U.S. Environmental Protection Agency, Office of Research and Development

SAFE AND SUSTAINABLE WATER RESOURCES RESEARCH PROGRAM

Treatment Options For HABs Impacted Waters

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Kansas AWWA Operator Certification Session

November 12, 2020

Outline

A. Background and definitions

B. Drinking water treatment options:

   i. Permanganate

   ii. Powdered activated carbon (PAC)

   iii. Coagulation/flocculation/sedimentation

   iv. Filtration

   v. Chlorination

   vi. UV/ozone/chlorine dioxide

Background

- All water bodies contain suspended (planktonic) micro-organisms. They are an essential part of the aquatic food web and include single-cell phototrophic micro-organisms such as:
  - Algae (eukaryotic)
  - Cyanobacteria (prokaryotic)
- A harmful algal bloom (HAB) occurs when these micro-organisms multiply to the point that they disturb the baseline ecology of the water body
- If a bloom is caused by cyanobacteria, why is it called a "harmful algal bloom?"
  - Prior to the use of DNA sequencing, cyanobacteria were classified as "blue-green algae"
  - Terms such as "cyanobacteria" and "blue-green algae" are still used interchangeably

Background

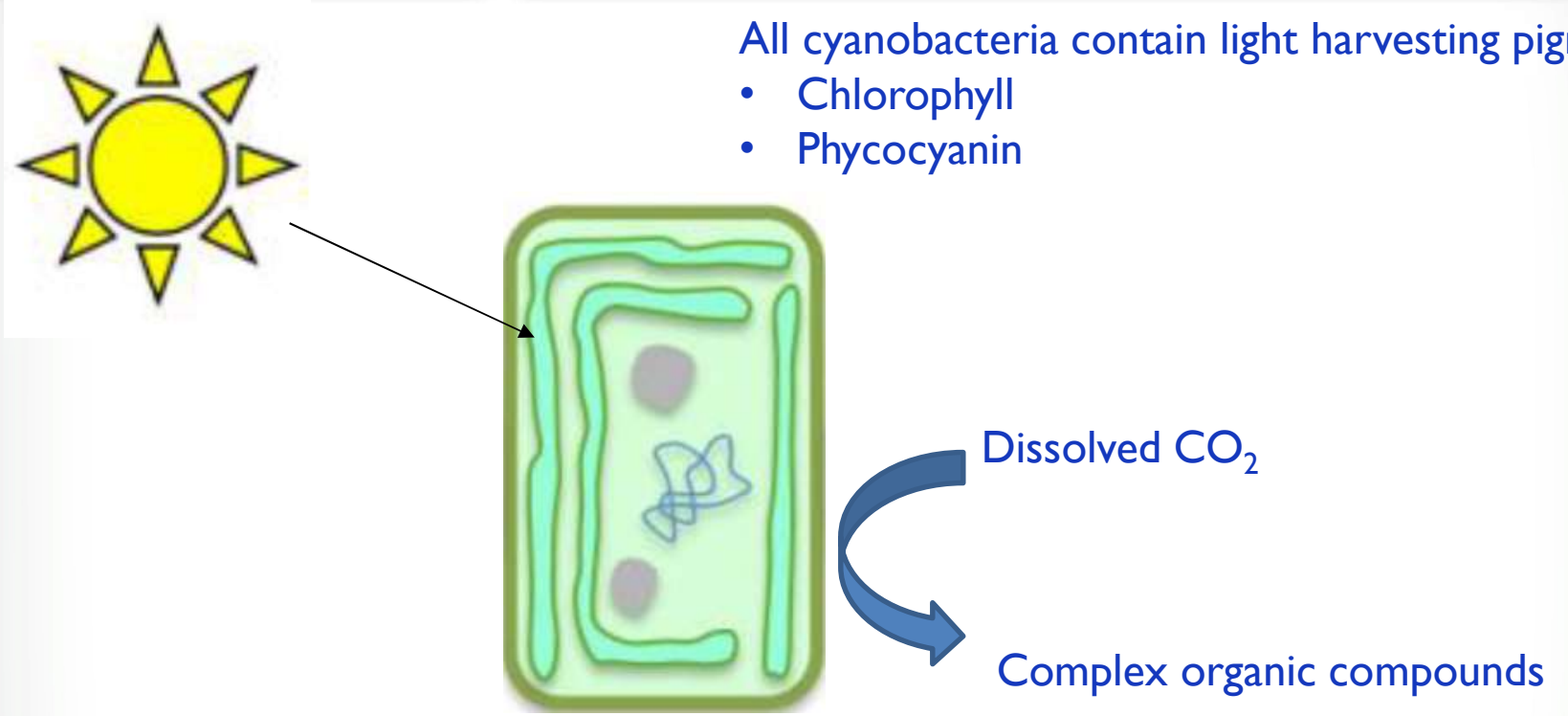
- Why is a bloom potentially harmful?
  - Unpleasant appearance
  - Unpleasant tastes and/or odors
  - Cyanobacterial toxins

    Water potentially unsuitable for body-contact recreation by humans and animals
  - Negative impacts on aquatic food web
  - Increased difficulty in treating drinking water:
    - Maintenance & operation issues
    - Potential for exceeding health advisory toxin concentration values
    - Potential for loss of confidence in the quality of treated drinking water

Background

All cyanobacteria contain light harvesting pigments:

- Chlorophyll
- Phycocyanin

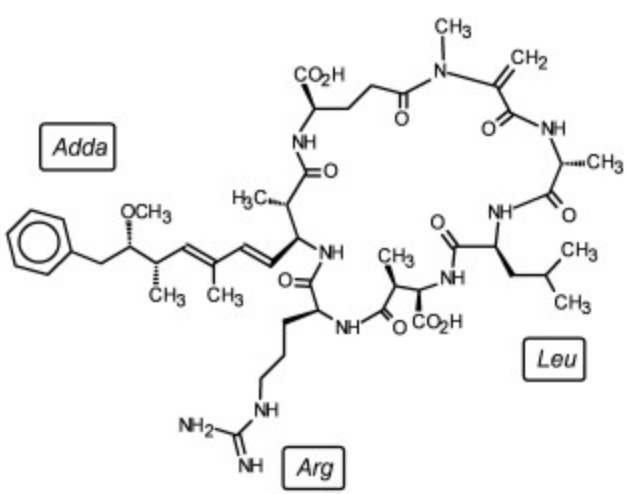


- Not all cyanobacteria produce toxins
- In toxin-producing cyanobacteria – timing of toxin production can vary
- When toxins produced, they are usually contained within the cell membrane
- Sometimes toxins released from cells into solution

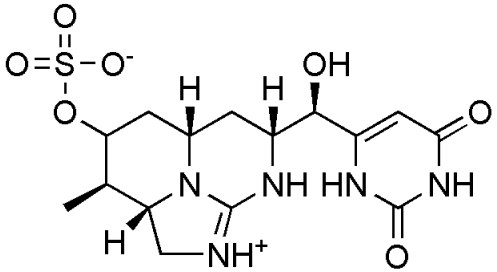
Figure adapted from: Kamennaya, N.A., et al; *Minerals* 2012:2:338-364

Background

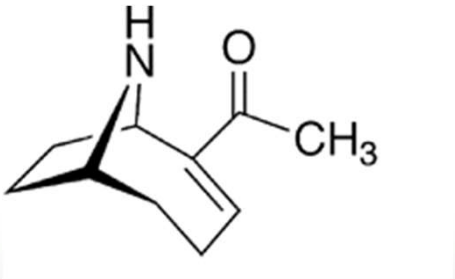
Microcystin → liver



Cylindrospermopsin → kidneys & liver



Anatoxin → central nervous system

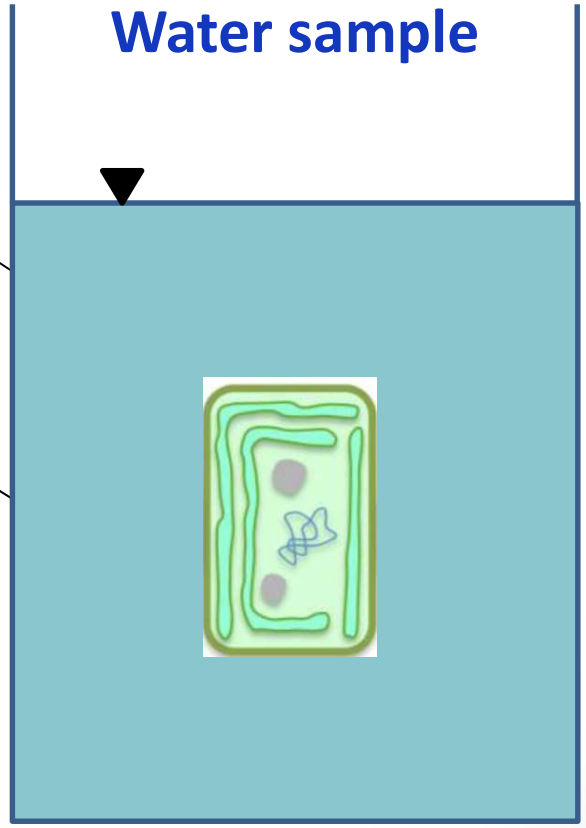


Background

Intracellular
Toxins contained inside the cell

Extracellular
Toxins in solution outside the cell

Combined
Extracellular + intracellular toxin

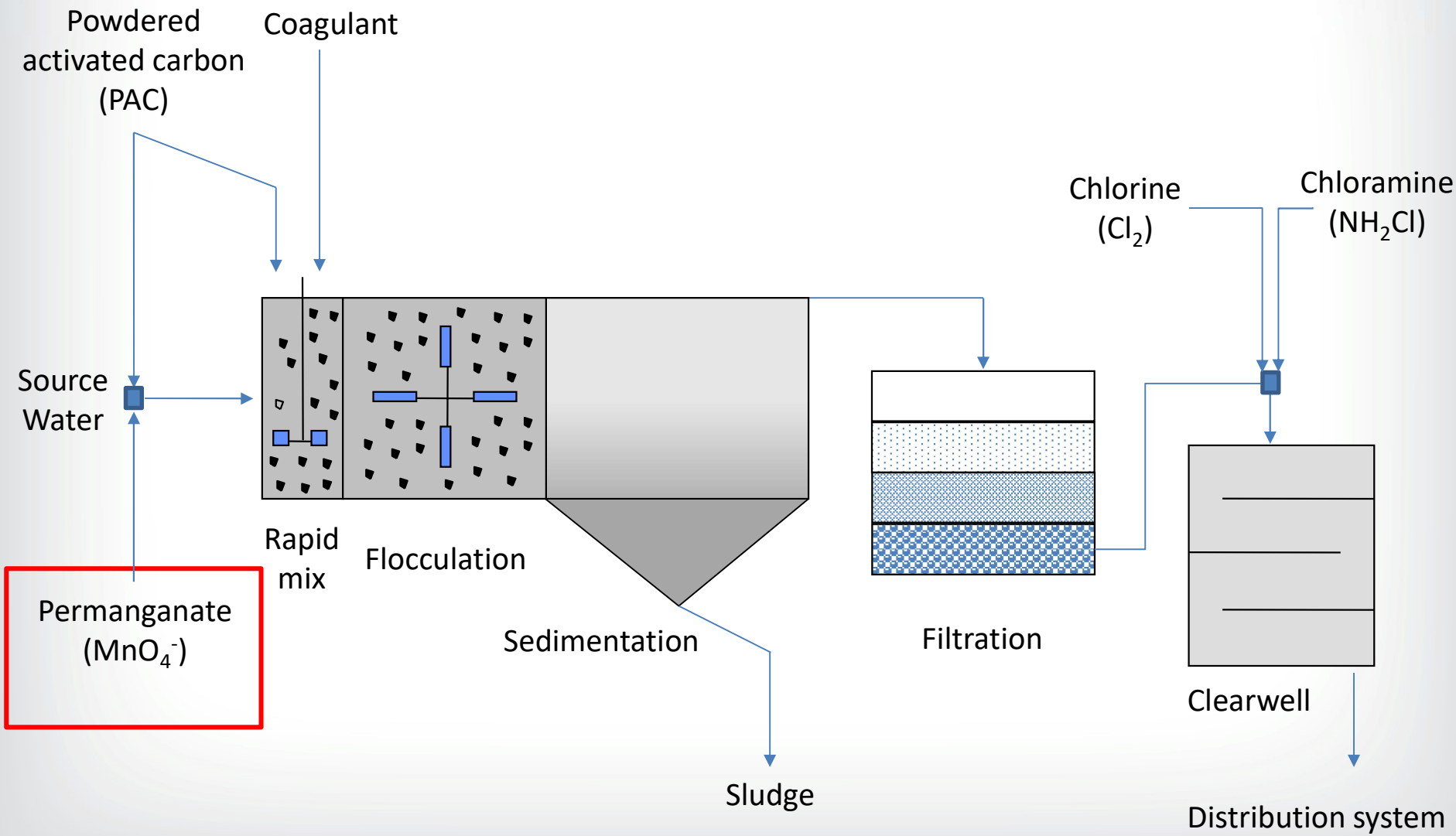


Federal Finished Drinking Water Toxin Health Advisory Levels

US EPA 10-day health advisory levels (µg/L)

