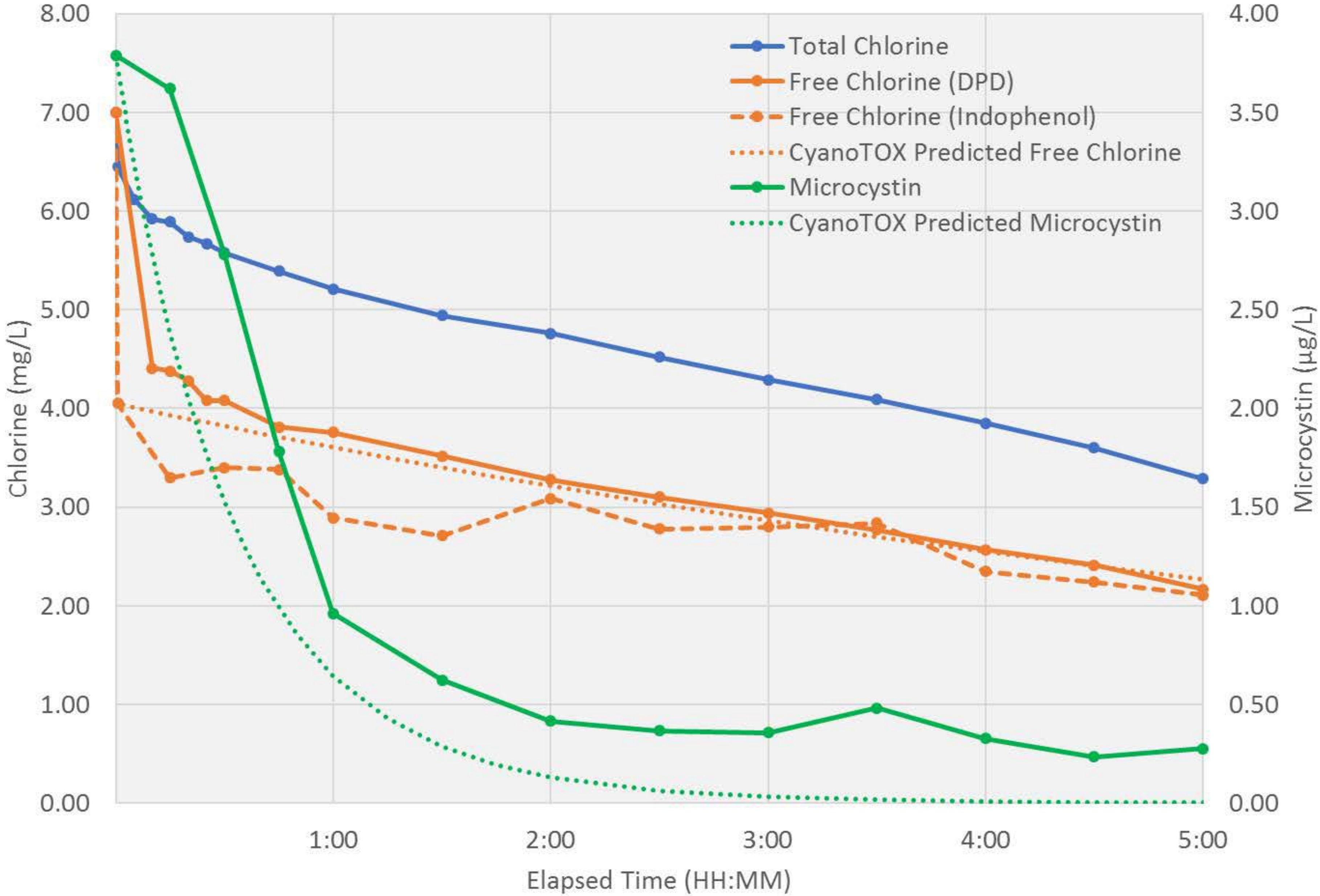
Evaluate Removal of Cylindrospermopsin With Three Different PAC Types and Two PAC Doses



Microcystins Chlorine Oxidation Study #1



Microcystins Chlorine Oxidation Study #2



Special Study Results Summary

- **Cyanotoxin removal estimated by jar tests is less than removal estimated by isotherm equations**
  - Potential impact of NOM/DOC
- Variable removal based on source of microcystins (different variants)
- Alum & lime did not impact PAC performance (one study)
- Blended coal/wood/coconut PAC performed well (OEPA Studies) and wood performed well (OSU Study) for microcystins adsorption
- **AWWA CyanoTOX calculator overestimated chlorine oxidation of microcystins.** Consider applying safety factor of 2 (one study- follow-up studies planned for this summer)

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Treatment Optimization: Next Steps

- Conduct additional hold time studies and jar tests, as needed
- Provide concentrated challenge water to PWSs
- Compare "real-world" experimental results to published isotherm data, AWWA Cyanotox Calculator, and results from OBHE funded research projects
- Develop modified Ohio EPA HAB CPE approach and consider offering to additional HAB impacted Ohio PWSs
- Revise guidance documents (partner with Ohio Section AWWA on White Paper revision)

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Microcystins Accumulations in Water Treatment Residuals (WTR)

Initial Findings

- Microcystins were detected in all WTR samples, regardless of WTR age.
- LC-MS analysis confirmed presence of microcystins variants in samples analyzed by ELISA.
- In general, microcystins concentrations in WTR were greater than concentrations in raw water.

