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CEE 697z
Organic Compounds in Water and Wastewater

Cyanotoxins
Removal in Water Treatment

Lecture #30

WRF Reports on Cyanotoxin Control

- Newcombe, 2002 (WRF 446) Removal of Algal Toxins from Drinking Water Using ozone and GAC
- WRF 2839; Treatability of Algal Toxins using Oxidation, Adsorption and Membrane Technologies (2010)
- Newcombe, 2009 (WRF 3148) International Guidance Manual for the Management of Toxic Cyanobacteria, Global Water Research Coalition Project (2010)
- WRF 4016; Evaluation of Integrated Membrane Systems for T&O and Algal Toxin Control (2012)
- Wert et al., 2014 (WRF 4406) Release of Intracellular metabolites from Cyanobacteria during Oxidation Processes
- Newcombe, 2015? (WRF 4315) Optimizing Conventional Treatment for Removal of Cyanobacteria and Toxins (in progress)

Water Treatment

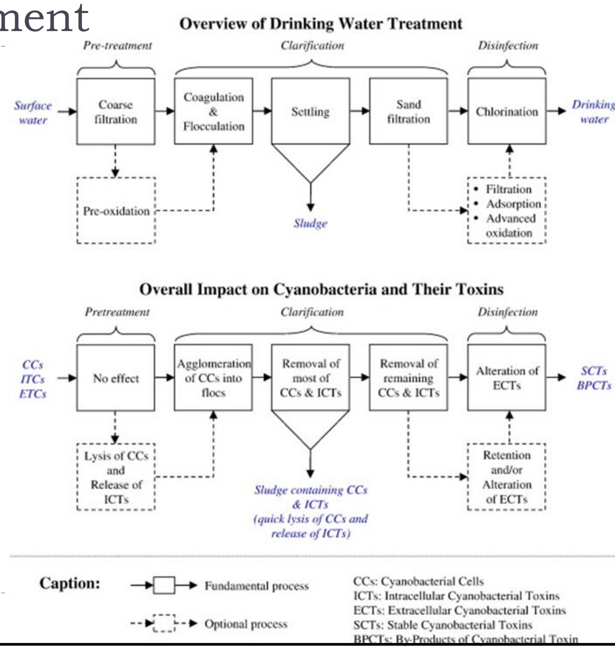
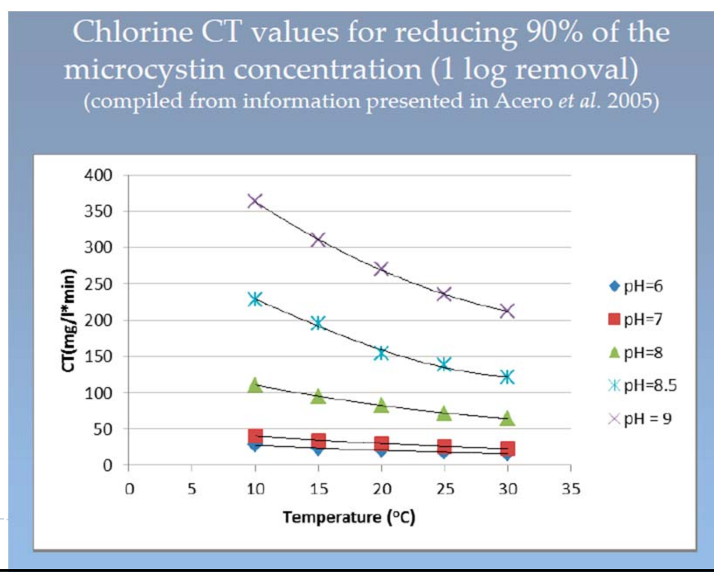


Fig. 6 Overview of drinking water treatment and the overall impact on cyanobacteria and cyanotoxins.

Merel, S., Walker, D., Chicana, R., Snyder, S., Baures, E. and Thomas, O. (2013) State of knowledge and concerns on cyanobacterial blooms and cyanotoxins. Environment International 59, 303-327.

Chlorine and Mycrosystins



Chlorination

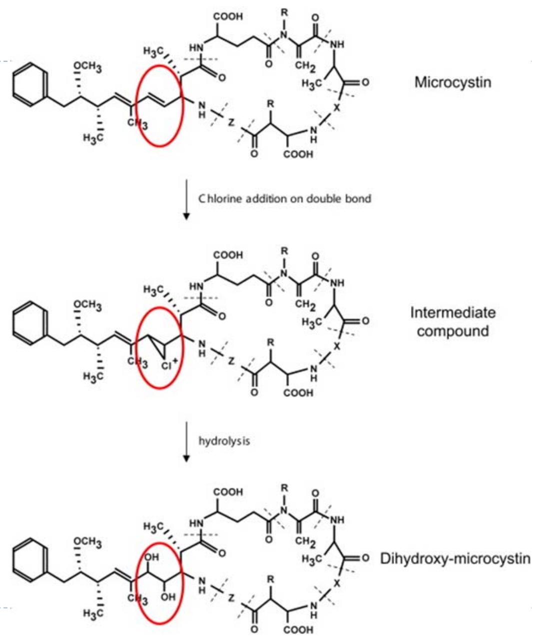


Fig. 2 Formation of dihydroxy-microcystin from reaction with chlorine

Merel, S., Walker, D., Chicana, R., Snyder, S., Baures, E. and Thomas, O. (2013) State of knowledge and concerns on cyanobacterial blooms and cyanotoxins. Environment International 59, 303-327.

