Ohio EPA HAB Update

OTCO Workshop

March 7, 2018

Heather Raymond
Ohio EPA HAB Coordinator

Ohio Environmental Protection Agency

Ohio EPA HAB Update

- 2017 HAB Monitoring Overview
- Cyanotoxin Treatment: Treatment technique rule requirements, CPE update, jar test results, University research
- Water Treatment Residuals
- Reservoir Management

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2017 HAB 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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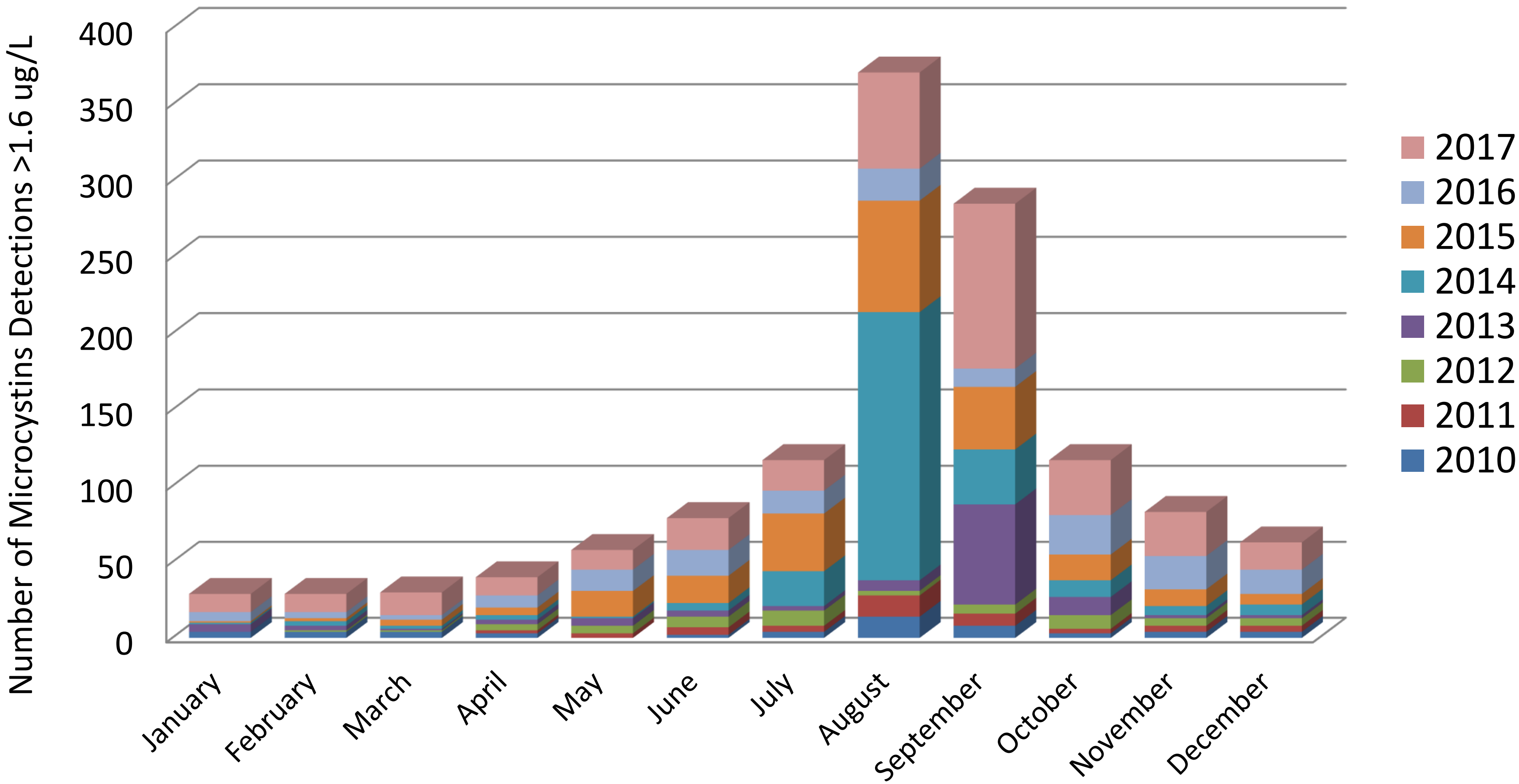
Frequency of Source Water Microcystins Detections > 1.6 ug/L in Ohio



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.

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2017 Lake Erie qPCR mcyE Data Summary

- **mcyE detections at 22 of 25 PWSs and Microcystins detections at 18 PWSs**
  - **West Basin**: mcyE preceded microcystins at all four water systems by 1-4 weeks.
  - **Central Basin (East of Cleveland):** mcyE preceded microcystins detections at 6 of 7 PWSs by 1-2 weeks. Trace detection (0.31 ug/L at Painesville not preceded by mcyE).
  - **Central Basin (Vermillion – Cleveland):** no microcystins
  - **Sandusky Subbasin:** mcyE preceded microcystins at half (3) PWSs. Trace detections at three PWSs not preceded by mcyE detections (impacted by Sandusky Bay bloom).

Photo Credit: Toledo Aerial Media

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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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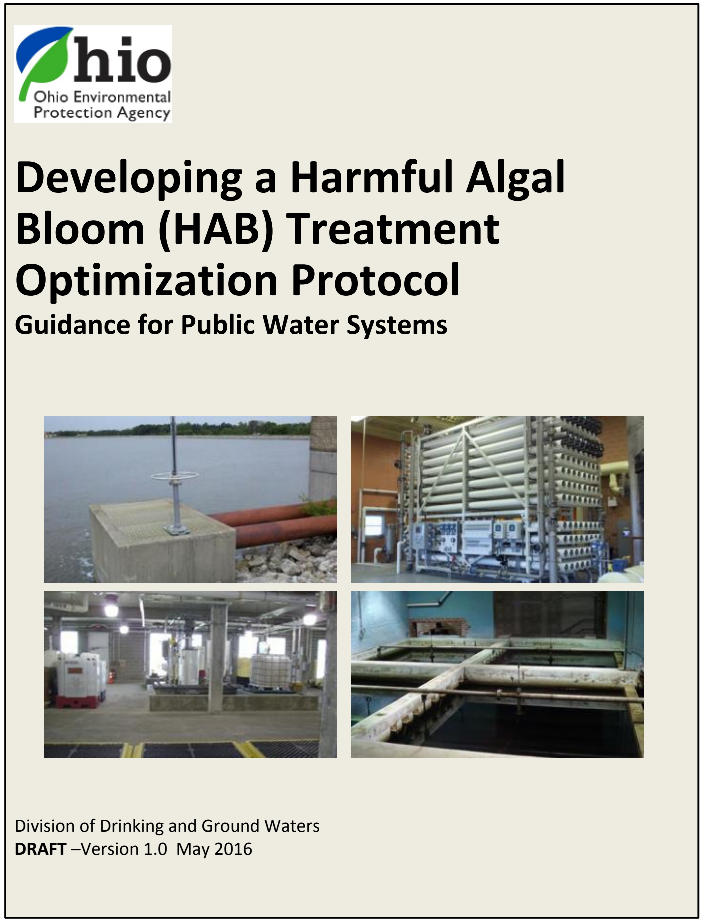
Treatment Optimization Guidance

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

Recommendations

– INTRAcellular (inside cyanobacteria cell) Cyanotoxins: optimize conventional treatment to enhance intact cell removal.

– EXTRAcellular (outside of cyanobacteria cell) Cyanotoxins: optimize for cyanotoxin adsorption, oxidation, or other advanced treatment.

64 PWSs triggered treatment optimization plan rule requirement

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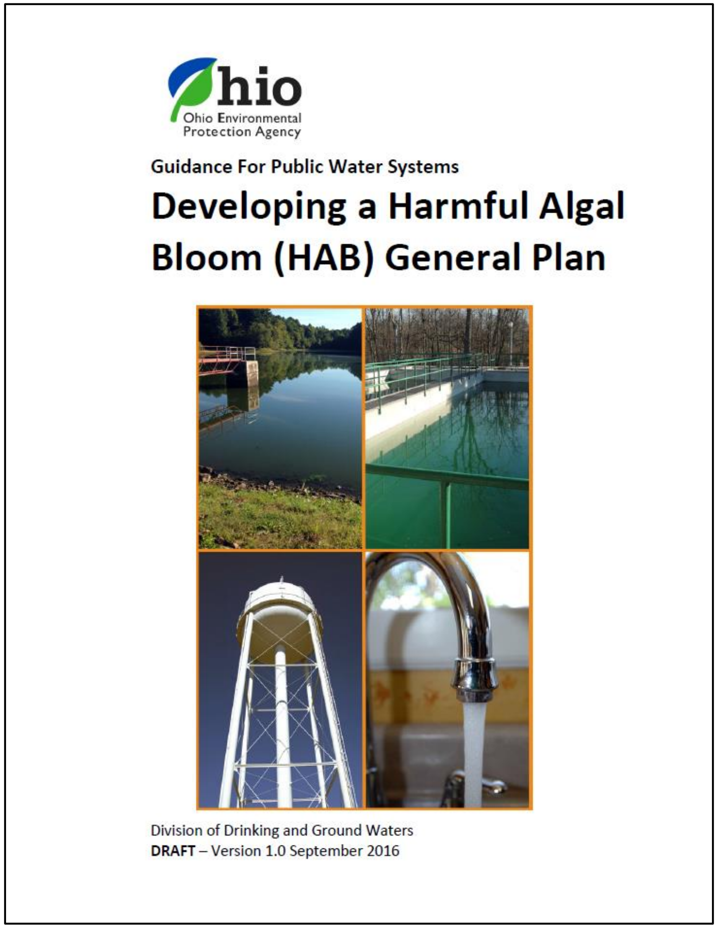
HAB General Plan Guidance

http://epa.ohio.gov/ddagw/HAB.aspx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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

Plan should include a combination of the following:

- Documentation that existing processes are effective at meeting challenge microcystins concentrations;
- Addition of new treatment processes or enhancement of existing processes;
- Avoidance strategies;
- Reservoir management; and/or
- Source water protection activities.

