American Water Works Association
Ohio Section Technology Committee

Ohio Environmental Protection Agency

DRAFT WHITE PAPER ON CYANOTOXIN TREATMENT

November, 2016

Introduction

Cyanobacteria (also known as blue-green algae) are microscopic organisms found naturally in surface water. True algae and cyanobacteria both utilize some form of chlorophyll to perform photosynthesis. True algae are essentially plants. Cyanobacteria are actually photosynthesizing bacteria. Cyanobacteria also contain the accessory pigment phycocyanin, that can give decaying blue-green algae a blue color. Some of the most commonly occurring cyanobacteria in Ohio waters include: microcystis, anabaena, pseudoanabaena, planktothrix, aphanizomenon, and cylindrospermopsis. True algae and cyanobacteria are very different organisms and therefore should not be treated the same. There are no known harmful toxins released by dying true algae. Cyanobacteria, however, can contain harmful cyanotoxins within the cell wall which may be released during cell growth or death.

Some species of cyanobacteria can produce cyanotoxins, including neurotoxins (nervous systems), hepatotoxins (liver) and dermatotoxins (skin irritant). Monitoring for cyanotoxins in Ohio is currently focused on the most prevalent cyanotoxins where reliable analytical capabilities exist, including microcystin, cylindrospermopsin, saxitoxin and anatoxin-a.

Cyanobacteria can be responsible for production of the problematic taste and odor compounds geosmin and 2-Methylisoborneol (MIB) in drinking water sources. A U.S. Geological Survey (USGS) study showed presence of taste and odor may serve as an indicator of the presence of cyanotoxins. Not all cyanobacteria are capable of producing geosmin or MIB, however, so cyanotoxins can occur in the absence of taste and odor compounds.

It is recommended that public water systems with a history of cyanobacteria in their drinking water sources monitor for cyanobacteria and the effectiveness of their current treatment processes to deal with cyanotoxin-producing blooms. Since some cyanobacteria do not produce scums and are often not visually apparent, routine microscopic identification is strongly recommended. During a significant bloom in the source water, it should be assumed cyanotoxins could be present. In Ohio, routine monitoring for microcystins is required by rule. Photographs of blooms, specific recommendations for cyanotoxin monitoring and how to respond in the event cyanotoxins are detected are available on Ohio EPA's website at www.epa.ohio.gov/ddagw/HAB.aspx.

This white paper is intended to assist public water system operators with evaluating and optimizing their treatment processes to deal with cyanotoxins. In general, the most effective way to remove cyanotoxins is while they are still encased within the intact cyanobacteria cells, or intracellular. Once cyanotoxins are released from the cells, or extracellular, they are much more difficult to remove. As the cyanobacteria cell cycles through its normal life cycle, or when it dies and lyses, it can release toxins. The coagulation, flocculation and sedimentation processes are effective at cyanobacteria cell

removal and thus intracellular toxin removal, but ineffective at removing extracellular toxins. Additional chemical processes will be needed to remove extracellular toxins. Therefore, the most efficient and cost effective method for cyanotoxin removal includes optimization of current treatment processes for intact cell removal. A multi-barrier approach which couples optimization of physical removal of intact cells with an oxidation/destruction and/or adsorption step(s) to remove extracellular toxins is the best defense.

Treatment

Source Water Protection & Algaecides

A watershed protection program can help reduce the nutrient load on the watershed area. An effective watershed management program will help identify specific environmental characteristics of the watershed and actions necessary to reduce or eliminate potential contaminants.

It is beyond the scope of this guidance to discuss all relevant reservoir management strategies, but algaecides are so commonly used they warrant mention. Algaecides (including copper sulfate and hydrogen peroxide), when applied to a drinking water source under controlled conditions, can effectively control the growth of algae and cyanobacteria. Water systems are required to submit a Notice of Intent (NOI) to Ohio EPA Division of Surface Water and obtain coverage under the pesticide general permit prior to applying algaecide to a source of drinking water. Before applying an algaecide it is important to closely read the pesticide label and be fully aware of both the environmental impact and practical problems with its use. Water systems must also follow the conditions outlined in the pesticide general permit. Treatment should be applied at the early stages of a bloom when cyanobacteria cell counts are low (<10,000 cells/ml) because: 1) this is when the potential for cyanotoxin release is not probable or low, and 2) if the treatment is applied at the early stages of a bloom, then the toxic compounds if released into the water can be removed effectively during the treatment processes. To keep the algae under control for extended periods of time, the algaecide applications should be performed at specific intervals based upon the pesticide label.

The pesticide general permit prohibits algaecide application to severe blooms (>100,000 cells/ml) or any scums that are within 500 yards of the intake or cover greater than 20% of the reservoir, unless information is provided to Ohio EPA prior to algaecide application that confirms: the bloom is not currently producing cyanotoxins, or the surface water will not be used as a source of drinking water until monitoring can confirm cyanotoxins are below levels of concern, or the water system has demonstrated that treatment is capable of removing high concentrations of cyanotoxins. More information is available in the Ohio EPA algaecide application fact sheet, available here: http://epa.ohio.gov/Portals/28/documents/HABs/Publications/AlgaecideApplicationFactSheet.pdf

Conventional Treatment

Conventional surface water treatment is defined as the sequential use of coagulation, flocculation, sedimentation, filtration, and disinfection (normally with chlorine) in drinking water treatment. With proper coagulation and flocculation, the sedimentation and filtration processes generally provide good cyanobacteria cell removal. Although many common cyanotoxins may be destroyed by the addition of chlorine, the disinfection process (based on the oxidation of the cyanotoxins) may or may not be sufficient (depending on disinfection method, cyanotoxin type and concentration, as well as other water quality parameters) and should not be relied upon as the sole barrier to contamination. If cyanotoxins are released into the water due to cell damage and/or natural decay,

sedimentation and filtration would not provide sufficient removal. The goal of conventional treatment should be undisruptive transport, removal, and disposal of healthy, intact cyanobacteria cells. Each process should be evaluated for cell removal performance and optimized to mitigate the risk of cell breakthrough and/or release of dissolved cyanotoxins. Note that if pre-oxidation of the raw water is practiced, special precautions must be taken (see the section on oxidation included herein).

Following are guidelines to consider when using conventional treatment on source waters which are known to contain cyanobacteria and may be prone to cyanobacteria blooms.

- Coagulation and flocculation generally provide a good preparatory step for cell removal in subsequent processes, although, depending on cell life stage and health, cyanotoxin release could occur from cell wall damage or natural decay. The following guidelines should be considered for process optimization.

    1. Process control parameters and targets (i.e., pH, settled turbidity, dissolved organic carbon removal, etc.) should be more closely monitored to ensure proper operation is maintained.
    2. Coagulation performance can be hindered by poor water quality conditions and/or high cell counts. Coagulant doses need to be optimized for the proper conditions of floc formation, which can be done through laboratory jar tests and verified under full scale operation.
    3. Mechanical and/or hydraulic disturbances could compromise the integrity of cells and floc particles. Flocculator speeds should be evaluated and optimized. If possible, minimize turbulence, maintain even flow distribution, and reduce flow velocities prior to sedimentation. Flocculator speeds up to 230 rpm (velocity gradient, G=480/s) were studied under bench and pilot scale conditions and did not cause additional release of microcystin-LR into water (Drikas, et al. 2001). Jar testing should be used to develop the appropriate velocity gradient (G) and detention time necessary for mixing to consider impacts on other treatment objectives (i.e., TOC and turbidity removal) when optimizing.

