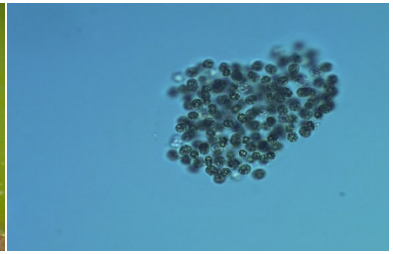
U.S. Environmental Projection Agency
Office of Research and Development & Office of Ground Water and Drinking Water

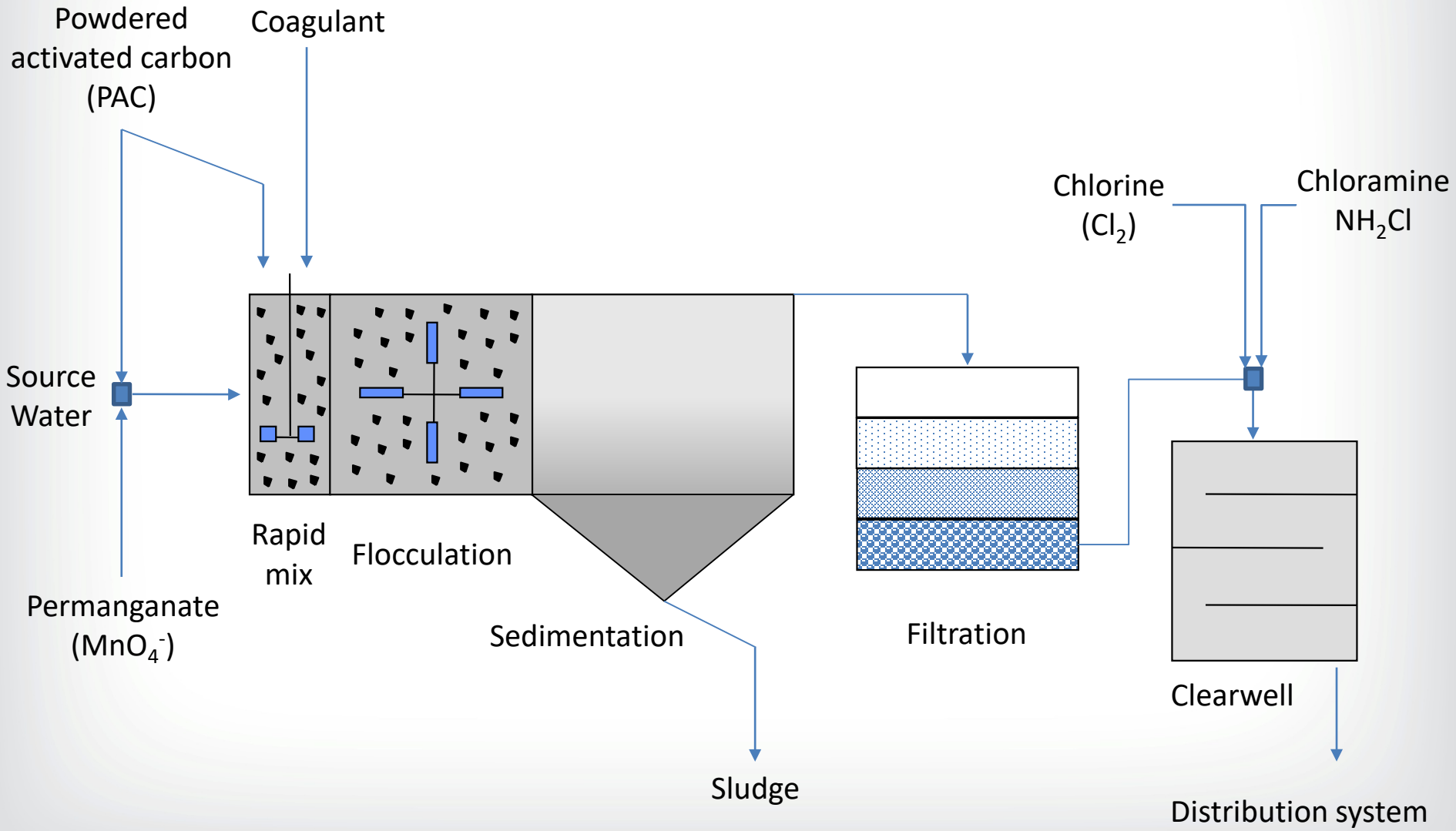



Conventional Treatment Options For HABs Impacted Waters

Nicholas Dugan, PE
Thomas Waters, PE

Conventional surface water treatment process



Definitions

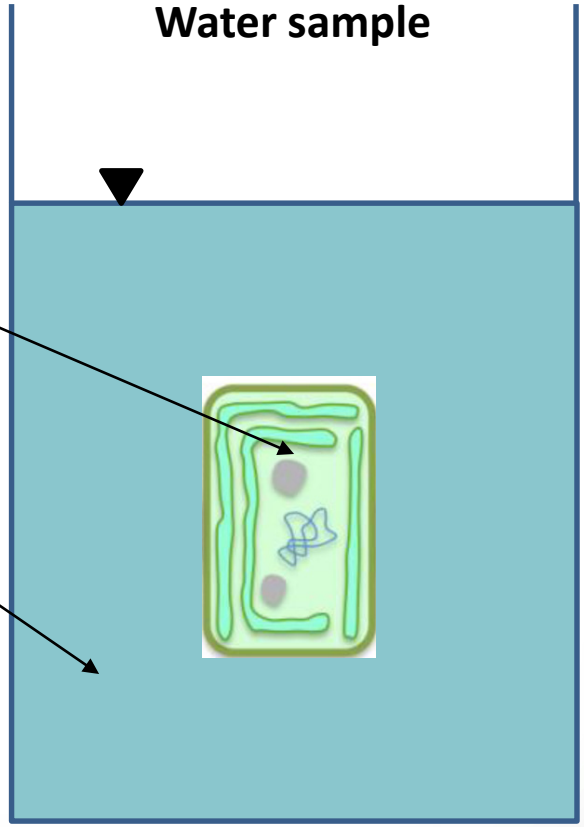
- Cell counts: direct counting of cells under a microscope
- Chlorophyll: pigment molecules in algae and cyanobacteria that play a role in photosynthesis
- Phycocyanin: pigment molecules in cyanobacteria that play a role in photosynthesis
- Microcystin: A type of toxin produced by cyanobacteria, most commonly detected, affects the liver

Combined, intracellular and extracellular toxins

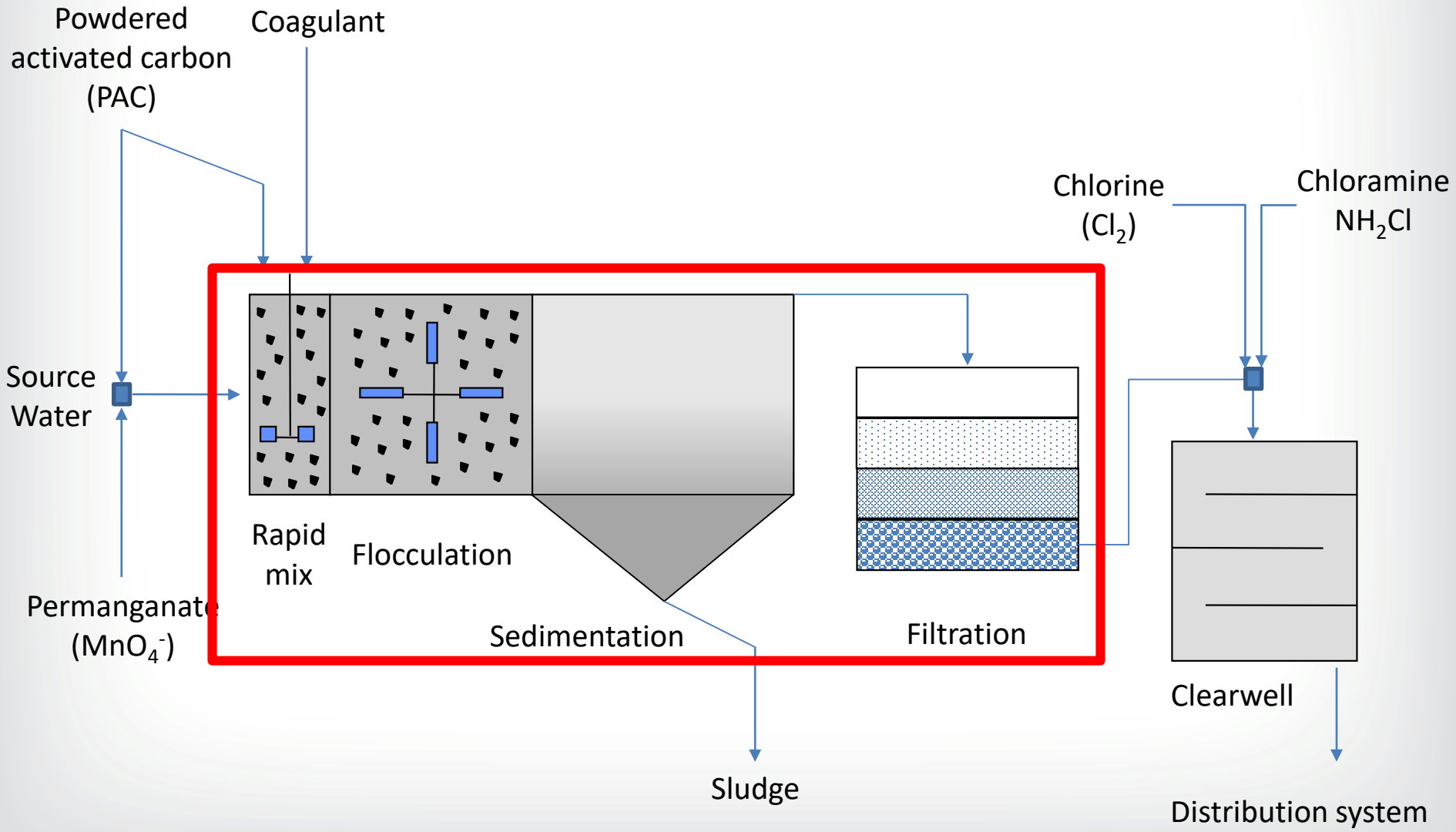
Intracellular
Toxins contained inside the cell