Toxin	Children < 6 years	Children ≥ 6 years & adults
Microcystin	0.3	1.6
Cylindrospermopsin	0.7	3.0

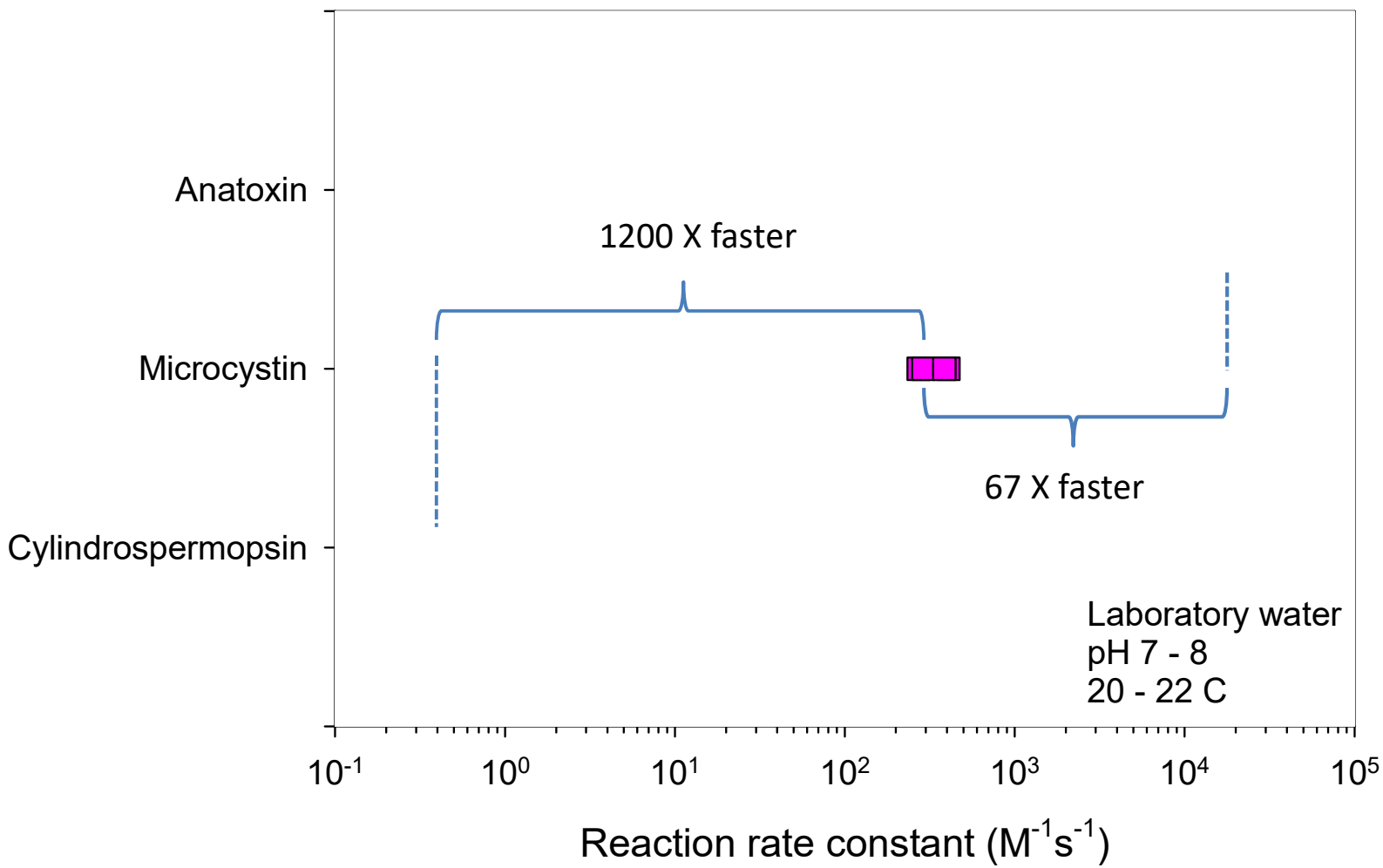
Conventional Surface Water Treatment



Permanganate

- Permanganate (MnO_4^-):
  - Applied early in the treatment process – often the 1st chemical added
  - Applied as a sodium or potassium salt
  - Taste and odor control
  - DBP precursor control
  - Iron and manganese control
  - Control of zebra mussels in intake structures
  - Induces oxidative stress in cyanobacterial cells → may lead to the release of toxins into solution
  - Oxidizes toxins released into solution

Permanganate – Reaction Rates



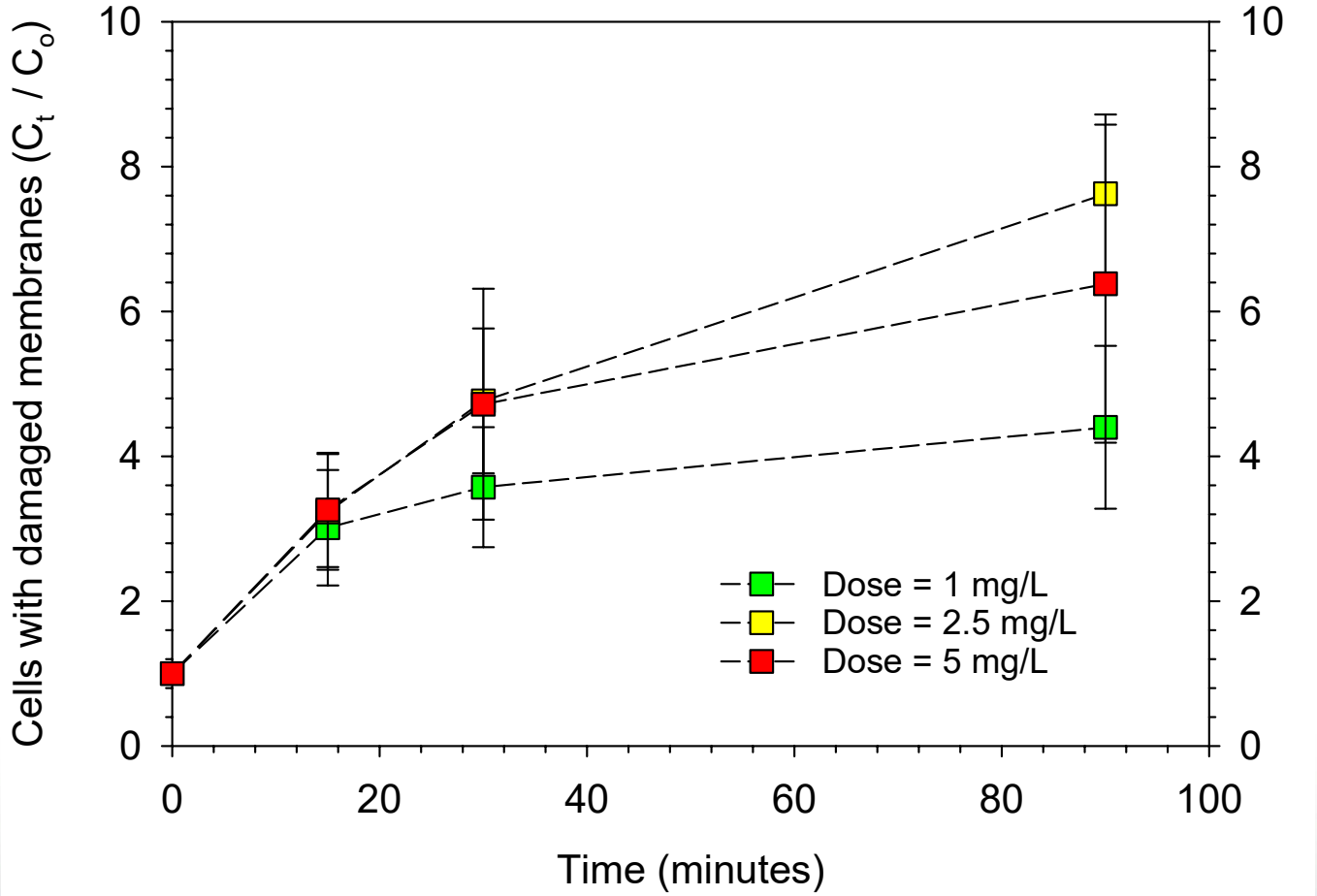
See bibliography slide (#55) for data sources

Permanganate – Reaction Rates

- The permanganate/toxin reaction rate depends on the type of toxin: anatoxin >> microcystin >> cylindrospermopsin
- The permanganate/toxin reaction rate will increase with increasing temperatures
- Within the pH range of 7 – 9, the permanganate/toxin reaction rate does not change significantly with pH
- Dissolved natural organic matter (NOM) and inorganic constituents such as iron and manganese can react with permanganate → possibility of competing reactions → potentially slower degradation of toxins