- Sedimentation sludge withdrawal cycles should be monitored and increased if necessary to avoid dissolved cyanotoxin release from decaying cells.
- The practice of chlorinating the filter influent should be evaluated, if high numbers of cells remain in the sedimentation basin. At certain doses, chlorine and other oxidants lyse (break open) cyanobacteria cells and increase dissolved cyanotoxin concentrations, which may pass through the filters. As a general recommendation, the practice of chlorination prior to filtration should cease, or at least be minimized, during the cyanobacteria bloom event when cyanotoxins are detected in the raw water supply.
- The rapid rate filtration process is generally effective for cell removal. The following guidelines should be followed to help optimize cell removal and prevent cyanotoxin release.

    1. Filter headloss, run-time, and effluent quality should be closely monitored for each filter. Backwash frequency should be increased, if necessary, to avoid the release of dissolved cyanotoxin due to cell lysis from long storage times and decay inside the filter bed. Filter

effluent should also be checked for cell breakthrough, and backwash frequency should be increased accordingly.

2. Hydraulic disturbances in the filters should be minimized to prevent cell breakthrough. Initial filter start-up, filter-to-waste cycles, flow rates, and backwash scheduling should be evaluated and optimized.
3. If high numbers of cells are being retained in the filters, the backwash water may contain a high concentration of cyanotoxins which may be released due to damaged and/or naturally decaying cells. Consider discontinuing backwash water recycling, if possible. Additional treatment and/or alternate disposal of backwash water may be necessary. See residuals section below for further considerations.

- The disinfection process should be evaluated for the removal of any dissolved cyanotoxins which may escape upstream processes. Proper chlorine application with sufficient contact time (or CT) is effective for the destruction of many cyanotoxins, particularly microcystins and cylindrospermopsin, and to a lesser degree, saxitoxins. Chlorine does not effectively eliminate anatoxin-a. For applicable cyanotoxins, necessary CT values can vary under site specific conditions considering pH, chlorine dose and residual, and temperature. Chloramines are not effective for cyanotoxin destruction in drinking water treatment applications. See Chlorination section below for further considerations.

Activated Carbon

The utilization of activated carbon is a well-accepted treatment technique for the removal of a wide range of organic compounds, including the removal of various cyanotoxins. Powdered activated carbon (PAC) and granular activated carbon (GAC) can both be used as a physical process to adsorb cyanotoxins present in source water. The effectiveness of the adsorption is highly influenced by the nature of the source water, primarily the type of cyanotoxins and competing natural organic matter (NOM) constituents present, and the type of carbon being utilized.

GAC can be used in a full depth contactor for adsorption and is often integrated into the treatment process for taste and odor and disinfection byproduct precursor removal following filtration. Typical empty bed contact times (EBCT) for these applications are a minimum of 10 minutes, and usually around 20 minutes. Literature suggests 15 minute EBCTs are effective for cyanotoxin removal. However, the GAC may not perform as long in removing cyanotoxins as compared to its use for other targeted parameters, such as NOM (literature reports weeks to six months) during a cyanotoxin event (U.S. EPA May 2015 webinar). If GAC is currently utilized, operators should consider optimizing reactivation and replacement frequency based on seasonal occurrence of cyanobacteria.

GAC can also be allowed to go biologically active, such as in biologically active filtration. GAC, as a cap on the filter media bed or at full depth, could be used in this manner. Facilitating a healthy biofilm growth on the GAC media (in lieu of a sand or anthracite layer) in rapid rate gravity filters has been shown to be effective for removal of taste and odor compounds and may have the ability to remove dissolved cyanotoxins. More information on biologically active filtration is found in the following section.

Since cyanotoxin events are periodic, or seasonal, the use of PAC can be advantageous since PAC can be added intermittently to the conventional treatment process to react to a situational presence

of cyanotoxins in a fairly cost effective approach. PAC can be added either prior to coagulation, and removed in the settling tanks, or it can be added to the settling tanks and removed through filtration. A consideration in using PAC is that it needs to be removed by a downstream process and discarded, as PAC is not typically reused or regenerated. Detention times are a consideration if using PAC to ensure that sufficient time is allotted to ensure adequate removal by adsorption. PAC basins are sometimes used prior to coagulation, however due care is needed to ensure that the PAC adsorption rate properly takes into account any competition that may occur for adsorption sites from NOM compounds.

If the treatment scheme includes a preoxidant it should ideally be separated from the PAC addition to allow the oxidant to react with the targeted constituent and thus avoid exhaustion of PAC adsorption sites with the oxidant. For example, potassium permanganate could be injected at the raw water intake crib and then PAC could be fed into an onshore wet well. If PAC is fed at the rapid mix process, coagulation may reduce its effectiveness by being incorporated into floc thus reducing its ability to contact microcystins for adsorption. PAC can also be applied after coagulation, which has a benefit of less competition with NOM that has already been removed by flocculation, but has a disadvantage of reduced contact time.

Overall, the ability to feed PAC at multiple points in the treatment train, prior to filtration, will provide for greater operational flexibility and opportunities to increase contact of PAC particles with extracellular toxins for removal. The earlier PAC is introduced into the treatment train, the greater is the potential contact time with the extracellular toxins. Adequate mixing and suspension of the PAC at the dosing location is also important.

Treatment plants utilizing PAC for microcystins removal should be equipped with the ability to feed PAC from 15 mg/L up to doses of 50 mg/L, or as determined by jar testing (U.S. EPA May 2015 webinar). US EPA's *Drinking Water Health Advisory for Cyanobacterial Microcystin Toxins* document suggests that, "According to Newcombe et al. (2010), a PAC dose of 20 mg/L and a contact time of at least 45 minutes should be considered for removal of most extracellular microcystins (with the exception of microcystin-LA)." This dose recommendation was based on raw water concentrations of dissolved (or extracellular) microcystins up to 4 μg/L. Some microcystin congeners are more difficult to remove, however, and removal efficiencies will depend on the toxins present as well as other water quality parameters. A summary table from WQRA (Newcombe et al, 2010), provided in the Appendix Table 7, shows ranges of PAC dosing for various microcystins congeners developed from numerous laboratory studies. Results from jar testing should be used to establish PAC dosing necessary to remove anticipated worst case cyanotoxin levels below the health advisory level of 0.3 μg/L (microcystin). This dosing rate may require upgrading existing feed equipment and storage capacity to accommodate the higher feed rate necessary for microcystin removal as compared to its use for taste and odor control.

The type of PAC chosen greatly impacts the removal efficiency of cyanotoxins from the water. According to *He X., et al., 2016*, who presented an article summarizing research findings, "mesoporous activated carbon (pore size 2–50 nm) is more effective in adsorbing microcystins than activated carbon dominated by macropores or micropores (Ho et al., 2011; Huang et al., 2007; Pendleton et al., 2001) since the mesopores more readily accommodate the approximately 1–3 nm sized microcystins (Donati et al., 1994; Pendleton et al., 2001)." Research has indicated that wood or lignite based PAC (similar in mesapore size to wood PAC) is better performing for microcystins adsorption as compared to other types, such as coconut based PAC, due to the greater percentage of

mesapore volumes typically present (Donati et al, 1994). For cylindrospermopsin, wood based PAC was also found to be more effective, similar to microcystin. For saxitoxins removal, GAC/PAC types typically used for taste and odor compounds (geosmin) were found to be effective and thought to be attributed to the similarity in smaller molecular size between the compounds. An activated carbon with a higher ratio of micropore to mesapore volumes appear to be better suited to saxitoxin removal (Ho, et al. 2009). Coconut based PACs typically have greater micropore volume making it better for saxitoxin removal (Walker 2015). Due to the varying nature of pore size, particle size, and material type among manufacturers, the best performing GAC/PAC should be determined from site-specific testing.

