EPA

Office of Ground Water and Drinking Water

Drinking Water Treatment for Cyanotoxins

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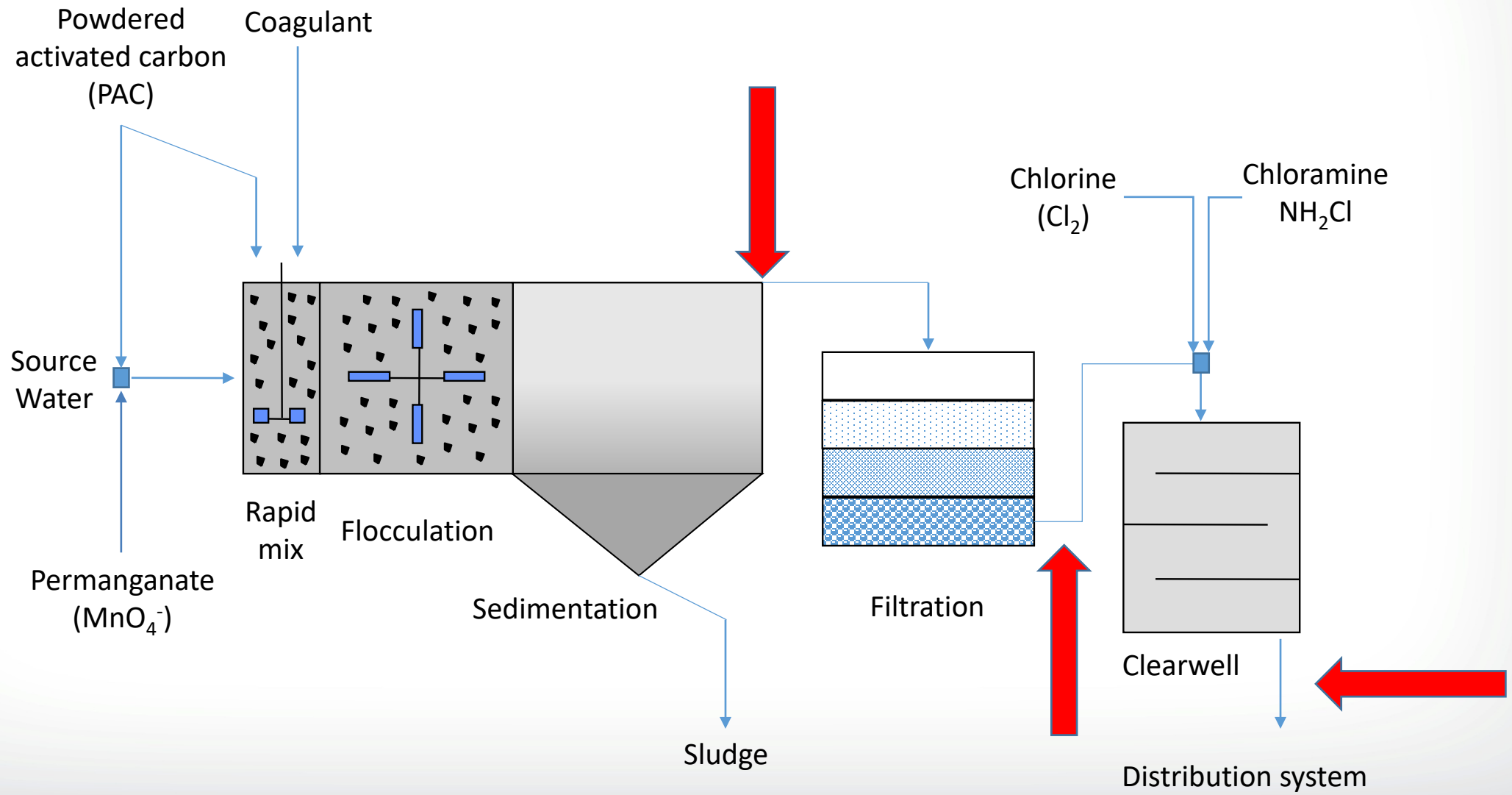
Office of Groundwater & Drinking Water

December 3, 2018

Conventional surface water treatment process



Definitions

Cell counts: direct counting of cells under a microscope

Chlorophyll: pigment molecules in algae and cyanobacteria that play a role in photosynthesis

Phycocyanin: pigment molecules in cyanobacteria that play a role in photosynthesis

Microcystins: A group of cyanotoxins produced by cyanobacteria, more commonly detected, affects the liver

ELISA: Enzyme-linked immunosorbent assay

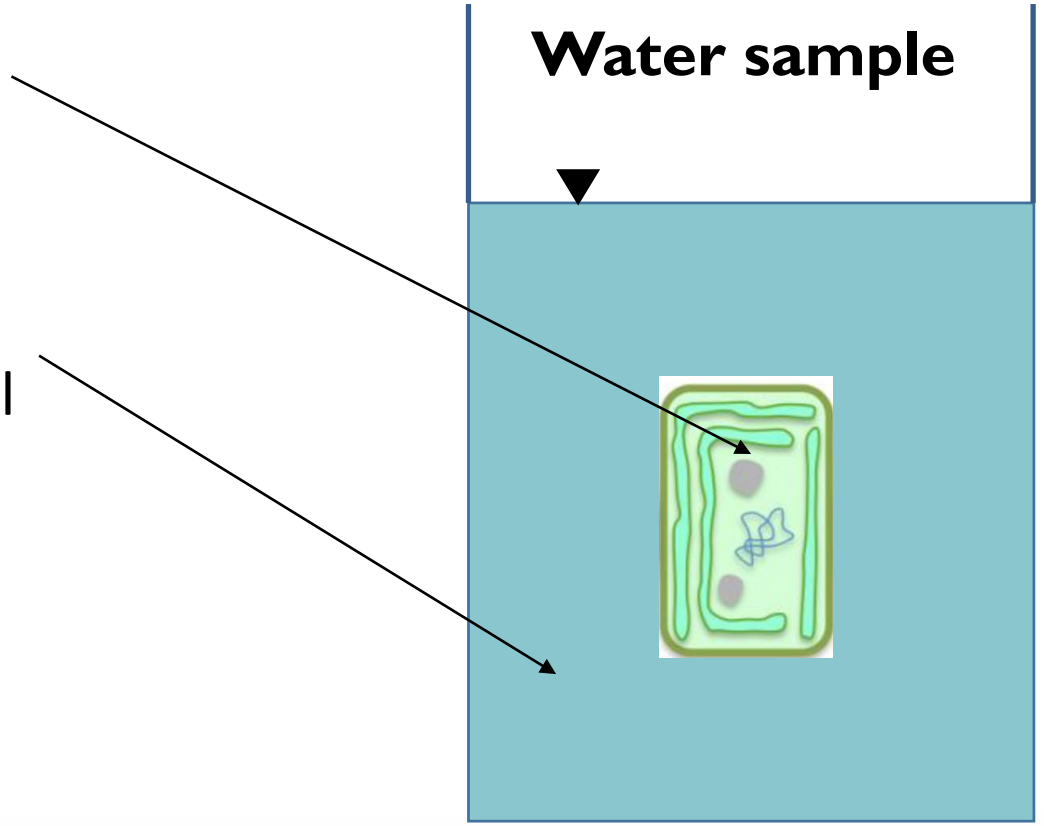
LC/MS/MS: Liquid chromatography, tandem mass spectrometry