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Microcystins Accumulations in Water Treatment Residuals: NEXT STEPS

Ohio Board of Higher Education HAB Grant:

- Further evaluate extraction and analytical methods for determining concentrations of microcystins in WTR
- Determine fate of microcystins in WTR
- Evaluate potential for plant uptake

Ohio EPA Lab:

- Finalize microcystins-ADDA ELISA method for WTR (DES Method 701.3)
- Analysts certified in water matrix ELISA method can perform analysis of WTR
- Requires determination of percent solids

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Microcystins Accumulations in Water Treatment Residuals: NEXT STEPS

Ohio EPA Division of Materials Waste Management:

- Addressing interested party comments to develop water treatment plant residuals beneficial reuse general permits:
  - Land application for agricultural benefit as a liming material
  - Land application in a soil blend
- Current LAMP Permits
  - When current LAMP Permits expire transition/apply for coverage under OAC 3745-599 (rules effective March 31, 2017)
  - 180 Days prior to expiration of LAMP apply for new permit
  - Maintain current operations until general or individual permit is issued

See Tomorrow's Ohio EPA Presentation!

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Emerging Contaminants

- Knows and unknowns
  - HABs
  - Per- and Polyfluoroalkyl Substances (PFAS)
  - Manganese
  - [fill in the blank]
- Expectations have changed after Toledo and Flint
- Need regulatory programs to evolve, focused research and innovation to meet challenges
- Role of Asset Management and Source Water Protection

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UCMR 4

(Unregulated Contaminant Monitoring Rule – 4th round)

- Monitoring begins 2018; Ends 2020
- All PWS >10,000; 1600 randomly selected PWS <10,000
- Monitoring Schedules in USEPA's Central Data Exchange (CDX): 10 cyanotoxins and 20 other
- epa.gov/dmucmr/fourth-unregulated-contaminant-monitoring-rule

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Manganese Strategy/Rule Development

- Developed a policy on addressing the HAL and secondary MCL issues with Manganese
- Coordinating with Ohio Department of Health
- Releasing an iron and manganese technical paper and fact sheet with the policy
- Will use strategy to develop/revise rules
- <u>Early Stakeholder Outreach began 5/29/18</u>

http://epa.ohio.gov/Portals/28/documents/rules/proposed/ESO_Manganese2018.pdf

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Per- and Polyfluoroalkyl Substances (PFAS)

- A broad family of synthetic organic chemicals first developed by 3M in the late 1940s and used worldwide since the 1950s
- The most common specific PFAS are PFOS and PFOA
- Benchmarking with other states to identify the industry types and potential sources

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PFAS Uses

Industry

- Many are used as surfactants
- Good for reducing friction, and are used in industries such as aerospace, automotive, construction, and electronics
- Aqueous film forming foam (AFFF) for fighting petroleum-based fires

Consumer Products

- Non-stick cookware and food packaging
- Soil-, stain-, water-resistant in homes, shoes, and clothing

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Known Ohio PFAS Contamination Sites

- DuPont/Chemours Washington Works Plant, Parkersburg, WV
- Newport Volunteer Fire Department
- Wright Patterson Air Force Base
- Dayton Fire Training Center
- Toledo Air National Guard Base

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PFAS

- May 22-23, 2018 National Leadership Summit
- Key issues:
  - Address as class vs individual
  - Conflicting state numbers
  - Analytical methods
  - Communicating unknowns and risk to the public

OEPA Director Craig Butler providing State's perspective at PFAS Summit 5/22/18

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PFAS - USEPA's Four-Step Action Plan

1. Initiate steps to evaluate the need for a maximum contaminant level (MCL) for PFOA and PFOS.
2. Begin the necessary steps to propose designating PFOA and PFOS as "hazardous substances" through one of the available statutory mechanisms, including potentially CERCLA Section 102.
3. Develop groundwater cleanup recommendations for PFOA and PFOS at contaminated sites and will complete this task by fall of this year.
4. Develop toxicity values for GenX and PFBS.

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PFAS

- Working with U.S. EPA and other states through participation on the ASDWA PFAS Workgroup and discussion on risk communication through ECOS
- Developing agency PFAS response strategy
- Ohio EPA’s laboratory has developed the capability to quantify PFOS and PFOA in drinking water samples and working on other media methods

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Future Activities

- Rule Implementation
- Integration of Asset Management -**Umbrella**
- Re-vision SWAP Program
- Certified Operator Workforce Summit (fall 2018)
- Administration transition
  - Drinking water will likely remain a priority
  - Strategic planning and transition documents

Training Opportunities

OSU Stone Lab (Gibralter Island)

- Algae ID (August 6-7)
- Dealing with Cyanotoxins and Taste and Odor Compounds (August 8-9)
- https://ohioseagrant.osu.edu/education/stonelab/courses/workshops

North America Lake Management Society National Conference "Innovations in Lake Management"

- Partnering with Ohio Lakes Management Society
- Cincinnati, Ohio
- October 30 –Applied Workshops
- October 31 through November 2 – Technical Sessions
- https://www.nalms.org/nalms2018/

HABs State of the Science Conference

- Toledo, Ohio
- September 13

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Questions?

www.epa.ohio.gov/ddagw/HAB.aspx

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