WATER TREATMENT CONSIDERATIONS FOR CYANOTOXINS

IN CLEAR LAKE **SWRCB DDW – MENDOCINO DISTRICT** **MAR 2019**

INTRODUCTION

Cyanobacteria (and associated toxins) have become an increasing problem in source waters and at some water treatment facilities in California over the last decade. The information provided in this document is an overview on water treatment considerations for cyanotoxins and is intended to bring awareness to water facilities in Clear Lake considering treatment optimization during a bloom, research findings, and potentially installing additional treatment to address these noxious blooms.

This document addresses only three cyanotoxins, anatoxin-a, cylindrospermopsin, and microcystin. The USEPA issued health advisories for cylindrospermopsin and microcystin. Research and knowledge on this topic is expanding rapidly. Consider reading the references cited and consult with other utilities, relevant agencies, consultants, researchers, and other water industry partners. The Division of Drinking Water recommends considering all treatment optimization adjustments on a case-by-case basis until treatment research is further developed and consensus is established. If cyanotoxins are present, we highly recommend learning more about that cyanotoxin, as treatment approaches widely vary based on the type of toxin. To learn more about potential toxins produced by different algal genera, use the SWRCB SWAMP guide.

Due to the documented presence of microcystins in Clear Lake, we recommend that all surface water treatment plants around Clear Lake develop a Cyanotoxin Management Plan. Several options are available:

- Reach out to Highlands Mutual Water Company or California Water Company – Lucerne
- Use a template generated by the USEPA
- Example plans are available from our District Office

Document Contents:

Treatment References:

- US EPA Cyanotoxin Tools for Drinking Water
- A Water Utility Manager's Guide to Cyanotoxins (AWWA/WRF)
- AWWA's Cyanotoxin Resource Community (AWWA)

GENERAL TREATMENT APPROACH FOR CYANOBACTERIA & CYANOTOXINS

To reduce risks associated with cyanotoxins, a multi-barrier approach is recommended, including prevention, source control, treatment optimization, and monitoring[1]. Depending on the severity of the bloom, one of these treatment options may address reduce cyanotoxin concentrations.

OPTION 1. AVOID TOXINS AT THE SOURCE

How? Evaluate alternate intake options and source treatment

If the intake is located in a reservoir prone to algal blooms for algal genera (or taxa) that potentially produce toxins, consider introducing an alternate intake location. Conduct water quality surveys to

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[1] Merel, S., Walker, D., Chicana, R., Snyder, S., Baures, E., and Thomas, O. (2013) State of knowledge and concerns on cyanobacteria blooms and cyanotoxins. *Environment International*, V59, 303-327.
He, X., Liu, Y.-L., Conklin, A., Westrick, J., Weavers, L., Dionysiou, D., Lenhart, J., Mouser, P., Szlag, D., Walker, H. (2016) *Harmful Algae* V54, 174-193.

assess optimal alternative intake locations while comparing to current intake conditions. Anticipate that a reducing environment may contribute to more dissolved metals (and potentially improved coagulant performance) if intake levels are shifted to water with lower pH. If intake adjustments do not lead to lower pH source water, evaluate whether acid additions (or a shift in coagulant) are (is) necessary for coagulants to operate optimally. Consider adding tools to monitor source waters to learn when algal blooms shift (e.g. fluorometers, satellite information, secchi depth, cell identification, visual observations, etc.).

If surveys above demonstrate no potential water quality improvements with an alternate intake, consider evaluating algal control measures at the source. Source control could include correctly timed chemical applications (e.g. copper sulfate, endothal, aluminum sulfate, etc.), biological measures (e.g. introducing organisms or planting submerged aquatic vegetation) or physical perturbations (e.g. aeration). Each measure may be subject to permit or regulation requirements by local, state, or federal authorities and other implications should be considered (e.g. sonication could destroy biota indiscriminately). Herbicides (e.g. Sonar) are recommended as a last resort rather than routine for maintenance. The Division recommends applications during the onset of an algal bloom as a preventive measure and NOT to apply during peak bloom periods as it may exacerbate conditions.

OPTION 2. KEEP ALGAL CELLS INTACT.