Chlorination

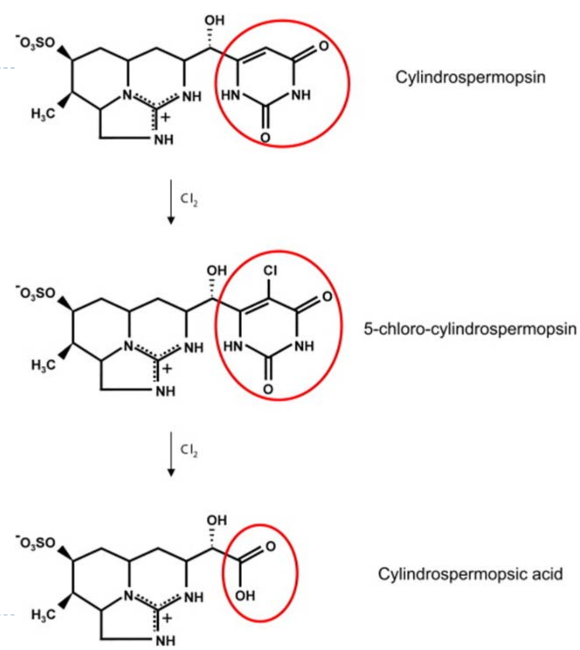


Fig. 3 Formation of 5-chloro-cylindrospermopsin and cylindrospermopsic acid from reaction with chlorine

Merel, S., Walker, D., Chicana, R., Snyder, S., Baures, E. and Thomas, O. (2013) State of knowledge and concerns on cyanobacterial blooms and cyanotoxins. Environment International 59, 303-327.

Ozone and Cyanotoxins

Newcombe, 2002 (WRF 446) Removal of Algal Toxins from Drinking Water Using ozone and GAC

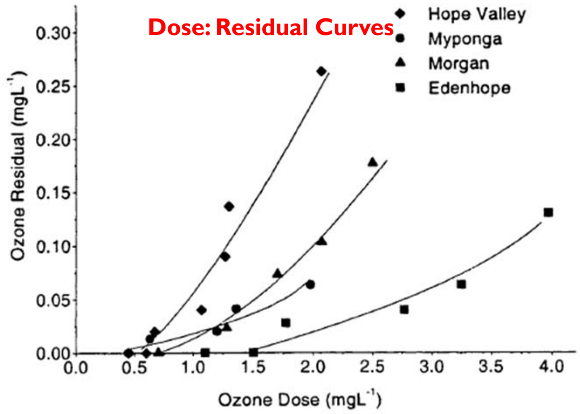


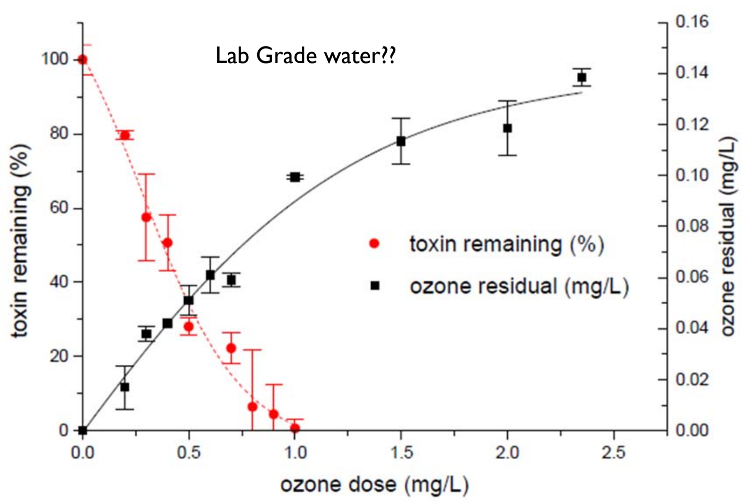
Table 3.1

Water quality parameters of four treated waters

Water	pH	Alkalinity (mg L^{-1} as $CaCO_3$)	DOC (mg L^{-1})	Colour (HU)	SUVA (Lm^{-1}mg^{-1})
Hope Valley	7.8	77	5.3	10	1.8
Myponga	7.5	30	4.6	7	2.1
Morgan	7.8	109	5.7	11	1.9
Edenhope	7.1	133	15.5	7	1.4

- Water Quality Characteristics

Ozone and Microsystin



Ozonation of Microsystin

Newcombe, 2002 (WRF 446) Removal of Algal Toxins from Drinking Water Using ozone and GAC