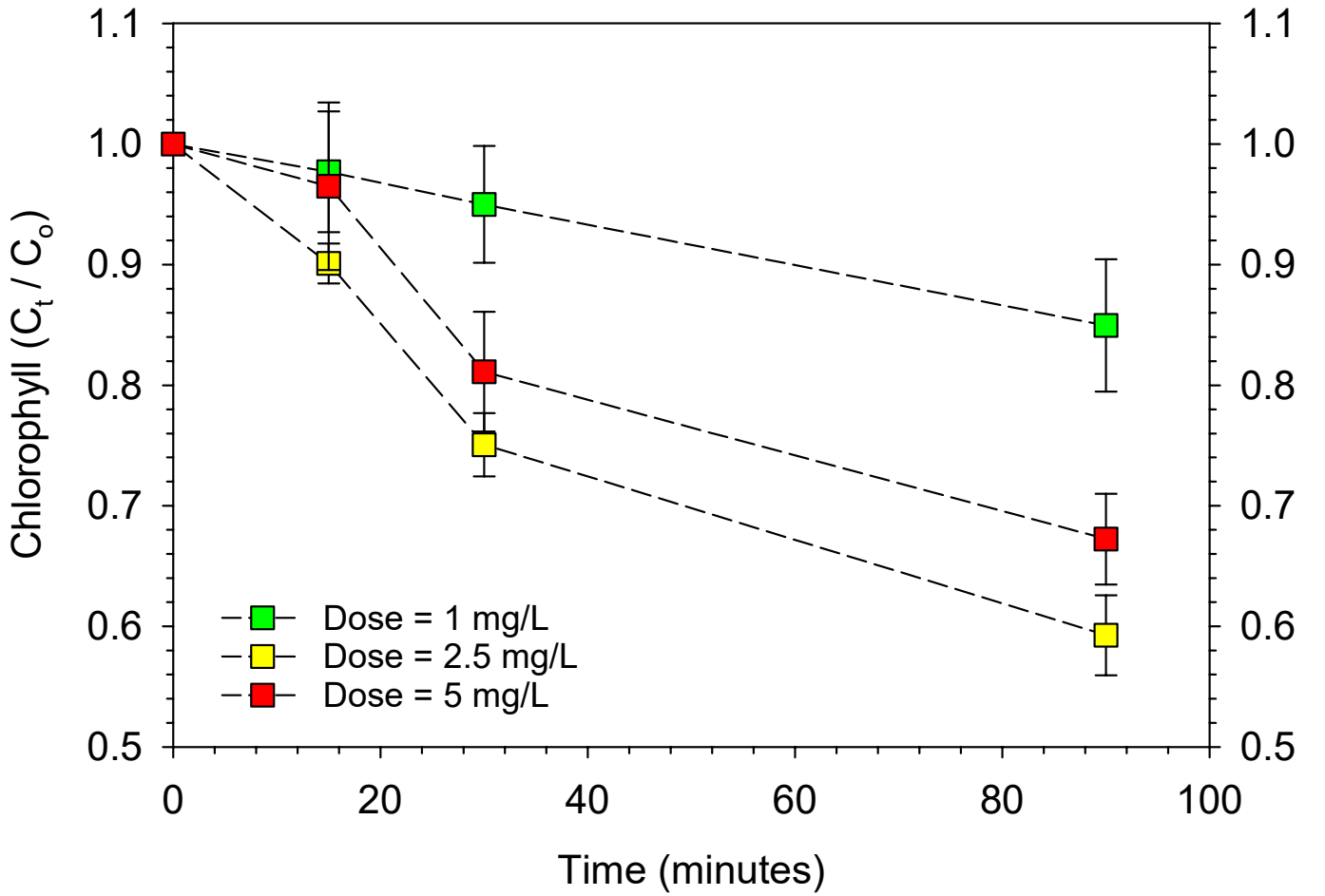
Impact of KMnO4 on Cyanobacterial Cell Membrane Integrity

Permanganate exposure increases the concentration of cells with membrane damage



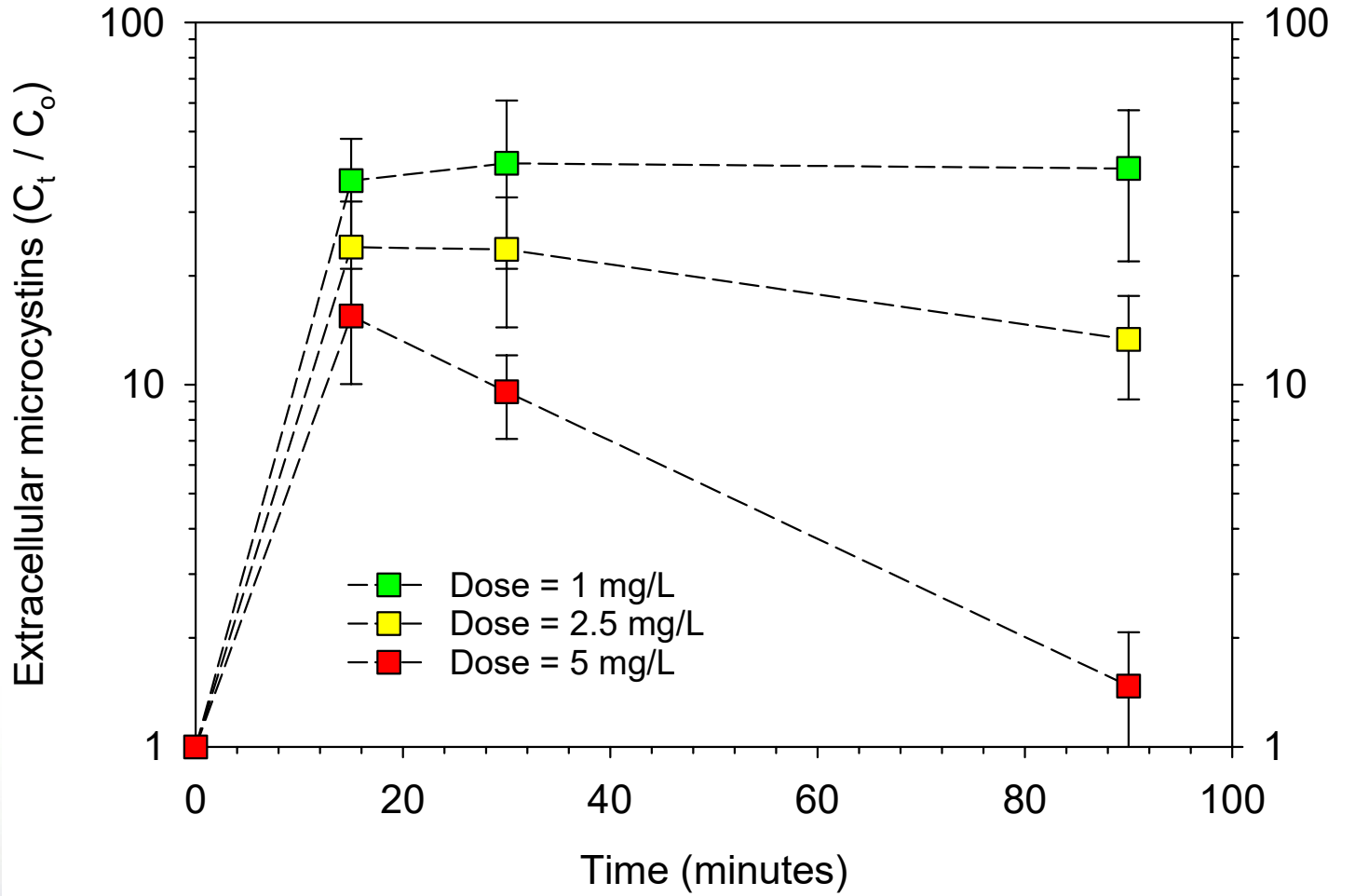
Impact of KMnO4 on Chlorophyll in Cyanobacterial Cells

Permanganate exposure decreases chlorophyll concentrations inside cells



Impact of KMnO4 on Toxin Release from Cyanobacterial Cells

Permanganate exposure increases extracellular microcystin concentration



Operational Considerations for Permanganate Pre-Oxidation

- If possible, monitor for toxins in the treatment plant influent in addition to the source water:
  - Extracellular toxins
  - Extra + intracellular toxins (requires freeze/thawing of samples)
- The degree to which toxins exist as extracellular versus intracellular may drive treatment decisions

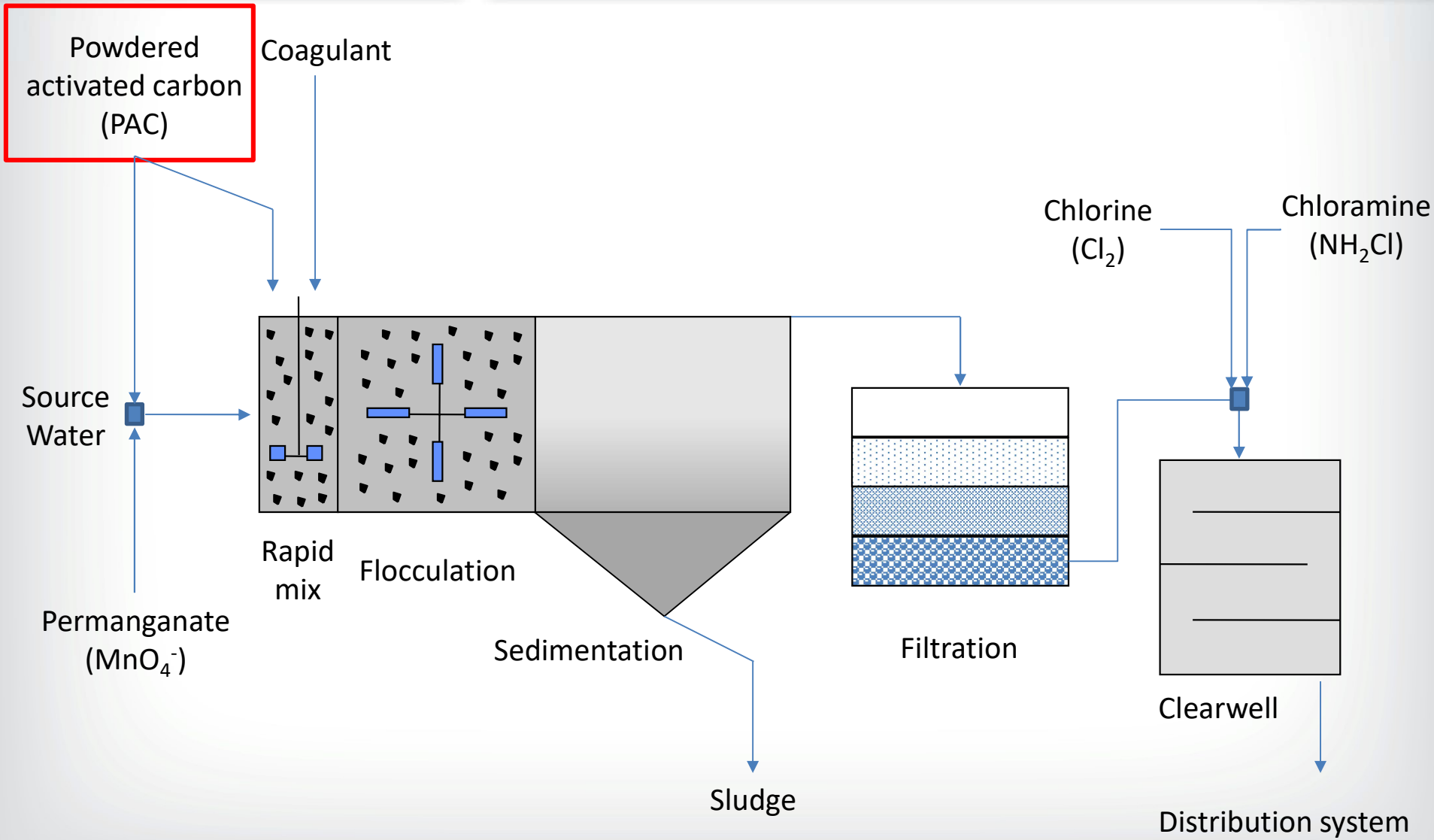
Operational Considerations for Permanganate Pre-Oxidation

- If primarily extracellular, continuing permanganate feed will not hurt and increasing the dose may help:
  - Consider site-specific considerations regarding production of colored water
  - Consider locations of permanganate and powdered activated carbon (PAC) application – PAC has the potential to adsorb toxins but also to neutralize permanganate

