Ohio EPA HAB Update

Lake Erie Water Plant Group Meeting
April 26, 2018

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Ohio EPA HAB Coordinator
Ohio EPA HAB Update

• 2018 HAB Season Monitoring Schedules
• 2017 HAB Monitoring Overview
• Cyanotoxin Treatment Update: Treatment technique, CPEs, jar test results, oxidation study results, University research results
• Water Treatment Residuals General Permit Update
• Training Opportunities
Revised HAB Season Monitoring Schedules

- Minimal changes from 2017 May-November schedules (new additional monitoring reductions for Schedule 3)
- Schedule assignments based on HAB occurrence and treatment risk. Available on Ohio EPA’s HAB website: [http://epa.ohio.gov/ddagw/HAB.aspx](http://epa.ohio.gov/ddagw/HAB.aspx)
## 2018 HAB Season Monitoring Schedules

<table>
<thead>
<tr>
<th>Schedule</th>
<th>Monitoring Requirements 5/1/18 – 10/31/18</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Follow Rule: Biweekly qPCR screening Weekly raw/finished microcystins <em>(paired with screening sample)</em></td>
</tr>
<tr>
<td>2</td>
<td>Biweekly qPCR screening Biweekly raw water microcystins (collected on alternate week as screening sample, <em>not paired</em>)</td>
</tr>
<tr>
<td>3</td>
<td>Monthly qPCR screening</td>
</tr>
</tbody>
</table>

**Schedules 1 and 2:**
NWDO: Collect first qPCR sample week of May 6
NEDO: Collect first qPCR sample week of May 13
Schedule 2- Implementation Notes

- If microcystins are detected in the raw water:
  - PWS must collect paired raw and finished water sample within 24 hours of receiving the result and complete analysis within five days.
  - If PWS collected a paired finished water sample with their initial raw water sample, an additional raw and finished sample is not required until the following week (unless raw water was > 5ug/L or any finished water detection).
  - PWS will be changed to Schedule 1 requirements for remainder of the season (though 10/31/2018).
If mycE genes are detected at high levels in the raw water (> 5 gene counts per uL):

- PWS collect raw/finished water microcystins sample within 24 hrs of receiving the result and complete analysis within five days.
  - If microcystins are not detected the PWS will remain on Schedule 2 monitoring requirements.
  - If microcystins are detected in either the raw or finished water, the PWS will be changed to Schedule 1 monitoring requirements for the remainder of the season.
All Schedules

- OAC Chapter 3745-90 additional monitoring requirements triggered if:
  - raw water microcystins > 5 ug/L
  - any finished water microcystins detection
- Ohio EPA will conduct follow up monitoring for saxitoxins or cylindrospermopsin based on gene detections.
- If data from source water monitoring or satellite data indicate that a HAB is present, Ohio EPA can request or require (depending on HAB severity and proximity to intake) the PWS sample for microcystins
  - Based on results could be switched to schedule 1
- As in past years, Ohio EPA will consider reduced monitoring options starting Nov. 1 and will notify PWS of option by the end of September 2018
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
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).
- 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.
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.
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
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
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

• **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
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
## Permanganate Impact on Coagulation and Cell Lysis

<table>
<thead>
<tr>
<th>Jar #</th>
<th>Coagulant (ACH) dose</th>
<th>Permanganate dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (control)</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>24 mg/L (plant’s dose)</td>
<td>None</td>
</tr>
<tr>
<td>3</td>
<td>24 mg/L (plant’s dose)</td>
<td><strong>1.2 mg/L</strong> (plant’s current dose)</td>
</tr>
<tr>
<td>4</td>
<td>24 mg/L (plant’s dose)</td>
<td><strong>3 mg/L</strong> (plant’s max. dose)</td>
</tr>
</tbody>
</table>
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
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**: $d < 2.0 \text{ nm}$

**Mesopores**: $2.0 \text{ nm} < d < 50.0 \text{ nm}$

**Macropores**: $d > 50.0 \text{ nm}$

Microcystin-LR:

$$1.2 < d < 2.6 \text{ nm}$$
### Estimating Dosages of PAC

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

<table>
<thead>
<tr>
<th>Activated Carbon</th>
<th>Microcystis Toxins&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Oscillatoria Toxins&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$</td>
<td>$1/n$</td>
</tr>
<tr>
<td>Wood GAC</td>
<td>501.2</td>
<td>0.36</td>
</tr>
<tr>
<td>Calgon coal GAC</td>
<td>512.9</td>
<td>0.36</td>
</tr>
<tr>
<td>Culligon coal GAC</td>
<td>126</td>
<td>0.57</td>
</tr>
<tr>
<td>Coconut GAC</td>
<td>331.1</td>
<td>0.44</td>
</tr>
<tr>
<td>Nonactivated GC</td>
<td>2.1</td>
<td>1.3</td>
</tr>
<tr>
<td>Wood PAC</td>
<td>6309</td>
<td>0.56</td>
</tr>
<tr>
<td>Calgon coal PAC</td>
<td>3630</td>
<td>0.9</td>
</tr>
<tr>
<td>Coconut PAC</td>
<td>1259</td>
<td>1</td>
</tr>
</tbody>
</table>