Jar testing is strongly recommended to compare the performance of different types of PAC and also to determine dosing needs for PAC to be an effective treatment barrier for the projected cyanotoxin concentrations that could occur. The jar testing protocol must consider the water quality conditions and contact time available at the possible points of application which could impact how well the PAC performs. A contact time of at least 45 to 60 minutes is recommended, as suggested by the literature (Newcombe et al, 2010 and USEPA May 2015 webinar).

Aside from jar testing, an empirical approach, through development of isotherms, has been used to predict the most effective PAC or GAC type. Mohamed et al, developed empirical constants for different carbons, as PAC or GAC or non-activated forms, to be used with the Freundlich isotherm equation to predict dosing requirements to meet final microcystins concentration goals. The Freundlich equation is applied in calculating the dose, as follows (see sample calculations in the Appendix):

(Equation 1) $q = K_f C_f^{1/n}$,

where q is the loading of microcystin on the carbon in micrograms per gram, K_f is an empirical constant for adsorption capacity of carbon, C_f is the equilibrium concentration of microcystin (mg/L) in solution, and $1/n$ is an empirical constant for intensity of adsorption. The K_f and $1/n$ constants are determined using the study results, and are provided in Table A of the Appendix. The PAC dose, in mg/L, is then calculated by taking the initial concentration (in mg/L) of microcystins in the water, or C_i, and subtracting it from the desired final concentration, or C_f, and dividing this result by the q calculated., as summarized in following equation:

(Equation 2) dose (mg/L) = $[(C_i - C_f)/q] \times 1000$

A comparison of the Freundlich isotherm parameters (K_f and $1/n$ constants) of Microcystis and Oscillatoria cyanotoxins adsorbed by different kinds of activated carbons from the Mohammed et al., is provided as Table A of the Appendix. The resulting dosing tables can be used as a starting point, or guideline, in determining PAC feed capacity needs and dosing requirements. See the Appendix for the full discussion on how to use the equation and table, and for dosing curves generated from this data.

The Mohamed study also indicated that wood based activated carbons, both in PAC and GAC form, performed best in adsorption capacities for microcystin, with the most pronounced efficacy found for wood-based PAC. For similar type carbons, the PAC outperformed the GAC in adsorption capacity, however, this study did not take into account typical contact times seen with PAC application versus empty bed contact time found with GAC filters (typically 10-20 minutes). In the Mohamed study, both PAC and GAC samples were gently mixed and held for seven days to

determine adsorption capabilities. As such, these isotherm results should not take the place of site specific jar testing for PAC or Rapid Rate Small Scale Column Tests (RSSCTs) for GAC contactor performance. An RSSCT or other demonstration study should be performed using actual settled water samples (for GAC filter caps) or filtered water samples (for post-filtration GAC contactors) during a HAB event. This is necessary to properly determine the size (EBCT) and projected replacement frequency (time-to-breakthrough for cyanotoxin) for a specific GAC and to estimate the projected operating (carbon replacement) costs of the treatment system.

AWWA has developed guidance for conducting jar testing to estimate PAC dosage, which is available at: http://www.awwa.org/resources-tools/water-knowledge/cyanotoxins.aspx Once you log in or register (free), click on the "Testing Protocols for Site-Specific Powdered Activated Carbon Assessments" and "Powder Activated Carbon Calculator for Site Specific Assessments" links.

As with other treatments, the presence of competing contaminants, such as NOM, must be considered, as they will compete for adsorption sites on the activated carbon, driving up the dose for PAC use) or reactivation frequency (for GAC use). When choosing GAC or PAC, overall treatment objectives and economics need to be considered.

Water systems should consider piloting higher dosages of PAC to determine impacts on downstream processes and the PAC feed system itself. For example, higher feed rates could blind filters or the feeder capability may not allow for dosing at these higher rates (i.e., carrier pipes can clog with additional PAC loading).

Oxidation

For the purposes of this section, oxidation will include the following: chlorination (gaseous elemental chlorine, liquid sodium hypochlorite, or calcium hypochlorite), chloramines, chlorine dioxide, potassium permanganate, and ozone. UV with hydrogen peroxide addition is also presented.

Preoxidation (the application of an oxidant at any point in the treatment process prior to filtration) is not recommended because most oxidants will lyse the cyanobacteria cells present and release their cyanotoxins (i.e., extracellular toxin). If at all possible, cyanobacteria cells should be removed through the coagulation/sedimentation process prior to adding an oxidant to keep the cell structure intact and the cyanotoxins contained (i.e., intracellular). If pre-oxidation is necessary for adequate turbidity and/or organic carbon removal, water systems should consider the use of a weaker oxidant such as potassium permanganate that is less likely to lyse cyanobacteria cells. When permanganate is used during a cyanobacteria bloom, it is recommended that powdered activated carbon (PAC) be used downstream so that any cyanotoxins released may be removed by the carbon. If a stronger oxidant is necessary, then the concentration of oxidant used must be high enough to: meet oxidative demand of compounds in the water (such as metal ions), lyse the cyanobacteria cells present, and have enough oxidant remaining to destroy the cyanotoxins.

Not all oxidants do a good job of destroying all cyanotoxins. It should be noted that increasing some oxidants will create higher levels of regulated disinfectant byproducts in finished water. Additionally, chemical oxidants vary in their reactivity to the different cyanotoxins. The level of reactivity is dependent on the type and dose of oxidant and also on the cyanotoxin's molecular structure, which are not discussed here.

Chlorine reactivity is influenced by pH of the water, temperature, and by the presence of NOM. Chlorine is reactive against microcystins, cylindrospermopsin, and to a lesser extent saxitoxins. Chlorine does not appear to react well with anatoxin-a. Additionally, saxitoxin inactivation is most effective at higher pH values [due to molecular structure of saxitoxin at higher pH (pH ≥ 9)], while microcystin inactivation is most effective at lower pH values [(pH <8) due to presence of greater concentration of the more reactive hypochlorous acid]. Contact time (CT) values required for destruction of microcystins with free chlorine may be many times higher than required for the surface water treatment rule depending on specific water quality conditions. See subsection on chlorination for more details and CT tables.

Commonly used doses of chloramine and **chlorine dioxide** have not been found to be effective against any of the four cyanotoxins. Very high doses and long contact times with chloramines are effective against microcystins but the doses are impractical (Newcombe, et al. 2010). Data for other cyanotoxins is limited. Effective doses of chlorine dioxide can create compliance issues with chlorite and chlorate.

Potassium permanganate can reduce microcystins, anatoxin-a, and possibly cylindrospermopsin concentrations, but data is limited on cylindrospermopsin. Saxitoxin is not oxidized by potassium permanganate. The data for potassium permanganate is not sufficient to recommend doses for cyanotoxin destruction. Free chlorine and potassium permanganate used in a multiple barrier program can be effective against all four cyanotoxins. See subsection on potassium permanganate for further considerations.

Ozone reacts more quickly with microcystins, anatoxin-a and cylindrospermopsin than do other common oxidants. Saxitoxin is the least susceptible to ozone destruction. Under comparable conditions where microcystins would be adequately destroyed, only 20% of saxitoxins present would be destroyed. Although hydrogen peroxide alone does little to remove cyanotoxins, ozone with hydrogen peroxide is even more effective than ozone alone. See subsection on ozone for further considerations.

UV with advanced oxidation using hydrogen peroxide is effective against cyanotoxins. However, the power requirement for advanced oxidation is many times greater than required for UV levels used in water disinfection.