How? Assess treatments: (1) minimize cell lysis and (2) optimize cell removal by relying on physical treatment processes: coagulation/flocculation/sedimentation/filtration/DAF/adsorption.

Consider the stage of the algal bloom. During the senescent phase of the bloom, the cells are lysing in their natural environmental and Option 3 below should be considered. More often than not, toxins are cell bound (Park et al., 1998; McQuaid et al., 2011). To minimize cell lysis during the onset of the bloom or during the peak, evaluate if pre-oxidants (KMnO4, ozone, NaOCl, etc.) are contributing to cell lysis or not. A few other places to watch closely include any sludge generated (e.g. clarifiers, membrane filtration, etc.) and recycled water. Minimize sludge contributions to cyanotoxin concentrations by monitoring and evaluating the frequency of disposal. One tool to consider using to monitor cell lysis is a special fluorometer.

At times, the algal cells, equipped with gas vacuoles, can regulate their buoyancy. This could potentially lead to the cells floating in clarifiers, wreaking havoc in treatment units collecting supernatant water. Consider installing a barrier or diverting water from a different location in the weir collection system.

Is the clarifier basin open to atmosphere and sunlight? If anatoxin is not a concern, consider covering the clarifier to minimize the incubator affect. There are several coagulant alternatives to consider to optimize treatment options.

TREATMENT FACTS:
Maximum algal cell removal via coagulation does not necessarily coincide with lowest turbidity results measured in jar tests but when the zeta potential reaches zero[2].

Coagulant additions have been shown to be a function of algae content and have reached 97-99.5% removal rates prior to filtration[3].

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[2] P. Mouchet and V. Bonnelye. Solving algae problems: French expertise and world-wide applications. *J Water SRT*, No. 3; 47: 125-141.

[3] Edzwald JK, Paralkar A. Algae, coagulations and ozonataion. In: Klute R, Hahn H, eds. *Chemical Water and Wastewater Treatment (5th Gothenburg Symposium);* 2: 263-279. Berlin/New York: Springer Verlag 1992.

OPTION 3. TREAT SOLUBLE COMPOUNDS.

How? Assess treatments specific to the cyanotoxin concentration detected. Physical treatment removal not likely to significantly decrease the concentration.

Treatment approaches are highly dependent on the type of toxin present and how it is distributed throughout the cell. Literature cites various algal genera have different expressions of the toxins – a percentage outside of the cell and a percentage in the cell. Chemical, biological, and physical (likely only membranes smaller than UF) can reduce dissolved toxins. Review the next section to understand and optimize for specific toxins detected. As a last resort, conditions may be such that adequate treatment is not possible and a Do Not Drink may be warranted. Contact our District Office if this is the case.

TREATMENT CHALLENGES AND CHANGES, INCLUDING UNIT TREATMENT PROCESSES

KNOW YOUR GENERAL ALGAL CELLS & TOXINS

GENERAL ALGAL CELL PROPERTIES

Size: µm to inches

Growth factors: light, nutrient availability (macro- and micro-), and temperature

Particle charge: typically negative (Yoo et al., 1995, Crittenden et al., 2005)

Learn more about harmful algal blooms and cyanobacteria toxins: USEPA Region 9 FAQ

All algal cells contain a specific pigment known as *chlorophyll a*.

Cyanobacteria (fresh water) contain *phycocyanin* pigments in addition to *chlorophyll a* and can be found in a unicellular, colonial, or filamentous form. Some contain gas vacuoles (aerotopes) which can help regulate optimal depth (e.g. light and nutrients), including *Microcystis*, *Anabaena*, *Aphanimenzomenon*, *Cylindrospermopsis*, and *Planktothrix*. Some can fix nitrogen (e.g. *Anabaena, Aphanizomenon, Cylindrospermopsis, Nodularia, and Nostoc*) using specialized cells called heterocysts. There are benthic blue green algal that are difficult to detect when sampling the water column.

Algal cells can contribute to producing taste & odor compounds but are not necessarily linked to cyanotoxins. One taste compound, β-cyclocitral, has been linked to *Microcystis* cell death.