Extracellular
Toxins in solution outside the cell

Combined
Extracellular + intracellular toxin



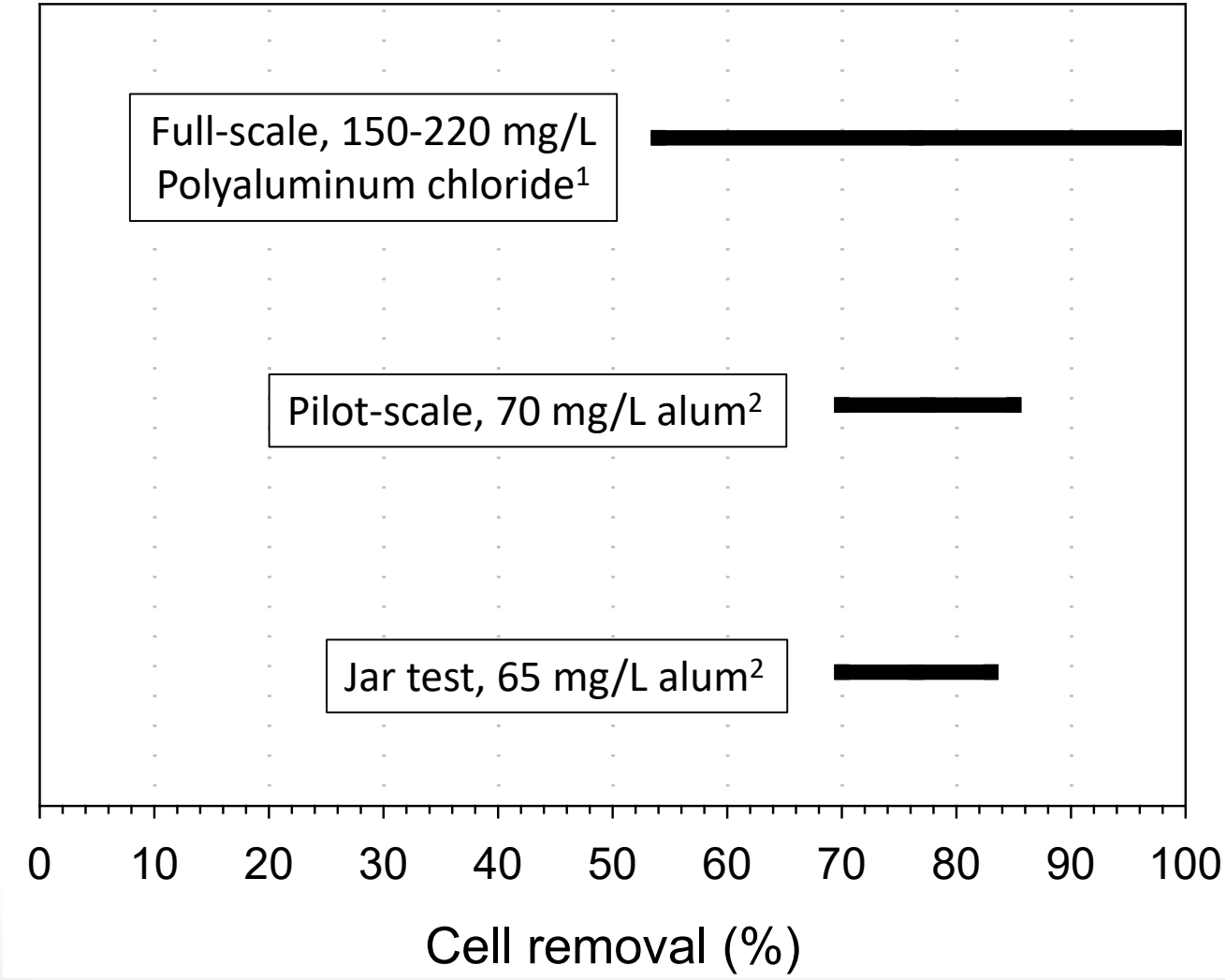
Conventional surface water treatment process



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, can evaluate:
  - Turbidity
  - NOM
  - Pigments (chlorophyll-*a*, phycocyanin)
  - Color
  - UV254
  - Particle counts
  - Streaming current or zeta potential

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

Toxin removals through pilot-scale coagulation, sedimentation and filtration

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

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

Toxin removals through pilot-scale coagulation, sedimentation and filtration

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

Source: 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

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

Jar testing case study

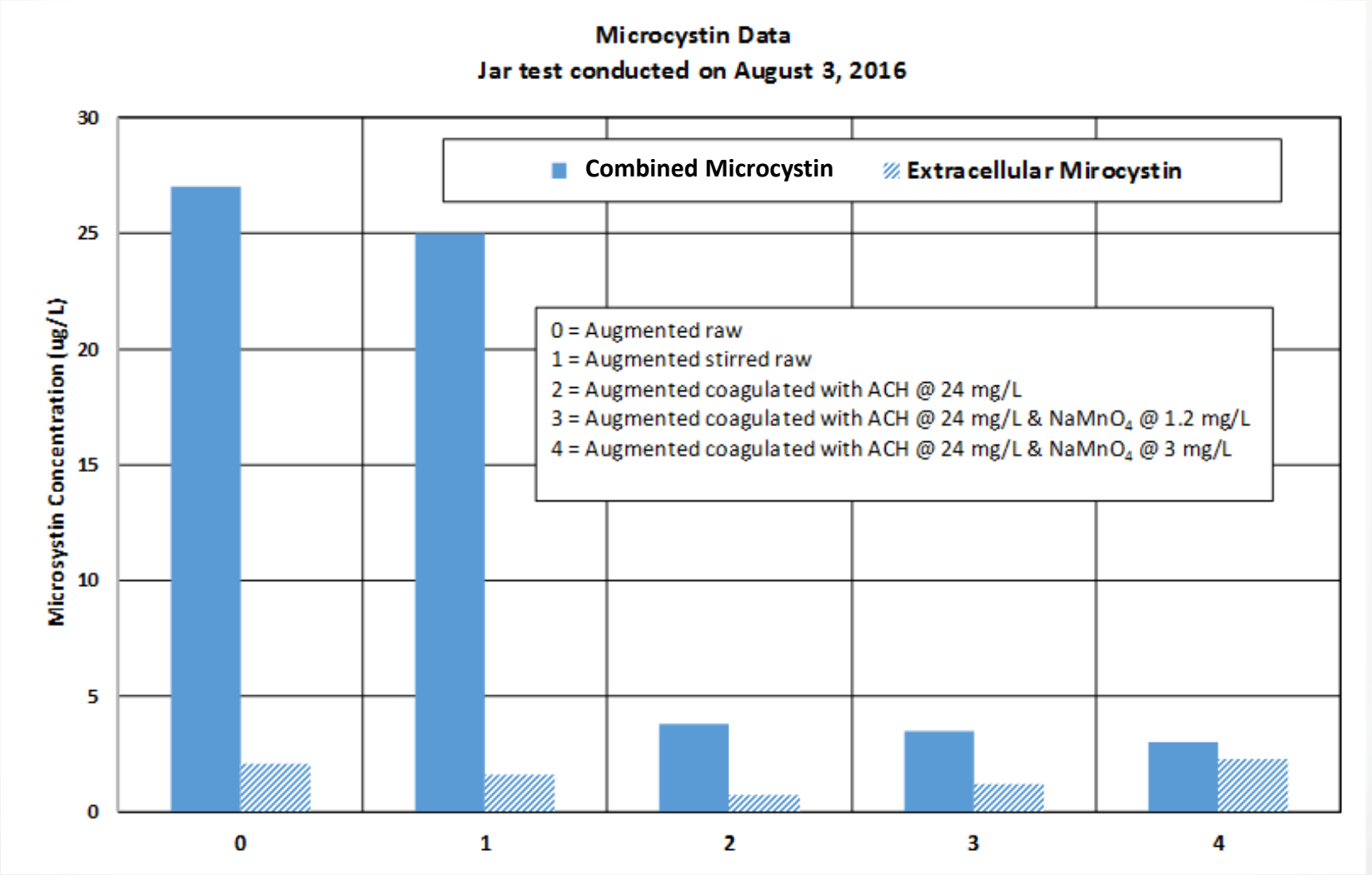
Experimental setup:

- 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

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

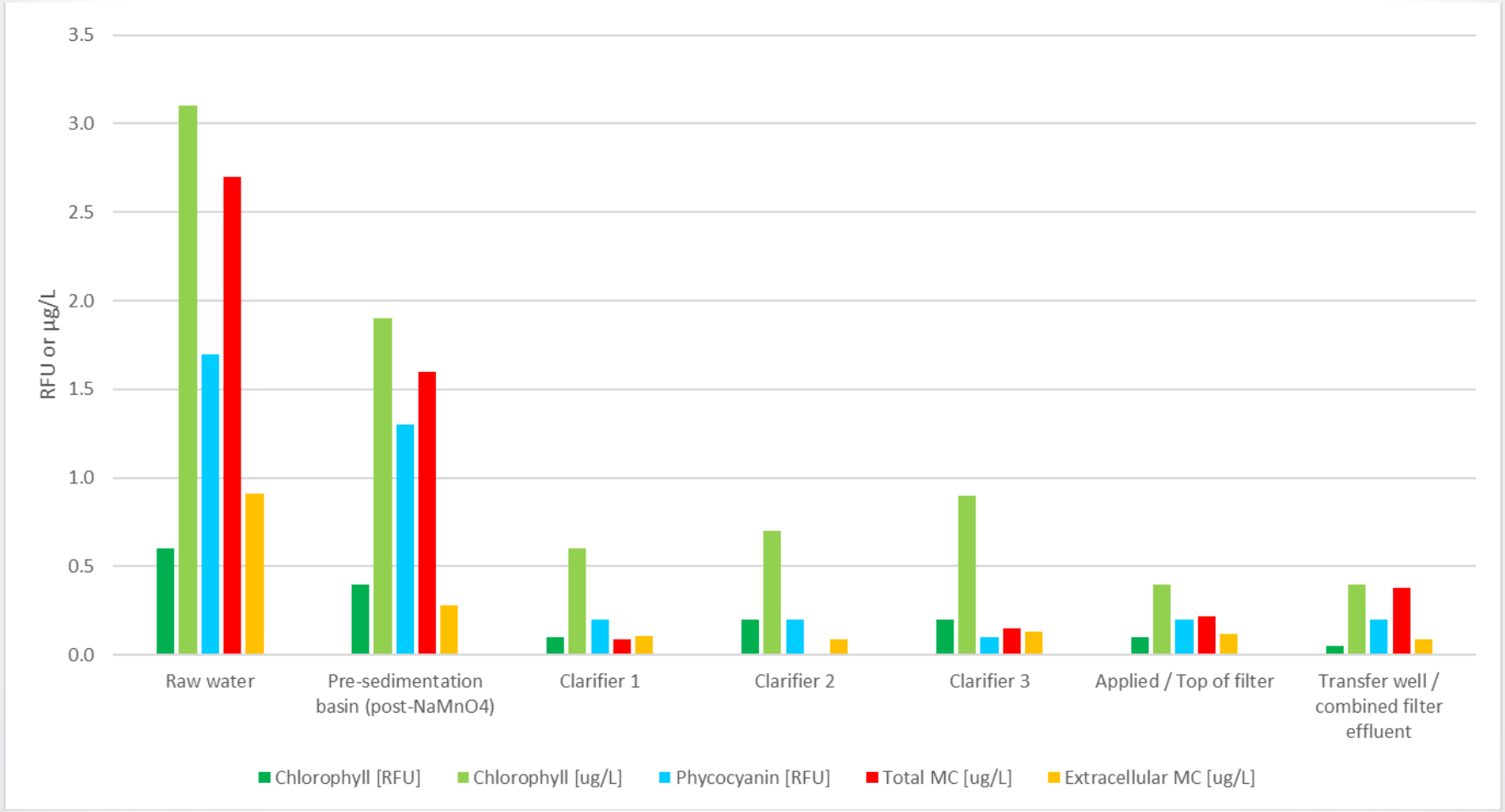
Bench-scale coagulation experiments with Lake Erie water and cyanobacteria



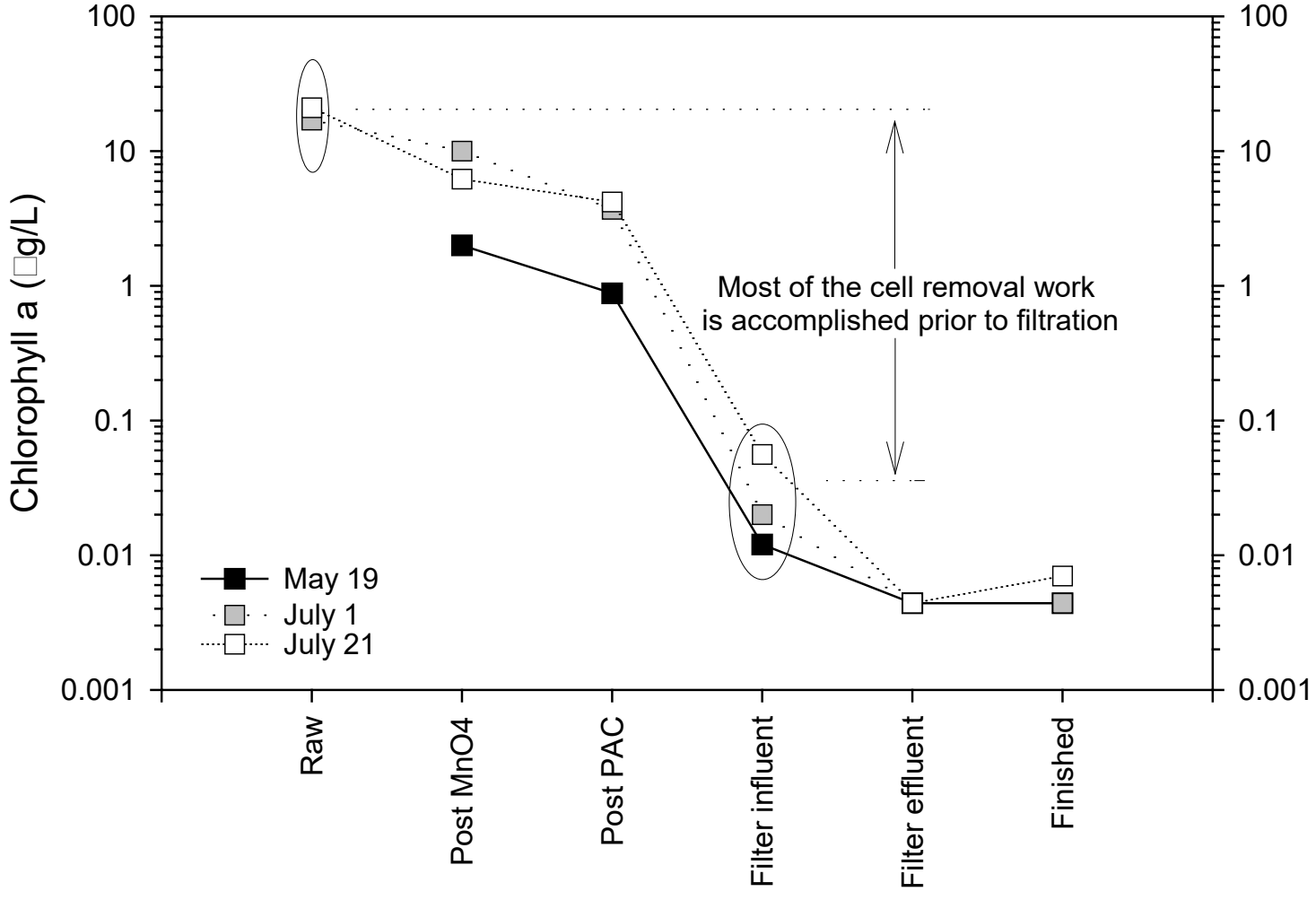
Unit process sampling

- YSI EXO sonde equipped with sensors:
  - Chlorophyll-*a (in-vivo, RFU)*
  - Phycocyanin ("blue-green algae") *(in-vivo, RFU)*
  - Dissolved oxygen
  - pH, temperature
  - Conductivity
  - Turbidity
- Sample in-situ at the following locations in the plant:
  - Raw water
  - Pre-sedimentation
  - Clarifier effluent
  - Top-of-filter
  - Combined filter effluent