Cyanotoxin treatment through the use of oxidants is effective if used as part of a more comprehensive, multi-barrier treatment strategy. When used alone, oxidation effectiveness can range from very effective to detrimental depending upon the process used and the cyanotoxins being treated. A summary of oxidation effectiveness is shown in Table 1 below.

AWWA has developed a calculator for estimating oxidant dose, which is available here: http://www.awwa.org/resources-tools/water-knowledge/cyanotoxins.aspx. Once you log in or register (free), click on the "Cyanotoxin Oxidation Calculator" link.

Table 1: General Effectiveness of Cyanotoxin Inactivation with Specific Oxidants

	Anatoxin-a	Cylindrospermopsin	Microcystin	Saxitoxin
Chlorine	Not Effective	Effective (at low pH)	Effective*	Somewhat Effective
Chloramine	Not Effective	Not Effective	Not Effective at normal levels	Inadequate Information
Chlorine Dioxide	Not Effective at normal levels	Not Effective	Not Effective at normal levels	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 Levels*	Inadequate Information

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

A comparative study was conducted on the kinetics of reactions of various oxidants with cyanotoxins. Table 2 below is presented to illustrate how long it takes, relatively, for a type of oxidant to degrade microcystin such that half of the cyanotoxin is remaining.

Table 2. Microcystin-LR half-lives for various oxidants
(assumes pH 8, 20 degrees C, and 1 mg/L oxidant concentration)

Oxidant	Microcystin-LR Half Life
HOCl	24.8 minutes
NH_2Cl	>14 hours
O_3	0.08 seconds
OH	5 minutes
MnO_4^-	5.2 minutes
ClO_2	13.1 hours

Taken from presentation, "Cyanobacterial Cell and Toxin Removal Options for Drinking Water Treatment Plants" by Harold Walker, Ph.D., P.E., [powerpoint slides], given at Stone Lab Algal Toxins Workshop, August 2012. Chart adapted from Acero et. al. 2005; Kull et al 2004; Onstad et al 2007; and Rodriguez et al 2007.

Using Chlorination for Microcystins destruction in a conventional plant

Since chlorination is widely used as a disinfectant in treatment plants, it is likely available for use toward microcystins reduction. Dosing of free chlorine residuals within existing contact basins used to achieve CT disinfection can be optimized to also address microcystins reduction. Acero et al, studied the rate of reaction of hypochlorous acid and hypochlorite with several microcystin (MC) congeners, or variants that make up the group of microcystins. The congeners studied included MC-LR, MC-RR and MC-YR over a wide pH range. From this study, CT tables were developed. The CT tables take into account whether the system is a plug flow or batch reactor, or if the system is a continuously stirred tank reactor (CSTR). Batch or plug flow is typically the flow pattern most representative when chlorine is added to reduce cyanotoxin concentrations, such as in detention pipes or clearwells following filtration. For plug flow, water flows through a long narrow channel, and chemical is added at the entrance and no mechanical agitation is present. In theory, each molecule remains in the plug flow for the same amount of time as flow continues through the basin.

The maximum chemical conversion will occur with plug flow since all the molecules have the maximum opportunity to react. In reality, aside from pipe flow, complete plug flow will not exist and is typically accounted for in using a baffling factor for the basin. The CT table for the batch or plug-flow reactor from this study is shown below:

Table 3A. CT chart for microcystin-LR in a batch or plug-flow reactor [1]
(Chlorine contact time values required for reducing microcystin LR concentration to 1 μg/L)

pH	Microcystin- LR Concentration	CT (mg/l x min.)			
		10° C	**15° C**	**20° C**	**25° C**
6	50 μg/L	46.6	40.2	34.8	30.3
	10 μg/L	27.4	23.6	20.5	17.8
7	50 μg/L	67.7	58.4	50.6	44.0
	10 μg/L	39.8	34.4	29.8	25.9
8	50 μg/L	187.1	161.3	139.8	121.8
	10 μg/L	110.3	94.9	82.3	71.1
9	50 μg/L	617.2	526.0	458.6	399.1
	10 μg/L	363.3	309.6	269.8	234.9

1 Acero et al., "Kinetics of reactions between chlorine and the cyanobacterial toxins microcystins," Water Res., 39, 1628-1638, 2005.

The following table represents CT for a CSTR. CSTR flow is typically the flow pattern most representative of a rapid mix tank or flocculation basin. For CSTR model, chemical is distributed throughout by impellers or paddles. Typically chlorine will not be added in a rapid mix or flocculation basin prior to filtration due to the possibility for cell lysing. As such, this CT table has limited application. In a CSTR, the contact time necessary to achieve reaction is much greater than is required for a batch or plug-flow reactor.

Table 3B. CT chart for microcystin-LR in a Continuously Stirred Tank Reactor (CSTR) reactor [1]
(Chlorine contact time values required for reducing microcystin LR concentration to 1 μg/L)

pH	Microcystin- LR Concentration	CT (mg/l x min.)			
		10° C	**15° C**	**20° C**	**25° C**
6	50 μg/L	583.9	503.3	436.3	380.0
	10 μg/L	107.2	92.4	80.1	69.8
7	50 μg/L	847.7	731.2	663.7	551.7
	10 μg/L	155.7	134.3	116.4	101.3
8	50 μg/L	2347.5	2020.3	1751.8	1525.9
	10 μg/L	431.2	371.1	321.7	280.3
9	50 μg/L	7731.1	6589.0	5740.9	4998.6
	10 μg/L	1420.0	1210.2	1054.4	918.1

1 Acero et al., "Kinetics of reactions between chlorine and the cyanobacterial toxins microcystins," Water Res., 39, 1628-1638, 2005.

An example of how to apply the CT tables to a particular situation is as follows:

A treatment plant doses a solution of sodium hypochlorite into the clearwell influent to achieve CT disinfection. The plant needs to optimize chlorine dosing for microcystin destruction. The expected minimum operating water level of the clearwell yields a volume of 0.10 Mgal. Maximum flow through the clearwell is expected to be 2.0 MGD. An effective volume factor applies to the

clearwell to account for baffling and is 0.6. Raw water entering the treatment plant has a detected microcystin toxin level of 50 μg/L, is at a temperature of 20 Celsius and a pH of 8. The goal is to reduce the level down to 1μg/L.

Table 3A would apply and a CT of at least 139.8 mg-min/L would have to be provided, assuming no further cell lysing and cyanotoxin release occurs during treatment and pH is maintained. If the volume of the clearwell at the water operating level is 0.10 Mgal and the flow through the clearwell is 2.0 MGD, a theoretical detention time of 72 minutes results. An effective volume factor, taking into account baffling, of 0.6 applies. As a result, the effective time is reduced by 0.6, and is 43.2 minutes. With a "T" of 43.2 minutes, a free chlorine residual, or "C" of 3.24 mg/L is necessary to yield a CT of at least 139.8 mg-min/L.

Higher pH water has a slower rate of reaction associated with the reactions of chlorine on microcystins and thus requires compensating with a higher free chlorine residual concentration and/or contact time to degrade microcystins. Acero et al[1], who studied reaction of MC-LR, MC-RR and MC-YR with chlorine, concluded that chlorination is a feasible option for microcystin degradation during oxidation and disinfection processes and can be applied in drinking water treatment to reduce cyanotoxin risk if pH is kept below 8. A significant increase in CT is evident between a pH of 8 versus pH of 9 from Table 3A.

The interference of other parameters in the water, such as natural organic matter, must be accounted for in dosing of chlorine to ensure the free chlorine residual goal is met. In addition, these CT tables should be used as a guideline, as they were developed to be applicable within a defined range of values and extrapolation may or may not apply correctly.