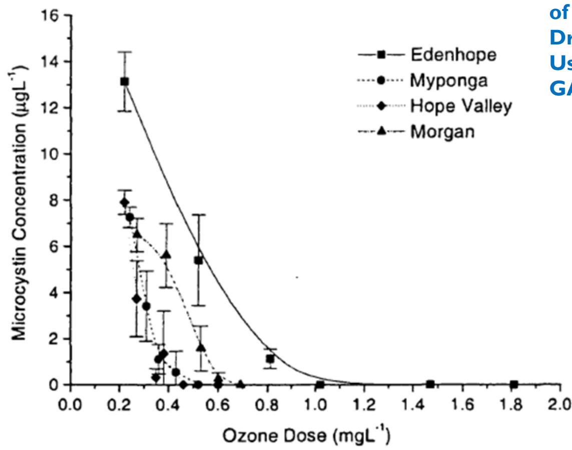


Figure 3.5 Microcystin concentration as a function of ozone dose

Ozonation of Anatoxin-a

Newcombe, 2002 (WRF 446) Removal of Algal Toxins from Drinking Water Using ozone and GAC

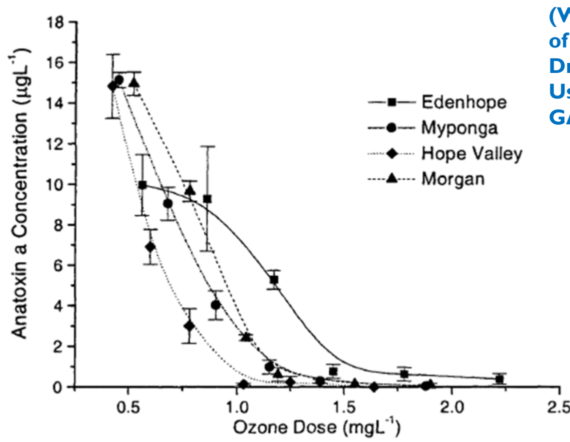


Figure 3.6 Anatoxin-a concentration as a function of ozone dose

Ozonation of Saxitoxins

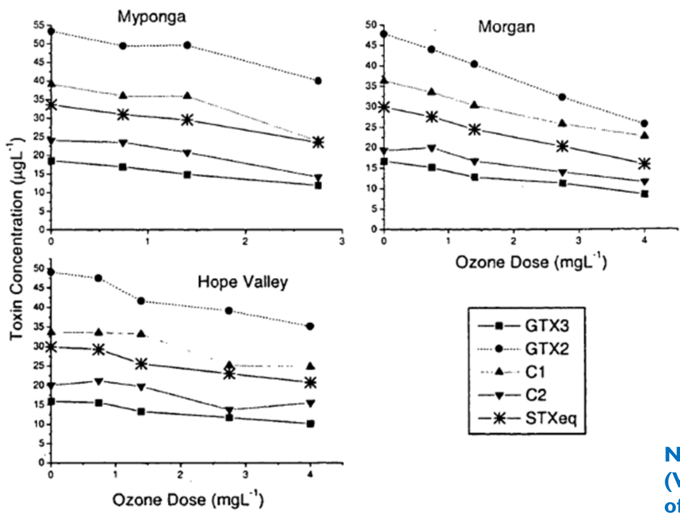
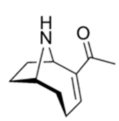


Figure 3.7 Saxitoxin concentration vs. ozone dose in three treated waters

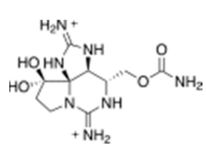
Newcombe, 2002 (WRF 446) Removal of Algal Toxins from Drinking Water Using ozone and