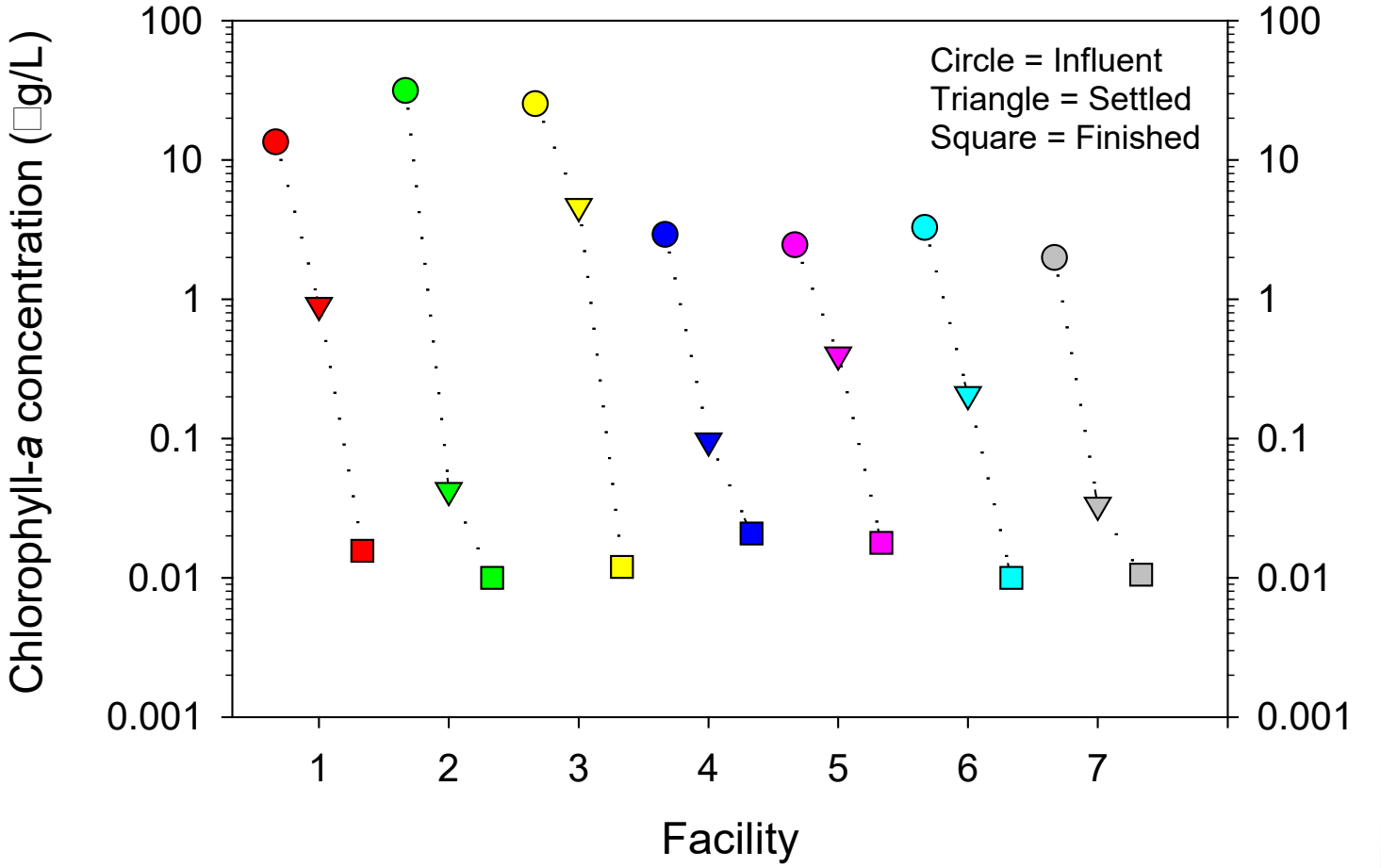
Through-plant sampling – Lake Erie water treatment plant



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

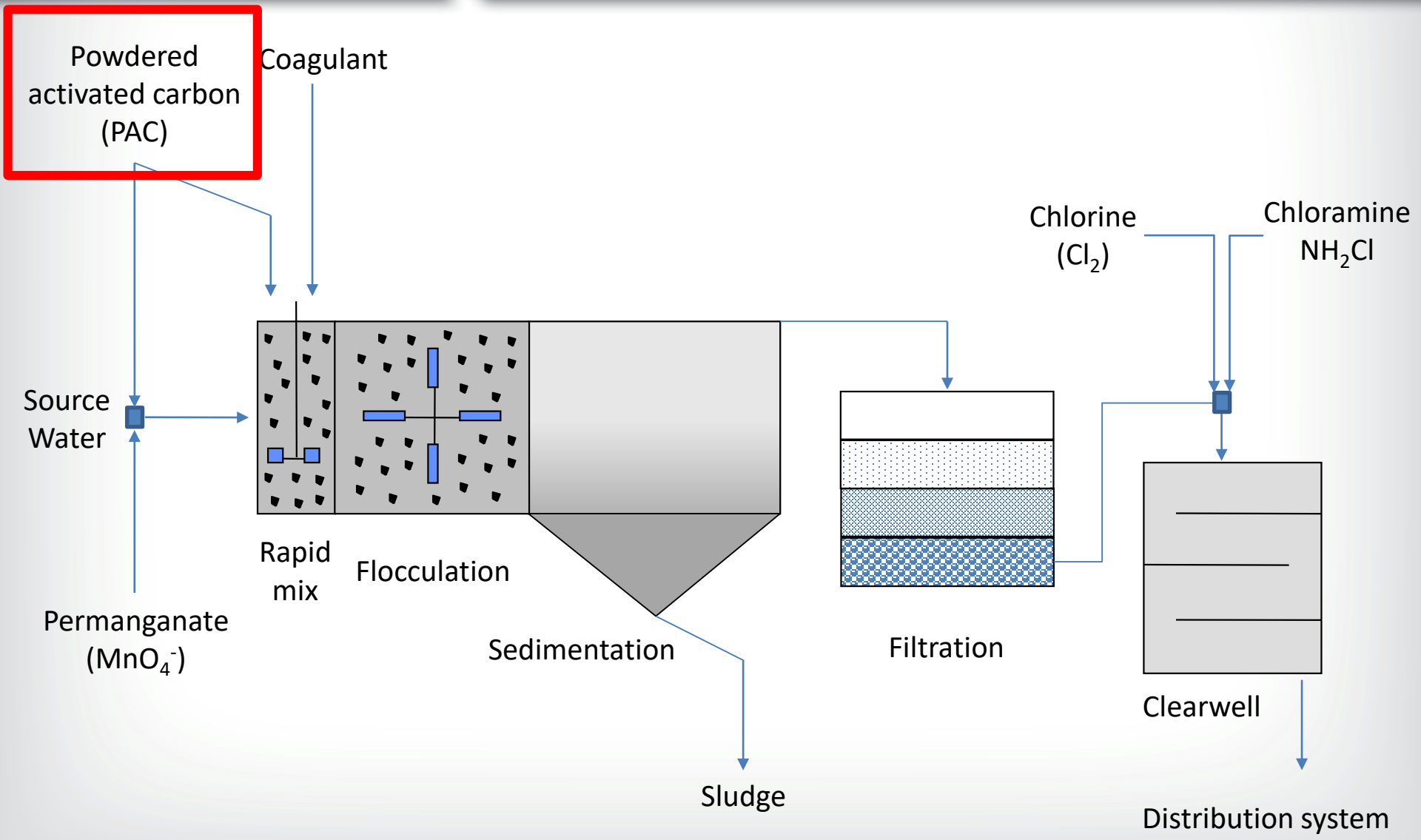
Coagulant	Baseline filter loading rate (m/hr)	Steady-state removal of chlorophyll-*a* (Δ log)
Alum + cationic polymer	7	2.8
	10	2.5
Ferric chloride + cationic polymer	7	2.9
	10	3.8