The AWWA oxidant dose calculator for estimating necessary CT for microcystins destruction will provide a similar calculation as the above referenced study. The AWWA calculator allows for inputs of pH, temperature, chlorine dose and contact time, as well as initial and targeted final microcystins concentrations. Only a handful of the microcystins congeners have been studied with regard to reaction rates and the effect of chlorine on their destruction. Any CT calculator for destruction of microcystins is limited by the availability of the research on the type of microcystins congener studied and the available input parameters for rates of reaction.

Given the lack of data for many microcystins congeners and other limitations associated with the existing calculator (limited data on high pH source water, NOM, etc.), water systems may want to consider adding a safety factor to the CTs generated by the calculator, or conduct plant-based jar test studies to confirm CT needed. The Appendix includes an additional graph, Figure 2, generated using the AWWA calculator. A safety factor of at least two times the results generated by the calculator is recommended to account for unknowns due to site specific water quality conditions and cyanotoxins variability.

The use of $KMnO_4$ as an oxidant

The use of $KMnO_4$ is common for control of zebra mussels, taste and odor compounds, iron and manganese, and assisting in better settling of floc. Dosing of $KMnO_4$ for typical applications can range from a continuous potassium permanganate dosing of 0.5 to 2.5 mg/L for control of adult zebra mussels, 0.25 to 20 mg/L to treat taste and odor causing compounds, to dosages relating back to iron and manganese concentrations required for oxidation at 0.94 mg/mg iron and 1.92 mg/mg manganese. (U.S. EPA, EPA Guidance Manual Alternative Disinfectants and Oxidants, EPA 815-

R-99-014, April 1999). Past literature has indicted KMnO4 is less apt to lyse cells than chlorine, however, recent laboratory studies have shown the potential for $KMnO_4$ to release cyanotoxins from intact cells by compromising the cell membrane (Dugen, N., U.S. EPA). The U.S. EPA study was conducted on cultures of Microcystis aeruginosa, which may be more prone to releasing cyanotoxins than filamentous cyanobacteria that often have thicker cell walls. Prior studies have indicated that cell lysis varies based on type (genera) of cyanobacteria present. The U.S.EPA study investigated water at pH of 7 and a pH of 9, dosed with varying concentrations of KMnO4 (1.0, 2.5 and 5 mg/L) with contact times of 15 minutes, 30 minutes and 90 minutes, to realize the impacts on cyanotoxin release from cyanobacteria, cyanotoxin destruction and cell integrity. Low doses of permanganate showed no chemical residual after 90 minutes, however did show an increase in extracellular cyanotoxins in the water with little to no consumption of the cyanotoxins at a pH of 7 and 9. The 2.5 mg/L and 5 mg/L dosages carried a permanganate residual after 90 minutes. Both of these dosages also showed increases in extracellular cyanotoxins. The 2.5 mg/L dose did show moderate destruction of cyanotoxins after 90 minutes at a pH of 7. The 5 mg/L dose showed significant destruction of cyanotoxins after 90 minutes at a pH 7. However, at a pH of 9, extracellular cyanotoxins were released but not significantly destroyed after 90 minutes with either dose. This study showed pH is a factor when considering the use of $KMnO_4$ and whether it can be expected to assist with any extracellur cyanotoxin destruction with further contact time. Also, at higher doses, residual permanganate is present which can impact downstream processes, such as PAC efficiency for cyanotoxin removal or precipitation of manganese oxide and/or accumulation of manganese in recycled streams. Because of the potential for $KMnO_4$ to release intracellular cyanotoxins, even at doses as low as 1 mg/L, PAC should be used downstream as an additional treatment barrier.

The use of ozone as an oxidant

Ozone is the most effective oxidant for the destruction of cyanotoxins (aside from saxitoxins). The ozone dose necessary to achieve a slight residual, to ensure cyanotoxins are targeted, is dependent on a number of factors, including other water quality constituents that consume ozone and contact time. Pilot testing to determine appropriate dosing is necessary. The goal should be for complete cell lyses and destruction of released total cyanotoxins. In general, an ozone residual dose of 0.2 mg/L with a contact time of five minutes will be necessary (Walker 2010). Water with DOC higher than 5 mg/L may require higher doses (Newcombe, G. et al., 2010). Ozone is an energy intensive application. Ozone breaks down organic matter and can effect biological growth within downstream processes, and as such, is often paired with biologically active filtration. The effect of ozone on bromate formation must be considered.

Membrane Filtration

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes use pressure to separate contaminants by size and charge, based on the chemical/physical characteristics of the membrane. In general, MF and UF membranes should be able to remove cyanobacteria cells effectively. However, because of their larger pore size they allow extracellular cyanotoxins to pass through. In addition, as the cyanobacteria cells concentrate near the membrane the cells may rupture, releasing their internal cyanotoxins. The extent of cell rupture will depend on the pressure and time period between backwashes. It has also been noted that the cells tend to foul the membrane and are difficult to remove from the membrane during backwashing. More frequent backwashing and concentrate wasting may be necessary. As with other filtration processes, backwash waste streams should not be recycled during a HAB event.

Submerged membrane systems may offer advantages over pressurized systems for waters with high numbers of cyanobacteria. Submerged membranes use lower pressures, so cell lysis may be reduced.

Several studies have shown that both NF and RO are effective at removing cyanotoxins. Membrane composition and operation criteria can affect removal, with results indicating 80% to complete cyanotoxin removal of microcystin and anatoxin-a. The removal of cylindrospermopsin and saxitoxins with NF and RO has not been studied as closely. Based solely upon cutoff values, NF and RO should also effectively remove cylindrospermopsin and saxitoxins.

Biological Filtration

Biologically active riverbank filtration, both slow and rapid filtration, as well as biologically active GAC filtration, has been reported to remove/inactivate microcystins and cylindrospermopsin. However, research suggests that saxitoxin variants may be transformed into a more potent variant. The amount of cyanotoxin degradation during filtration is dependent upon the conditioning and growth of a microbial population capable of metabolizing the cyanotoxins as well as other environmental variables including temperature, pH, and other organisms present. Several researchers recommended that due to the physiological requirements, biological filtration of cyanotoxins should be used as only a polishing step following another primary removal treatment. Biologically active rapid rate filtration is often seen following ozonation as an effective method to remove the assimilable organic matter that results following ozonation of natural organic matter, and aids in prevention of disinfection byproducts formation. Further studies on the effectiveness of biologically active rapid rate filtration in cyanotoxin reduction, and the microorganisms that metabolize the cyanotoxins, are ongoing.

Residuals Handling Issues

The goal in residuals handling is to prevent cyanobacteria cells or cyanotoxins from reentering plant processes once they have been removed. Operators experiencing high levels of cyanobacteria in their plants should consider modifying their backwash and sludge recycling processes to prevent the cyanobacteria cells or their cyanotoxins from being continuously recycled through the plant. This can cause the cyanotoxins to accumulate in the plant and can encourage unruptured cells captured by the filters to lyse open during repeated backwashes and recycling. If possible, operators may want to consider discontinuing backwash and sludge recycle during cyanobacteria bloom events.

WTP operators should also consider increasing the frequency with which they remove sludge from their sedimentation basins. Cyanobacteria cells successfully removed from the water during the sedimentation stage are at risk of lysis over time thereby releasing the cyanotoxins into the water heading for the filters. A sludge management strategy that focuses on minimizing sludge age within the sedimentation basins may be prudent, especially during acual cyanobacteria bloom events or during high risk seasons.