Structural Refresher

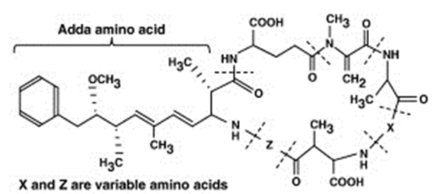
- Anatoxin-a



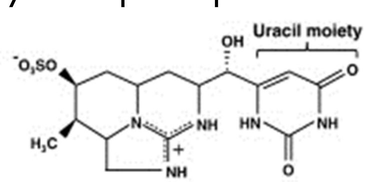
- Saxitoxin



- Microsystin



- Cylindrospermopsin



Comparison in Myponga Water

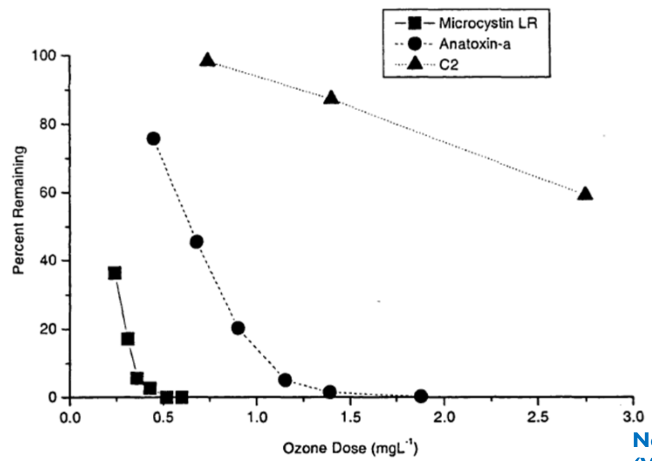
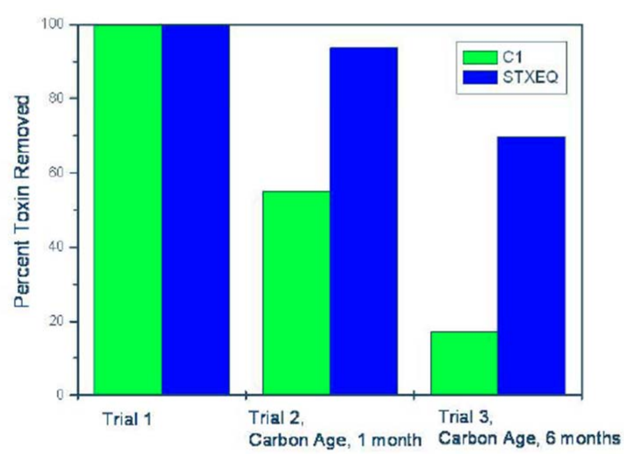


Figure 3.10 Comparison of the destruction, by ozone, of three toxins

Newcombe, 2002 (WRF 446) Removal of Algal Toxins from Drinking Water Using ozone and

GAC removal of Saxitoxins

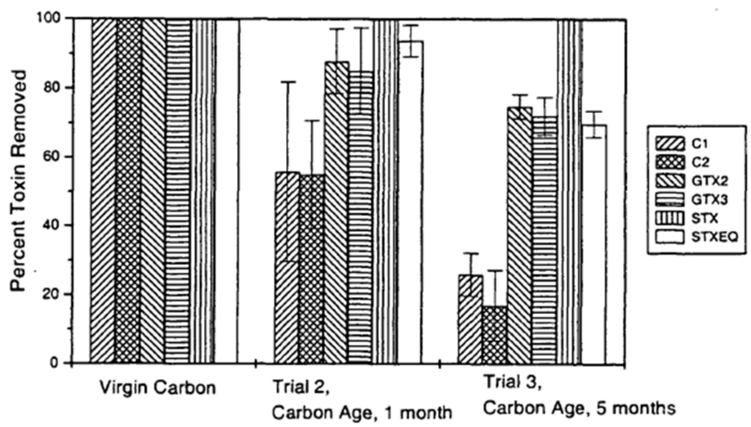
- Hope Valley water



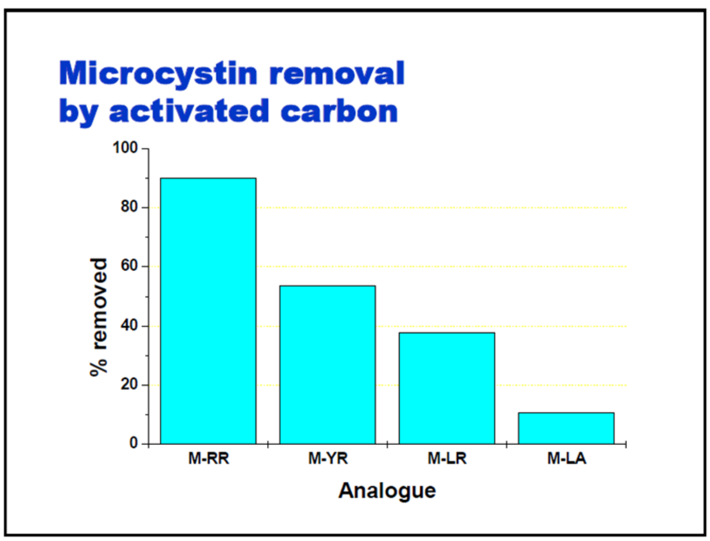
GAC and more Saxitoxins

- Hope Valley Water

Newcombe, 2002 (WRF 446) Removal of Algal Toxins from Drinking Water Using ozone and GAC



GAC removal of Microsystins



Summary

Newcombe, 2002 (WRF 446) Removal of Algal Toxins from Drinking Water Using ozone and GAC

Table 7.1

Recommendations for treatment options for cyanotoxins. GAC_{adsn} - GAC functioning in adsorption mode, $GAC_{degradn}$ - GAC functioning as a biofilter. ND - not determined. ✔ - recommended ✖ - not recommended. Multiple symbols represent strength of recommendation (eg. ✖ represents some removal, but not recommended alone as an option, whereas ✖✖✖ indicates negligible effect)

Toxin	Ozone	Ozone/GAC	GAC_{adsn}	$GAC_{degradn}$
M-LR	✔✔	✔✔	✖✖	✔✔✔* (potentially)
M-LA	✔✔	✔✔	✖✖✖	✔✔✔* (potentially)
Saxitoxins	✖	✔✔	✔	✖✖
Anatoxin-a	✔✔	✔✔	ND	ND