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

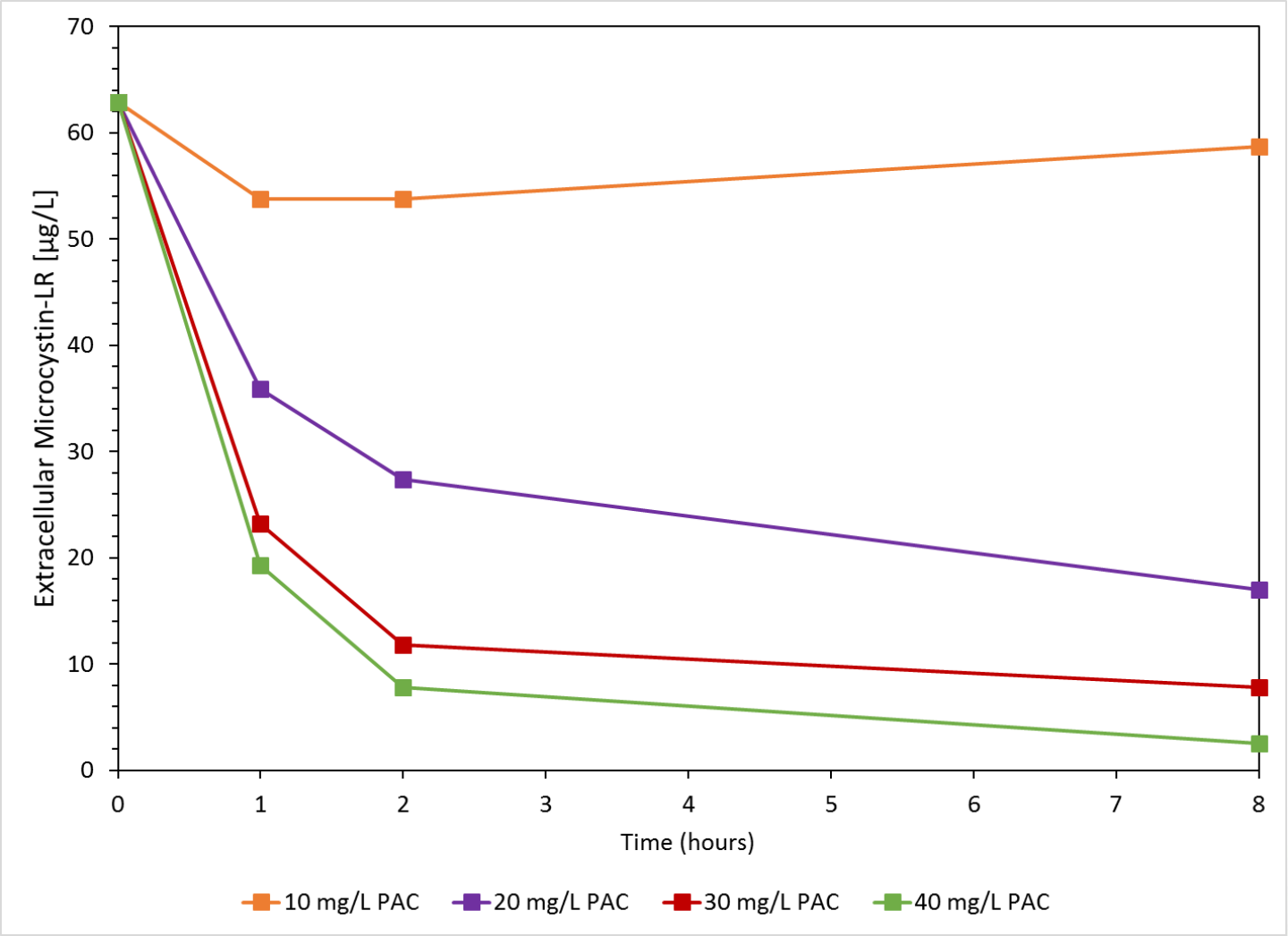
Operational considerations for coagulation, flocculation, sedimentation and filtration

- 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

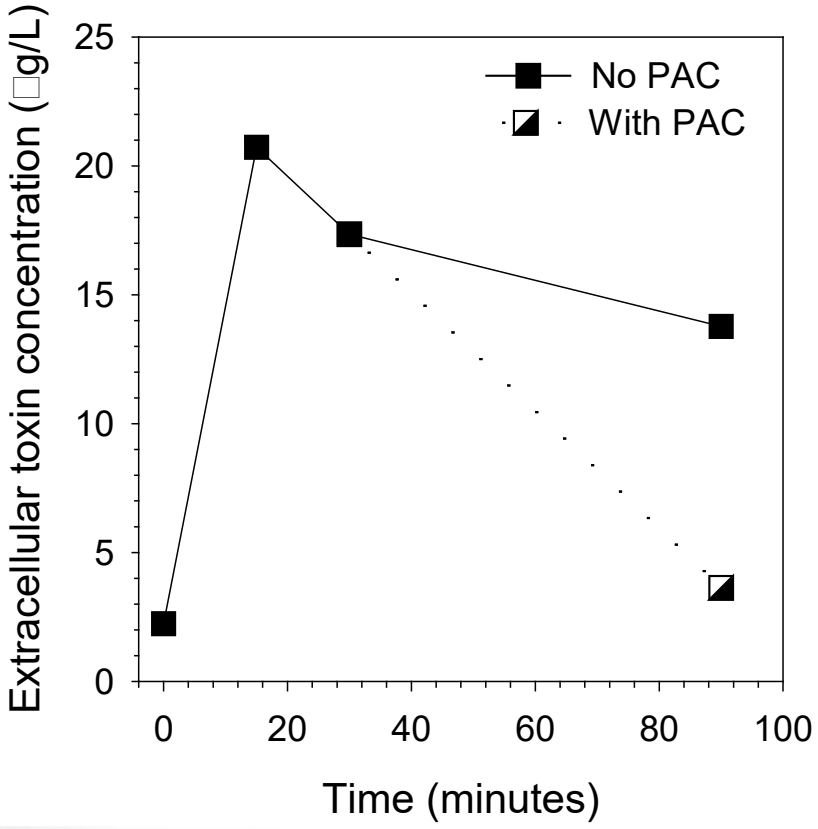
Conventional surface water treatment process

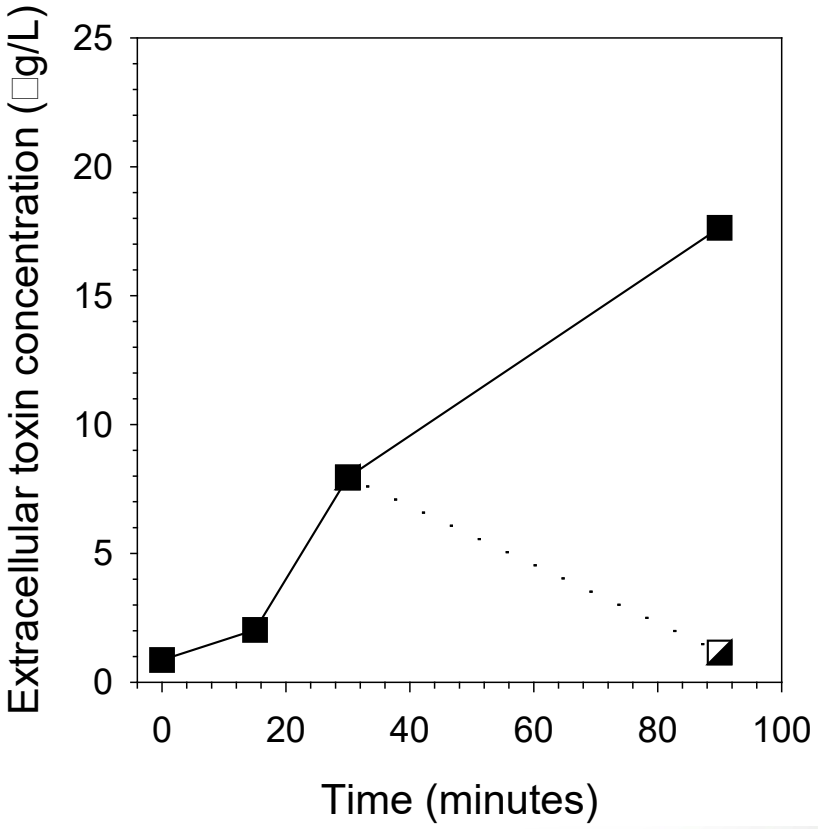


Impact of powdered activated carbon (PAC) addition – microcystin spiked into raw surface water



Impact of powdered activated carbon (PAC) addition – carbon added after toxin release from cyanobacterial cells