Table 4: Summary of Water Treatment Processes for Removal of Cyanotoxins

INTACT CYANOBACTERIA CELLS		
Treatment Process	**Treatment Efficiency**	
Coagulation/sedimentation	Very effective for the removal of intracellular cyanotoxins provided cells accumulated in sludge are isolated from the plant	
Rapid filtration	Very effective for the removal of intracellular cyanotoxins provided cells are not allowed to accumulate on filter for prolonged periods	
Slow sand filtration	As for rapid sand filtration, with the additional possibility of biological degradation of dissolved cyanotoxins	
Combined coagulation/ sedimentation/filtration	Extremely effective for the removal of intracellular cyanotoxins provided cells accumulated in sludge are isolated from the plant cells and any free cells are not allowed to accumulate on filter for prolonged periods	
Membrane processes	Very effective for the removal of intracellular cyanotoxins provided cells are not allowed to accumulate on membrane for prolonged periods	
Dissolved Air Flotation	Same as coagulation/sedimentation	
EXTRACELLULAR CYANOTOXINS		
Treatment Process	**Cyanotoxin**	**Treatment Efficiency**
PAC (dose required varies with water quality)	Microcystins (except m-LA)	Wood-based, chemically activated carbon is the most effective, or similar, 60 minutes contact time recommended
	Microcystin LA	High doses recommended
	Cylindrospermopsin	Wood-based, chemically activated carbon is the most effective, or similar, 60 minutes contact time recommended
	Saxitoxins	A microporous carbon (coconut or coal based, steam activated wood) 60 minutes contact time recommended effective for the most toxic of the variants
GAC	All dissolved cyanotoxins	GAC adsorption displays a limited lifetime for all cyanotoxins. Research suggests that GAC is less efficient at removing cyanotoxins than other commonly targeted contaminants such as DBP precursors. Bench or pilot scale testing (RSSCTs) is needed to determine design and GAC replacement frequency
Biological filtration	All dissolved cyanotoxins	When optimized this process can be effective for the removal of most cyanotoxins. However, factors affecting the removal such as biofilm mass and composition, acclimation periods, temperature and water quality cannot be easily controlled.
Membrane processes	All dissolved cyanotoxins	Depends on membrane pore size distribution
Oxidation	All dissolved cyanotoxins	See Table 2

Newcombe G., House J., Ho L., Baker P. and Burch M., 2009. Management Strategies for Cyanobacteria (Blue-Green Algae) and their Toxins: A Guide for Water Utilities. WQRA research report 74.

Other Resources

- Ohio Public Water System Harmful Algal Blooms (HAB) Website: http://www.epa.ohio.gov/ddagw/HAB.aspx

- Water Research Foundation. List of cyanotoxin-related applied research reports: http://www.waterrf.org/resources/StateOfTheScienceReports/Cyanotoxins_StateOfTheScience.pdf
  - Algae: Source to Treatment (M57), 2010
  - Removal of Algal Toxins From Drinking Water Using Ozone and GAC, 2002
  - Reservoir Management Strategies for Control and Degradation of Algal Toxins, 2009
  - Early Warning and Management of Surface Water Taste & Odor Events, AwwaRF 2006
  - Identification of Algae in Water Supplies (CD-ROM), AWWA 2001

- World Health Organization (WHO), 1999. Toxic Cyanobacteria in Water: A Guide to their Public Health Consequences, Monitoring and Management www.who.int/water_sanitation_health/resources/toxicyanbact/en/

- Water Quality Research Australia (WQRA) http://www.wqra.com.au/publications/document-search/

- Newcombe G., House J., Ho L., Baker P. and Burch M., 2010. Management Strategies for Cyanobacteria (Blue-Green Algae) and their Toxins: A Guide for Water Utilities. WQRA research report 74. WATERRA [Online]. Available at: http://www.waterra.com.au/publications/document-search/?download=106

- WQRA International Guidance Manual for the Management of Toxic Cyanobacteria, 2009, edited by Dr. Gayle Newcombe, Global Water Research Coalition and Water Quality Research Australia. WATERRA [Online]. Available at: http://www.waterra.com.au/cyanobacteria-manual/PDF/GWRCGuidanceManualLevel1.pdf

- 2008 International Symposium on Cyanobacterial Harmful Algal Blooms (ISOC-HAB) www.epa.gov/cyano_habs_symposium/monograph.html

- ISOC-HAB Chapter 13: Cyanobacterial toxin removal in drinking water treatment processes and recreational waters. Westrick, Judy A.

- U.S. Geological Survey Algal Toxins Research Team http://ks.water.usgs.gov/studies/qw/cyanobacteria/

- Graham, J, Loftin, K., Meyer, M., Ziegler, A., 2010. Cyanotoxin Mixtures and Taste-and-Odor Compounds in Cyanobacterial Blooms from the Midwestern United States, Environmental Science and Technology http://pubs.acs.org/doi/abs/10.1021/es1008938

- Acero, J. L., Rodriquez, E., Meriluoto, J., 2005. "Kinetics of reactions between chlorine and the cyanobacterial toxins microcystins," Water Res., **39**, 1628-1638.

- Mohamed, Z. A., Carmichael, W. W., An, J., El-Sharouny , H. M., 1999. "Activated Carbon Removal Efficiency of Microcystins in an Aqueous Cell Extract of Microcystis aeruginosa and Oscillatoria tenuis Strains Isolated from Egyptian Freshwaters", Env. Toxicol., **14(5)**, 197-201.

- U.S. EPA. (May 26, 2015) Webinar on *Current Water Treatment and Distribution System Optimization for Cyanotoxins*. [PowerPoint slides]. Obtained from webinar organizer, Cadmus Group: webcastinfo@cadmusgroup.com.
  - "Treatment Strategies to Remove Algal Toxins from Drinking Water". Lili Wang , P.E., EPA's Office of Water.
    "Removal of Cyanobacteria and Cyanotoxins Through Drinking Water Treatment". Nicholas Dugan, P.E., EPA's Office of Research and Development.

- U.S. EPA. *Drinking Water Health Advisory for the Cyanobacterial Microcystin Toxins*. EPA Document Number: 820R15100. June 15, 2015.

- Walker, Harold W. "Cyanobacterial Cell and Toxin Removal Options for Drinking Water Treatment Plants", [Powerpoint Slides]. Taken from materials presented at The Ohio State University's Stone Lab Algal Toxins Workshop, August 2010.

- Walker, Harold W. Harmful Algal Blooms in Drinking Water: Removal of Cyanobacterial Cells and Toxins. Boca Raton, FL: CRC Press, 2015.

- Lionel Ho, Paul Tanis-Plant, Nawal Kayal, Najwa Slyman and Gayle Newcombe**. 2009. "Optimising water treatment practices for the removal of Anabaena circinalis and its associated metabolites", Journal of Water and Health. 7(4), 544-556.**

- AWWA Cyanotoxins resource site: http://www.awwa.org/resources-tools/water-knowledge/cyanotoxins.aspx

- Drikas, M., Chow, C.W.K, House, J., Burch, M.D., 2001. "Using Coagulation, Flocculation, and Settling to Remove Toxic Cyanobacteria", Journal AWWA. **February 2001**, 100-111.

- He, X., Liu, Y., Conklin, A., Westrick, J., Weavers, L. K., Dionysios D. D., Lenhart, J. J., Mouser, P. J., Szlag, D., Walker, H. W. 2016. "Toxic cyanobacteria and drinking water: Impacts, detection, and treatment", Harmful Algae **54 (2016)**, 174–193.

- Donati, C., Drikas, M., Hayes, R., Newcombe, G. 1994. "Microcystin-LR Adsorption by Powdered Activated Carbon", Wat. Res. **28(8)**, 1735-1742.