Operational Considerations for Permanganate Pre-Oxidation

- If significant intracellular toxins, have a contingency plan in place for temporarily suspending permanganate application:
  - Potential for color, taste & odor (T & O), DBP, or operational issues if permanganate is used for T & O, iron, DBP precursor, or color control
  - Be prepared to increase PAC dose and modify coagulation conditions to maximize removals of extracellular toxins and toxin-containing cells through coagulation, flocculation, and sedimentation
  - If possible, increase post-filtration chlorine dose

Conventional Surface Water Treatment

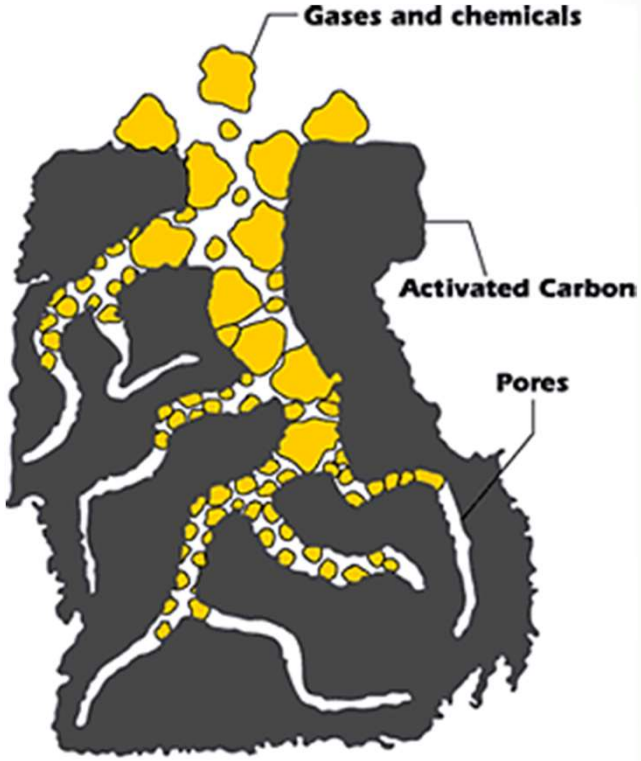


Background: Powdered Activated Carbon

- Powdered activated carbon (PAC):
  - Taste and odor control
  - Seasonal control of trace organics (herbicides, insecticides, etc.)
  - Adsorbs cyanobacterial toxins released into solution
  - Neutralizes MnO_4^-

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



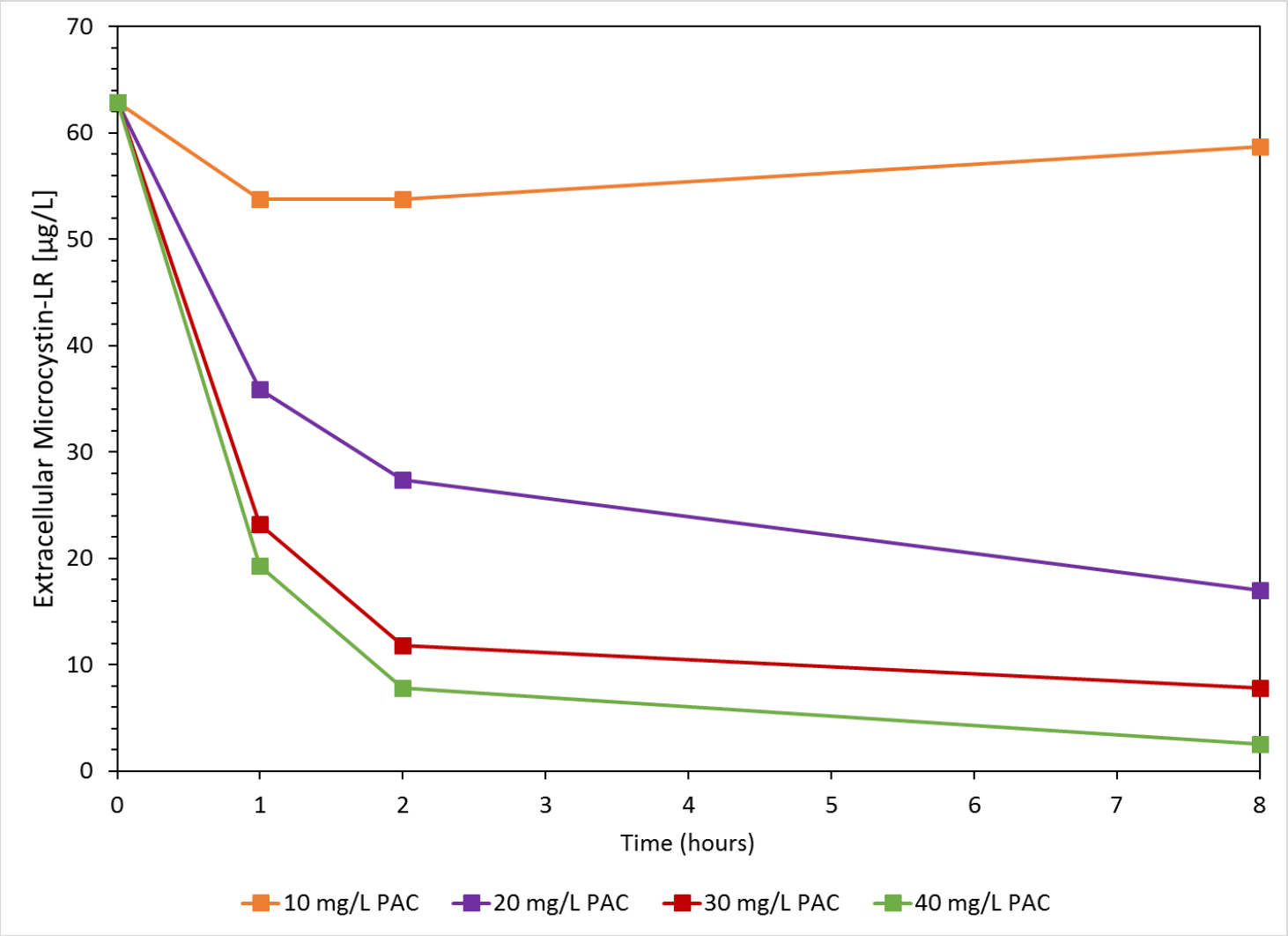
Micropores: < 2 nm
Mesopores: 2 - 50 nm vs. microcystin-LR: 1-3 nm
Macropores: > 50 nm

Effectiveness of PAC in Natural Waters

Toxin	Toxin concentration (µg/L)	PAC type	PAC dose (mg/L)	Contact time (min)	% Removal
MYC	5	?	10	60	92
MYC	22	?	10	15	41
MYC	22	Coal	10	60	30 – 60
MYC	22	Coal	50	60	≥ 90
CYL	20	Coal	25	30	60 - > 90
ANA	73	Coal	30	864*	> 80