* more research is required before a general recommendation can be confidently made

Oxidation: Summary Kinetics

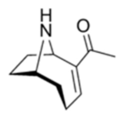
Table 1.1
Apparent second-order rate constants for the reaction of oxidants with cyanotoxins (Adapted from Rodriguez et al. 2007)

	Apparent second-order rate constant (kapp) at pH=8 at 20°C		
Oxidant	Microcystin-LR	Anatoxin-a	Cylindrospermopsin
Ozone	4.1×10^5	6.4×10^4	3.4×10^5
Hydroxyl radical	1.1×10^{10}	3.0×10^9	5.5×10^9
Chlorine	33	< 1	490
Chloramine	< 1	< 1	< 1
Permanganate	357	2.3×10^4	0.3
Chlorine dioxide	1	Low	0.9

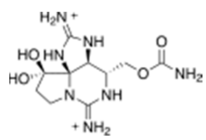
Wert et al., 2014 (WRF 4406) Release of Intracellular metabolites from Cyanobacteria during

Structural Refresher

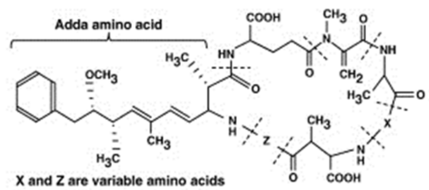
- Anatoxin-a



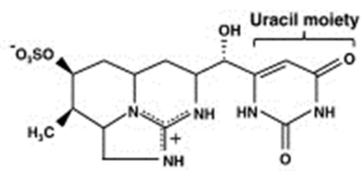
- Saxitoxin



- Microsystin



- Cylindrospermopsin



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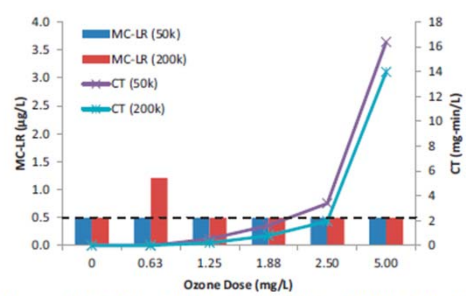


Figure 4.4 Release of MC-LR from 50,000 cells/mL (50k) and 200,000 cells/mL (200k) of MA after ozone oxidation (Note: MRL of 0.5 µg/L indicated by dashed line)

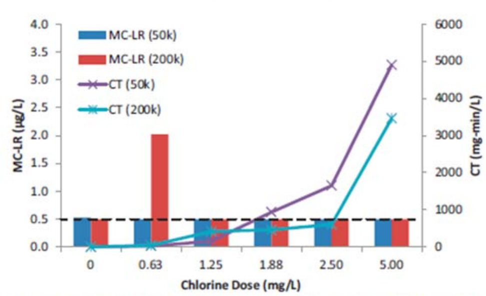


Figure 4.5 Release of MC-LR from 50,000 cells/mL (50k) and 200,000 cells/mL (200k) of MA after chlorine oxidation (Note: MRL of 0.5 µg/L indicated by dashed line)

Wert et al., 2014 (WRF 4406) Release of Intracellular metabolites from Cyanobacteria during Oxidation Processes

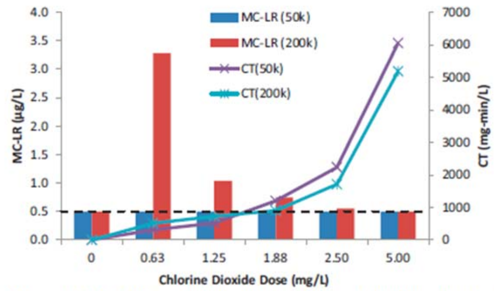


Figure 4.6 Release of MC-LR from 50,000 cells/mL (50k) and 200,000 cells/mL (200k) of MA after chlorine dioxide oxidation (Note: MRL of 0.5 µg/L indicated by dashed line)

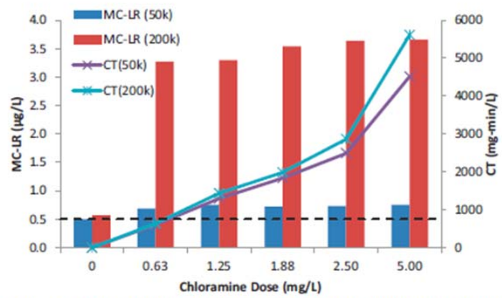
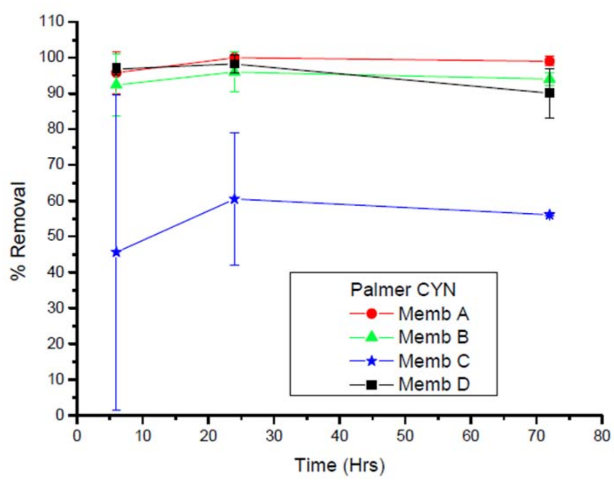