An implementation schedule is required if existing practices are not capable of meeting microcystins challenge concentrations.

19 PWSs triggered general plan rule requirements.

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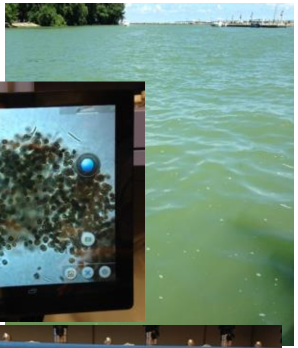
Comprehensive Performance Evaluation (CPE) Approach to Addressing HABs

- Partnering with USEPA & Process Applications, Inc.

- 4 pilot HAB CPEs at Ohio WTPs
- 3 out of 4 Pilot HAB CPEs Completed
  - Final Pilot at Delphos in March 2018

- Develop protocol for conducting a HAB CPE by modifying the existing microbial CPE guidance to address both cyanobacteria cell removal and extracellular cyanotoxins
- 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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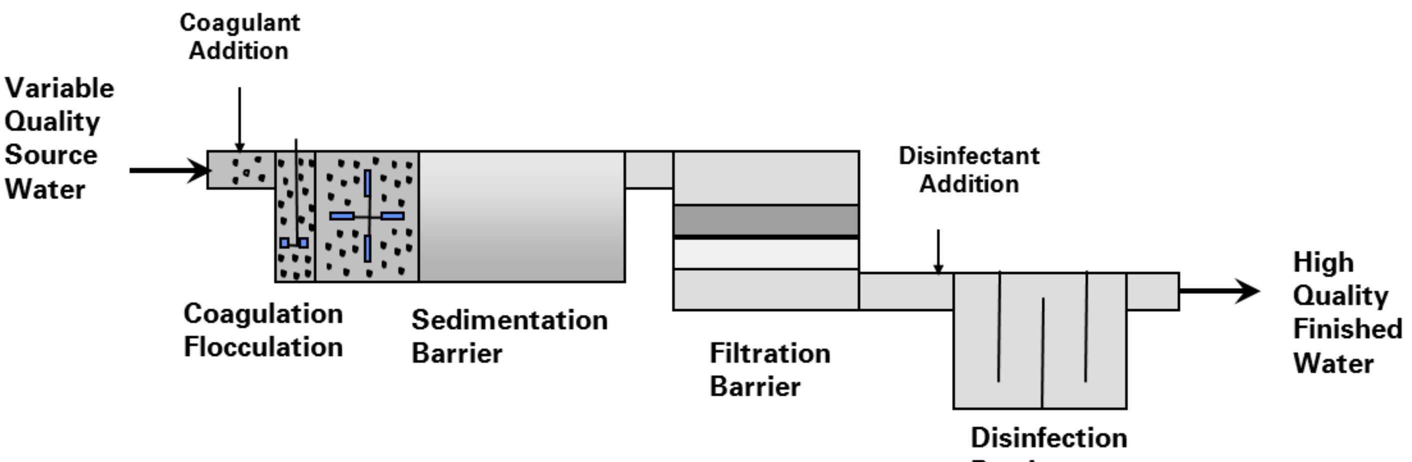
Applying the CPE to Address Cyanotoxins

- <u>Optimize Existing Facilities</u> for cyanobacteria cell removal
  - 50-95% of cyanotoxins are typically intracellular
  - Avoid/Minimize pre-oxidation and release of cyanotoxins
  - Optimize cell removal through improved coagulation, sedimentation and filtration processes
- 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
- 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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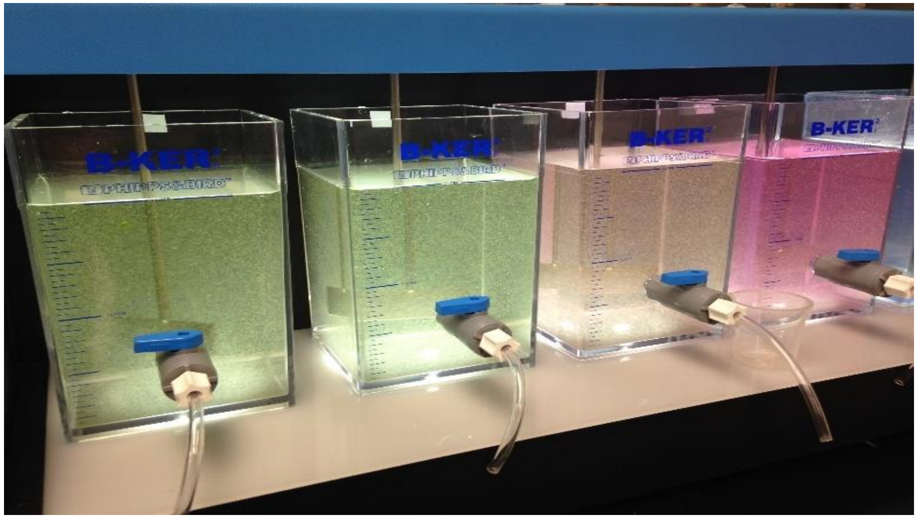
1: Permanganate Impact on Coagulation and Cell Lysis

Jar #	Coagulant (ACH) dose	Permanganate dose
1 (control)	None	None
2	24 mg/L (plant's dose)	None
3	24 mg/L (plant's dose)	**1.2 mg/L** (plant's current dose)
4	24 mg/L (plant's dose)	**3 mg/L** (plant's max. dose)



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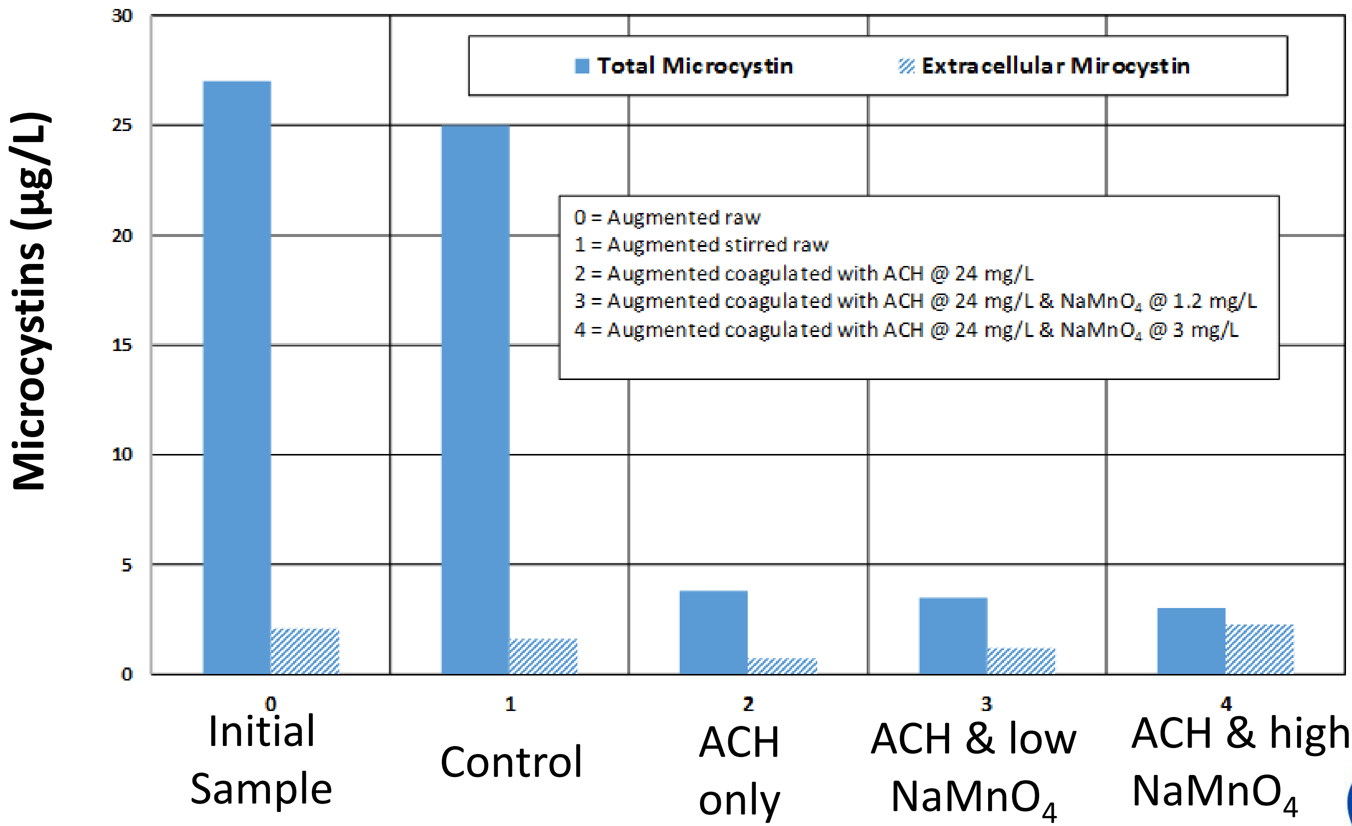
Permanganate Study Results