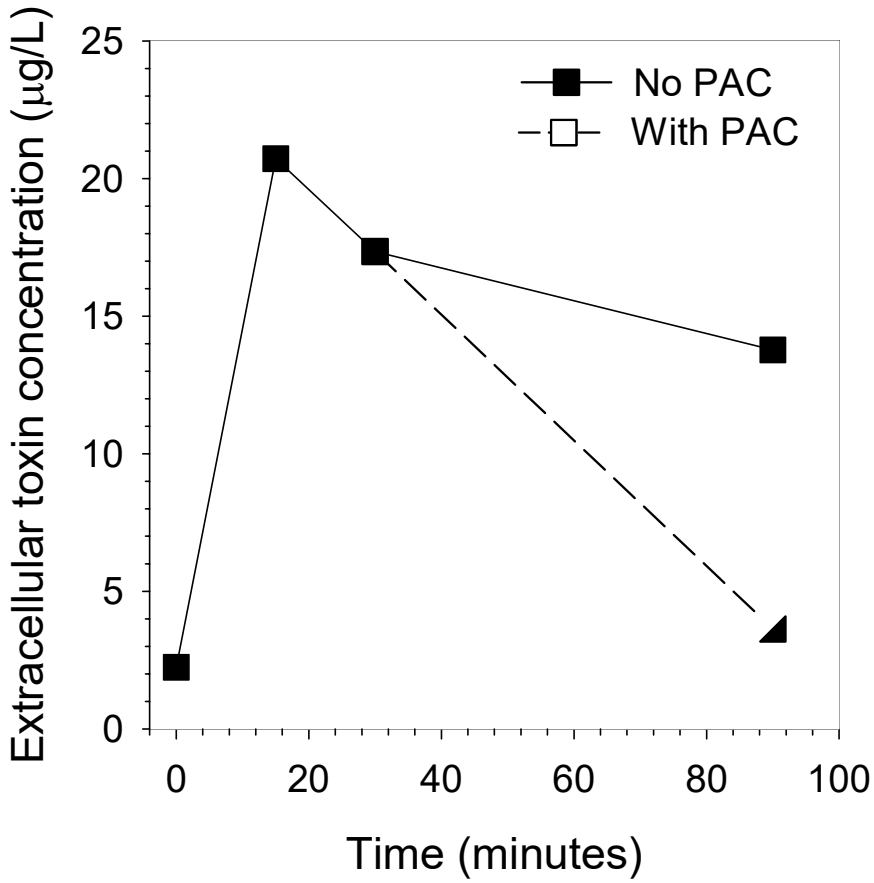
* Approximately 14 hours

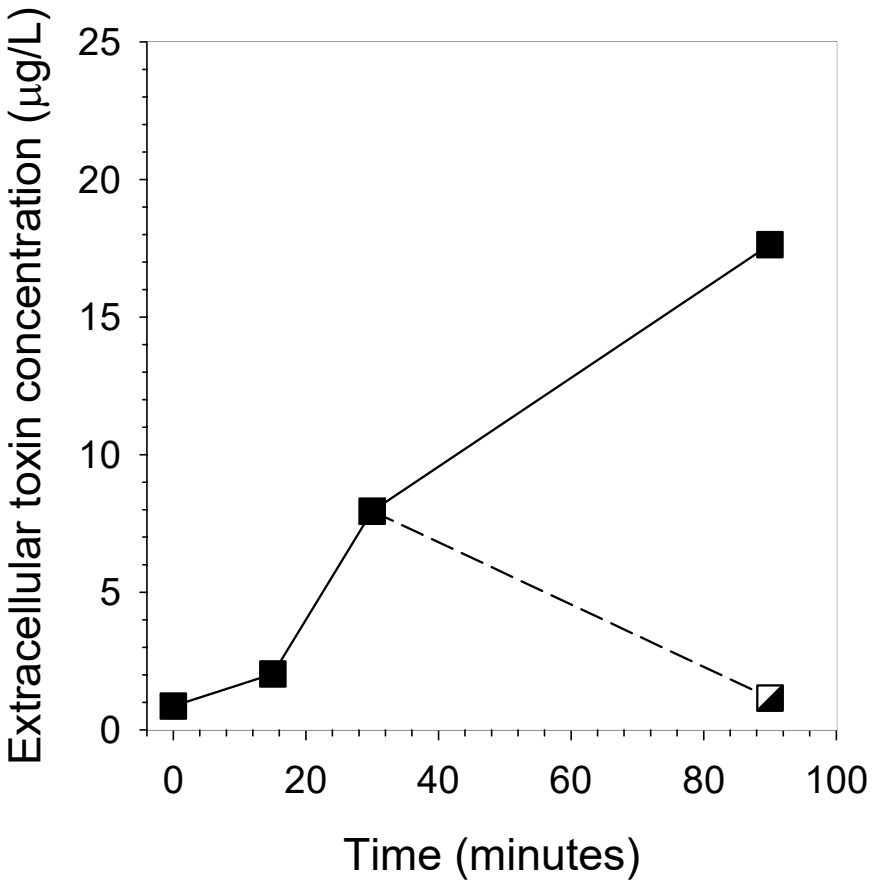
Impact of PAC Addition



Impact of PAC Addition

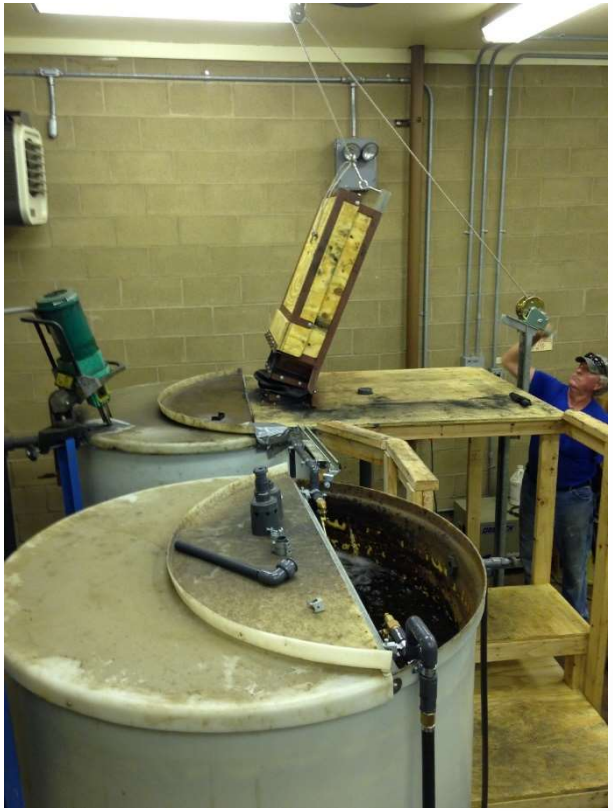
– Carbon added after toxin release from cyanobacterial cells



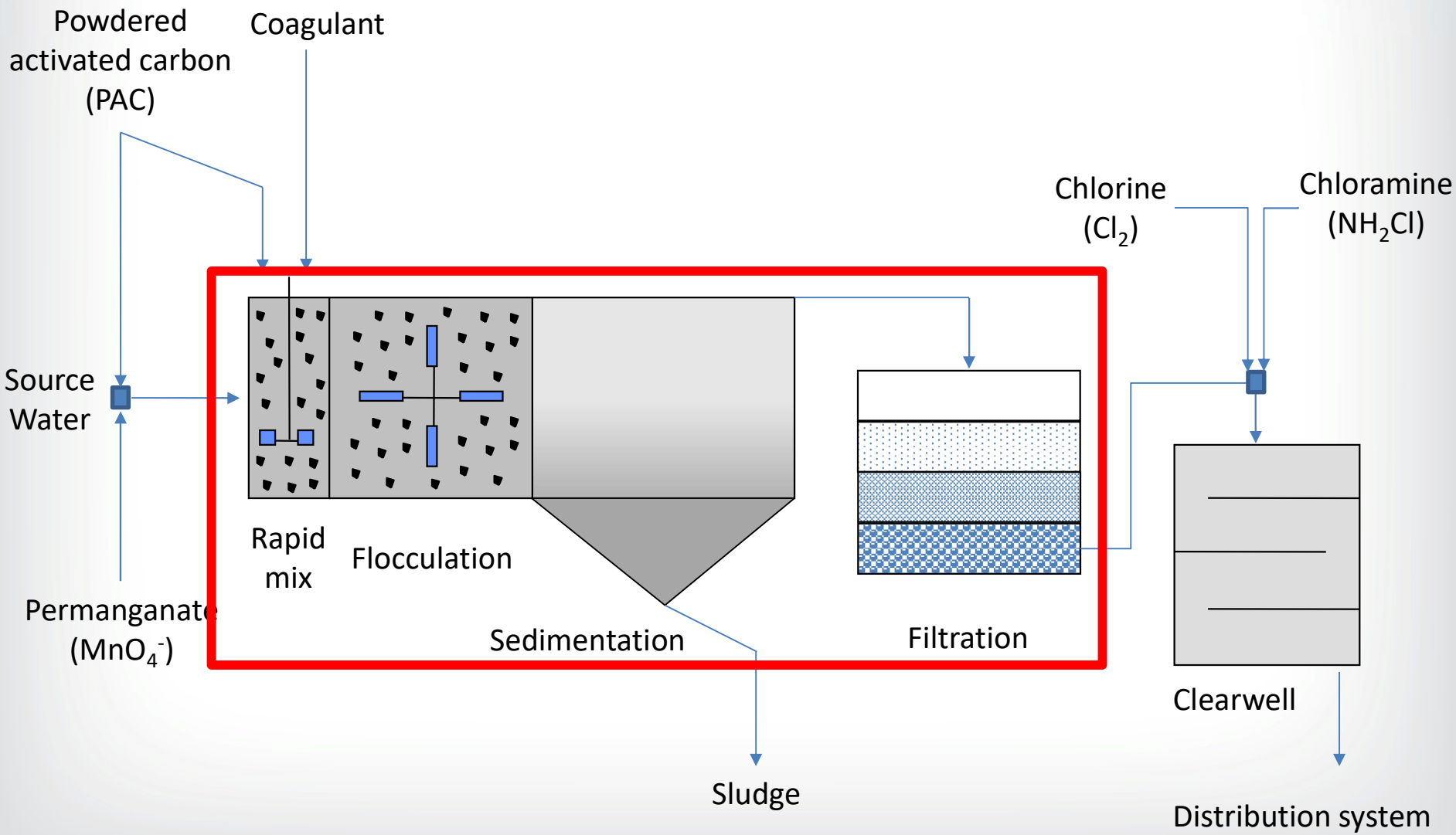


Operational Considerations for PAC

- 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



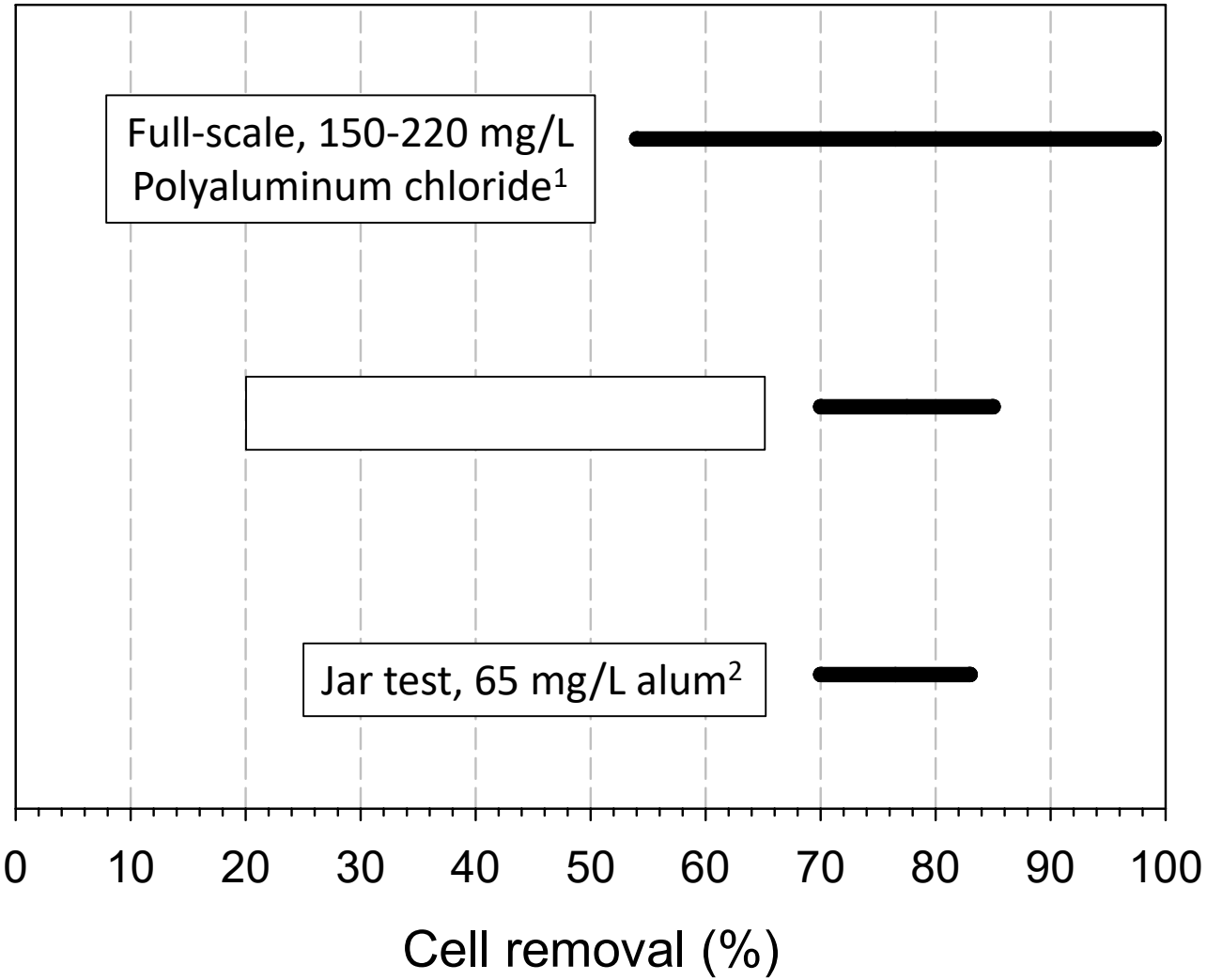
Conventional Surface Water Treatment



Background: Coagulation/Flocculation/Sedimentation

- Particulate removal (turbidity)
- DBP precursor removal
  - To some degree when adding coagulant with primary goal of optimizing settled water turbidity
  - To a greater degree when increasing coagulant dose and lowering pH in order to achieve enhanced coagulation
- Physical removal of *Giardia* cysts and *Cryptosporidium* oocysts
- Coagulant chemical addition destabilizes particles → particles remaining after sedimentation are more amenable to filtration
- Sedimentation basin provides contact time for PAC and permanganate
- Potentially effective barrier to the passage of cyanobacterial cells

Cell Removals through Coagulation and Sedimentation



[1]Zamyadi et al; *Species Dependence of Cyanobacteria Removal Efficiency by Different Drinking Water Treatment Processes*; Water Research; 2013:47:2689-2700
[2]Drikas et al; *Using Coagulation, Flocculation and Settling to Remove Toxic Cyanobacteria*; Journal AWWA; 2001:93:2:100-111

Bench-Scale Coagulation Experiments with *M. aeruginosa*

Water source/pH	Dose necessary to achieve 80% removal of cells (mg/L)		
	Aluminum chlorohydrate (ACH)	Ferric chloride	Aluminum sulfate
Myponga Reservoir			
pH 7.5 – 7.8	40	40	60
pH 6.3	20	40	60
River Murray			
pH 7.2 – 7.6	20	40	80
pH 6.3	20	20	60

Myponga turbidity = 1.2 – 8.7 NTU, DOC = 10 – 12 mg/L
Murray turbidity = 23 – 101 NTU, DOC = 5.3 - 17

Newcombe, G. et al; *Optimizing Conventional Treatment for the Removal of Cyanobacteria and Toxins*; Water Research Foundation, Denver CO; 2015

Toxin Removals through Pilot-Scale Coagulation, Sedimentation, and Filtration

		Microcystin-LR concentration (µg/L)	
Sample point	**Toxin type**	**Trial 1**	**Trial 2**
Influent	Combined	119	60
	Extracellular	3	2
Effluent	Combined	3	2
	Extracellular	3	2