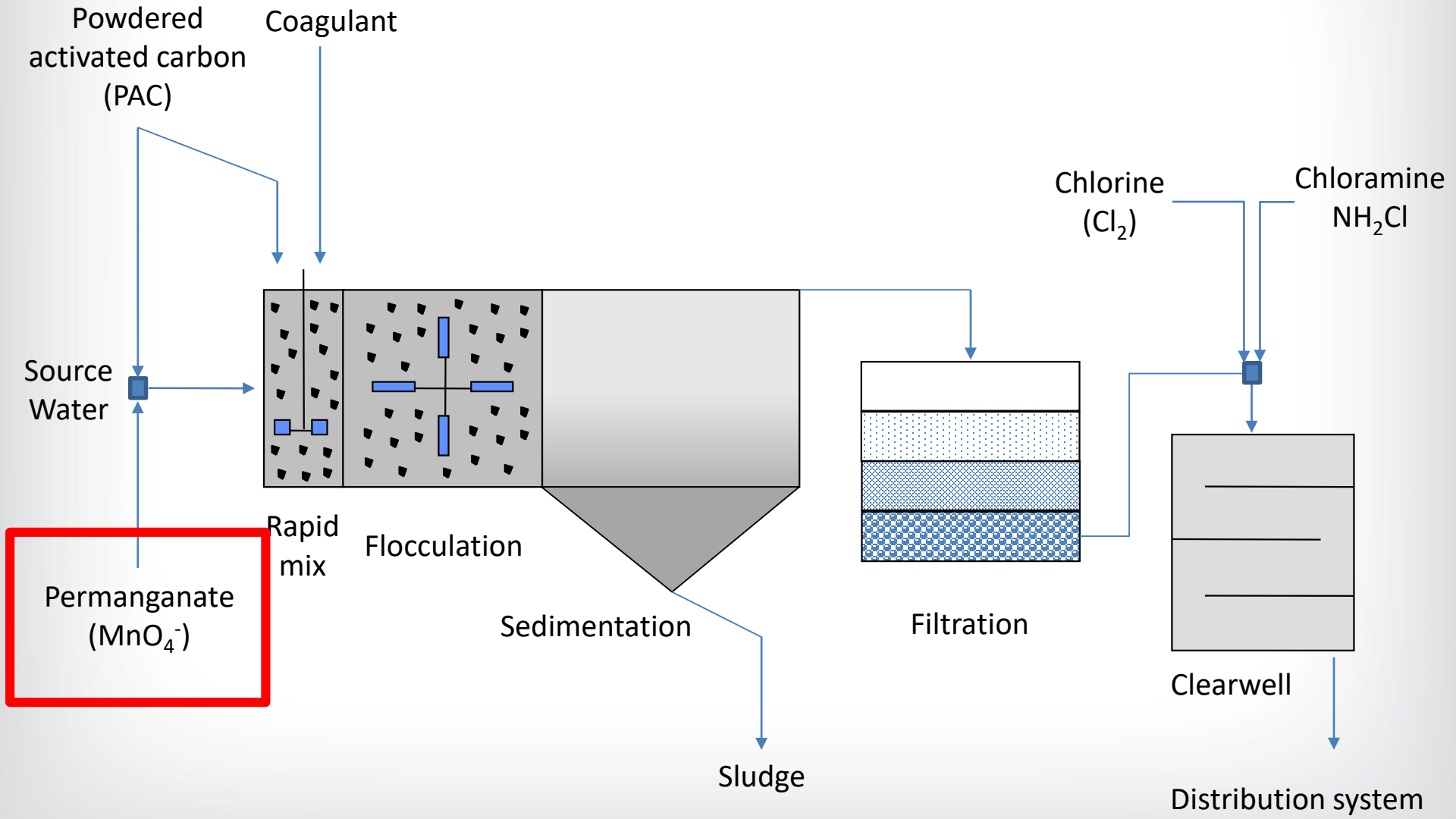




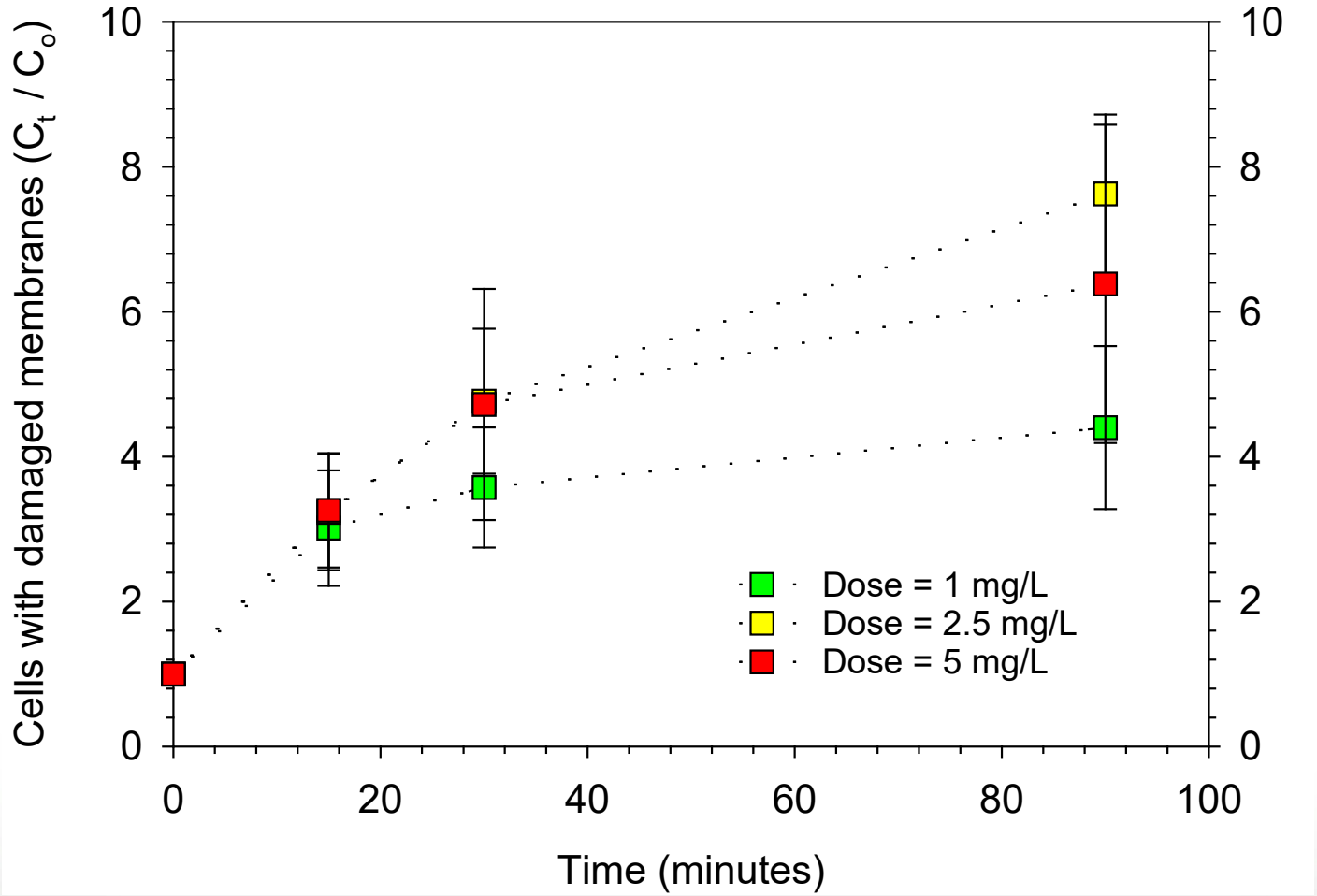
Operational considerations for PAC

- Consider sufficient supply, storage space, and safety prior to HAB season
- Consider operational impacts of adding PAC on sedimentation and filtration processes

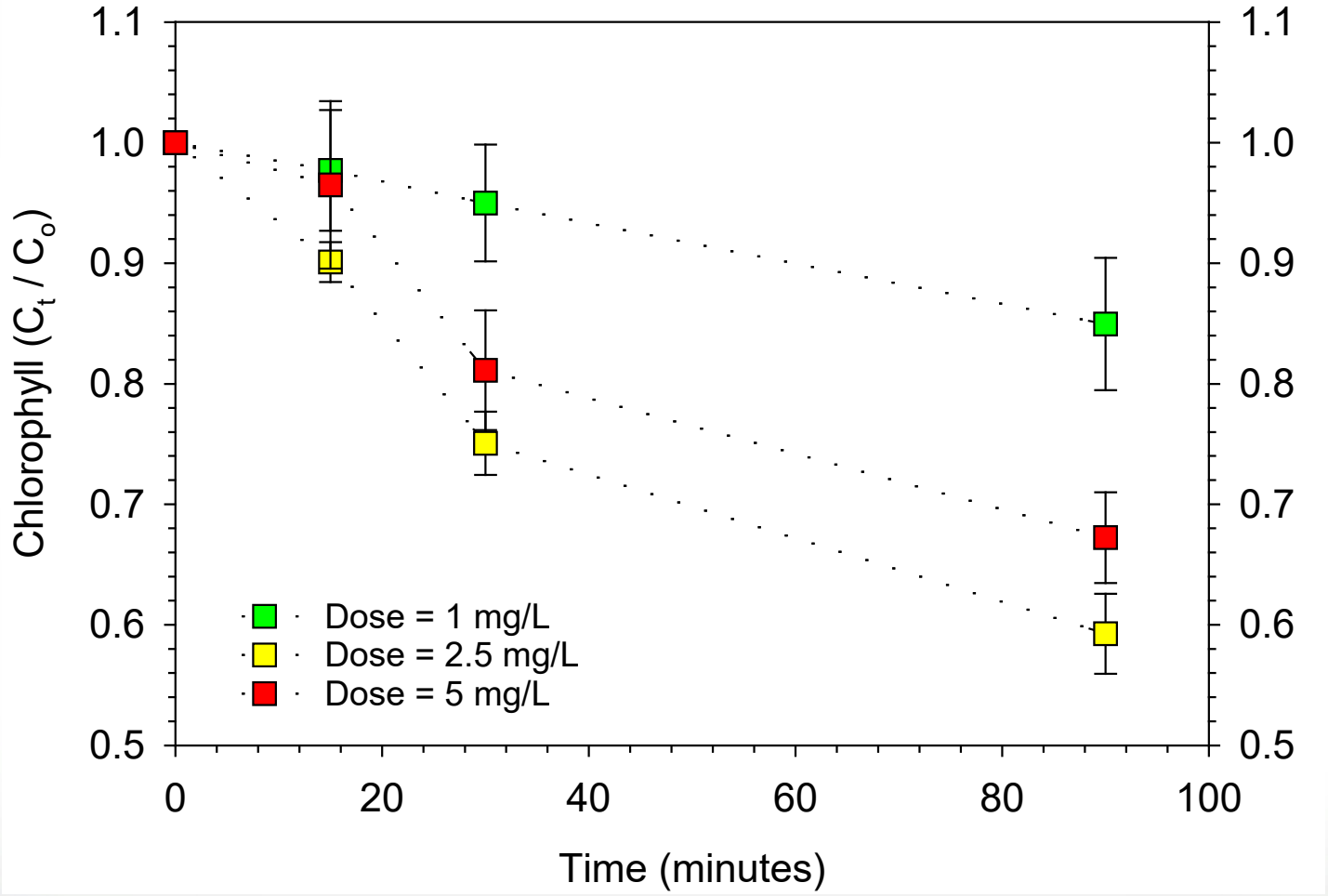
Conventional surface water treatment process