Appendix

Table A is a summary of Freundlich isotherm parameters developed by Mohamed et al, for different carbons, as PAC or GAC or non-activated forms, and can be used as a guideline, or starting point, in determining PAC feed capacity needs and dosing requirements.

Table A. Comparison of Freundlich isotherm parameters of Microcystis and Oscillatoria cyanotoxins adsorbed by different kinds of activated carbons.[2]

Activated Carbon	Microcystin Toxins[a]		Oscillatoria Toxins[a]	
	K_f (μg/g)(L/μg)	$1/n$ (Unit less)	K_f (μg/g)(L/μg)	$1/n$ (Unit less)
Wood GAC	501.2	0.36	15.5	0.99
Calgon coal GAC	512.9	0.36	83.2	0.53
Culligan coal GAC	126	0.57	2.0	1.24
Coconut GAC	331.1	0.44	12.6	1.1
Nonactivated GC	2.1	1.3	1.48	1.4
Wood PAC	6309	0.56	1259	0.9
Calgon coal PAC	3630	0.9	955	2
Coconut PAC	1259	1	1000	1

[a]K_f, adsorption capacity in (μg/g)(L/μg) ; $1/n$, adsorption intensity.

[2] Mohamed et al., "Activated Carbon Removal Efficiency of Microcystins in an Aqueous Cell Extract of Microcystis aeruginosa and Oscillatoria tenuis Strains Isolated from Egyptian Freshwaters,: Env. Toxicol., 14(5), 197-201, 1999.

Example Calculations using Table A.

Raw water source has a microcystin detection of 25 μg/L and the goal is to reduce the cyanotoxin level to 0.3 μg/L using a wood-based PAC. **Strongly recommended that a safety factor of 2-3 be used in application to account for unknowns, such as differences in properties that occur in manufacturing of PAC material, impact of water quality and competing contaminants, and contact time.**

-Using Wood PAC

K_f = 6309 (μg/g)(L/μg)

$1/n$ = 0.56

(Equation 1) $q = K_f C_f^{1/n}$

$q = (6309)(0.3)^{0.56} = 3{,}215$ (μg/g)(L/μg)

(Equation 2) dose (mg/L) = $[(C_i - C_f)/q] * 1000$(μg/mg)

dose (mg/L) = [(25 μg/L - 0.3 μg/L)/ 3,215 (μg/g)(L/μg)]* 1000(μg/mg)

dose (mg/L) = 7.7 mg/L

Safety Factor 2x dose(mg/L) = 2(7.7 mg/L) = 15.4 mg/L

3x dose(mg/L) = 3(7.7 mg/L) = 23.1 mg/L

-Using Calgon Coal PAC
K_f = 3630 (μg/g)(L/μg)

$1/n = 0.9$

(Equation 1) $q = K_f C_f^{1/n}$
$q = (3630)(0.3)^{0.9} = 1228$ (μg/g)(L/μg)

(Equation 2) dose (mg/L) = $[(C_i - C_f)/q] * 1000$(μg/mg)
dose (mg/L) = [(25 μg/L - 0.3 μg/L)/ 1228 (μg/g)(L/μg)]* 1000(μg/mg)

dose (mg/L) = 20.1 mg/L

Safety Factor 2x dose(mg/L) = 2(20.1 mg/L) = 40.2 mg/L
3x dose(mg/L) = 3(20.1 mg/L) = 60.3 mg/L

-Using Coconut PAC
K_f = 1259 (μg/g)(L/μg)

$1/n = 1$

(Equation 1) $q = K_f C_f^{1/n}$
$q = (1259)(0.3)^{1} = 378$ (μg/g)(L/μg)

(Equation 2) dose (mg/L) = $[(C_i - C_f)/q] * 1000$(μg/mg)
dose (mg/L) = [(25 μg/L - 0.3 μg/L)/ 378 (μg/g)(L/μg)]* 1000(μg/mg)

dose (mg/L) = 65.3 mg/L

Safety Factor 2x dose(mg/L) = 2(65.3 mg/L) = 130.6 mg/L
3x dose(mg/L) = 3(65.3 mg/L) = 195.9 mg/L

Table B: Dosage of PAC for percent removal of microcystin
(values do not include recommended safety factor of 2x-3x these values shown in sample calculations above)

Dosage wood PAC	Dosage coal PAC	Dosage Coconut PAC	Microcystin Removed (%)
0.00	0.00	0.00	0
0.03	0.02	0.04	5
0.07	0.04	0.09	10
0.11	0.07	0.14	15
0.15	0.09	0.20	20
0.19	0.12	0.26	25
0.24	0.16	0.34	30
0.29	0.20	0.43	35
0.35	0.24	0.53	40
0.41	0.29	0.65	45
0.48	0.35	0.79	50
0.56	0.43	0.97	55
0.65	0.52	1.19	60
0.76	0.64	1.48	65
0.90	0.79	1.85	70
1.06	0.99	2.38	75
1.29	1.29	3.18	80
1.61	1.78	4.50	85
2.13	2.72	7.15	90
3.32	5.35	15.09	95
8.53	23.74	78.63	99