Figure 4.7 Release of MC-LR from 50,000 cells/mL (50k) and 200,000 cells/mL (200k) of MA after chloramine oxidation (Note: MRL of 0.5 µg/L indicated by dashed line)

Wert et al., 2014 (WRF 4406) Release of Intracellular metabolites from Cyanobacteria during Oxidation Processes

Membrane removal of Cylindrospermopsin



Control of Intracellular cyanotoxins

Treatment Process	Relative Effectiveness
Intracellular Cyanotoxins Removal (Intact Cells)	
Pretreatment oxidation	Avoid pre-oxidation that lyses cells; removing intact cells is: 1) more cost effective than chemical inactivation/degradation; 2) removes a higher fraction of DBP precursors; 3) removes a higher fraction of intracellular taste and odor compounds; and 4) it is easier to monitor removal.
Coagulation/Sedimentation/Filtration	Effective for the removal of intracellular/particulate toxins.
Membranes	Microfiltration and ultrafiltration are effective at removing intracellular/particulate toxins. Typically, pretreatment is used.
Flotation	Flotation processes, such as Dissolved Air Flotation (DAF), are effective for removal of intracellular cyanotoxins since many of the toxin-forming cyanobacteria are buoyant.

Control of Extracellular Cyanotoxins

Treatment Process	Relative Effectiveness
Extracellular Cyanotoxins Removal	
Membranes	Typically, nanofiltration has a molecular weight cut off of 200 to 2000 Daltons; individual membranes must be piloted to verify toxin removal. Anatoxin-a has a molecular weight of 165 Daltons. Reverse osmosis is effective.
Potassium Permanganate	Effective for oxidizing microcystins and anatoxins. Not effective for cylindrospermopsin and saxitoxins.
Ozone	Very effective for oxidizing extracellular microcystin, anatoxin-a and cylindrospermopsin.
Chloramines	Not effective.
Chlorine dioxide	Not effective with doses typically used for drinking water treatment.
Chlorination	Effective for oxidizing extracellular cyanotoxins as long as the pH is below 8, ineffective for anatoxin-a.
UV Radiation	Effective at degrading toxins but at impractically high doses.
Activated Carbon	PAC/GAC: Most types are generally effective for removal of microcystin, anatoxin-a, saxitoxins and cylindrospermopsin. Because adsorption varies by carbon type and source *water* chemistry, each application is unique; activated carbons must be tested to determine effectiveness. Mesoporous carbon for microcystin and cylindrospermopsin. Microporous carbon for anatoxin-a.

Cylindrospermopsin

Initial conditions	PAC	MF/UF	Chlorine	Final		
MIB, 100 ng/L 100% EC	60	60	60	60 ng/L		
Geosmin, 100 ng/L, 30% EC	79	9	9	9 ng/L		
CYN, 20 ug/L, 50% EC	14	4	0.8	<1 ug/L		
	PAC	Coagulation	MF/UF	Chlorine	Final	
MIB, 100 ng/L 100% EC	60	60	60	60	60 ng/L	
Geosmin, 100 ng/L, 30% EC	79	16	9	9	9 ng/L	
CYN, 20 ug/L, 50% EC	14	5	4	0.8	<1 ug/L	
	Coagulation	MF/UF	GAC	Chlorine	Final	
MIB, 100 ng/L 100% EC	100	100	30	30	30 ng/L	
Geosmin, 100 ng/L, 30% EC	37	30	6	6	6 ng/L	
CYN, 20 ug/L, 50% EC	11	10	5	1	1 ug/L	
	Coagulation	MF/UF	Ozone	GAC	Chlorine	Final
MIB, 100 ng/L 100% EC	100	100	50	15	15	15 ng/L
Geosmin, 100 ng/L, 30% EC	37	30	15	3	3	3 ng/L
CYN, 20 ug/L, 50% EC	11	10	0.1	0.5	0.1	<<1 ug/L
	MF/UF	NF/RO*	Chlorine	Final		
MIB, 100 ng/L 100% EC	100	60	60	60 ng/L		
Geosmin, 100 ng/L, 30% EC	30	18	18	18 ng/L		
CYN, 20 ug/L, 50% EC	10	4	0.8	<1 ug/L		
	Coagulation	MF/UF	NF/RO*	Chlorine	Final	
MIB, 100 ng/L 100% EC	100	100	60	60 ng/L	60 ng/L	
Geosmin, 100 ng/L, 30% EC	37	30	18	18	18 ng/L	
CYN, 20 ug/L, 50% EC	11	10	4	0.8	<1 ug/L	