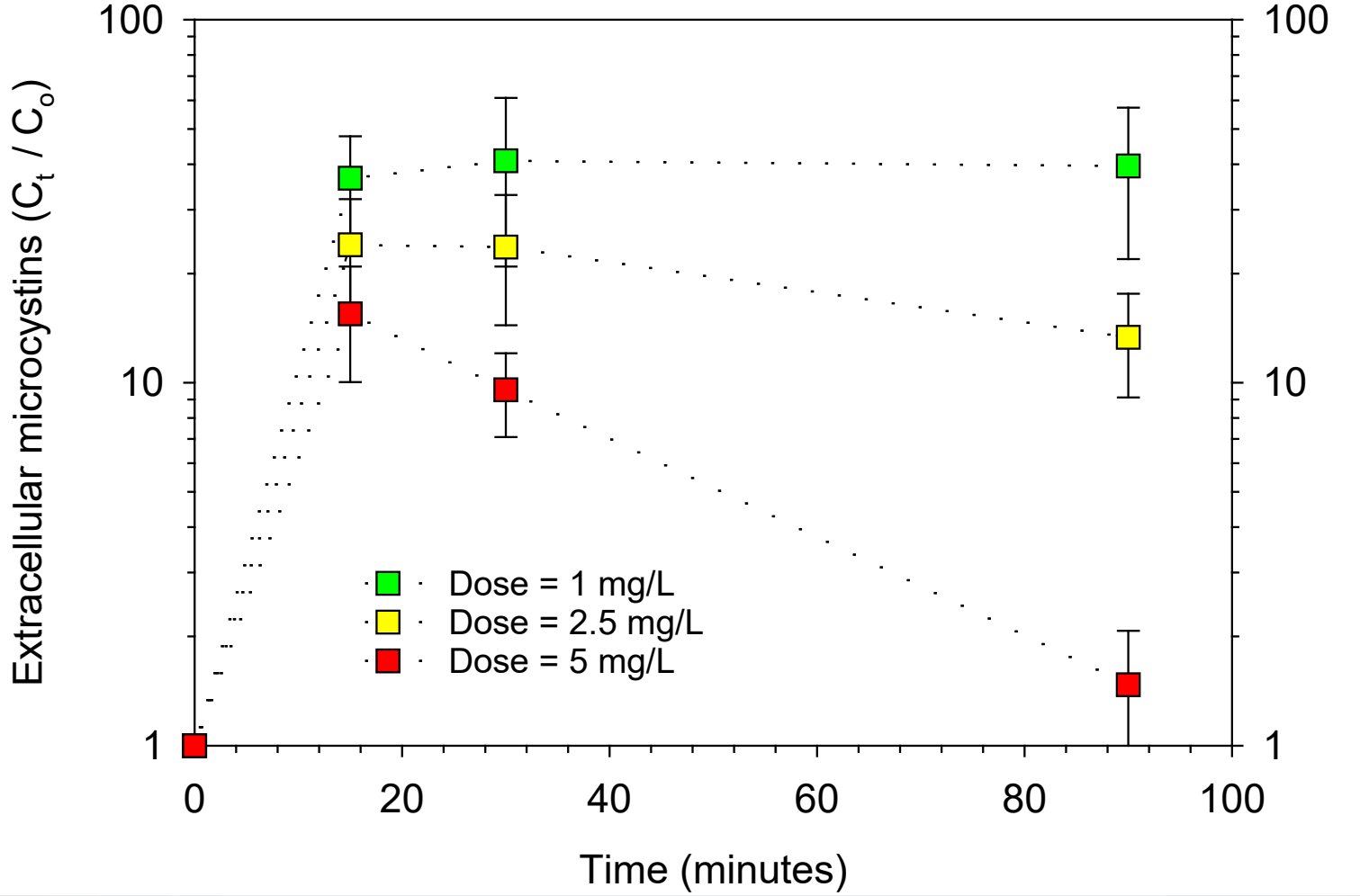
Impact of $KMnO_4$ on cyanobacterial cell membrane integrity



Impact of $KMnO_4$ on chlorophyll in cyanobacterial cells



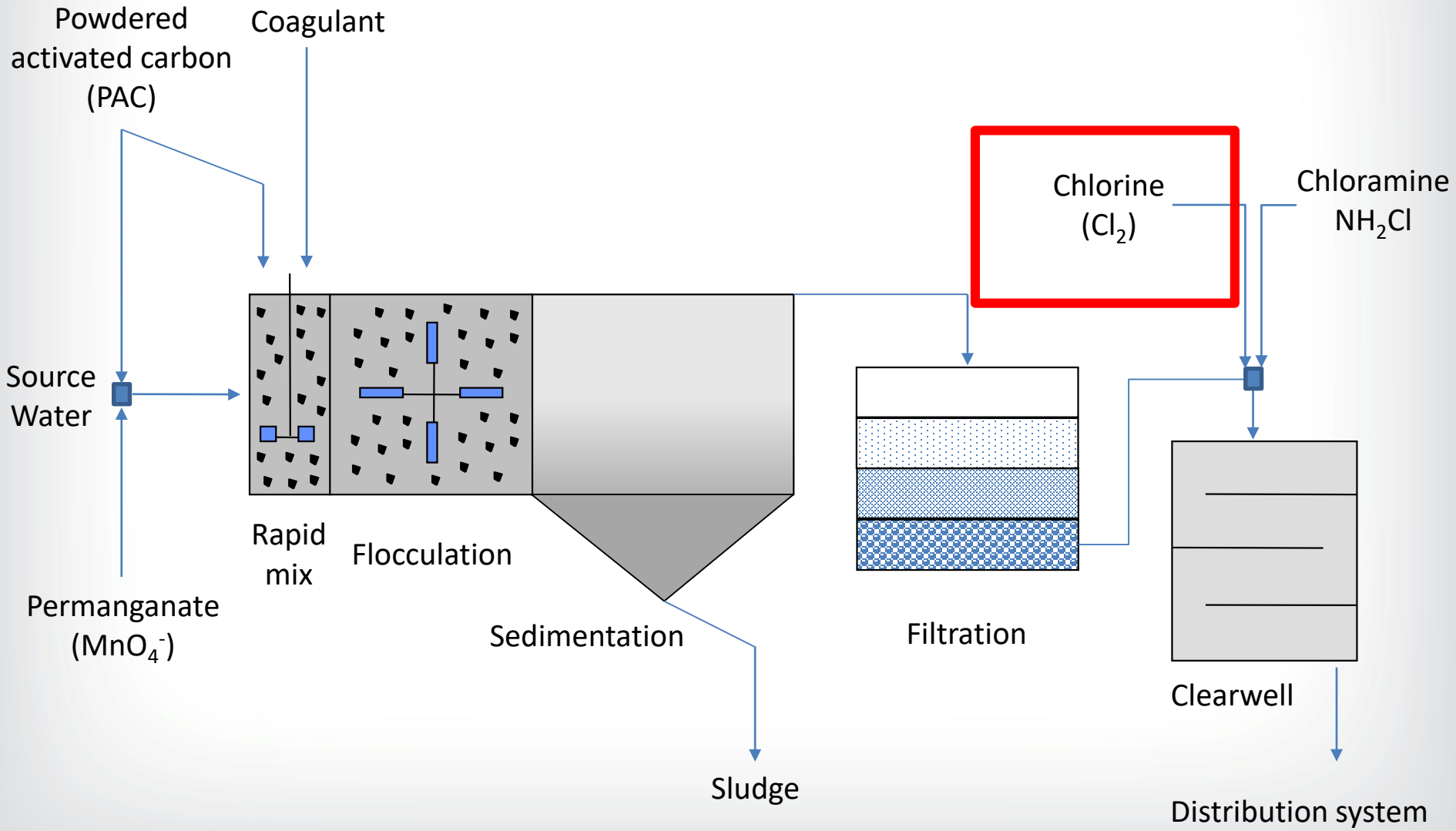
Impact of $KMnO_4$ on toxin release from cyanobacterial cells and subsequent degradation