- 85% of Microcystins removed by coagulation, no clear coagulation benefit from permanganate addition
- Extracellular microcystins increased to 80% of total with high permanganate dose



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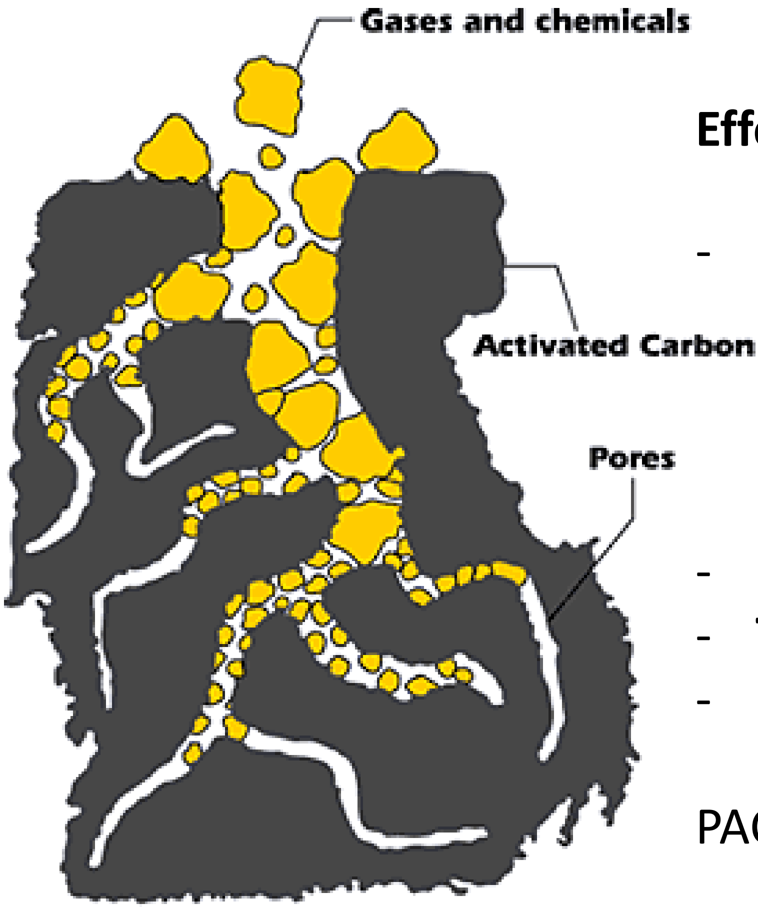
Powdered Activated Carbon (PAC)



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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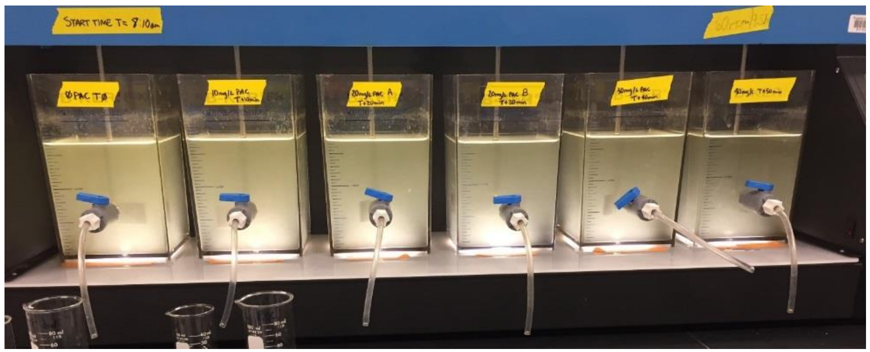
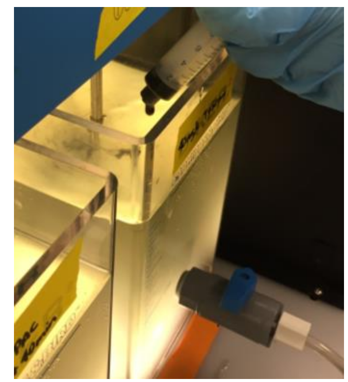
2: Carbon Dose and Contact Time Impact on Microcystins Adsorption

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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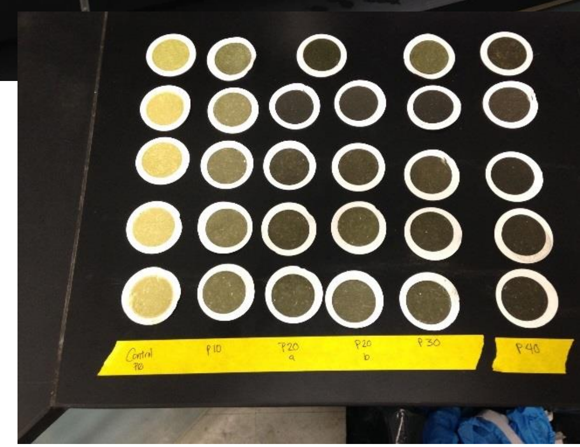
PAC Jar Testing

- 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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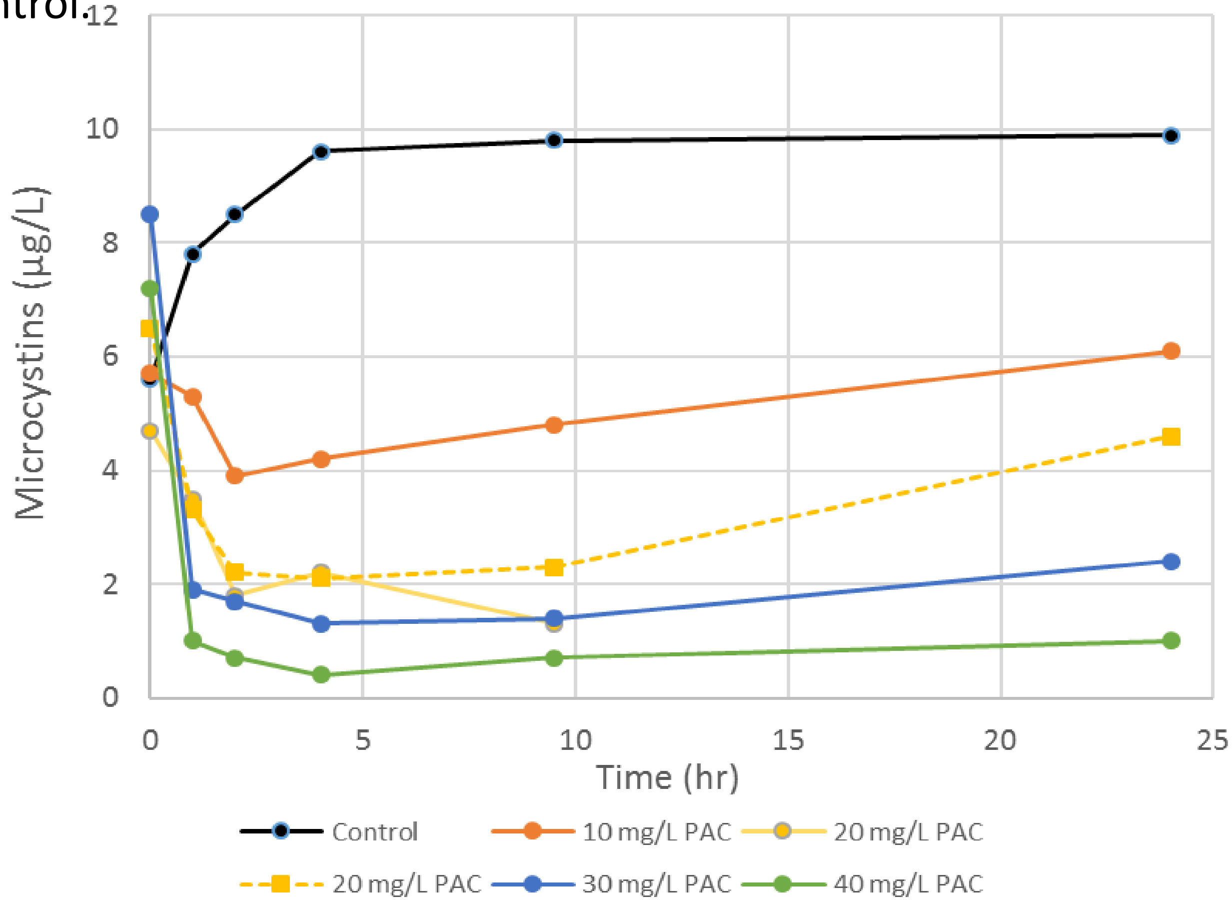
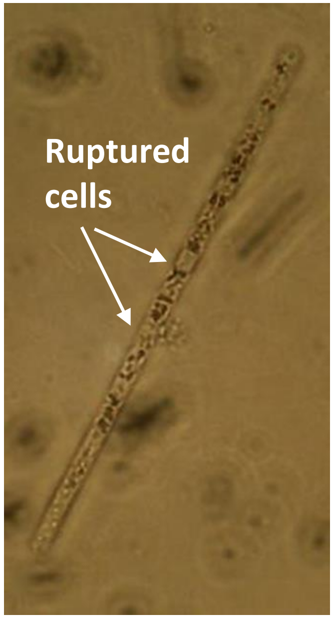
PAC Dose Study Results