Drikas et al; *Using Coagulation, Flocculation and Settling to Remove Toxic Cyanobacteria*; Journal AWWA; 2001:93:2:100-111

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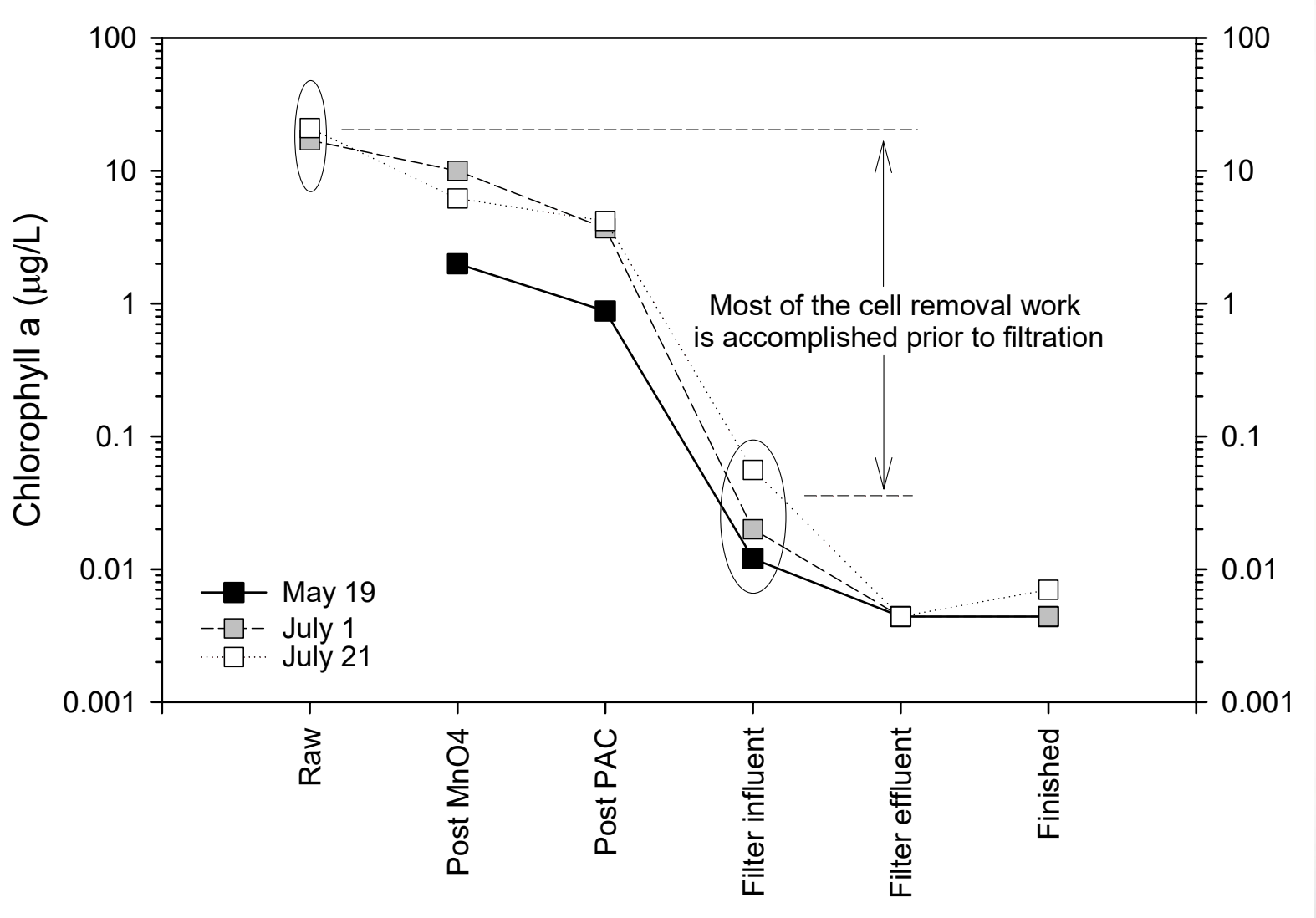
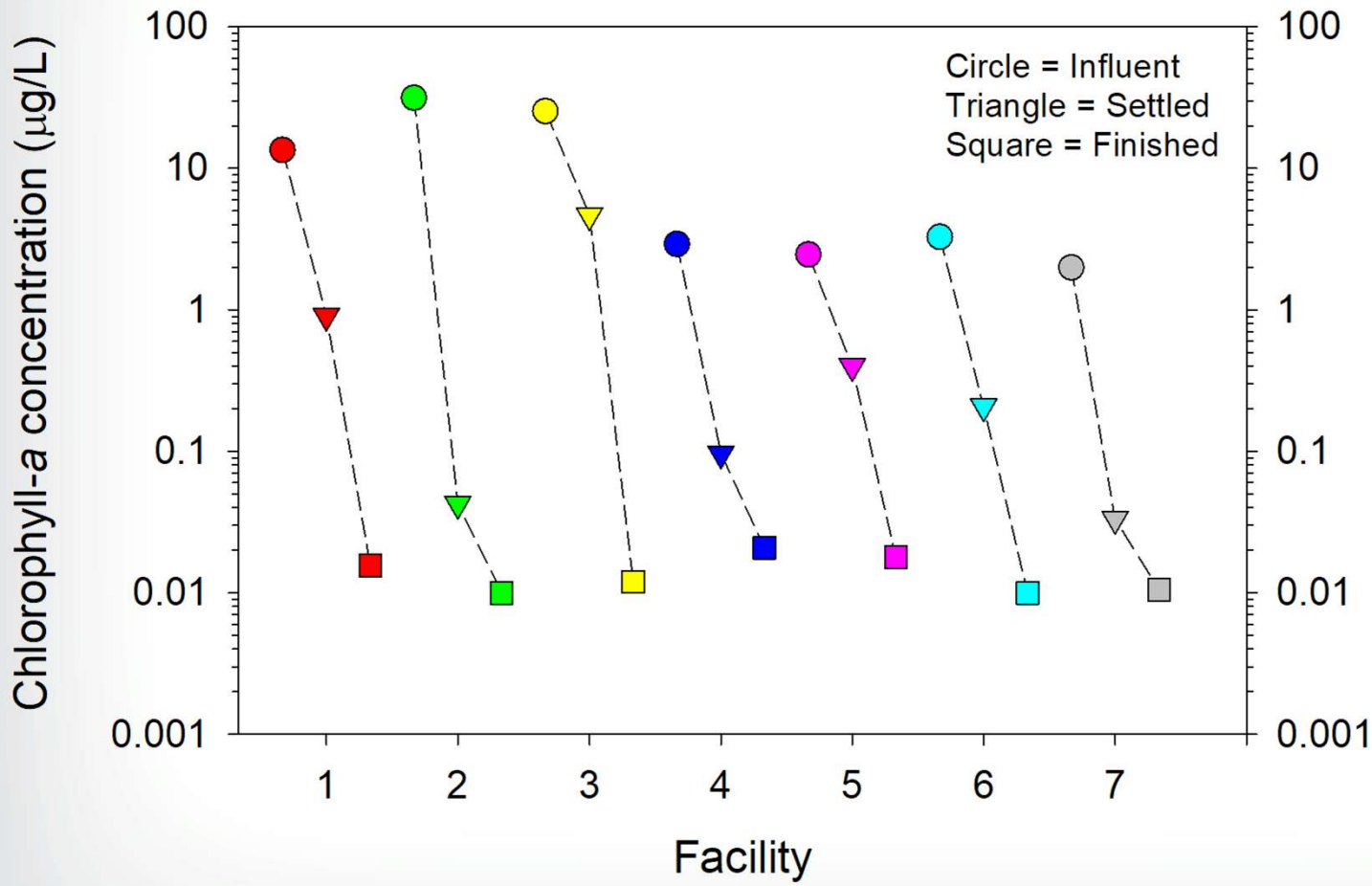
Cell Propagation through a Full-Scale Lake Erie Treatment Facility



Physical Removal of Cells through Seven Full-Scale Lake Erie Facilities



Each data point represents the average of 5 – 7 samples collected between May and October

West → 150 miles → East

Filtration of *M. aeruginosa* Pilot-Scale Seeding Trial Results

Coagulant	Baseline filter loading rate (m/hr)	Steady-state removal of chlorophyll-*a* (Δ log)
Alum + cationic polymer	7	2.8
	10	2.5
Ferric chloride + cationic polymer	7	2.9
	10	3.8

- Average influent chlorophyll-*a* concentration = 26 µg/L (SD = 12 µg/L)
- 1 m/hr = 0.41 gal/min•ft^2

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

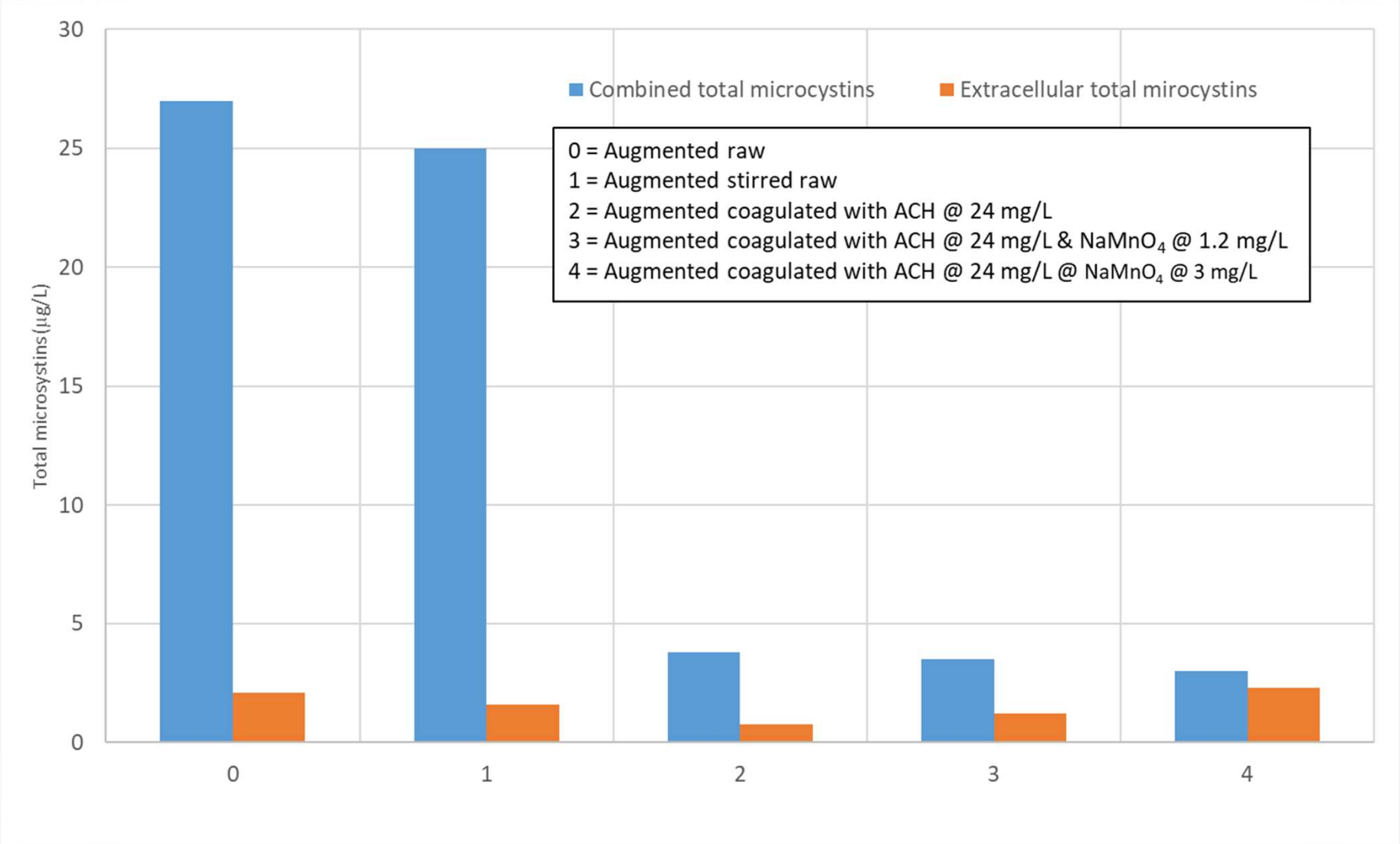
Objectives:

- Understand effect of coagulant on cyanobacteria cell removal.
- 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



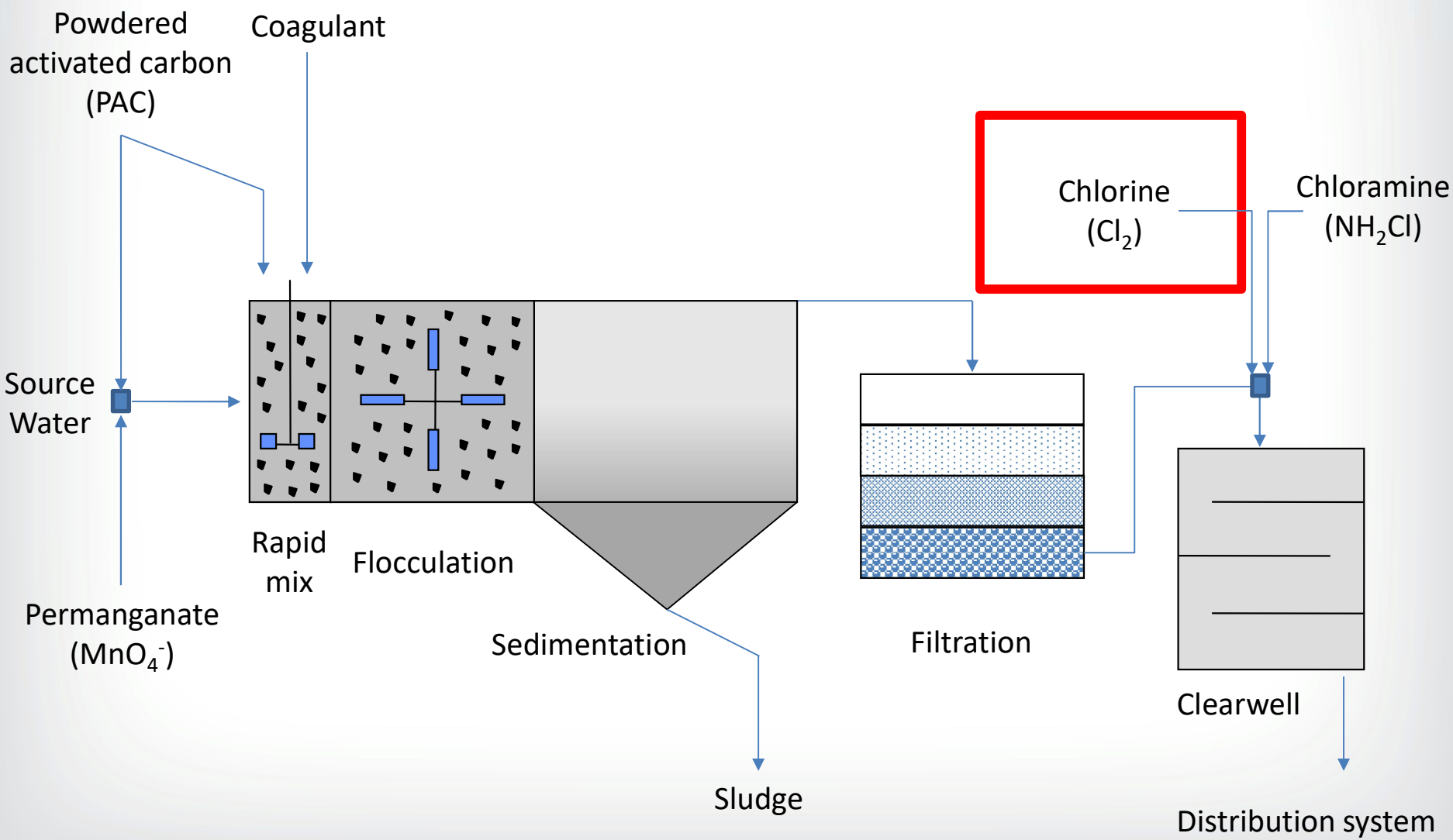
Operational considerations for Coagulation, Flocculation, Sedimentation and Filtration

- Cyanobacterial cells may have different surface chemistry than suspended clay and silt
- Cyanobacterial cells will have lower specific gravity (1.0 – 1.1) than inorganic particles (> 2)
- Some species of cyanobacteria have gas vacuoles → positive buoyancy
- Cyanobacteria can be found as single cells, "clumps" of individual cells, individual filaments, or "mats" of filaments
- For the reasons outlined above, different coagulation chemicals and doses may be required during blooms
- Optimizing coagulation conditions for cyanobacterial cell removal during sedimentation is worth the effort because it will protect the filters

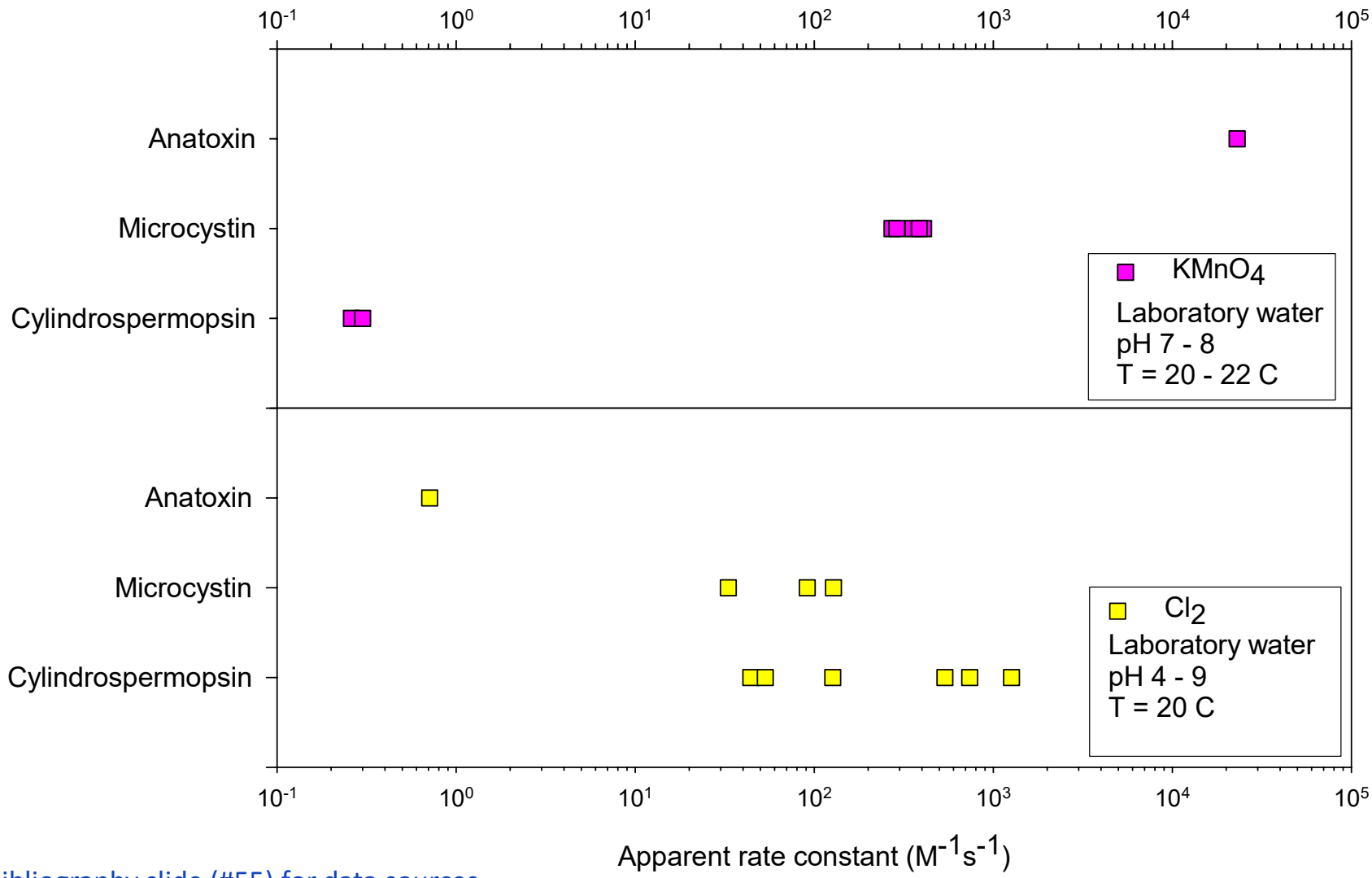
Operational considerations for Coagulation, Flocculation, Sedimentation and Filtration