*Values based on lower level of removals expected for loose NF membranes

EC: extracellular

Treatment summary

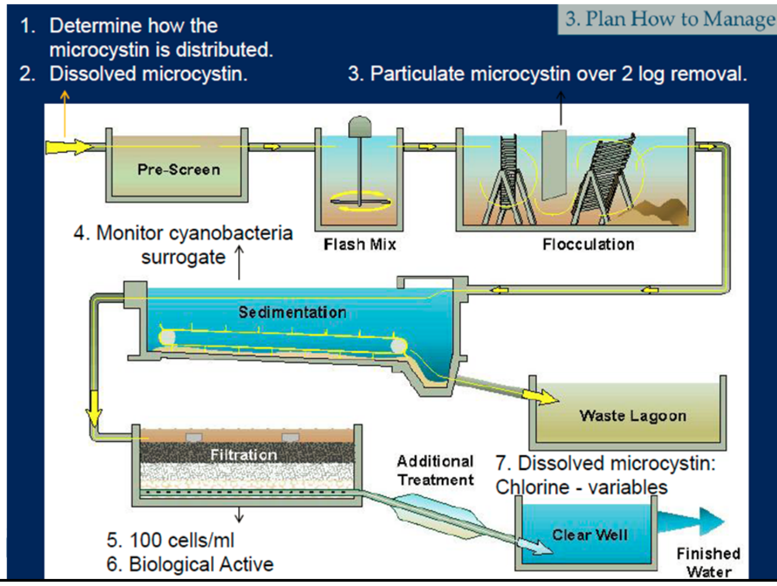
From: Cyanobacteria and Cyanotoxins: Information for Drinking Water Systems , USEPA , July 2012

Table 2. Cyanotoxin Treatment Processes and Relative Effectiveness

Treatment Process	Relative Effectiveness
Intracellular Cyanotoxins Removal (Intact Cells)	
Pretreatment oxidation	Avoid pre-oxidation because often lyses cyanobacteria cells releasing the cyanotoxin to the water column.
Coagulation/Sedimentation/ Filtration	Effective for the removal of intracellular toxins when cells accumulated in sludge are isolated from the plant and the sludge is not returned to the supply after sludge separation.
Membranes	Study data is scarce; it is assumed that membranes would be effective for removal of intracellular cyanotoxins. Microfiltration and ultrafiltration are effective when cells are not allowed to accumulate on membranes for long periods of time.
Flotation	Flotation processes, such as Dissolved Air Flotation (DAF), are effective for removal of intracellular cyanotoxins since many of the toxin-forming cyanobacteria are buoyant.
Oxidation processes	Avoid because often lyses cyanobacteria cells releasing the cyanotoxin to the water column.
Extracellular Cyanotoxins Removal	
Membranes	Depends on the material, membrane pore size distribution, and water quality. Nanofiltration and ultrafiltration are likely effective in removing extracellular microcystin. Reverse osmosis filtration would likely only be applicable for removal of some extracellular cyanotoxins like cylindrospermopsin. Cell lysis is highly likely. Further research is needed to characterize performance.
Potassium Permanganate	Effective for oxidizing microcystins and anatoxins. Further research is needed for cylindrospermopsin.
Ozone	Very effective for oxidizing extracellular microcystin, anatoxin-a and cylindrospermopsin.
Chloramines	Not effective
Chlorine dioxide	Not effective with doses used in drinking water treatment.
Chlorination	Effective for oxidizing extracellular cyanotoxins as long as the pH is below 8, ineffective for anatoxin-a.
UV Radiation	Effective of degrading microcystin and cylindrospermopsin but at impractically high doses.
Activated Carbon	PAC: Most types are generally effective for removal of microcystin, anatoxin-a and cylindrospermopsin, especially wood-based activated carbon. GAC: Effective for microcystin but less effective for anatoxin-a and cylindrospermopsins.

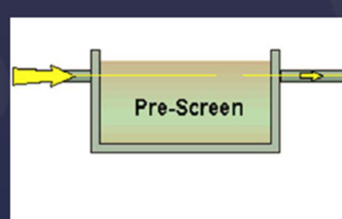
From: Sklener, Westrick & Szlag, 2014

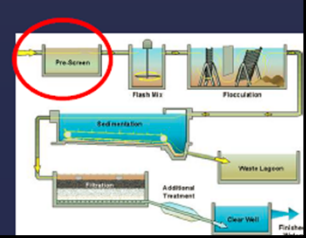
Managing a Cyanotoxin Event



<u>Intake Avoidance/Management Strategies</u>:

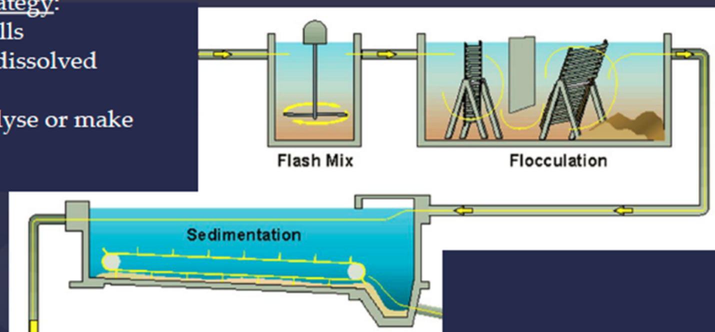
- Multiple sources
- Different depths
- Blending sources





From: Sklenar, Westrick & Szlag, 2014

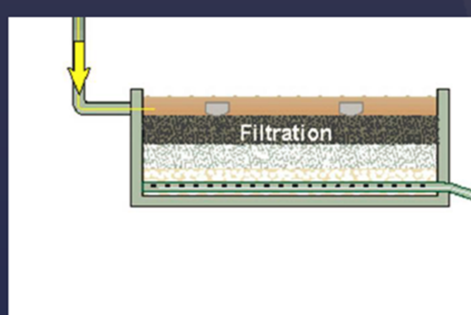
Pretreatment Strategy:
- Do not lyse cells
- PAC adsorbs dissolved cyanotoxins
- Oxidants can lyse or make cells leaky

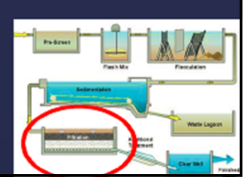


Coagulation/Sedimentation Strategy:
- Remove intact cells if you can
- Low pH (< 6.3) can increase release of cyanotoxins
- < 100 cell/mL onto filters
- Sweep coagulation may be a consideration to remove floating colonies
- Optimize treatment using a cyanobacteria surrogate (phycocyanin, cell counts, chlorophyll, particle counts, streaming current)

From: Sklenar, Westrick & Szlag, 2014

Filtration Removal Strategy:
- Standard sand, anthracite, multimedia that meet state standards are effective at removing cyanobacteria cells
- GAC may be biologically active; media becomes spent within weeks
- If possible, do not recycle filter backwash, sludge supernatant, etc. during a cyanobacterial bloom

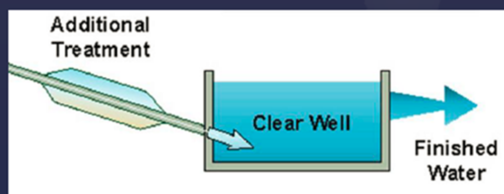


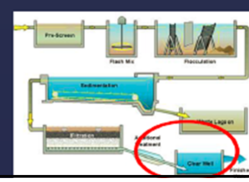


From: Sklenar, Westrick & Szlag, 2014

Clearwell Disinfection Strategy:

Ozone	Very effective for oxidizing extracellular microcystin, anatoxin-a and cylindrospermopsin.
Chloramines	Not effective.
Chlorine dioxide	Not effective with doses typically used for drinking water treatment.
Chlorine	Effective for oxidizing extracellular microcystin and cylindrospermopsin, however it is highly pH and temperature dependent, ineffective for anatoxin-a.
UV Radiation	Not effective at doses typically used for disinfection.





From: Sklenar, Westrick & Szlag, 2014

WTP Response to an HAB Event

- Do not use pre-chlorination for improved coagulation or reduced coagulant dosing during a cyanobacterial bloom unless comprehensive testing has identified a dose high enough to destroy released toxins. Do not apply pre-chlorination when cyanobacteria producing MIB or geosmin are present.
- Potassium permanganate dosing may be applied for the control of manganese and iron in the presence of A. circinalis and M. aeruginosa.
- Practice pH control to pH > 6 if this is not part of normal operations. This will reduce the risk of cell lysis and metabolite release during treatment.
- Optimize NOM removal using the criteria ΔC/C0 DOC, UV, and color ≤ 0.05 and the cell removal should be optimized as well.
- While turbidity cannot be used as an indicator of the presence of cyanobacteria or cell concentration, use the decrease in settled water turbidity with coagulant dose as a surrogate for, or indicator of, cell removal if the initial turbidity is ≈10 NTU or above.
- If the presence of cyanobacteria results in increased coagulant demand to achieve improved settled water turbidity the application of a particulate settling aid, or even powdered activated carbon, may lead to improvements.
- Although removal of cyanobacteria through conventional coagulation can be very effective, 100% cell removal is unlikely in normal full scale operations. In the event of high cell numbers entering the plant monitor for cell carryover and accumulation in clarifiers, this can lead to serious water quality problems if not rectified.
- Once captured in the sludge, cyanobacteria can remain viable and multiply over a period of at least 2–3 weeks. Simultaneously, within one day some cells in the sludge will lyse and release NOM and metabolites.

Newcombe, 2014 (WRF 4315, in progress) Optimizing Conventional Treatment for Removal of Cyanobacteria and Toxins

- To next lecture