- Increasing PAC dose improved microcystins removal, but even highest dose did not achieve total removal. Isotherm equation estimated only 2.5 mg/L PAC needed to reduce 10 ug/L to 1 ug/L microcystins.
- 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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3: 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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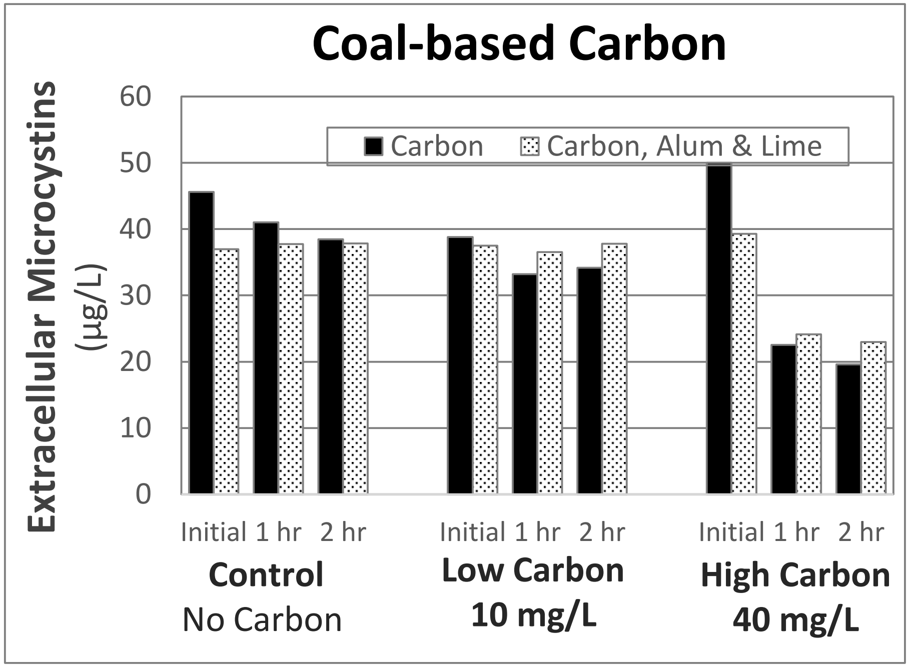
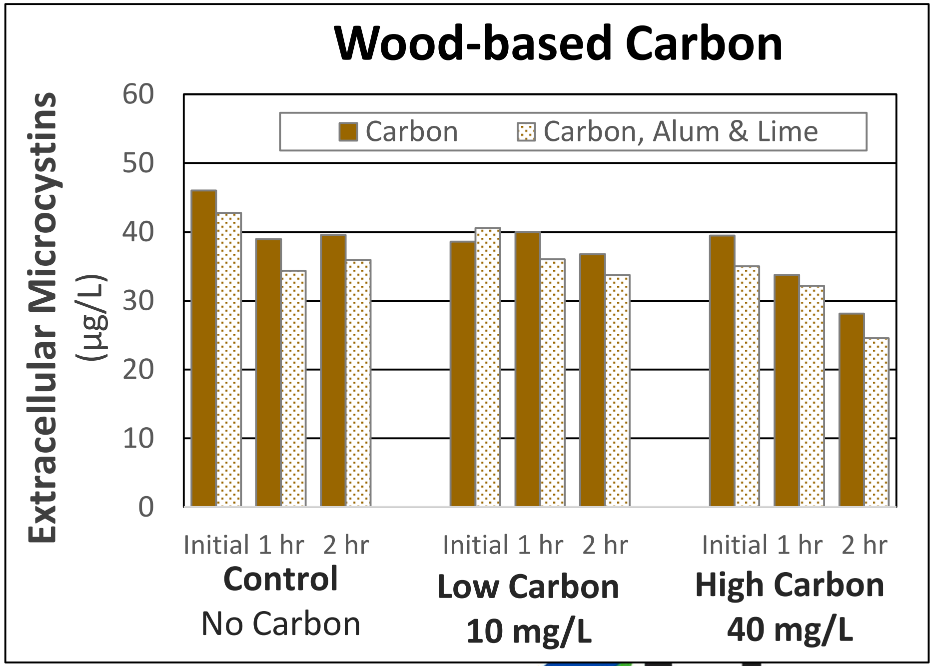
PAC Type, Dose, and Treatment Chemical Study Results

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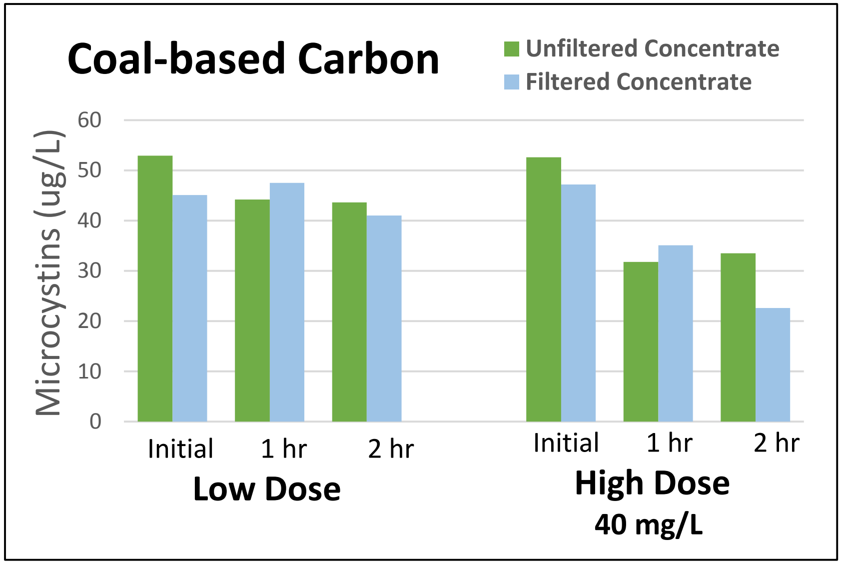
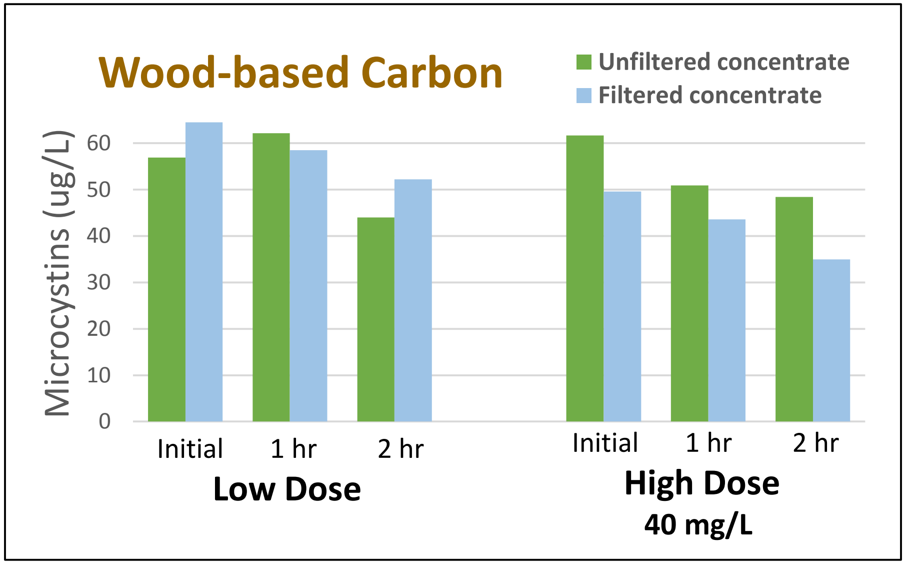
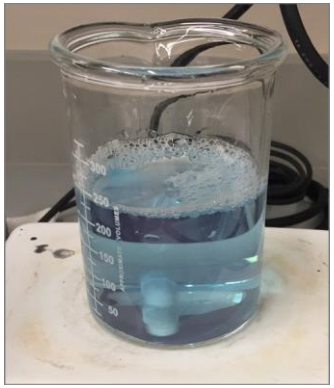
4: Evaluate Filtered vs Unfiltered Concentrate Spike, Carbon Types (Coal & Wood), and Dose (10 & 40 mg/L)