Combined, intracellular, and extracellular toxins

Intracellular
Toxins contained inside the cell

Extracellular
Toxins in solution outside the cell

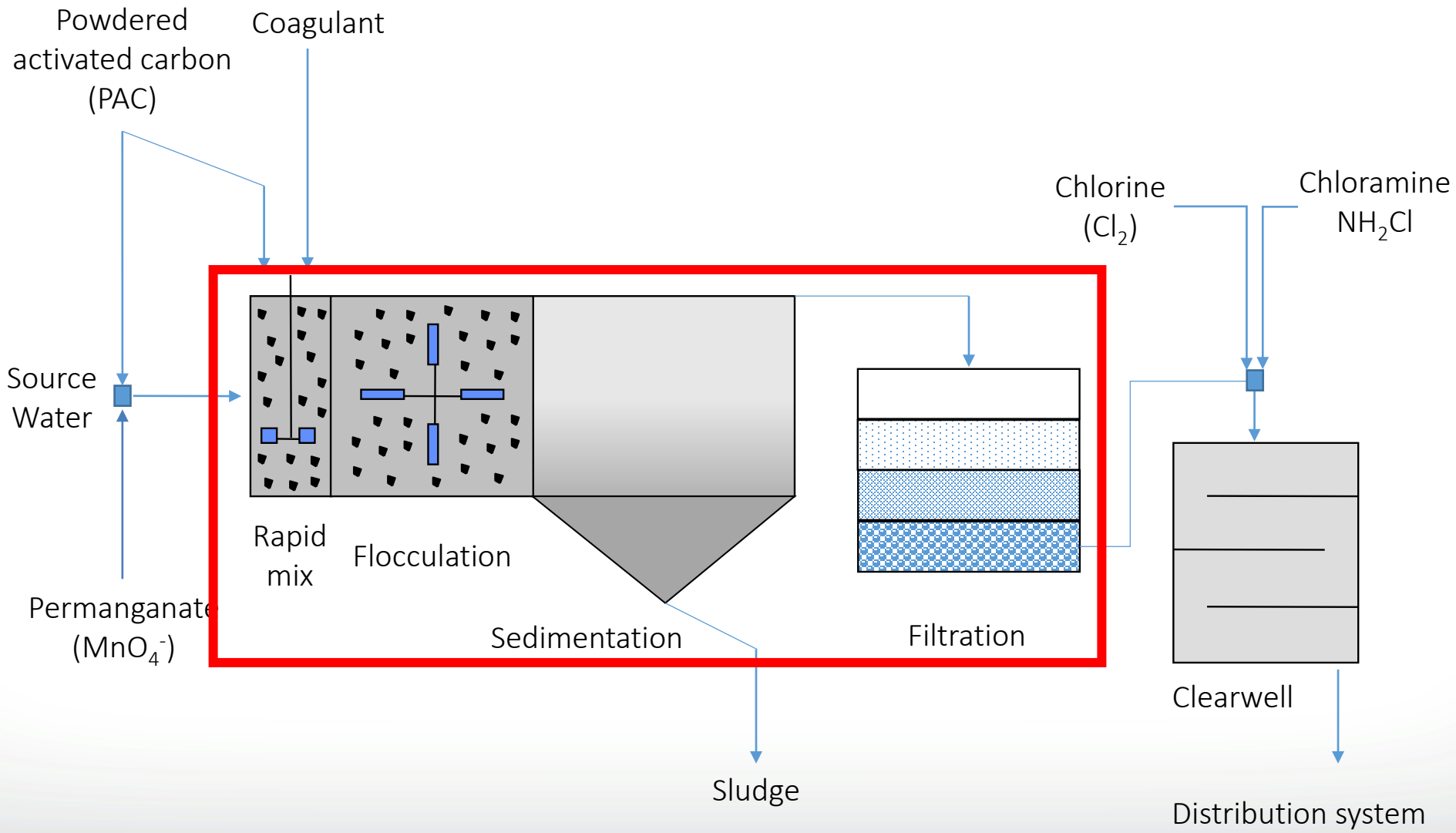
Combined
Extracellular + intracellular toxin



Multiple barrier strategy for cyanobacteria & cyanotoxin removal

- **Cyanobacteria cell removal**
  - Potential monitoring indicators include turbidity, particle counts, phycocyanin, chlorophyll-*a*, NOM, UV254, color
  - Treatment options focus on particle removal
    - Coagulation/flocculation, clarification, and filtration
    - Membranes
- **Cyanotoxin removal**
  - Analytical measurement by ADDA-ELISA, LC/MS/MS
  - Adsorption: powdered activated carbon (PAC) and granular activated carbon (GAC)
  - Oxidation / disinfection: adequate CT for pathogen inactivation and cyanotoxin oxidation

Conventional surface water treatment process



Unit process sampling

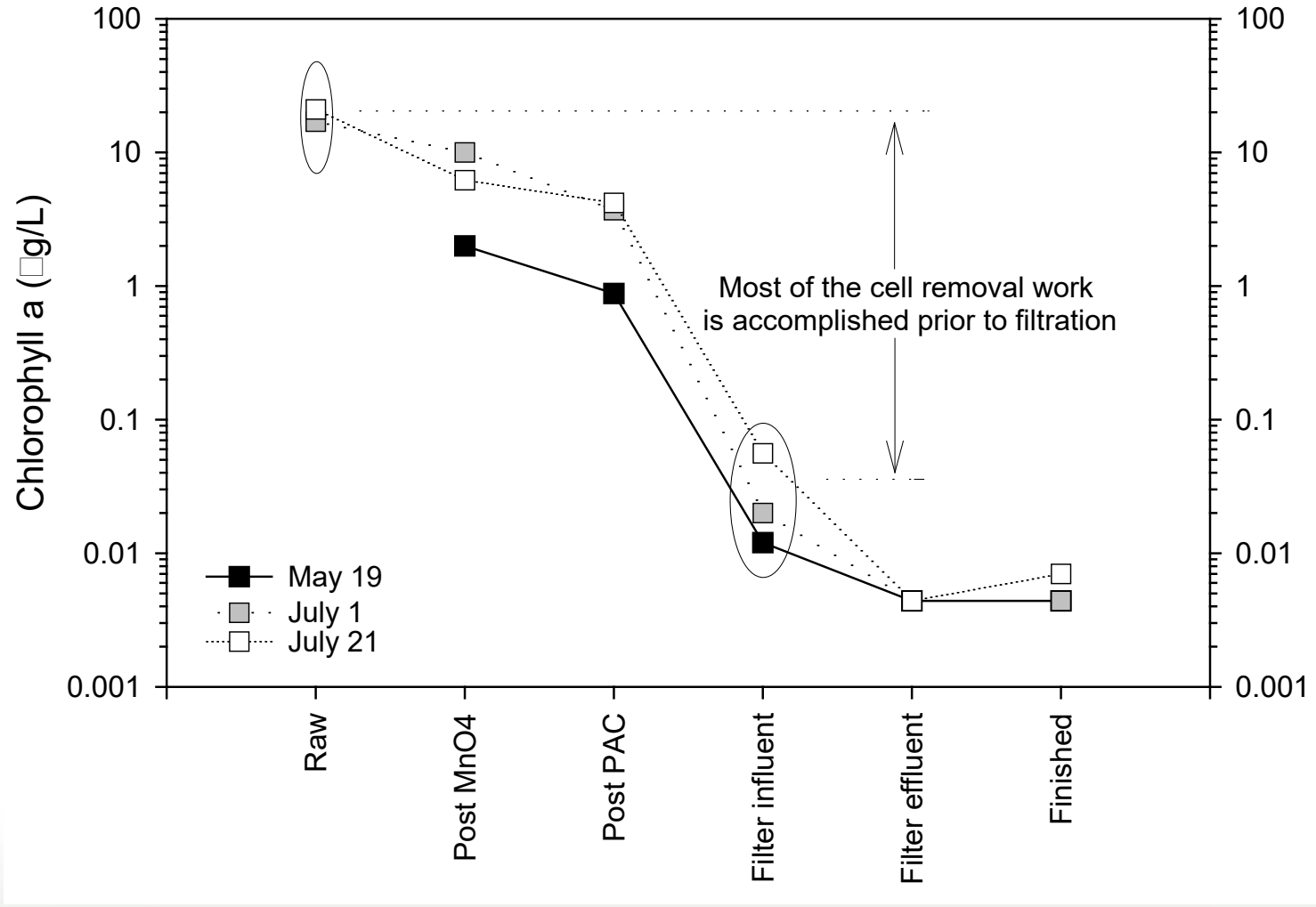
<u>YSI EXO sonde equipped with sensors</u>:

- Chlorophyll-*a (in-vivo, RFU)*
- Phycocyanin ("blue-green algae") *(in-vivo, RFU)*
- pH, temperature
- Turbidity