One advantage to the cells containing pigments is our ability to monitor them using fluorometers which can serve as an excellent tool to oversee operations at a water treatment plant utilizing source water with dynamic algal blooms. Some fluorometers have the ability to detect when cells lyse and potentially associated toxin producing complex exits the cell. Regardless, cell size, charge, motility, morphology, and resistance to sheer stress and pressure play an important role in accumulation and removal at the WTP and vary widely by species (Drikas et al., 2001; Dickens and Graham, 1995; Bernhardt and Clasen, 1991).

GENERAL TOXIN PROPERTIES

Boiling cyanotoxins does not reduce the concentration and can increase it.

The same toxin can be produced by many different genera of cyanobacteria.

Cyanobacteria produce toxins that can either remain within the cell (intracellular) or be associated with the outside of the cell (extracellular or exogenous). Researchers are expanding our understanding of how toxins are distributed. The distribution can play a role in how water treatment strategies are implemented.

There is some evidence that extracellular toxins may be more persistent in the environment[4].

Based on research in Australia[5], it was found that primary routes of exposure to cyanotoxins were during recreation, inhalation, and skin absorption. However, He, et al. (2016) indicates that the primary source of microcystin exposure for humans is through drinking water.

TREATMENT APPROACHES ARE LARGELY BASED ON THE TOXIN TYPE

If present, it is critical to know the type of cyanotoxin, as this will largely influence potential treatment approaches. Research and knowledge on this topic is expanding rapidly (and at times is inconsistent; e.g. charges of coagulant aids, efficiencies in reductions). Consider reading the general references and references cited directly to learn the circumstances in which it applies. The Division recommends considering all treatment adjustments on a case-by-case basis until treatment research is further developed and consensus is established.

If cyanobacteria genera are known, it may be helpful to rely on this table to learn which potential toxins it may produce. This may help guide which cyanotoxins to monitor. **If a cyanotoxin is detected, it is important to understand that treatment efficiencies are different for each cyanotoxin.**

ANATOXIN-A

An alkaloid toxin; a potent neurotoxin; associated with dog deaths; smallest of the cyanotoxins

Charge: neutral

Molecular Weight: 165.2 g/mol

Solubility: 7.2×10^4 at 25°C

Structure: $C_{10}H_{15}NO$

Vapor Pressure: 5.8×10^{-3} mm Hg at 25°C

Henry's Law constant: $6.6\text{X}10^{-9}$ atm-cu m/mol

Hydroxyl radical reaction rate constant: 1.2 x 10-10 cu cm/mole sec at 25°C

Detections in Clear Lake? Aware of one instance that was localized and short-lived

RESEARCH NOTES:

Treatment Related Properties:

- Half-life ranges from 1-2 hours (biological conditions) to several days (no exposure to sunlight) [Stevens and Krieger, 1991]
- Sunlight photolysis is concluded to be an important detoxification route [Stevens and Krieger, 1990] or up to 14 days under normal conditions (day/night, pH 8-10, low concentration 10 ug/L) [Smith and Sutton, 1993]; it does degrade rapidly in basic solutions [Matsunaga+, 1989, WHO 1999 and Stevens and Krieger, 1991]

Health:

- **Ingestion of water contaminated with anatoxin-a has resulted in death by respiratory arrest of livestock, pets, and wildlife [Carmichael, 1981, Carmichael *et. al.*, 1975]**
- LD50 = 0.2 – 0.25 mg/kg i.p. mouse [Carmichael, 1982, 1988]

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[4] Lahti, K. et al., 1997. Persistence of Cyanobacterial Hepatotoxin, Microcystin-LR in Particulate Material and Dissolved in Lake Water. *Water Research*, 31:5:1005-1012.

[5] Falconer, I.R. 2001. Toxic cyanobacterial bloom problems in Australian waters: Risks and impacts on human health. *Phycologia*, 40: 228-233.

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CYLINDROSPERMOPSIN[6] (CYN)

DOI: 10.1039/C3EM00353A

"Cylindrospermopsin has been shown to be cytotoxic, dermatotoxic, genotoxic, hepatotoxic *in vivo*, developmentally toxic, and may be carcinogenic." Exposure can be through recreation, food consumption (bioaccumulation), or drinking water. To date, only three variants of cylindrospermopsin are known.