Coal test DOC range: 11.4—13.1 mg/L





Unfiltered Concentrated Spike Solution



Filtered Concentrated Spike Solution

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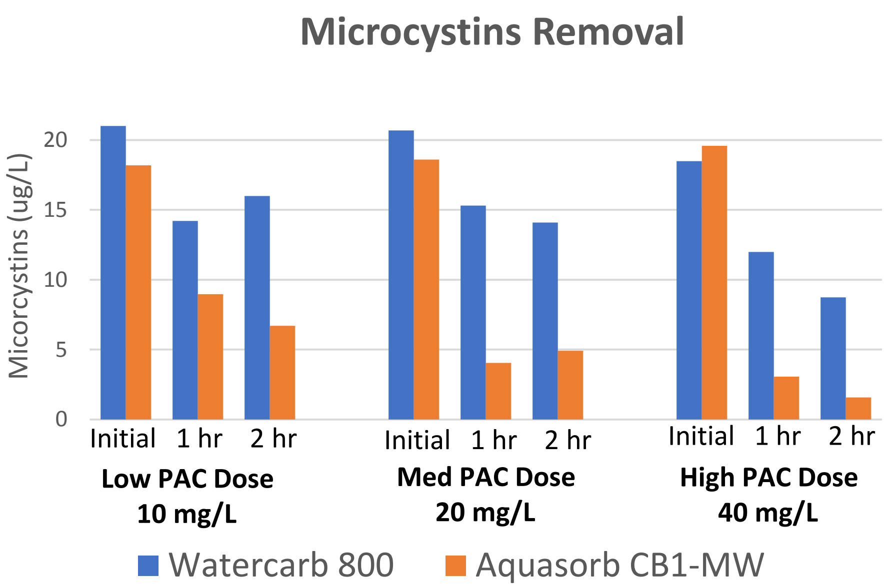
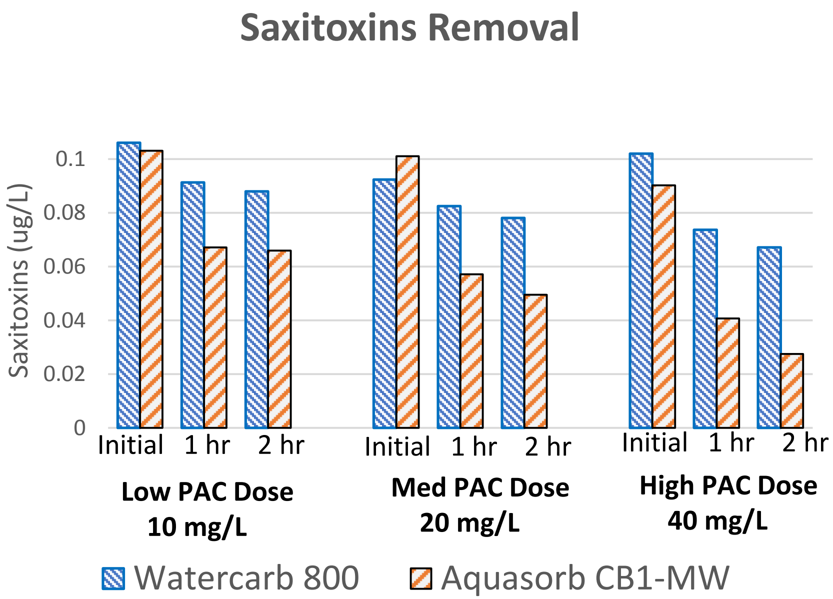
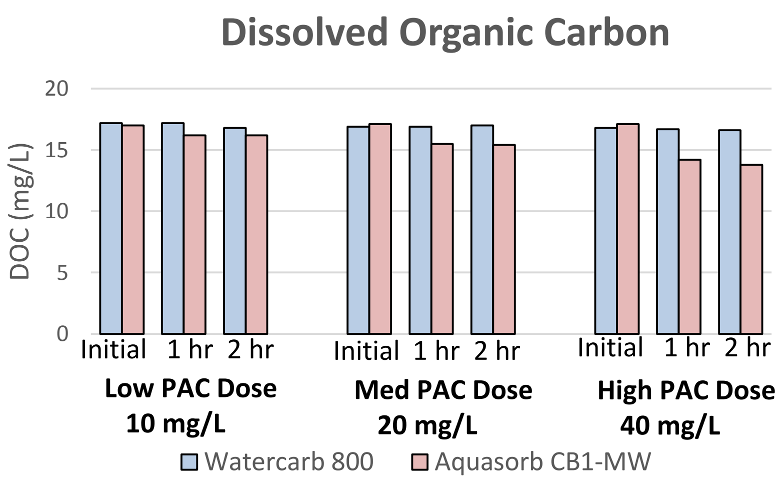
5a: Evaluate Impact of PAC Type and Contact Time on Removal of Microcystins, Saxitoxins, and DOC





WaterCarb 800:
Coal Blend

Aquasorb:
Wood/Coal/Coconut Blend



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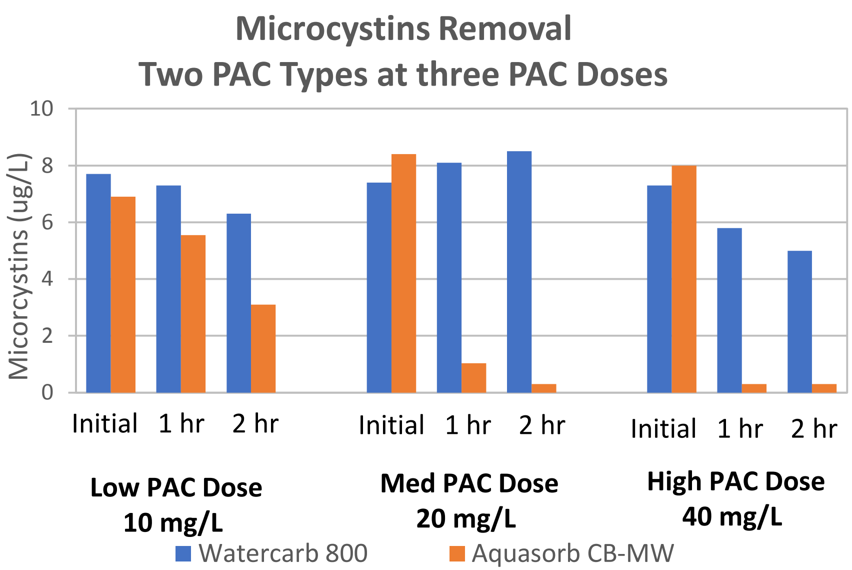
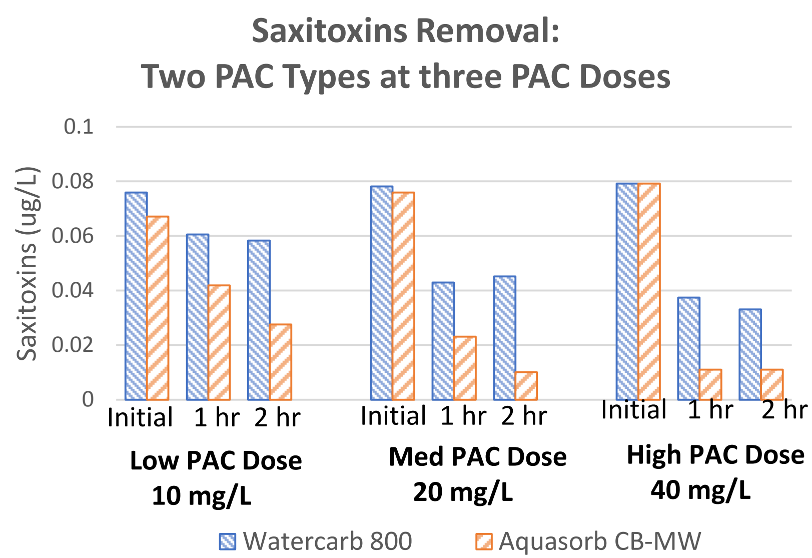
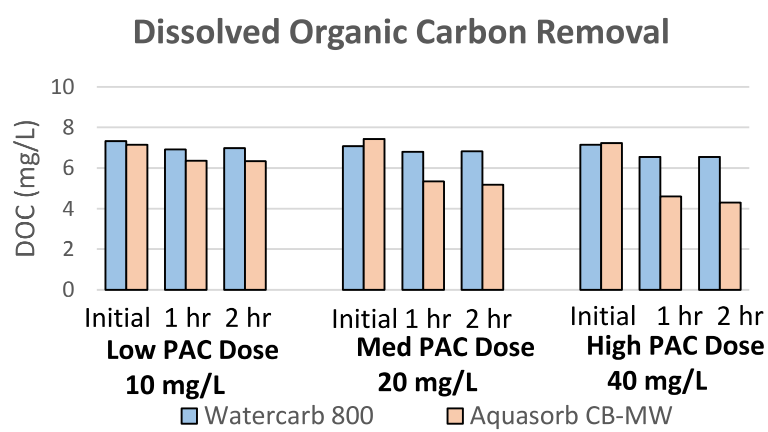
5a: Evaluate Impact of PAC Type and Contact Time on Removal of Microcystins, Saxitoxins, and DOC (Raw Water, No Spike)