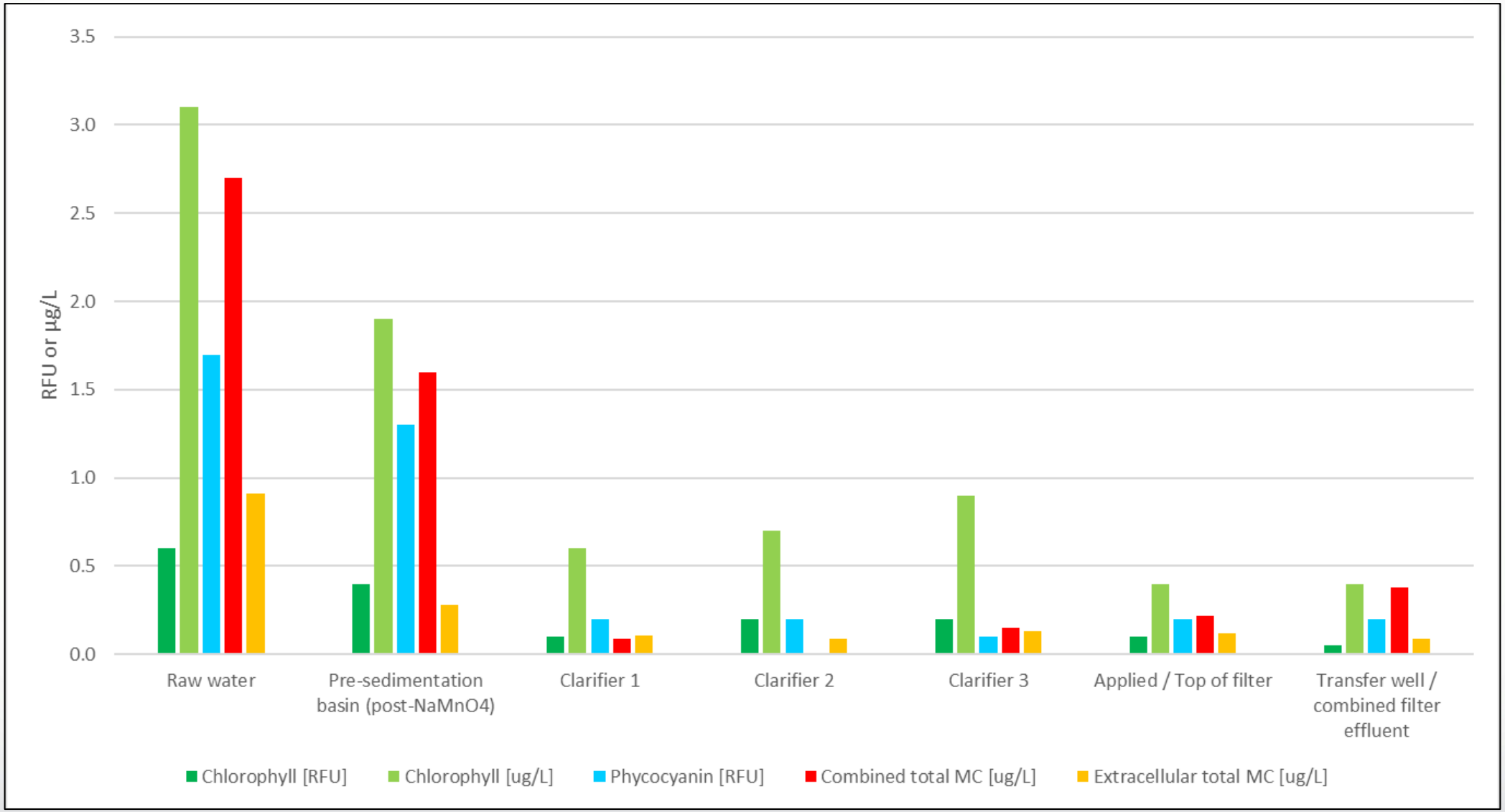
<u>Sample in-situ at the following locations in the plant</u>:

- Raw water
- Pre-sedimentation
- Clarifier effluent
- Top-of-filter
- Combined filter effluent

Cell propagation through a full-scale Lake Erie treatment facility



Through-plant sampling: Lake Erie water treatment plant



Jar testing

- Optimizing coagulant and polymer dosing can maximize cell removal through the treatment process. This can be effectively evaluated in most plants using jar testing.

- To evaluate optimal coagulant and polymer dosing for cyanobacteria cell removal, the following parameters can be monitored:
  - Turbidity
  - NOM
  - Pigments (chlorophyll-*a*, phycocyanin)
  - Color
  - UV254
  - Particle counts
  - Streaming current or zeta potential

Jar testing case study

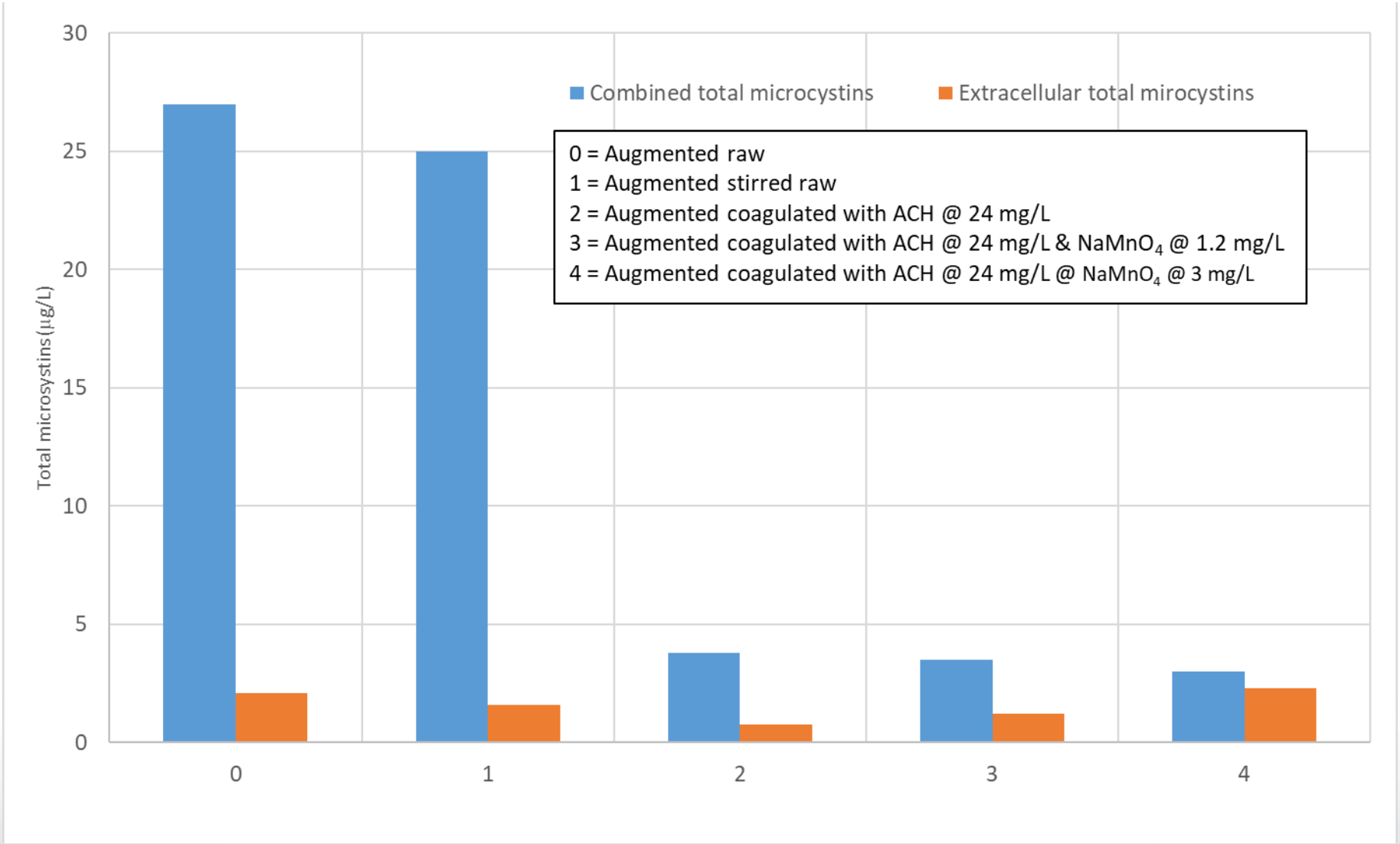
Objectives:

1. Understand effect of coagulant on cyanobacteria cell removal.
2. Understand effect of $KMnO_4$ on coagulation efficacy and cyanotoxin release from cyanobacteria cells.

Experimental setup:

- 4 jars stirred at mixing speed equivalent to turbulence in raw water main.
- Raw water sample augmented with concentrated cyanobacteria solution obtained with a phytoplankton net.
- Coagulant added at plant's dose.
- $KMnO_4$ added at plant dose and high dose.