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

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

\[ q = 6309 \cdot C_f^{0.56} = 6309(1)^{0.56} \]
\[ q = 6309 \mu g/g \]
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

\[ q = 1259 \cdot C_f^{1.0} = 1259(1)^{1.0} \]
\[ q = 1259 \mu g/g \]
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
Carbon Dose and Contact Time Impact on Microcystins Adsorption

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

Challenge Water: Simulated bloom by concentrating cyanobacteria in raw water using phytoplankton net, lysing concentrate using freeze/thaw, and adding concentrate to raw water
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
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 µg/L to 1 µg/L microcystins.

• Most removal occurs during first four hours of contact time.

• Unexpected high variability between jars and increase in extracellular microcystins in control.
Carbon Type (Coal vs. Wood), Dose, and Treatment Chemical (alum & lime) Impact on Microcystins Adsorption
## Jar Test Setup

<table>
<thead>
<tr>
<th>Jar Set</th>
<th>PAC Dose mg/L</th>
<th>Alum mg/L</th>
<th>Lime mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>20</td>
<td>120</td>
</tr>
<tr>
<td>Low</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbon</td>
<td>10</td>
<td>20</td>
<td>120</td>
</tr>
<tr>
<td>High</td>
<td>40</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbon</td>
<td>40</td>
<td>20</td>
<td>120</td>
</tr>
</tbody>
</table>

Evaluated both wood and coal-based PAC
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

![Graph showing extracellular microcystins for coal-based and wood-based carbon.](image)

Isotherm equation estimates (40 µg/L to 1 µg/L):
Coal PAC: 11 mg/L; Wood PAC: 6 mg/L
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
Evaluate Impact of PAC Type and Contact Time on Removal of Microcystins, Saxitoxins, and DOC

**Microcystins Removal**

- **Watercarb 800**: Coal Blend
- **Aquasorb**: Wood/Coal/Coconut Blend

**Saxitoxins Removal**

**Dissolved Organic Carbon**

- **Watercarb 800**: Coal Blend
- **Aquasorb**: Wood/Coal/Coconut Blend
Evaluate Impact of PAC Type and Contact Time on Removal of Microcystins, Saxitoxins, and DOC (Raw Water, No Spike)

**Microcystins Removal**
- Two PAC Types at three PAC Doses
- Low PAC Dose: 10 mg/L
- Med PAC Dose: 20 mg/L
- High PAC Dose: 40 mg/L

**Saxitoxins Removal**
- Two PAC Types at three PAC Doses
- Low PAC Dose: 10 mg/L
- Med PAC Dose: 20 mg/L
- High PAC Dose: 40 mg/L

**Dissolved Organic Carbon Removal**
- Two PAC Types at three PAC Doses
- Low PAC Dose: 10 mg/L
- Med PAC Dose: 20 mg/L
- High PAC Dose: 40 mg/L

Ohio Environmental Protection Agency
High Microcystins Challenge
Evaluate Removal of Microcystins and DOC from Lake Erie 2017 Harmful Algal Bloom

**Microcystins Removal**

- **PAC: 10 mg/L**
  - Initial
  - 0.5 hr
  - 1.5 hr
  - 3.5 hr

- **PAC: 40 mg/L**
  - Initial
  - 0.5 hr
  - 1.5 hr
  - 3.5 hr

**DOC Removal**

- **PAC: 10 mg/L**
  - Initial
  - 0.5 hr
  - 1.5 hr
  - 3.5 hr

- **PAC: 40 mg/L**
  - Initial
  - 0.5 hr
  - 1.5 hr
  - 3.5 hr

Legend:
- Calgon WPH1000
- Watercarb 900
- BioReagent 700

Ohio Environmental Protection Agency
Moderate Microcystins Challenge
Evaluate Removal of Microcystins and DOC from Lake Erie 2017 Harmful Algal Bloom