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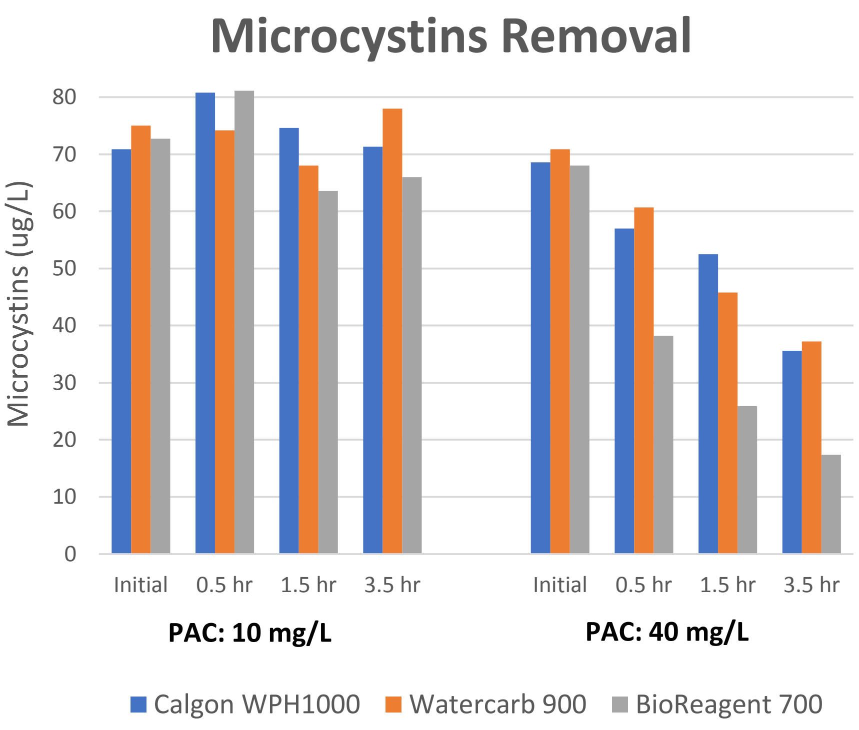
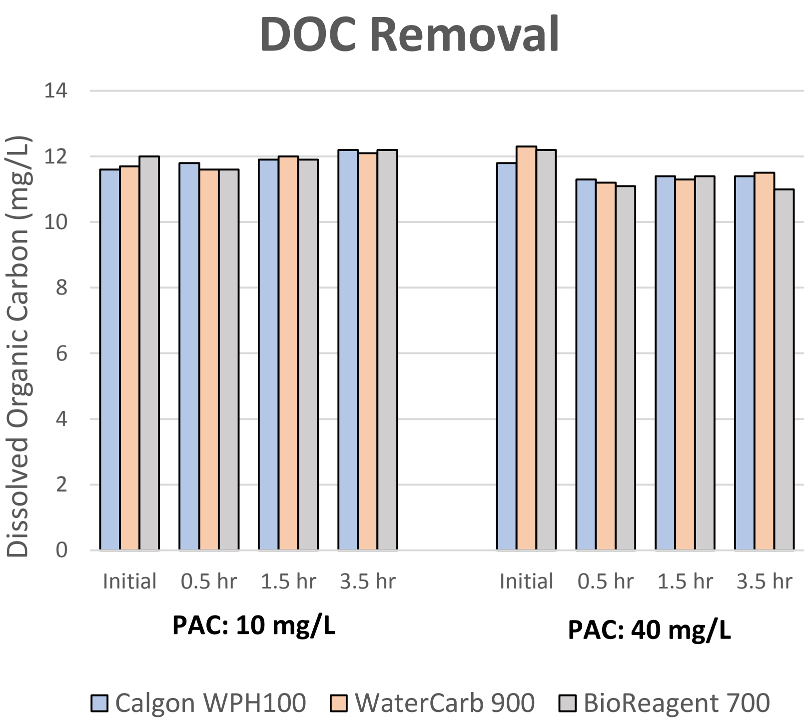
6: High Microcystins Challenge
Evaluate Removal of Microcystins and DOC from Lake Erie 2017 Harmful Algal Bloom





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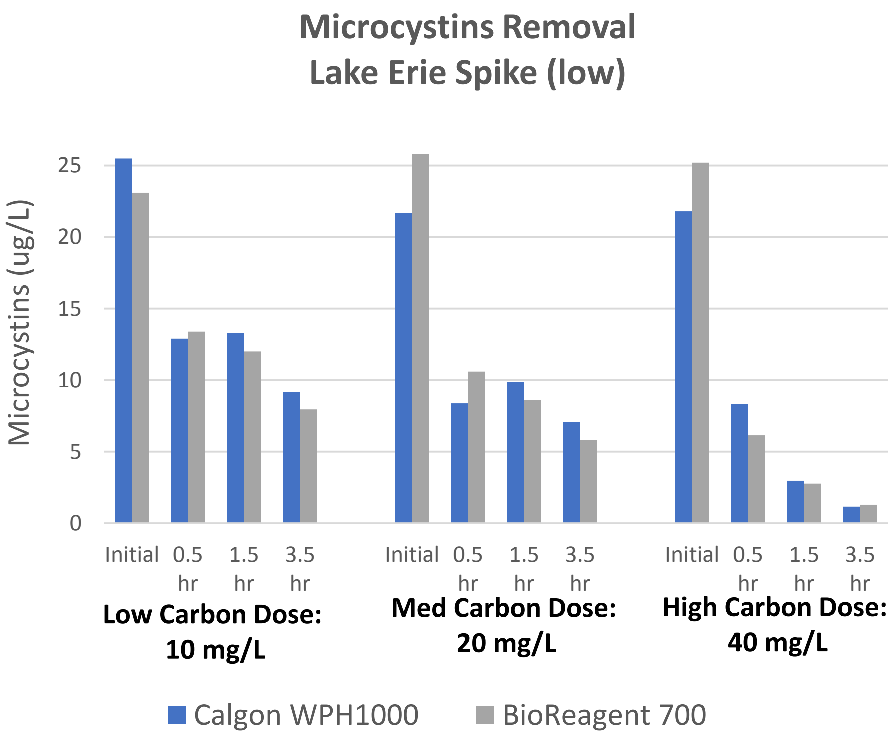
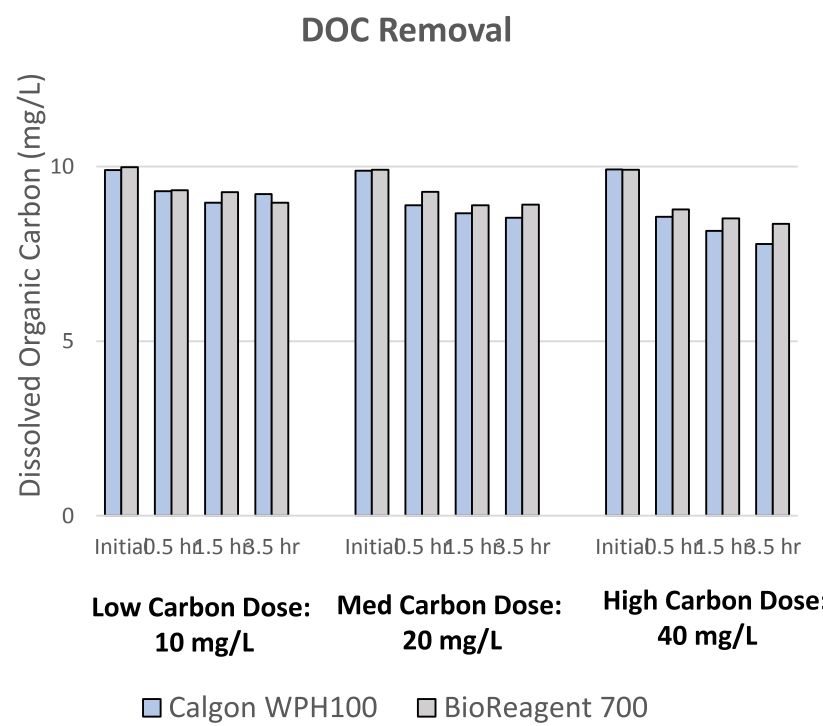
6b: Moderate Microcystins Challenge

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





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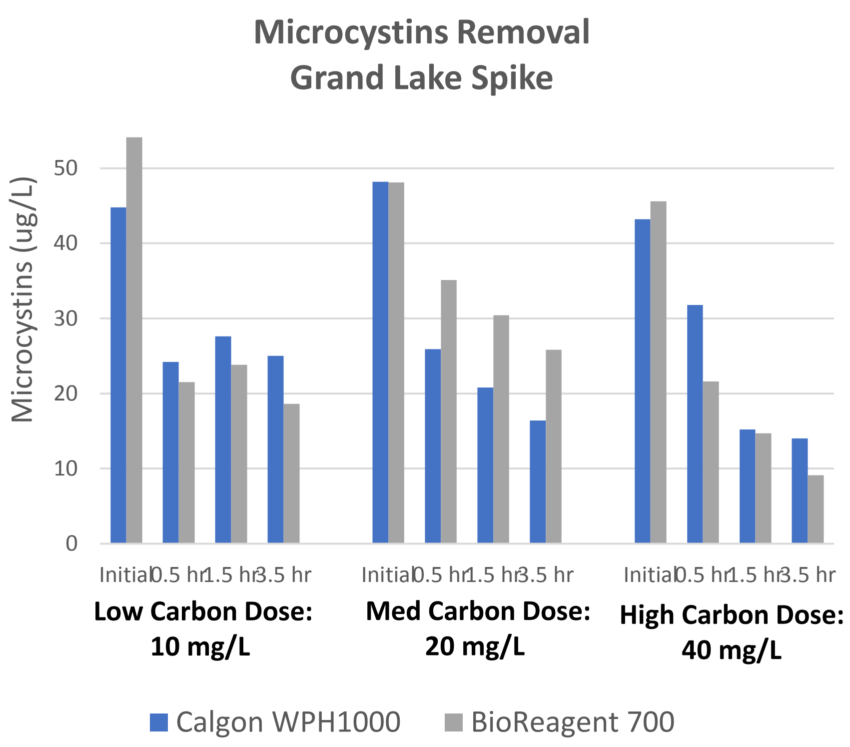
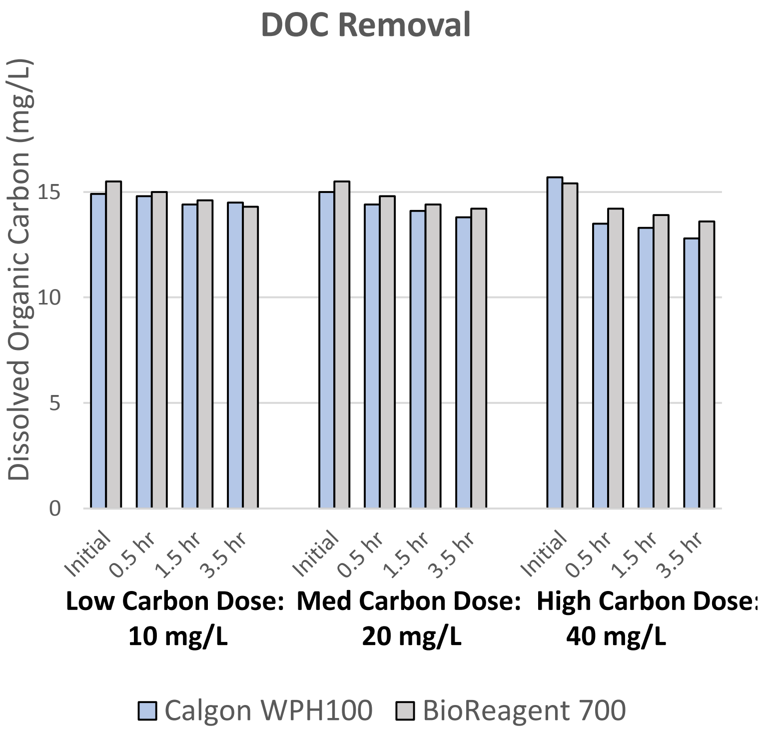
6c: High Microcystins Challenge
Evaluate Removal of Microcystins and DOC from Grand Lake 2017 Harmful Algal Bloom