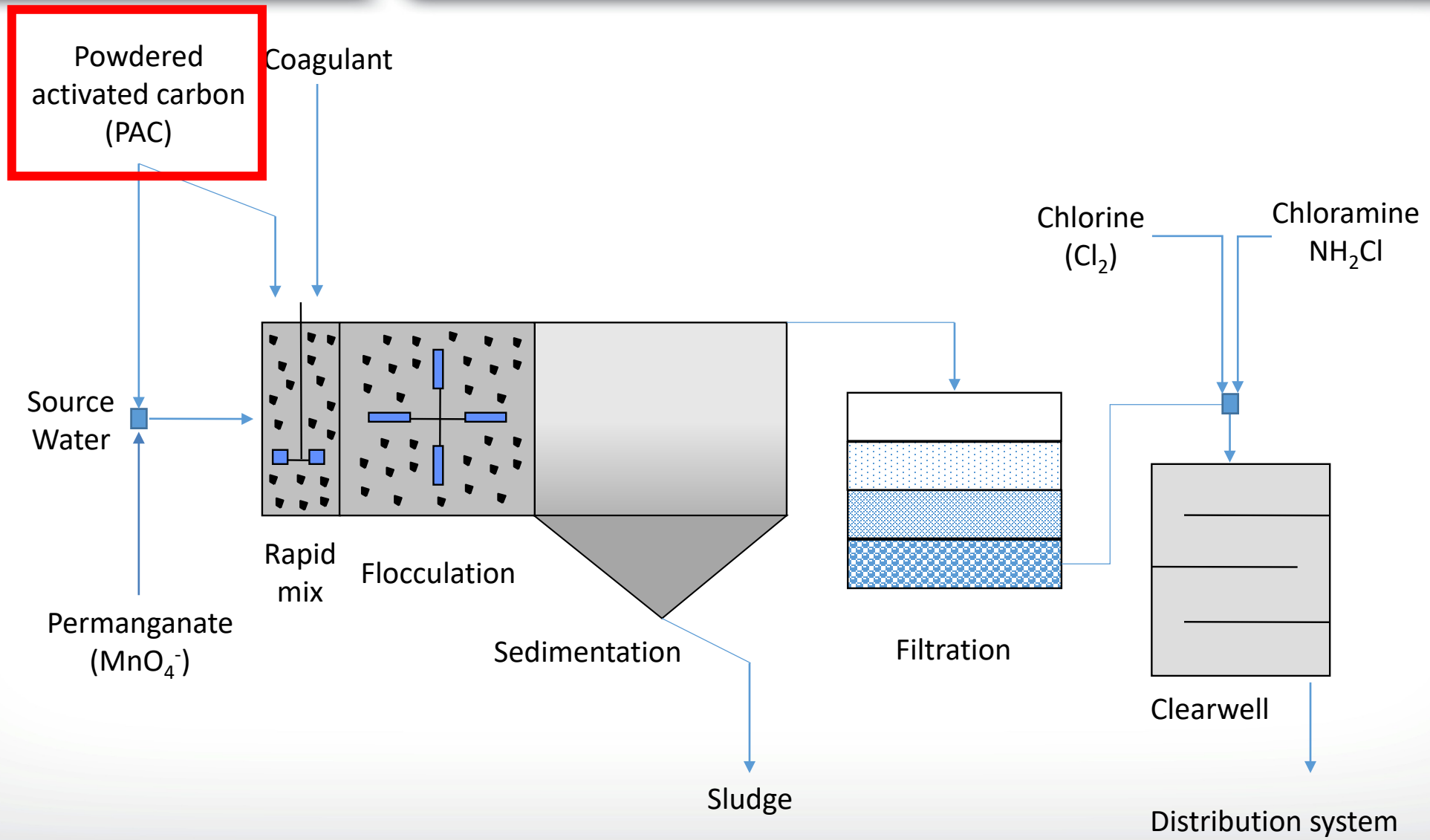
Bench-scale coagulation experiments with Lake Erie water and cyanobacteria



Operational considerations for coagulation, flocculation, sedimentation and filtration

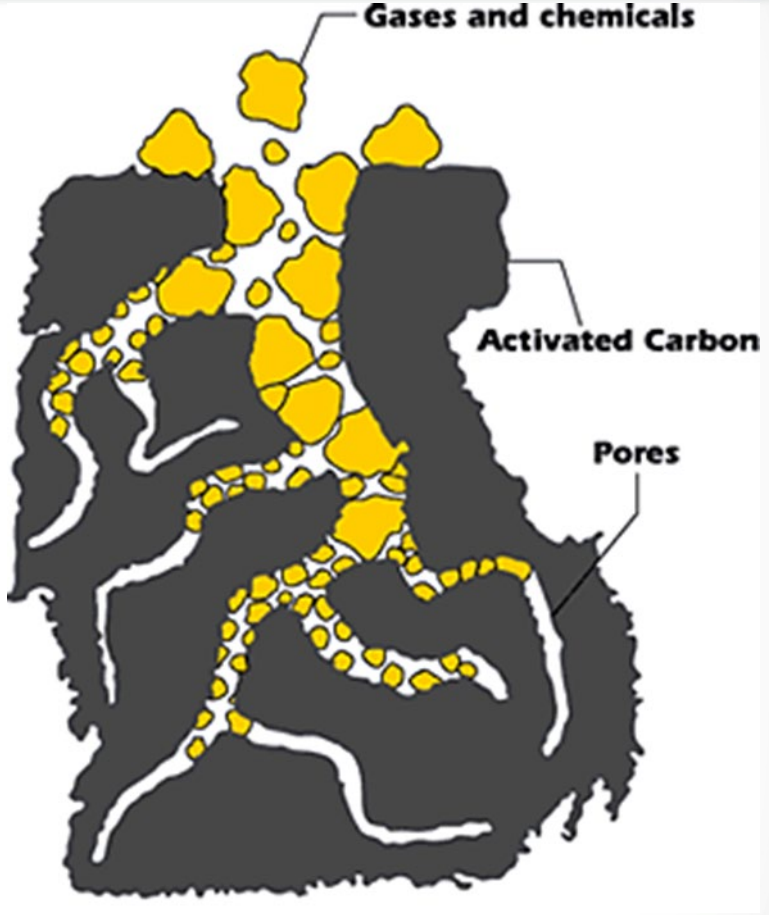
- Optimize coagulation, flocculation and sedimentation process through jar testing
- Filters that regularly achieve turbidity ≤ 0.10 NTU are better suited to remove cyanobacteria in the event of a HAB
- Backwashing filters based on water quality data, such as effluent turbidity, rather than length of time in service can lead to more optimal filter operation
- Trend water quality data regularly to understand baseline operation
- More frequent clarifier sludge removal may be necessary during a HAB

Conventional surface water treatment process



PAC treatment

- PAC effectiveness depends on:
  - Type of carbon (wood, coconut, coal)
  - Type of cyanotoxin or other compounds to be adsorbed
  - Dose and contact time
  - Natural organic matter (NOM) interference
- Jar testing best for assessing PAC type and dose
- AWWA PAC Jar Testing Protocol for Cyanotoxin Removal in Drinking Water



Micropores: < 2 nm
Mesopores: 2 - 50 nm **vs. microcystin-LR: 1-3 nm**
Macropores: > 50 nm

Operational considerations for PAC

- Consider sufficient supply, storage space, and safety prior to HAB season
- Consider operational impacts of adding PAC on sedimentation and filtration processes
  - More frequent sludge removal, higher volumes
  - Potential for filter clogging
  - Test higher PAC feed rates, if needed, prior to HAB season to evaluate potential for line clogging at higher doses