Charge: neutral	**Molecular Weight: 415.4 g/mol**
Stable in light, pH, and temperature	**Structure: $C_{15}H_{21}N_5O_7S$**
Toxin Distribution: 50% extra-:50% intra-	**Detected in Lake Berryessa (2017)**

Cell distribution: 50/50 during exponential phase and increasing extracellular with senescence[7]

Cylindrospermopsin producers bloom below the surface[8], making visual observations difficult for assessment.

RESEARCH NOTES:

- Natural attenuation in source waters of CYN is poor.
- Copper treatment (dosage of 0.5 mg/L) actually inhibited CYN degradation by interfering with beneficial organisms[9].
- Adequate destratification of source water (and the presence of silica) by aeration replaced the dominant cyanobacteria species but inadequate aeration could lead to an increase in phytoplankton biomass.
- Kinetic table available for various oxidants for CYN but the hypochlorous acid (derived from chlorine), ozone, and hydroxide-AOPs appear quite effective. Many factors play a role in the effectiveness, including pH, temperature, and [NOM] and byproducts should be considered. Ozone was considered the best option due the destruction of the toxic structure of CYN.
- Media based filtration has not been shown to be effective at reducing CYN. Nanofilration (90-100% reduction of CYN reported) and reverse osmosis have not been thoroughly evaluated but might be effective (half-life at pH 8 within seconds to minutes).
- Limited information on granular activated carbon effectiveness.
- Powder activated carbon is expected to be effective due to a high mesopore volume (ø2-50 nm) and no differences were observed in contact times between 30 and 60 minutes[10]. CYN=MCRR>MCYR>MCLR>MCLA
- Aluminum sulfate application was found to contribute to 46% reduction in CYN for an Australian plant and was in alignment with toxin distribution of extra- and intracellular described above.

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[6] Much of the background material for cylindrospermopsin derives from *A review on cylindrospermopsin: the global occurrence, detection, toxicity and degradation of a potent cyanotoxin* by de la Cruz, A. et al on August 29, 2013

[7] *Griffiths, D.J. and M.L. Saker, The Palm Island mystery disease 20 years on: A review of research on the cyanotoxin cylindrospermopsin. Environmental Toxicology 18(2): 78-93 (2003)*

[8] H. J. Kling, Fottea, 2009, 9, 45–47

[9] MJ Smith, GR Shaw, GK Eaglesham, L Ho and JD Brookes, 2008. Elucidating the factors influencing the biodegradation of cylindrospermopsin in drinking water sources, *Enviro. Toxicol.*, 2008, 23, 413-421.

[10] J. A. Westrick, D. C. Szlag, B. J. Southwell and J. Sinclair, *Anal. Bioanal. Chem.*, 2010, 397, 1705–1714; L. Ho, P. Lambling, H. Bustamante, P. Duker and G. Newcombe. Application of powdered activated carbon for the adsorption of cylindrospermopsin and microcystin toxins from drinking water supplies. *Water Res.*, 2011, 45, 2954–2964.

- CYN (article abstract DOES NOT reference CYN, only T&O compounds) competition demonstrated for sites on powder activated carbon[11]
- Raw [CYN] of 1.3 µg/L in Australia demonstrated reduction (<1 µg/L) through conventional treatment and disinfection.[12]
- KMnO4 is not ideal to oxidize CYN (Rodriguez et al., 2007c).

TOTAL MICROCYSTINS (MC) (-LR WHEN SPECIFIC)

Microcystins has numerous cogeners and is the most commonly studied cyanotoxin. While coagulation is effective for cells intact, coagulation is likely not effective at reducing extracellular dissolved toxins (typically toxins are less than 1,000 g/mol).

Charge: neutral	**Molecular Weight: 900-1,200 (995.17) g/mol**
Solubility: 7.2 x 10^4 at 25°C	**Structure: seven amino acids; “adda” group contributes to toxicity ($C_{49}H_{74}N_{10}O_{12}$)**
~Hydrophobic but varies with specific toxin	**Susceptible to oxidants, e.g. O_3 and NaOCl**

Cell distribution: 95% intracellular during healthy bloom and decreasing with senescence[13]

RESEARCH NOTES:

- A SWRCB - DDW 2016 snapshot evaluation of the Clearlake Oak facility found that while total MC was non-detect in raw water, the clarifier sludge exceeded 0.3 ug/L. The total MC overflowing through the weirs was non-detect, illustrating a successful sludge removal operation.
- KMnO4 is effective (oxidation of extra-cellular MC-LR and anatoxin-a) at ~ 1mg/L dosage if oxidant demand in water is low. Addition of KMnO4 to intact algae cells can cause the release of intracellular toxins.[14]

TREATMENT CHANGES AND CHALLENGES

During algal blooms, operating a drinking water treatment plant can be challenging. Below are events observed at treatment plants and references to potentially describe ways to mitigate these challenges.