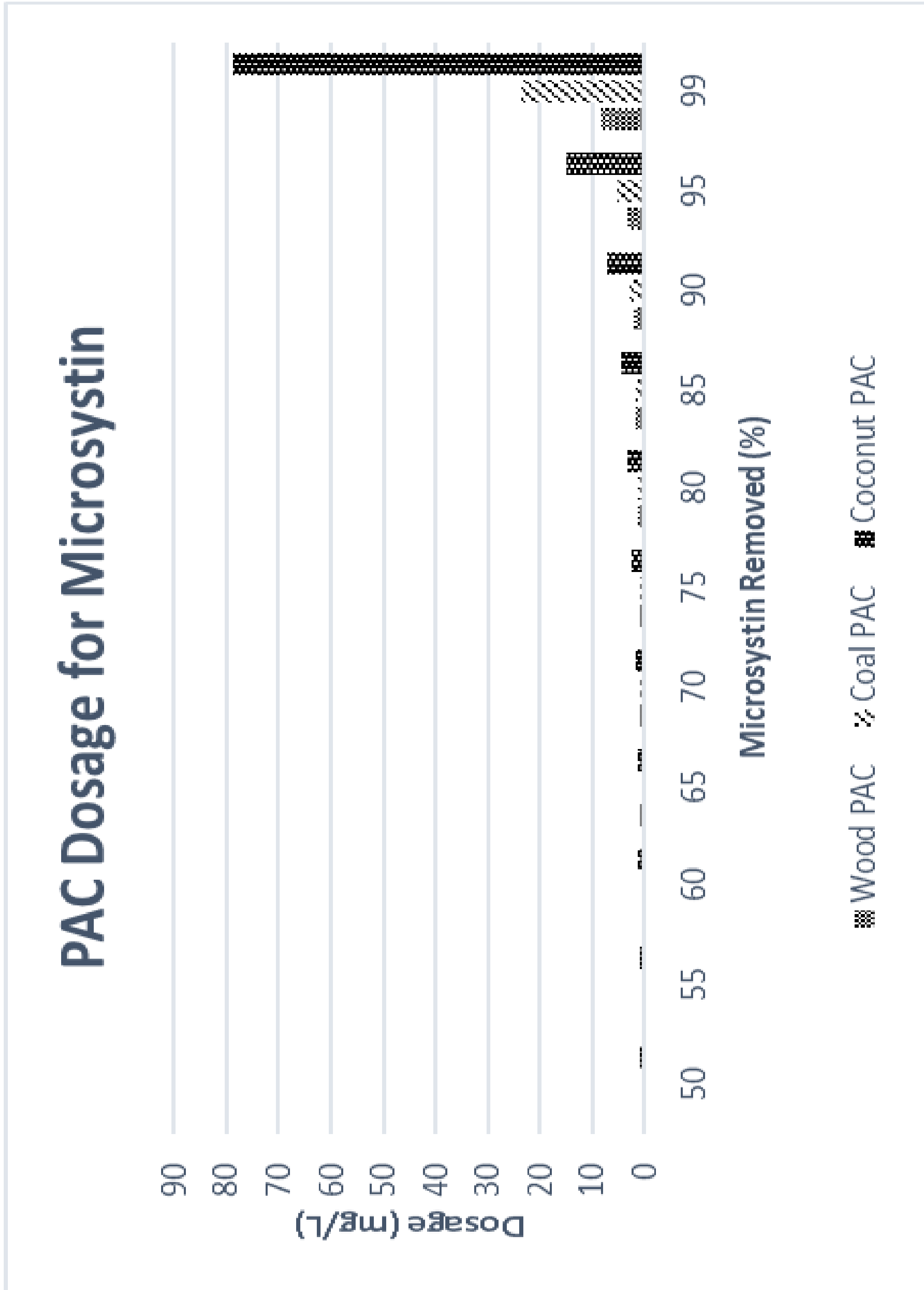


Figure 1: Visual representation of dosages for different types of PAC *_without safety factor_*

The following table, Table C, provides general recommendations for PAC doses based on microcystin congeners. The table illustrates the variability of adsorption to PAC based on the differences in the chemical properties of the congeners. In Ohio, 17 different microcystin congeners have been detected in source waters and many source waters have a mix of these different congeners. In addition, some source waters (especially those with *Planktothrix* blooms) may be dominated by microcystin congeners other than microcystin-LR. Adsorption data is not available for the majority of microcystin congeners.

Table C: General recommendations for PAC doses for microcystin toxins (dissolved) in source water with a DOC of 5 mg L-1 or less, and contact time 60 minutes * (taken from Newcombe et.al, 2010)

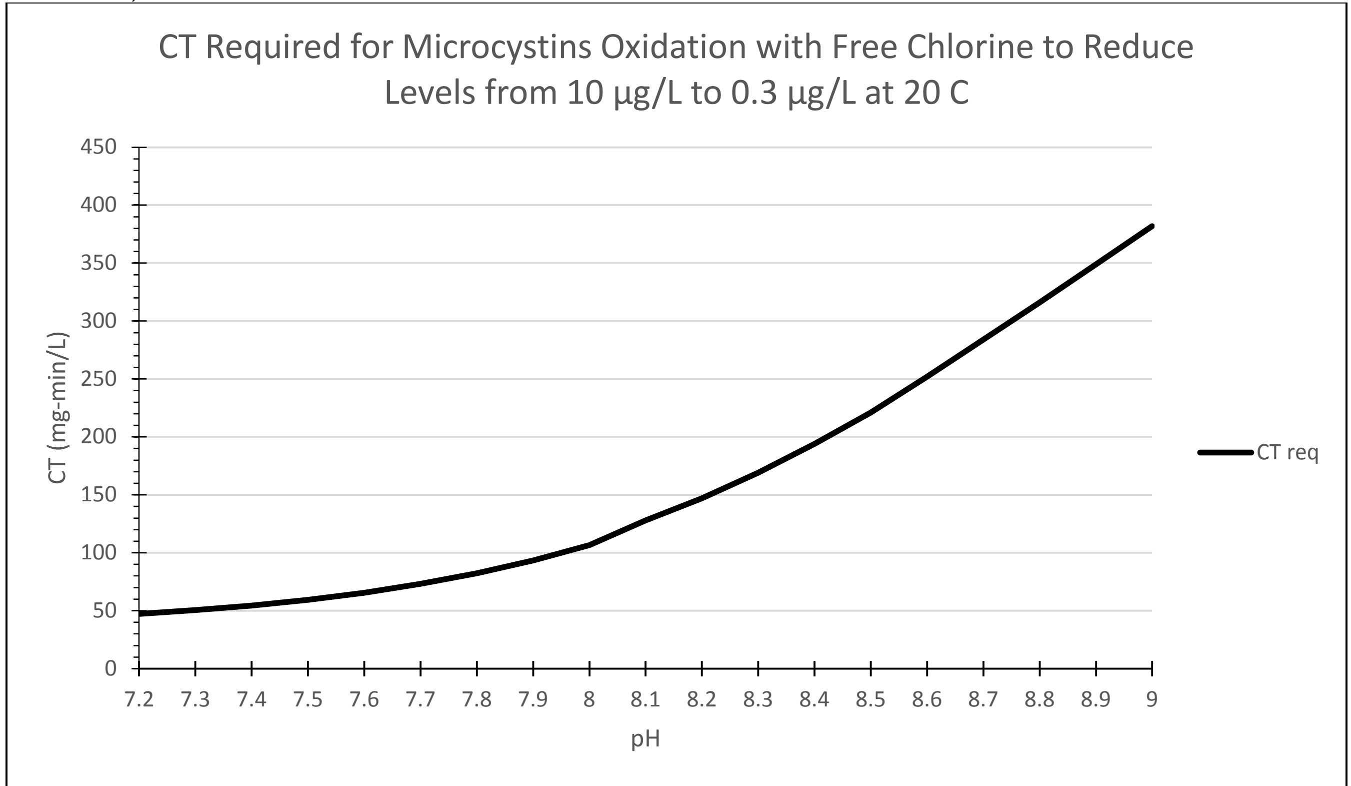
Microcystin Congener	**Inlet concentration 1-2 μg L-1**	**Inlet concentration 3-4 μg L-1**
MC-LA	**30-50**	**Not recommended**
MC-LR	**12-15**	**15-25**
MC-YR	**10**	**10-15**
MC-RR	**8**	**10**

***These doses were estimated from many laboratory experiments but the actual doses required will depend strongly on water quality. Site specific testing is recommended.**
The following stipulations were also noted:

- The presence of a mixture of cyanotoxins does not appear to affect the doses, therefore, for a mixture of MC-LR and MC-LA at 1 μg L-1 each, add the doses for each toxin individually, i.e. approximately 40 mg L-1.
- It should also be noted that if dissolved microcystins concentrations > 4 μg L-1 occur on a regular basis, other advanced treatments would be recommended.

The following figure, Figure 2, provides a graphical depiction of the CT that is necessary to reduce a dissolved (extracellular) microcystins concentration of 10 μg/L to 0.3 μg/L at a water temperature of 20 Celsius. The oxidant concentration and contact time that provides the CT is from free chlorine and the effective detention time of the finished water storage or clearwell, respectively. The results are from outputs generated by the AWWA Cyanotoxin Oxidation Calculator, using a microcystins mix in the input values, along with varying pH levels, and constant values of 20 C for water temperature and 10 μg/L for initial concentration and 0.3 μg/L for target concentration. The CT outputs were generated by selecting the CT based option of the calculator and recording the effective CT to achieve target value.

Figure 2: CT Required for Microcystins Oxidation with Free Chlorine to Reduce Levels from 10 µg/L to 0.3 µg/L at 20 C (Results generated using AWWA Cyanotoxin Oxidation Calculator)*



* Figure 2 provides the CT requirement without the recommended safety multiplication factor to account for unknowns related to site specific water quality conditions and cyanotoxins variability. A safety factor of two times these calculated CT values is recommended be available, or achievable (i.e., increasing CT through flow reduction or increasing depth of water for increased contact time or increasing free chlorine concentration). This figure illustrates how the increase in required CT becomes more pronounced with a pH 8 or higher.