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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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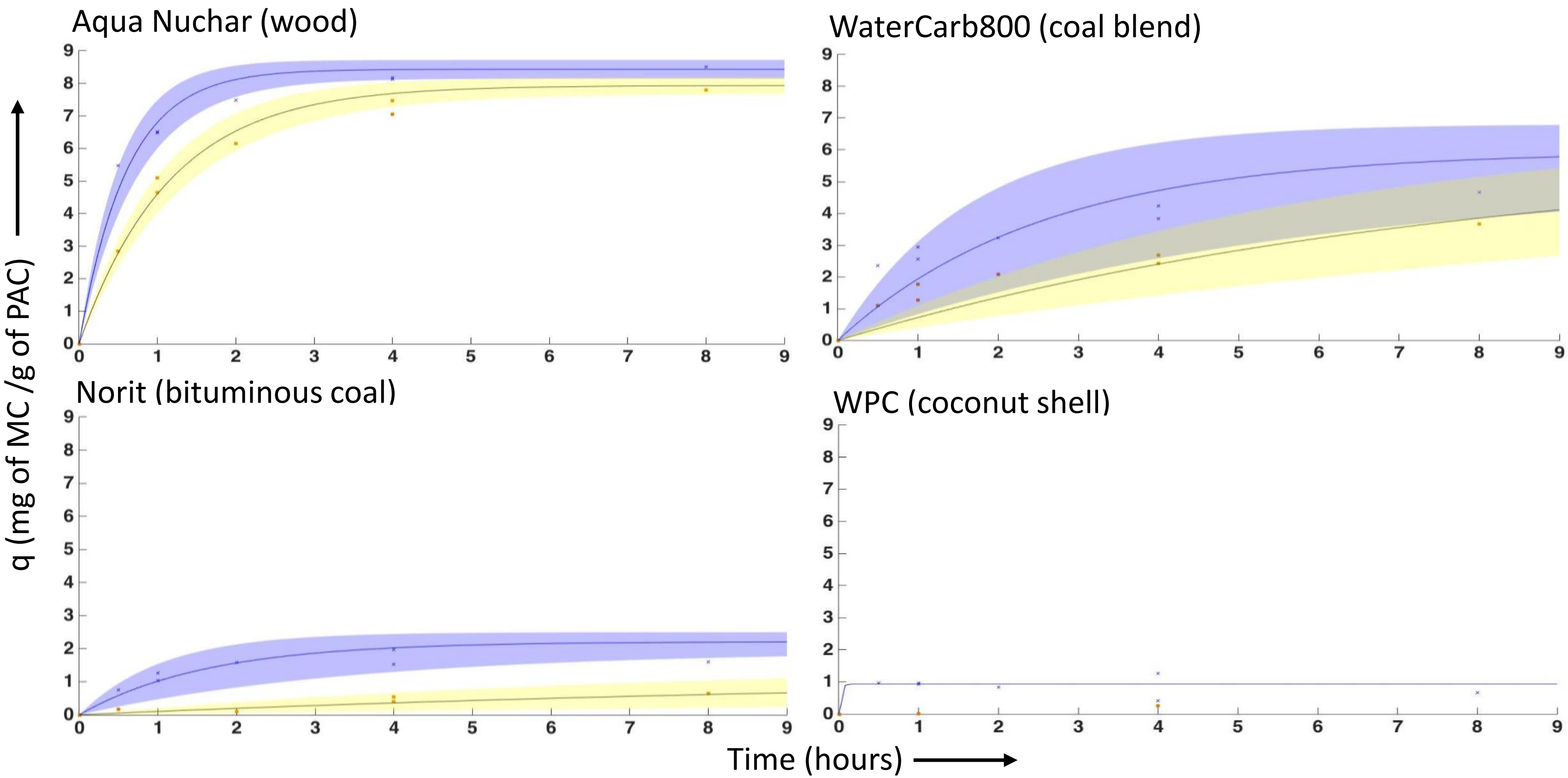
NOM Type Effect (vs. ≅ 5ppm)



Slide courtesy:
Asnika Bajracharya, OSU

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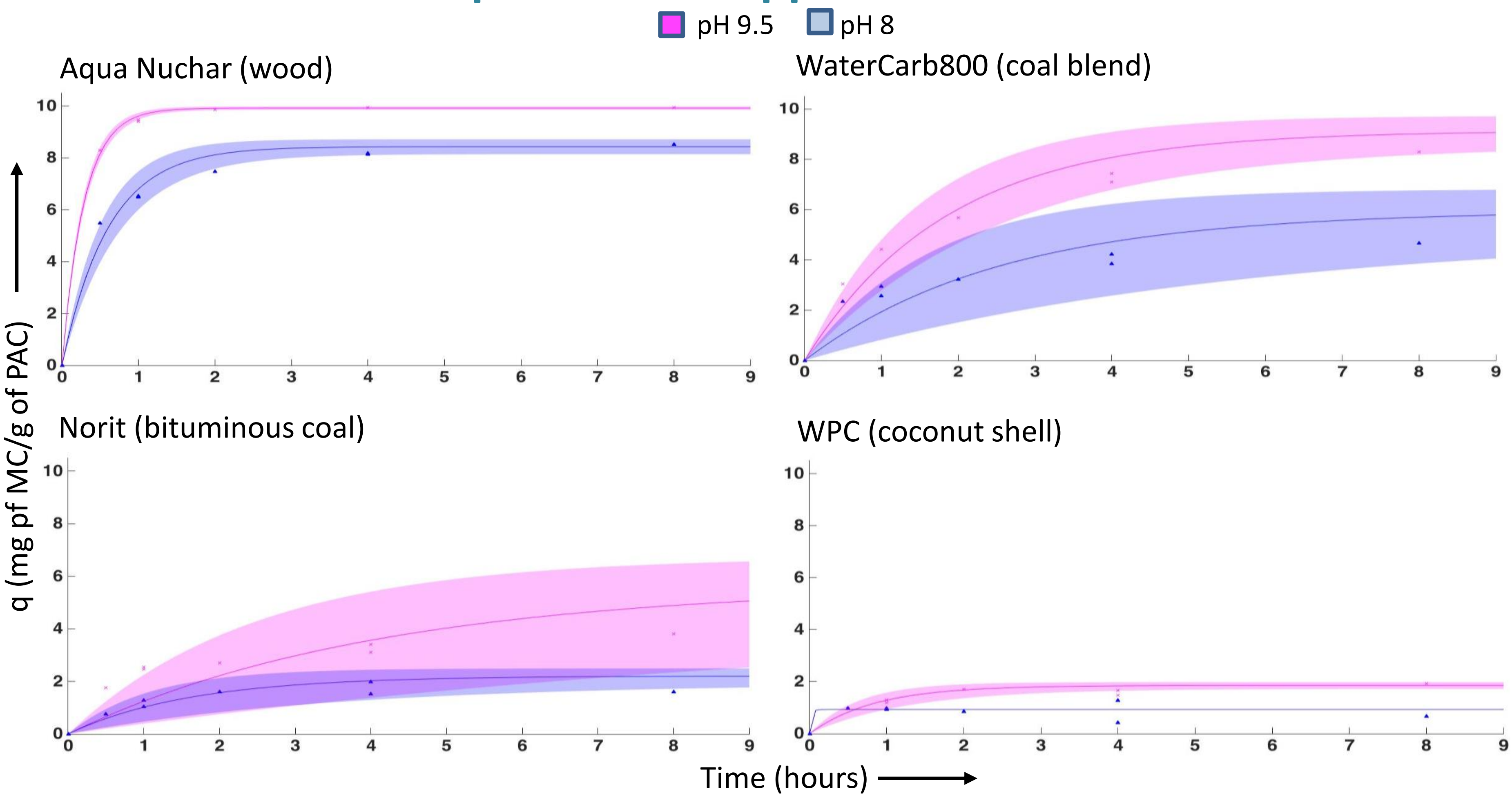
pH Effect at 5ppm of NOM