**Microcystins Removal**
Lake Erie Spike (low)

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Initial</th>
<th>0.5</th>
<th>1.5</th>
<th>3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Carbon Dose: 10 mg/L</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Med Carbon Dose: 20 mg/L</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>High Carbon Dose: 40 mg/L</td>
<td>15</td>
<td>10</td>
<td>5</td>
<td>0</td>
</tr>
</tbody>
</table>

**DOC Removal**

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Initial</th>
<th>0.5</th>
<th>1.5</th>
<th>3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Carbon Dose: 10 mg/L</td>
<td>10</td>
<td>8</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Med Carbon Dose: 20 mg/L</td>
<td>8</td>
<td>5</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>High Carbon Dose: 40 mg/L</td>
<td>5</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
High Microcystins Challenge
Evaluate Removal of Microcystins and DOC from Grand Lake 2017 Harmful Algal Bloom

Microcystins Removal
Grand Lake Spike

DOC Removal

Microcystins (ug/L)

Doc Removal

Calgon WPH1000  BioReagent 700

Low Carbon Dose: 10 mg/L
Med Carbon Dose: 20 mg/L
High Carbon Dose: 40 mg/L

Low Carbon Dose: 10 mg/L
Med Carbon Dose: 20 mg/L
High Carbon Dose: 40 mg/L

Calgon WPH1000  BioReagent 700
Preliminary Natural Organic Matter (NOM) Effect Data

Slides courtesy: Asnika Bajracharya

The Ohio State University
Environmental Engineering Graduate Research Assistant
NOM Type Effect ($\text{ vs. } \approx 5 \text{ ppm}$)

- **Aqua Nuchar** (wood)
- **WaterCarb800** (coal blend)
- **Norit** (bituminous coal)
- **WPC** (coconut shell)

$q$ (mg of MC/g of PAC)

Time (hours)

Slide courtesy:
Asnika Bajracharya, OSU
pH Effect at 5ppm of NOM

Aqua Nuchar (wood)

WaterCarb800 (coal blend)

Norit (bituminous coal)

WPC (coconut shell)

Slide courtesy: Asnika Bajracharya, OSU
NOM Concentration Effect

- Aqua Nuchar (wood)
- WaterCarb800 (coal blend)
- Norit (bituminous coal)
- WPC (coconut shell)

Slide courtesy: Asnika Bajracharya, OSU
Evaluate Removal of Cylindrospermopsin With Three Different PAC Types and Two PAC Doses

- **Low Carbon Dose: 5 mg/L**
  - Initial: 0.85 ug/L
  - 0.5 hr: 0.75 ug/L
  - 1 hr: 0.65 ug/L
  - 2 hr: 0.55 ug/L

- **Carbon Dose: 10 mg/L**
  - Initial: 0.90 ug/L
  - 0.5 hr: 0.80 ug/L
  - 1 hr: 0.70 ug/L
  - 2 hr: 0.60 ug/L

- **PAC Types:**
  - Coal PAC
  - Wood PAC
  - AquaSorb CB1-MW
Microcystins Chlorine Oxidation Study #1

Graph showing the change in chlorine and microcystin levels over time:
- Total Chlorine
- Free Chlorine (DPD)
- CyanoTOX Predicted Free Chlorine
- Microcystin
- CyanoTOX Predicted Microcystin

Y-axis: Chlorine (mg/L) and Microcystin (μg/L)
X-axis: Elapsed Time (HH:MM)
Microcystins Chlorine Oxidation Study #2

The graph shows the progression of chlorine and microcystin levels over time. The y-axis represents the concentration of chlorine (mg/L) and microcystin (μg/L), while the x-axis represents elapsed time (HH:MM) from 1:00 to 5:00.

Key lines:
- **Total Chlorine** (blue line)
- **Free Chlorine (DPD)** (orange line)
- **Free Chlorine (Indophenol)** (red line)
- **CyanoTOX Predicted Free Chlorine** (dotted orange line)
- **Microcystin** (green line)
- **CyanoTOX Predicted Microcystin** (dotted green line)
Special Study Results 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
  – Potential impact of NOM/DOC
• 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 adsorption
• AWWA CyanoTOX calculator overestimated chlorine oxidation of microcystins. Consider applying safety factor of 2 (one study-follow-up studies planned for this summer)
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)
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.
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.
Educational Opportunities

Stone Lab Algae ID and HABs Courses, August 6-7, 8-9, 2018
• https://ohioseagrant.osu.edu/education/stonelab/courses/workshops

Akron Smart Water Conference
• May 30-31
• https://www.agwaevent.net/program

North America Lakes Management Society Annual Conference:
• Cincinnati, Ohio
• October 30 – November 2, 2018
• https://www.nalms.org/nalms2018/
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