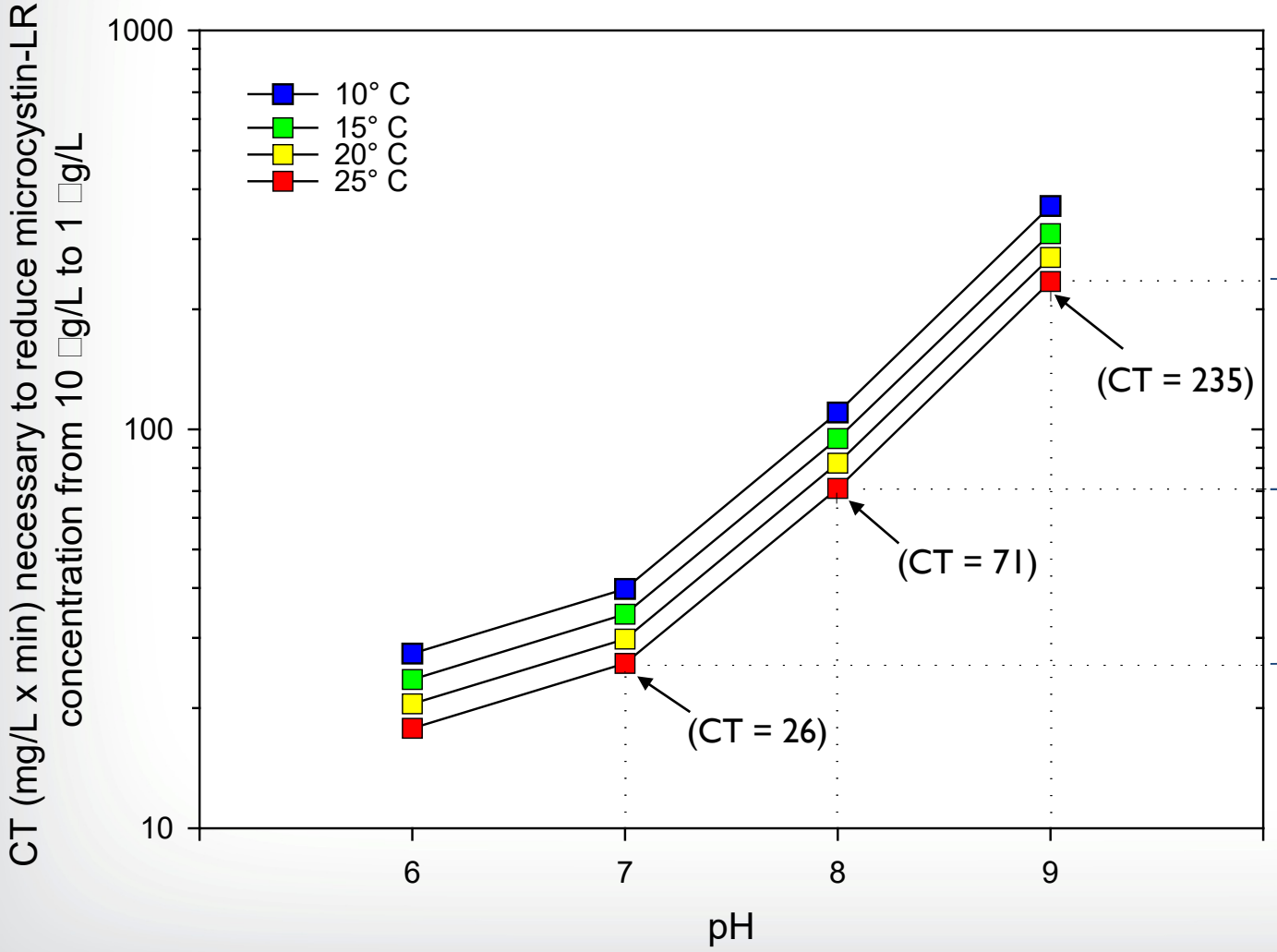
Operational considerations for permanganate pre-oxidation

- 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

Oxidation of microcystins with chlorine kinetic study

- Objective: evaluate microcystins 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 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 WTP

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

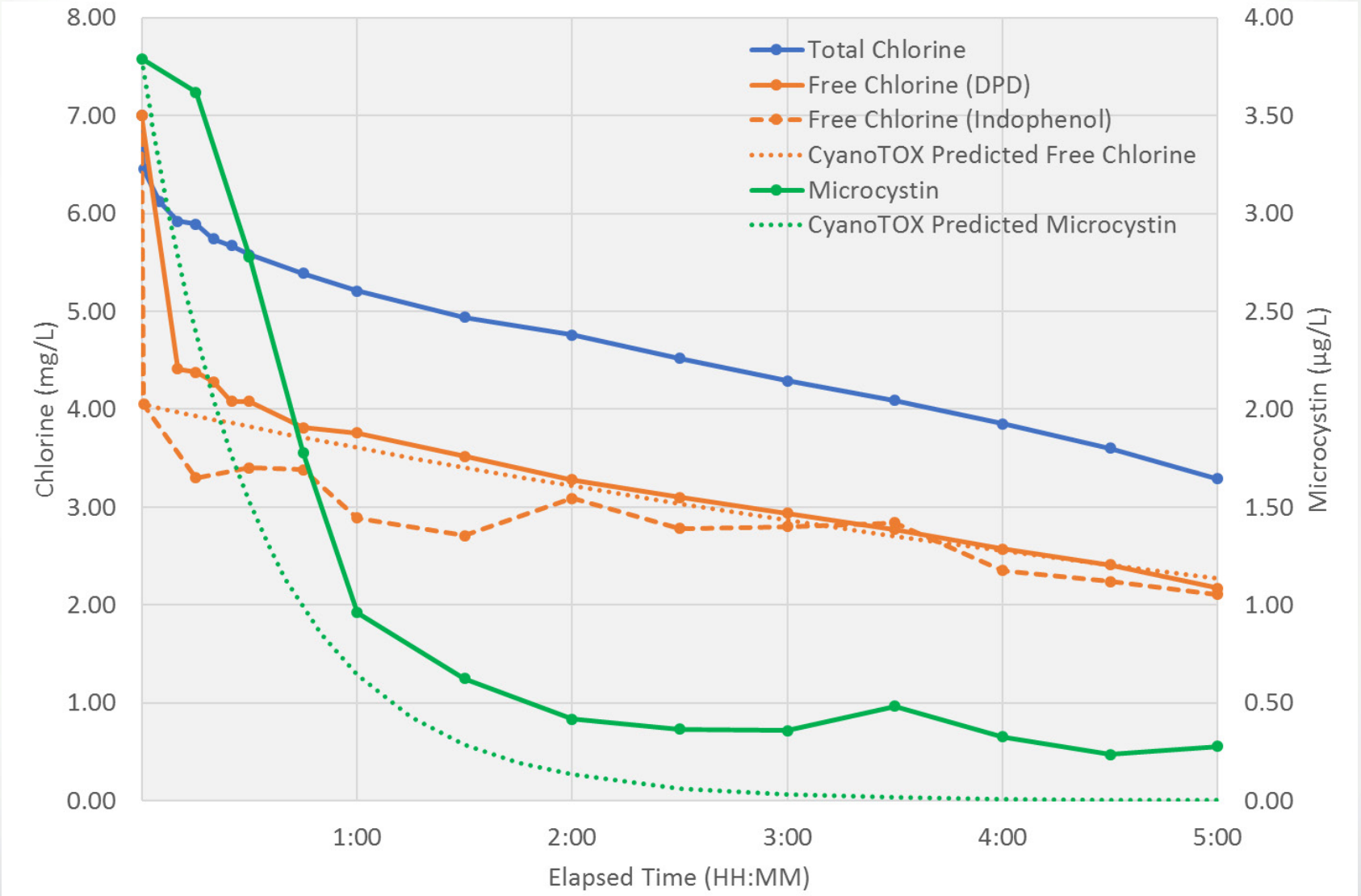
STEP 6. Go to your chosen calculator version: CT based or Dose-decay based (tabs in blue)

STEP 7. Input the following parameters

Baffling Factor	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")

Chlorine & microcystins kinetic study at a WTP



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

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

- Core conventional treatment processes – coagulation, flocculation, sedimentation, filtration - are highly effective at removing cyanobacterial cells – shown to work across a range of coagulants
- PAC effectively adsorbs microcystins – however, the exact carbon dose will vary depending on the type of carbon and the concentration of background of organic material

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

The U.S. Environmental Protection Agency, through its Office of Research and Development, funded and managed, or partially funded and collaborated in, the research described herein. It has been subjected to the Agency's peer and administrative review and has been approved for external publication. Any opinions expressed in this paper are those of the author(s) and do not necessarily reflect the views of the Agency, therefore, no official endorsement should be inferred. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Contact information

Nicholas Dugan

dugan.nicholas@epa.gov
513-569-7239

US Environmental Protection Agency
Water Supply and Water Resources Division
26 West Martin Luther King Drive
Cincinnati, OH 45268