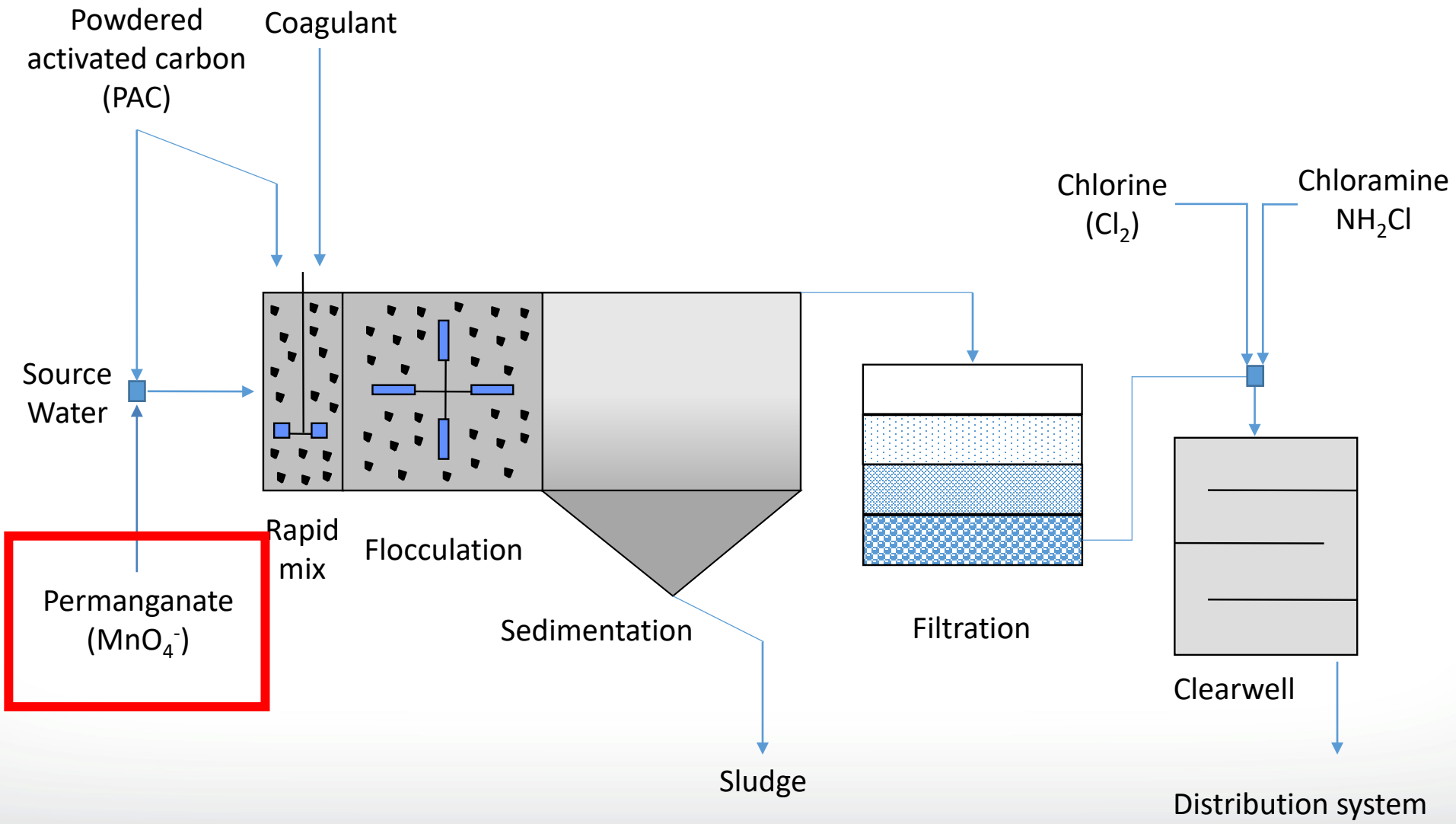
Oxidation treatment resources

Oxidant	Anatoxin-a	Cylindrospermopsin	Microcystins	Saxitoxin
Chlorine	Not effective	Effective (at low pH)	Effective*	Somewhat effective
Chloramine	Not effective	Not effective	Not effective at normal doses	Inadequate information
Chlorine dioxide	Not effective at normal doses	Not effective	Not effective at normal doses	Inadequate information
Potassium permanganate	Effective	Data ranges from not effective to possibly effective	Effective*	Not effective
Ozone	Effective	Effective	Very effective	Not effective
UV / advanced oxidation	Effective	Effective	Effective at high UV doses*	Inadequate information

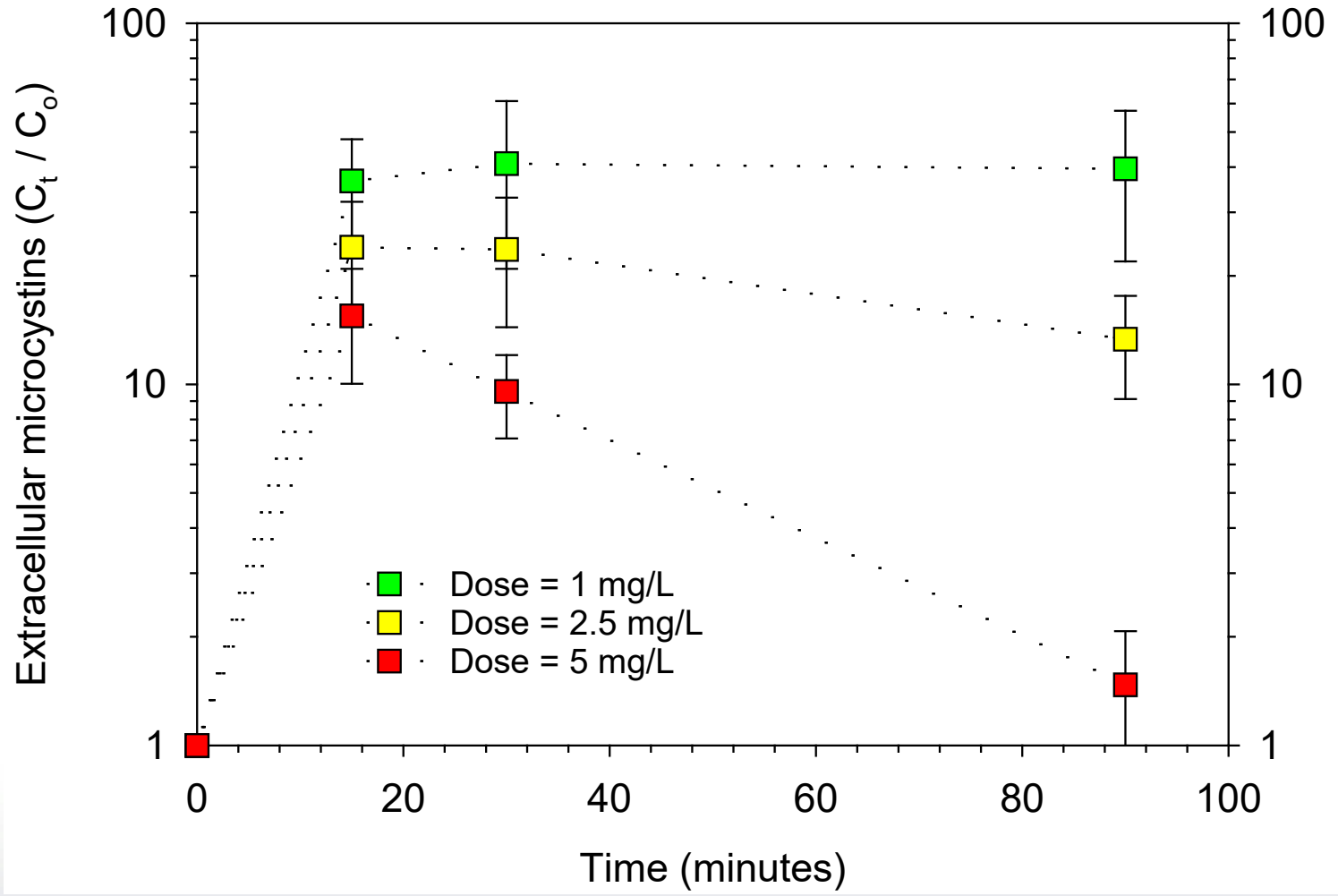
* Dependent on initial cyanotoxin concentration, pH, temperature, and presence of NOM.