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Asnika Bajracharya, OSU

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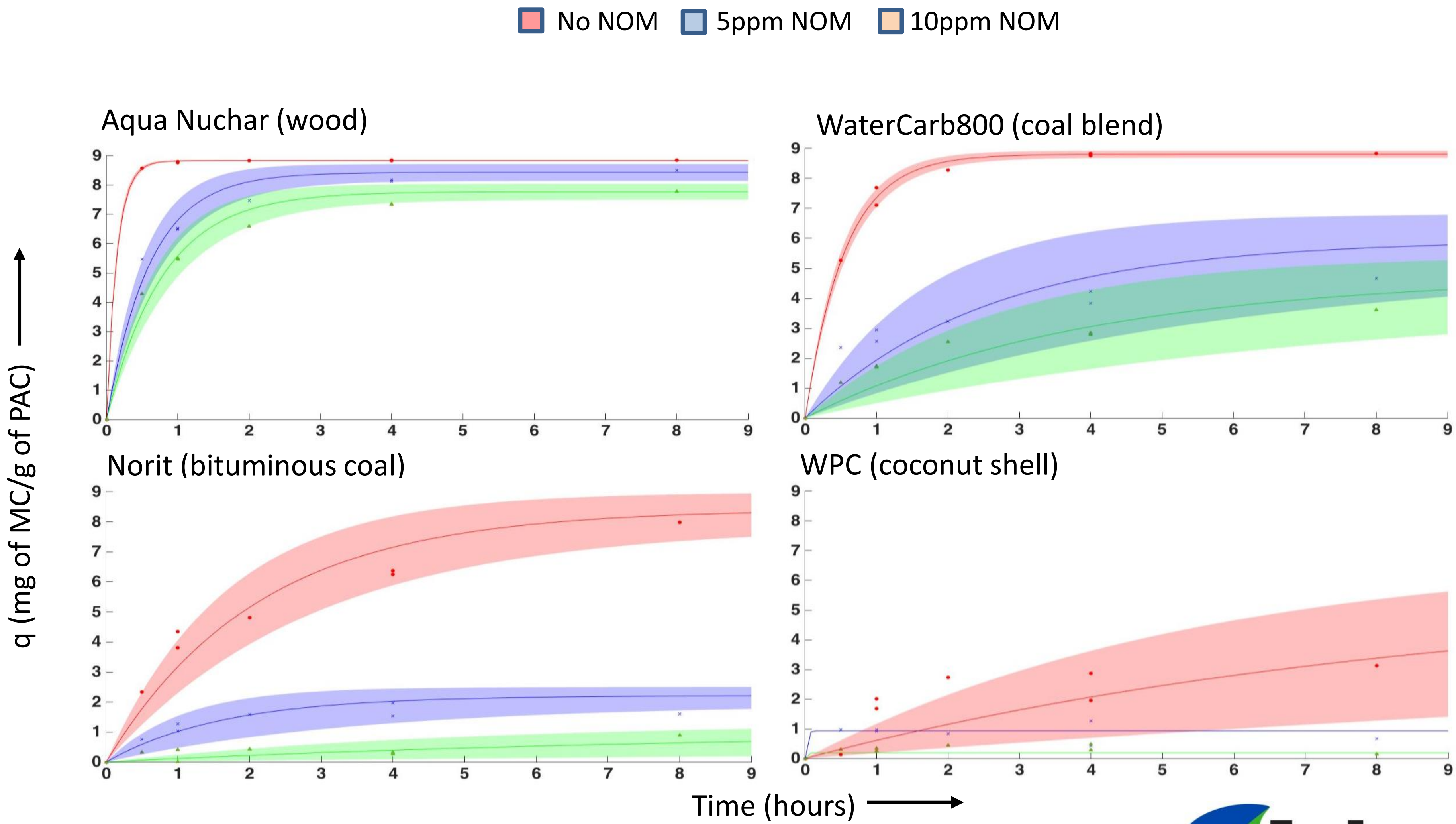
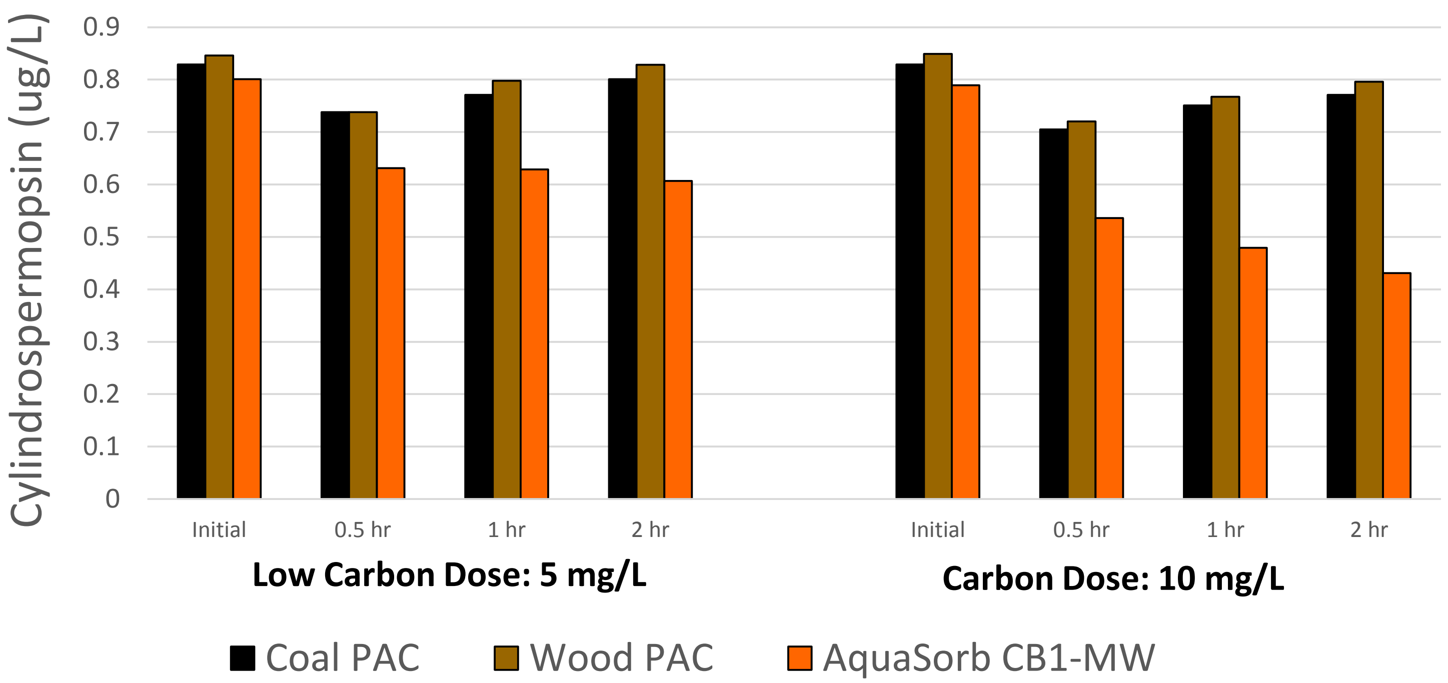
NOM Concentration Effect



Slide courtesy:

Asnika Bajracharya, OSU

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



Summary

- Higher doses of permanganate led to increase in extracellular microcystins with minimal benefit to coagulation.
- Cyanotoxin removal estimated by jar tests is less than removal estimated by isotherm equations
  - <u>Potential impact of NOM/DOC</u>
- Treatment chemicals did not impact PAC performance (one study)
- Blended coal/wood/coconut PAC performed well (OEPA Studies) and wood performed well (OSU Study) for microcystins adsoprtion
- Recommend PAC jar testing to better estimate cyanotoxin removal potential (variability between PACs)

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Treatment Optimization: Next Steps

- 4th Pilot CPE this month (evaluate GAC and UV processes)
  - GAC Study by OSU
- Conduct "real world" oxidation kinetics study during next CPE (microcystins) and compare to AWWA calculator and results from OBHE funded projects
  - Oxidation Study by OSU and UC
- Conduct additional jar test experiments, as needed
- Provide concentrated challenge water to PWSs
- Compare "real-world" experimental results to published isotherm data and results from OBHE funded research projects
- Develop modified Ohio EPA HAB CPE approach and consider conducting HAB CPEs at additional Ohio water systems, as needed
- Release revised guidance documents

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Microcystins Accumulations in Water Treatment Plant Residuals

Study Goals

- Determine microcystins occurrence in a variety of water treatment residual (WTR) types: with and without lime soda softening, with and without PAC.
- Investigate persistence of microcystins in WTR over time.
- Evaluate microcystins (MCs) analytical methods for water treatment residual (WTR) matrices.

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 Plant Residuals: NEXT STEPS

Ohio Board of Higher Education HAB Grant:

- Further evaluate extraction and analytical methods for determining concentrations of microcystins in water treatment residuals (WTR).
- Determine fate of microcystins in WTR.
- Identify potential for biodegradation of microcystins in WTR.
- Evaluate potential for plant uptake.

Ohio EPA Division of Materials Waste Management:
Address interested party comments and develop revised water treatment plant residuals beneficial reuse general permits.

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Reservoir Management

ODHE HAB grants: algaecide application and sonication studies

Stone Lab HABs Courses, August 6-7, 8-9, 2018

- https://ohioseagrant.osu.edu/education/stonelab/courses/workshops

North America Lakes Management Society Annual Conference:

- Cincinnati, Ohio
- October 30 – November 2, 2018
- https://www.nalms.org/nalms2018/

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Questions?

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

Heather.Raymond@epa.ohio.gov

(614) 644-2752

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