- 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

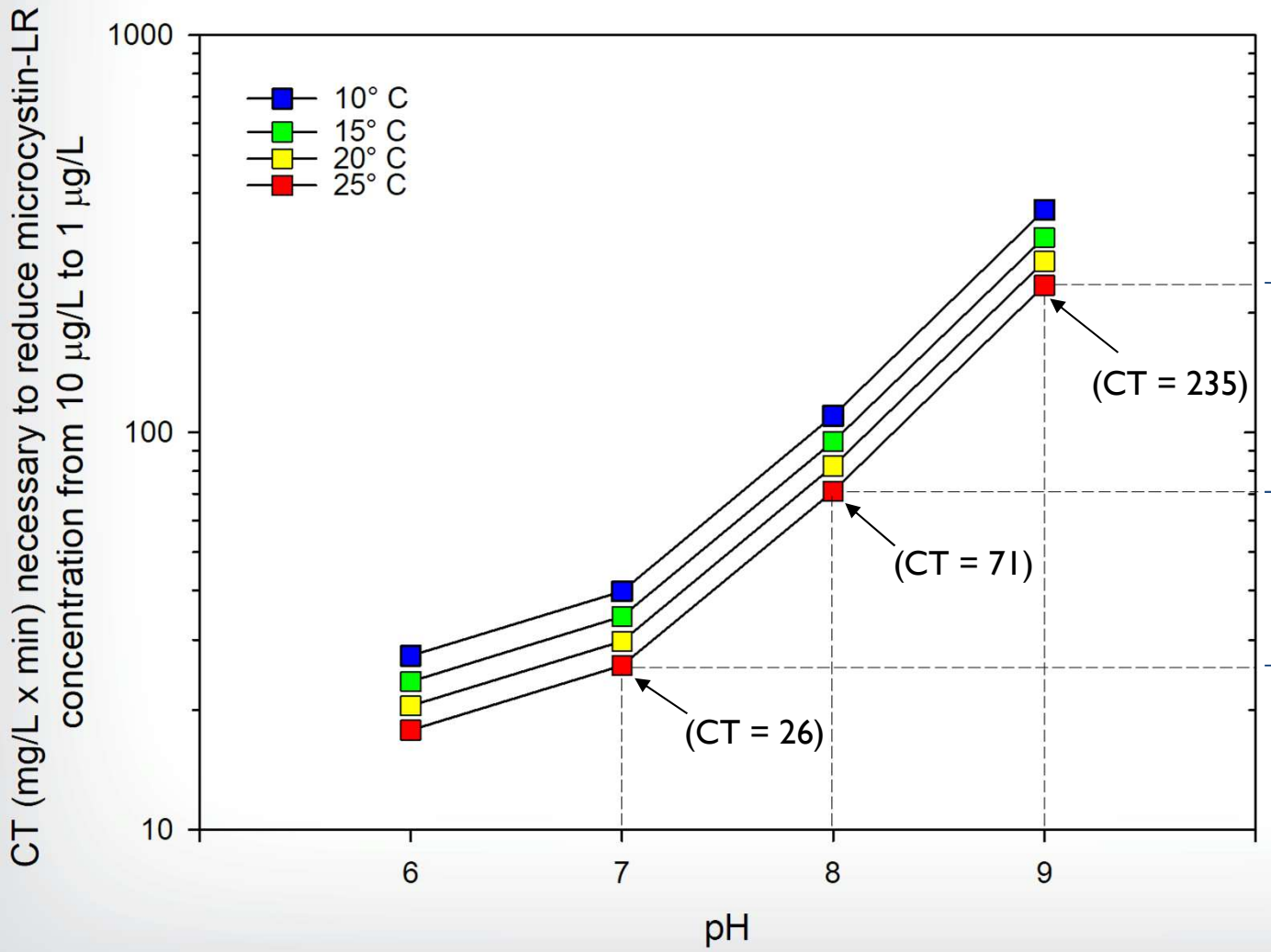


Permanganate and Chlorine – Reaction rates



See bibliography slide (#55) for data sources

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

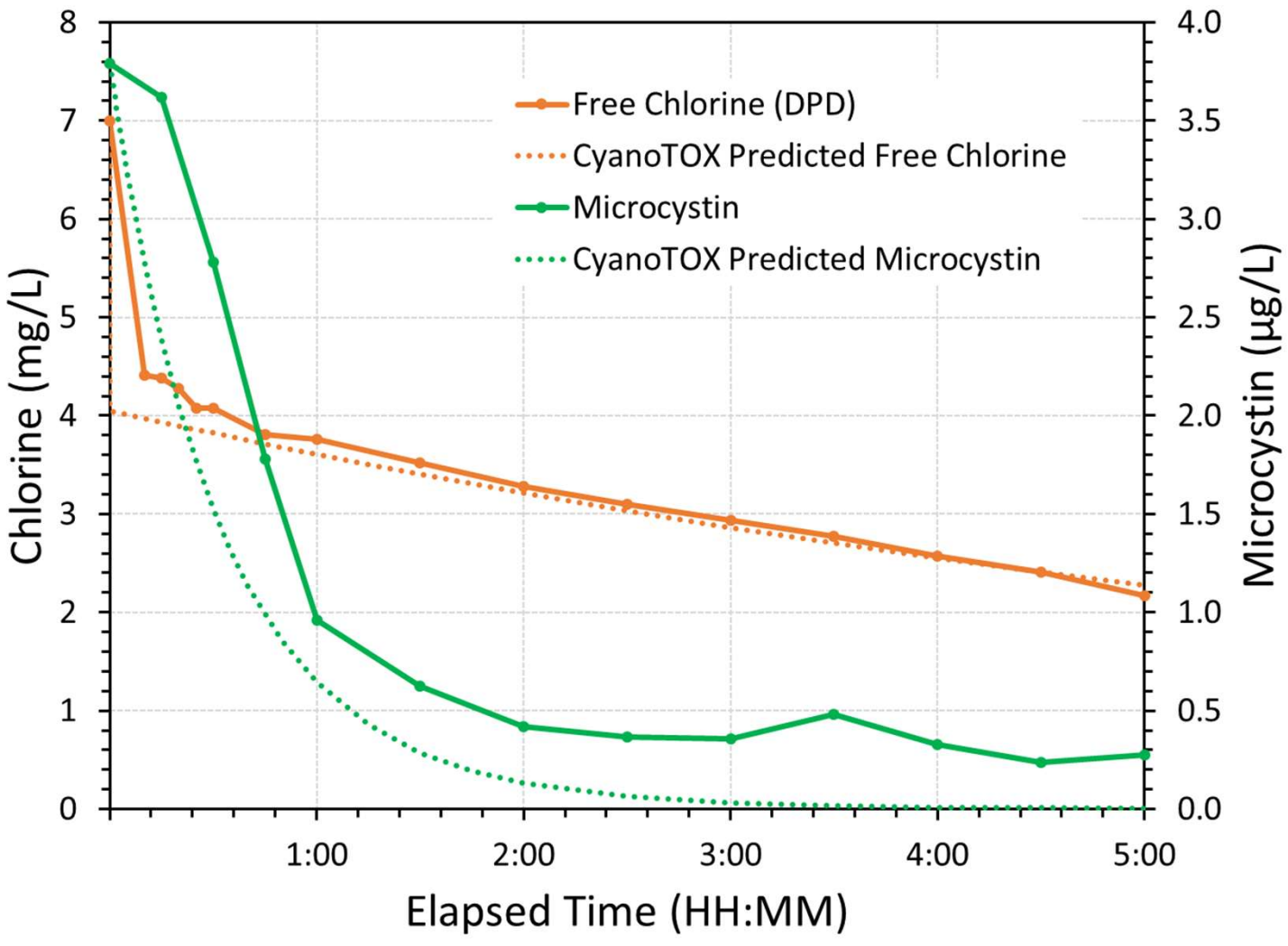
*Figure based on data from Acero et al, *Water Research*, 2005:39:1628-1638

Oxidation of Microcystins with Chlorine: Kinetic Study

Objective: evaluate microcystin oxidation by chlorine in the plant's raw water at the plant's typical chlorine dose.

- Augmented a raw water sample with concentrated solution of cyanotoxins obtained from another water body that was experiencing a HAB.
- Cyanobacteria subjected to freeze/thaw and a filtration step to ensure that toxins were extracellular.
- Compared experimental results with AWWA's CyanoTOX model results:
  - Calibrated "model" using free chlorine sample results.
  - Interested in predicted vs. observed microcystins.
  - Difference is raw water vs. lab water.
  - Presence of ammonia, other inorganics, and NOM in raw water reduces efficacy of chlorine against microcystins.
  - Understand if a safety factor necessary when predicting chlorine dose necessary to oxidize extracellular microcystins in a full-scale wastewater treatment plant (WTP).

Chlorine and Microcystins Kinetic Study



CyanoTOX Inputs

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.

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:

Oxidant Dose (mg/L):

Instantaneous oxidant demand (mg/L):

Contact Time (i.e., hydraulic detent. time, min):

Effective Oxidant Half Life (min):

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

CyanoTOX Oxidation Calculator

CT-based results:

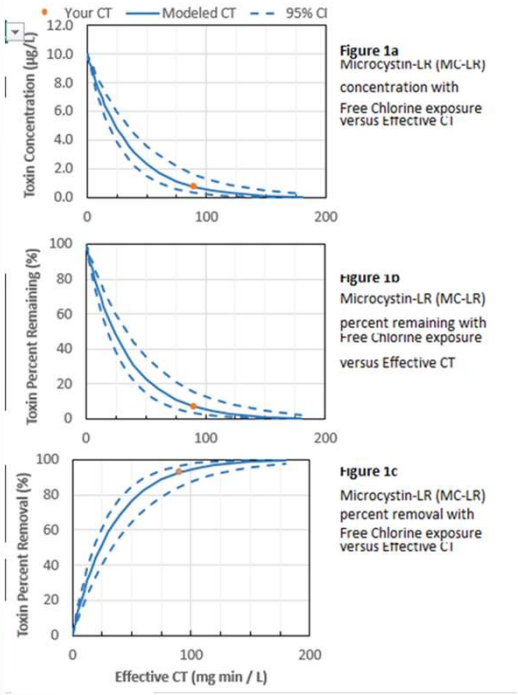


Figure 1a
Microcystin-LR (MC-LR) concentration with Free Chlorine exposure versus Effective CT

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:

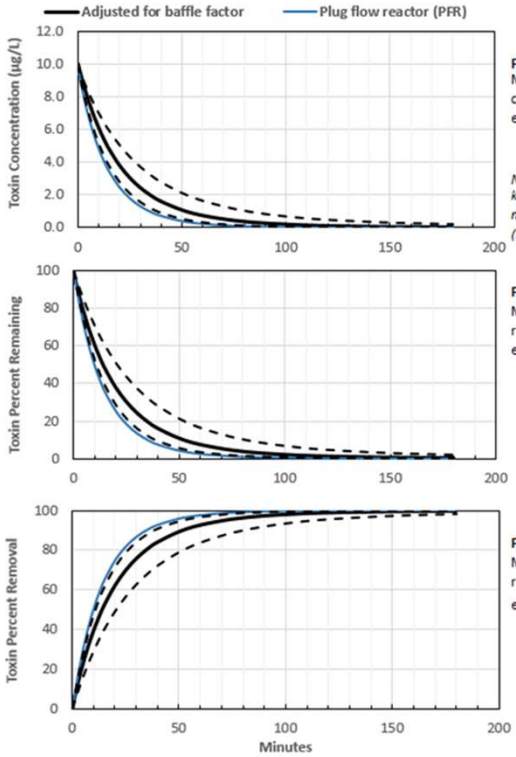


Figure 3a
Microcystin-LR (MC-LR) concentration with Free Chlorine exposure versus time

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 the toxin:
  - Chlorine is effective for microcystin and cylindrospermopsin
  - Chlorine is not effective for anatoxin
- Consider pH:
  - As pH increases, chlorine reaction rate with microcystin decreases
  - As pH increases, chlorine reaction rate with cylindrospermopsin increases and peaks at pH = 7, then begins to decrease
- Consider temperature – all reaction rates increase with temperature

Operational Considerations for Chlorination

- Consider competing oxidant demands:
  - NOM
  - Iron, manganese
  - Ammonia
- Consider the potential for formation of disinfection byproducts
- Consider contact time:
  - In the treatment plant
  - Between the treatment plant and the first connection
  - Other locations in the distribution system (storage tanks)
- Consider where chlorine is dosed and if any competing technologies would limit its effectiveness

UV Irradiation

- UV contactors installed toward the end of the treatment process – cells and intracellular toxins have been removed, only extracellular toxin remaining.
- Required UV doses for 2-log disinfection of *Cryptosporidium* = 5.8 mJ/cm^2, *Giardia* = 5.2 mJ/cm^2, virus = 100 mJ/cm^2.
- These doses drive full-scale UV contactor design.
- UV doses required for microcystin degradation are significantly higher – existing UV infrastructure not a barrier to toxin passage.

Ozone and Chlorine Dioxide

- Chlorine dioxide, at the doses used in drinking water treatment (to limit the formation of chlorite) is not considered effective against microcystins – reaction rate is approximately 3 orders of magnitude lower than permanganate.
- Ozone has been proven effective at degrading microcystins as well as cylindrospermopsins and anatoxin – reaction rate is sufficient to achieve degradation within the confines of ozone contactors used in full-scale drinking water treatment.

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.

Disclaimer

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EPA Water Treatment Document

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Water Treatment Optimization for
Cyanotoxins
Version 1.0

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https://www.epa.gov/sites/production/files/2018-11/documents/water_treatment_optimization_for_cyanotoxins.pdf

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