Source: Ohio EPA and Ohio AWWA "White Paper on Algal Toxin Treatment", 2015

Conventional surface water treatment process



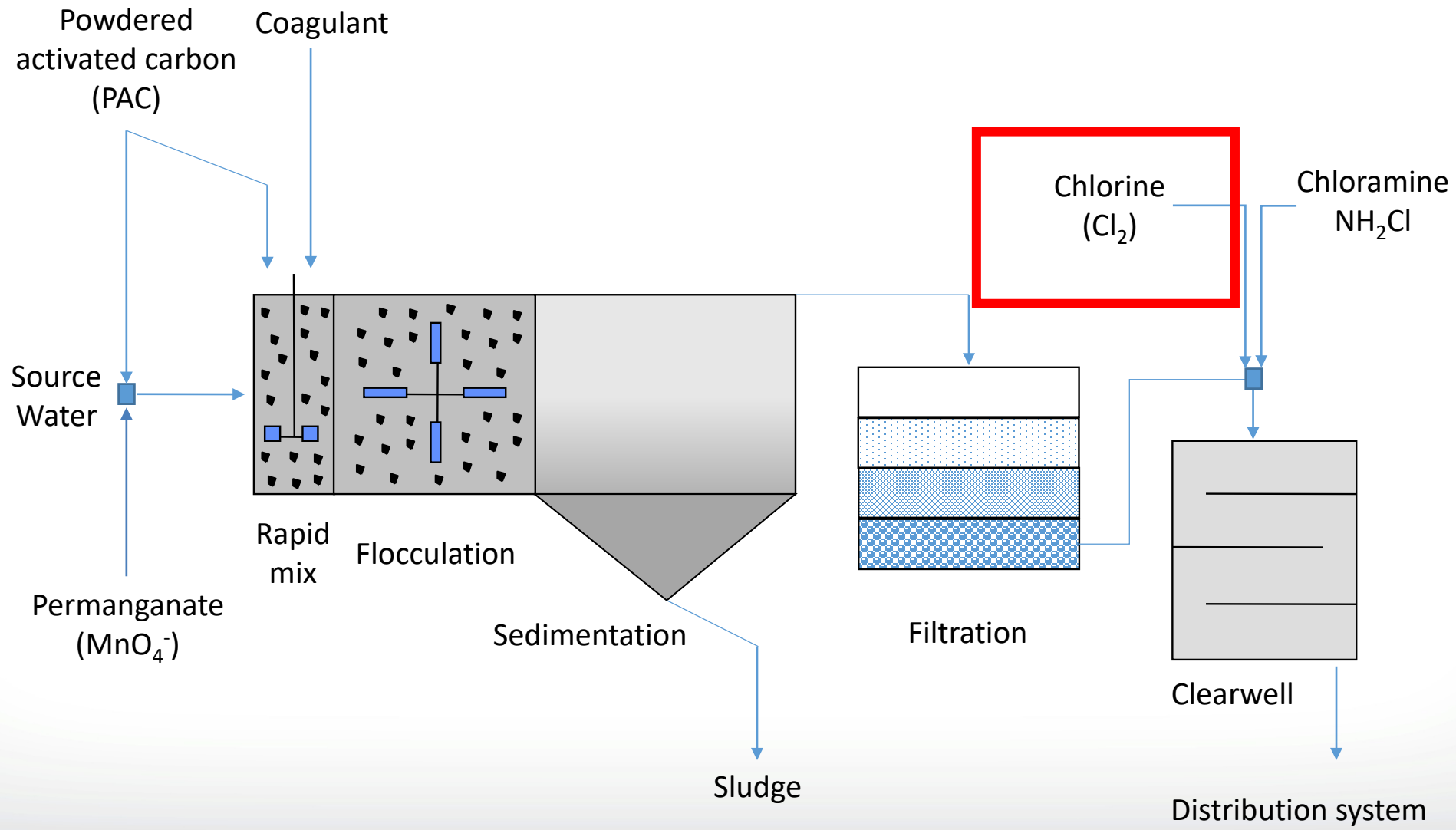
Impact of KMnO4 on Toxin Release from Cyanobacterial Cells and Subsequent Degradation



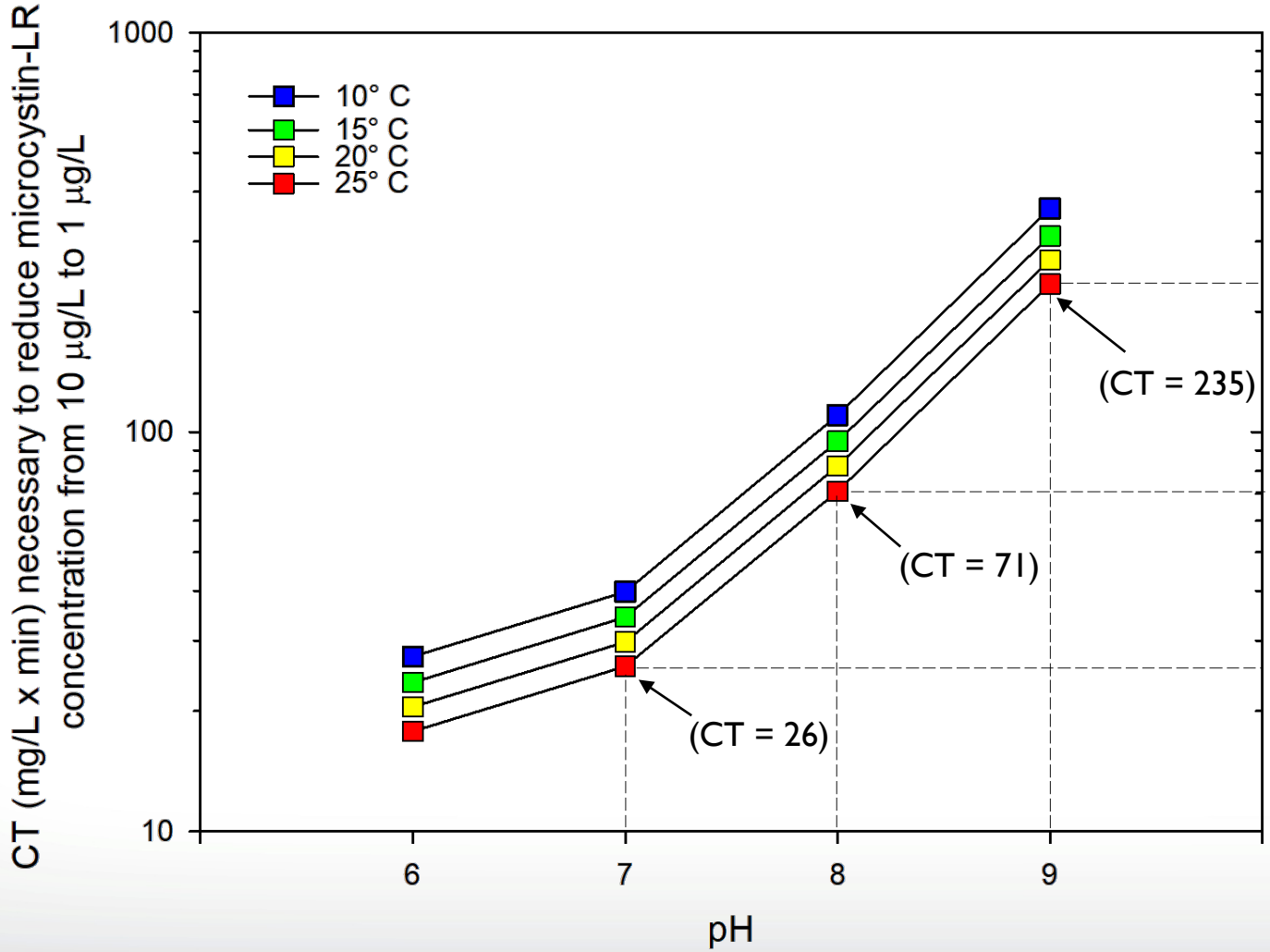
Operational considerations for permanganate pre-oxidation

- Consider reducing or stopping pre-oxidant use to minimize toxin release from cyanobacteria cells.
- Consider the impact of doing so on other treatment objectives that the pre-oxidant may be used to achieve (e.g., turbidity, TOC, and manganese removal; algae control in the plant; mussel control in intake line).
- Planning for and considering how these objectives will be achieved prior to the bloom season is critical.

Conventional surface water treatment process



Impact of chlorination on microcystin concentrations



CT for 3-log *Giardia* inactivation @ 1.0 mg/L Cl_2, t = 25° C:

- pH 7: 37
- pH 8: 54
- pH 9: 78

> 3X increase in CT

> 2X increase in CT

*Figure based on data from Acero et al, *Water Research*, 2005:39:1628-1638

AWWA CyanoTOX oxidation calculator

CALCULATOR INPUT PAGE

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

Cyanotoxin Type: Microcystin-Mix (MC-Mix) →

Variant	MC-LR	MC-RR	MC-YR	MC-LA	MC-LY	MC-LF	MC-Mix
Percent	5%	20%	50%	10%	5%	10%	100%

STEP 2. Input the following system parameters

pH (between 6-10)	9.2
Temperature (between 10-30°C)	10

STEP 3. Input the initial cyanotoxin concentration

Cyanotoxin Initial Concentration (µg/L): 3.79

(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. 1) 2)

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)

STEP 7. Input the following parameters

Baffling Factor	1
Oxidant Dose (mg/L)	7
Instantaneous oxidant demand (mg/L)	2.95
Contact Time (i.e., hydraulic detent. time, min)	300
Effective Oxidant Half Life (min)	360

(Enter a value in minutes OR "ND" for No Decay")

AWWA CyanoTOX oxidation calculator

CT-based results:

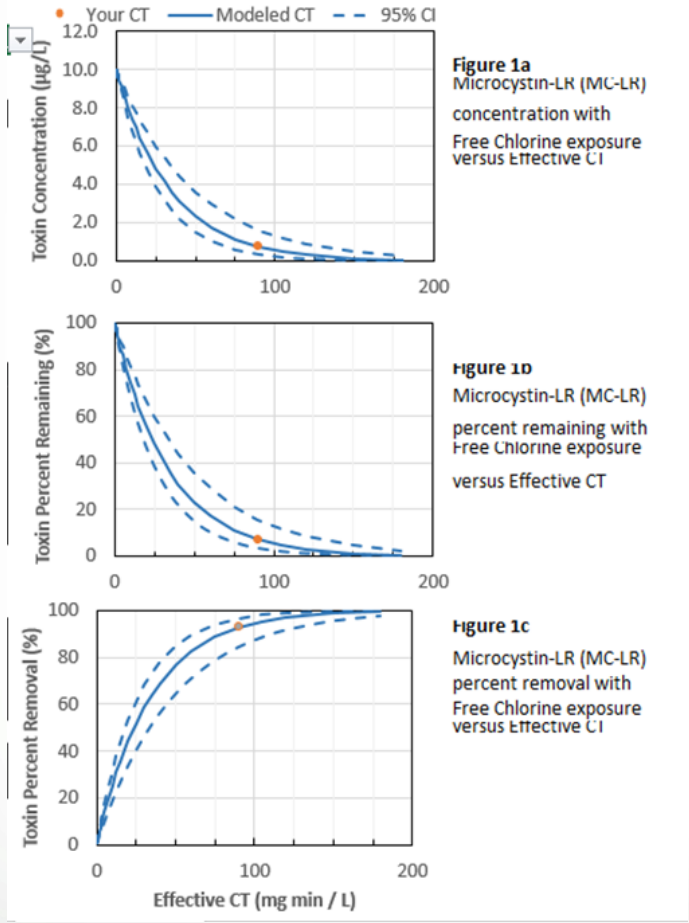


Figure 1a
Microcystin-LR (MC-LR) concentration with Free Chlorine exposure versus Effective CT

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

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

Dose-decay based results:

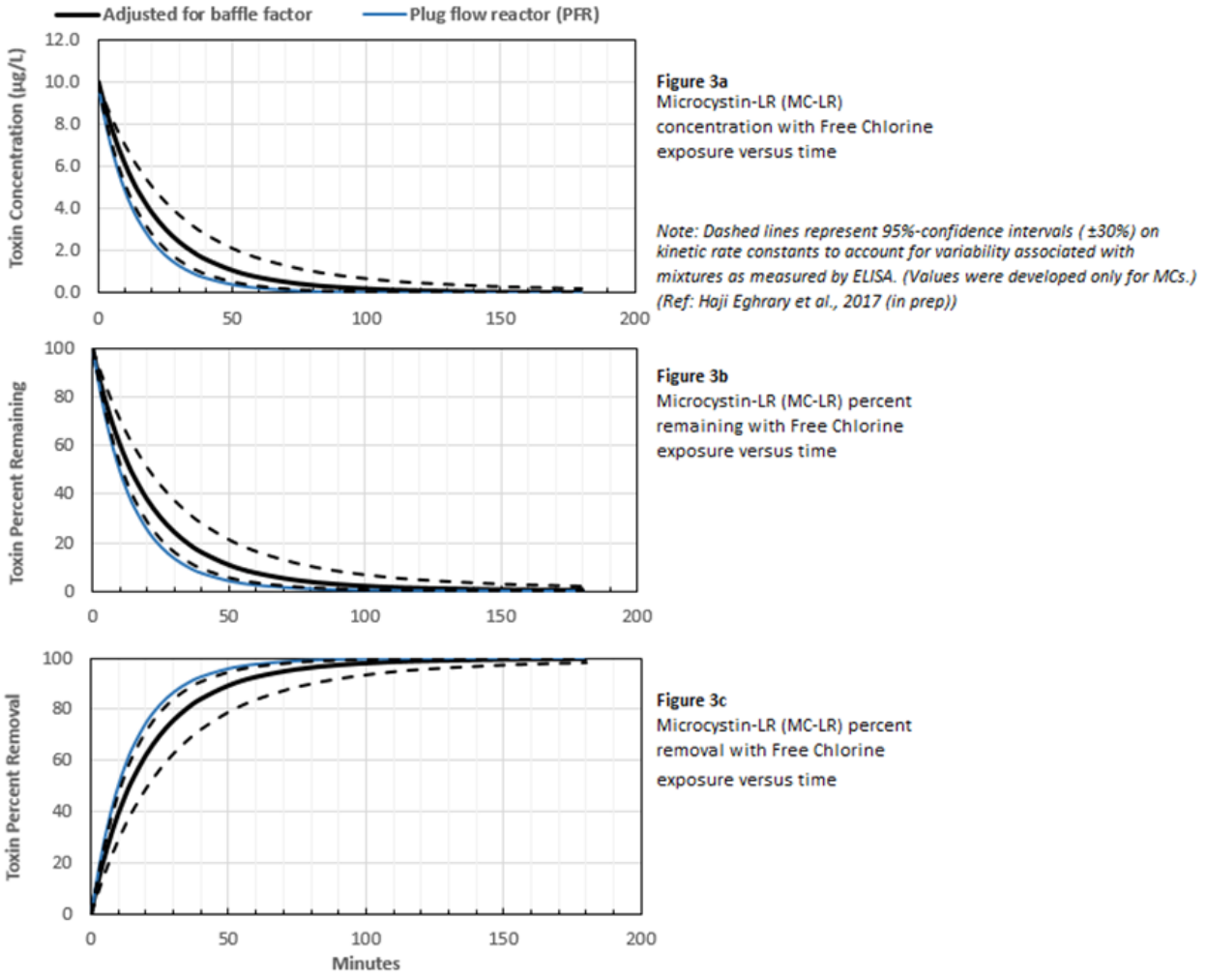


Figure 3a
Microcystin-LR (MC-LR) concentration with Free Chlorine exposure versus time

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

Figure 3b
Microcystin-LR (MC-LR) percent remaining with Free Chlorine exposure versus time

Figure 3c
Microcystin-LR (MC-LR) percent removal with Free Chlorine exposure versus time

Operational considerations for chlorination

- Consider where chlorine is dosed and if any competing technologies that would limit its effectiveness.
- Consider the potential for formation of disinfection byproducts.

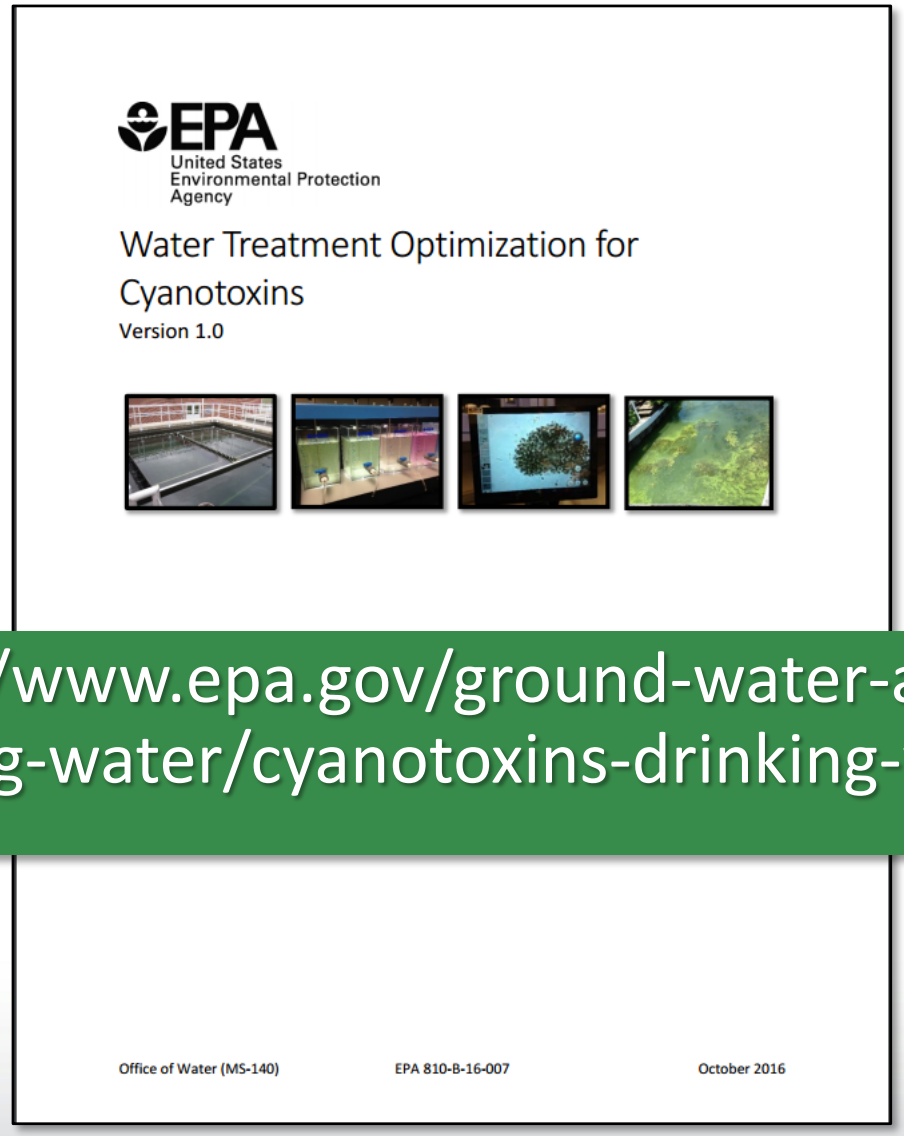
Conclusions

- When optimized, conventional treatment processes (coagulation, flocculation, sedimentation, filtration) are highly effective at removing cyanobacterial cells.
- PAC effectively adsorbs microcystins however, the exact carbon dose will vary depending on the type of cyanotoxin, type of carbon, and the NOM background.

Conclusions

- Chlorine effectively degrades microcystins – but the rate of degradation is temperature and pH dependent.
- Ozone effectively degrades microcystins.
- Chlorine dioxide and UV, at the dose levels commonly employed in drinking water treatment, are not effective.
- Permanganate effectively degrades dissolved microcystins – however, the typical location for permanganate addition, early in the treatment process where cyanobacterial cell concentrations are still high, sets up a potential for toxin release – vigilance is recommended.

EPA document

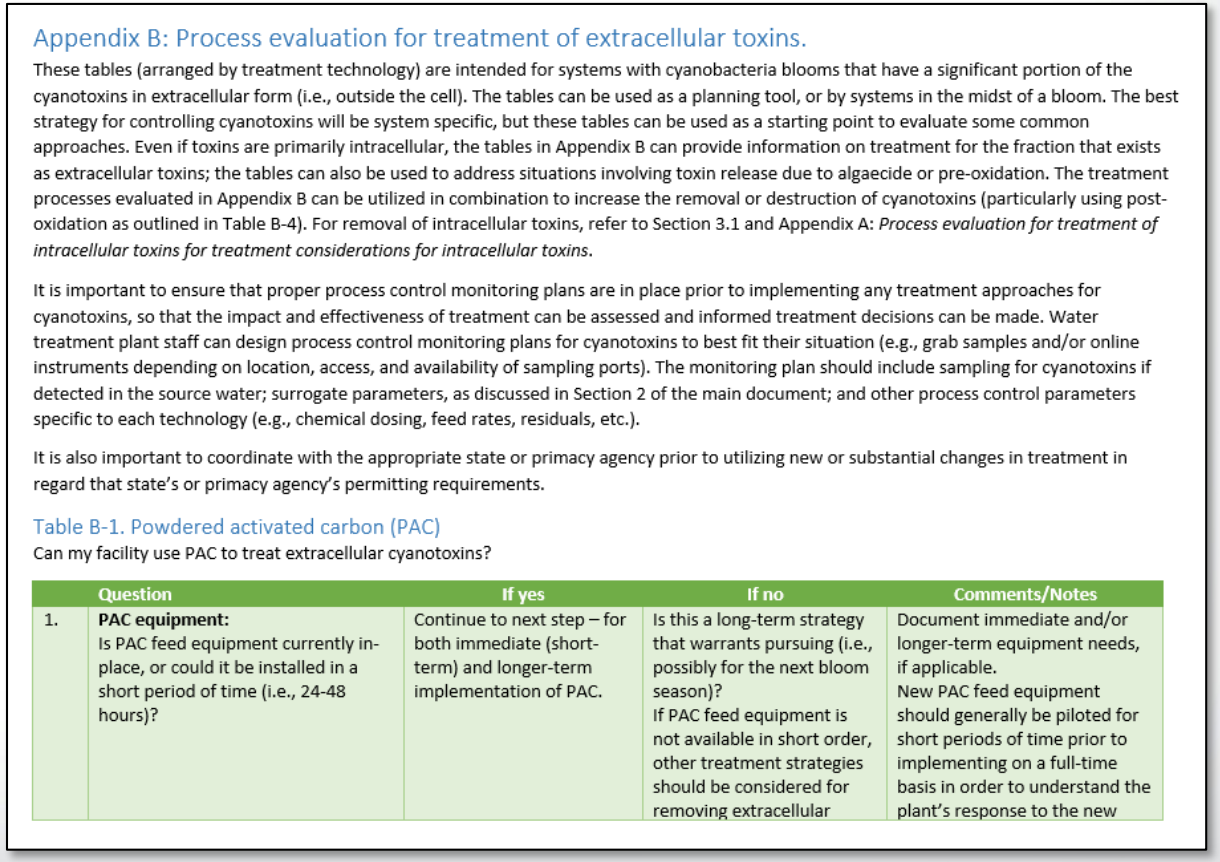


https://www.epa.gov/ground-water-and-drinking-water/cyanotoxins-drinking-water

EPA document appendices

Process evaluation for various types of treatment:

- For intracellular cyanotoxins:
  - Conventional treatment (coagulation, flocculation, sedimentation and filtration)
  - Membranes
- For extracellular cyanotoxins:
  - Powdered activated carbon (PAC)
  - Granular activated carbon (GAC)
  - Membranes (RO, NF)
  - Oxidation



Appendix B: Process evaluation for treatment of extracellular toxins.

These tables (arranged by treatment technology) are intended for systems with cyanobacteria blooms that have a significant portion of the cyanotoxins in extracellular form (i.e., outside the cell). The tables can be used as a planning tool, or by systems in the midst of a bloom. The best strategy for controlling cyanotoxins will be system specific, but these tables can be used as a starting point to evaluate some common approaches. Even if toxins are primarily intracellular, the tables in Appendix B can provide information on treatment for the fraction that exists as extracellular toxins; the tables can also be used to address situations involving toxin release due to algaecide or pre-oxidation. The treatment processes evaluated in Appendix B can be utilized in combination to increase the removal or destruction of cyanotoxins (particularly using post-oxidation as outlined in Table B-4). For removal of intracellular toxins, refer to Section 3.1 and Appendix A: *Process evaluation for treatment of intracellular toxins for treatment considerations for intracellular toxins*.

It is important to ensure that proper process control monitoring plans are in place prior to implementing any treatment approaches for cyanotoxins, so that the impact and effectiveness of treatment can be assessed and informed treatment decisions can be made. Water treatment plant staff can design process control monitoring plans for cyanotoxins to best fit their situation (e.g., grab samples and/or online instruments depending on location, access, and availability of sampling ports). The monitoring plan should include sampling for cyanotoxins if detected in the source water; surrogate parameters, as discussed in Section 2 of the main document; and other process control parameters specific to each technology (e.g., chemical dosing, feed rates, residuals, etc.).

It is also important to coordinate with the appropriate state or primacy agency prior to utilizing new or substantial changes in treatment in regard that state's or primacy agency's permitting requirements.

Table B-1. Powdered activated carbon (PAC)

Can my facility use PAC to treat extracellular cyanotoxins?

	Question	If yes	If no	Comments/Notes
1.	**PAC equipment:** Is PAC feed equipment currently in-place, or could it be installed in a short period of time (i.e., 24-48 hours)?	Continue to next step – for both immediate (short-term) and longer-term implementation of PAC.	Is this a long-term strategy that warrants pursuing (i.e., possibly for the next bloom season)? If PAC feed equipment is not available in short order, other treatment strategies should be considered for removing extracellular	Document immediate and/or longer-term equipment needs, if applicable. New PAC feed equipment should generally be piloted for short periods of time prior to implementing on a full-time basis in order to understand the plant's response to the new

HAB CPE development pilot project

- Partnering with Ohio EPA
- Series of 4 pilot HAB CPEs at Ohio WTPs
- Develop protocol for conducting a HAB CPE by modifying the existing microbial CPE framework
- Transfer capability to conduct CPEs to Ohio EPA staff, and other states (long-term)
- Ohio EPA HAB water treatment experience at plant level

Questions?

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