MONITOR COAGULANT DOSAGE

When coagulant demands are too high and sufficient preoxidation treatment is applied, polymers play an important role in reducing dissolved natural organic matter (from 2006 Konocti CWD treatment recommendations). Coagulation followed by sedimentation is more effective at removing intact cells rather than dissolved toxins (Yoo, et al., 1995, Hoeger et al., 2004, Jurczak et al., 2005). An increase in coagulant dosage is likely during bloom events due to the low settling velocity of algal floc (at times it can even reverse direction).

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[11] D. Cook, G. Newcombe and P. Sztajnbok. The application of powdered activated carbon for 2-MIB and geosmin removal: predicting PAC doses in four raw waters. *Water Res.*, 2001,35, 1325–1333.

[12] Hoeger, SJ, Shaw, G, BC Hitzfeld and DR Dietrich, 2004. Occurrence and elimination of cyanobacterial toxins in two Australian drinking water treatment plants. Toxicon 43, 639-649.

[13] *Chorus, I. and J.F. Bartram. Toxic cyanobacteria in water: A guide to their public health consequences, monitoring, and management. London: E&FN Spon (1999)*

[14] AWWA Research Foundation (2004) Algae Detection and Removal Strategies for Drinking Water Treatment Plants.

Compared to the use of aluminum sulfate as a primary coagulant, use of coagulant aids can improve treatment during algal blooms[15]. Filter and coagulant aids can improve treatment performance at conventional plants. Jar testing, bench top charge analyzers, and modeling the filtrate can all be critical to successfully evaluate water treatment performances.

No cell lysis attributed to aluminum sulfate (up to 200 mg/L[16]) and ferric chloride (up to 30 mg/L) primary coagulant additions nor mixing up to a G value of 480 s^{-1}[17]. However, cell integrity may depend on the growth stage of the cells.[18]

DISINFECTION DEMAND INCREASES

Residual algae in treated water may explain an increase in disinfection and elevated trihalomethanes[19].

TASTE AND ODOR COMPOUNDS DETECTED

- Combining hydrogen peroxide with ozone (~ 0.4:1 by weight) is highly effective at breaking down cyanobacteria toxic compounds, geosmin and 2-MIB[20]. Ozone alone is not able to complete the oxidation[21].
- 90-100% removal of geosmin and 2-MIB was documented in a granular activated carbon filter with an empty bed contact time of 10 minutes but saturation can be achieved in several months.[22].

UNIT TREATMENT PROCESS CONSIDERATIONS

X. He et al. (2016) states "While the use of many of the advanced oxidation processes [including ozone] *as a pre-treatment step may alter cell properties and enhance solid-liquid separation, the potential for cell disruption and release of cyanobacterial toxins requires special attention. Additional research is needed to better understand treatment kinetics and mechanisms, and for finding a good correlation of various pre-treatment methods on cyanobacteria-flocculation efficiency. Further, different flocculants applied in water treatment plants may exhibit different efficiencies depending on cyanobacteria types and pre-treatment approaches. An effective combination of pre-treatment and flocculation methods may be worthy of investigation."*

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[15] Zhao, X, Zhang, Y., Li, X., Liu, C., and L. Zhu, July 2010. Algae removal efficiencies of AS/PDMDAAC coagulants. *AWWA* 102:7, 119-128.

[16] Lam, A, K.-Y. et al., 1995. Chemical Control of Hepatotoxic Phytoplankton Blooms: Implications for Human Health. Water Research, 29:8:1845-1854.

[17] Chow, CWK et al., 1999. The Impact of Conventional Water Treatment Processes on Cells of the Cyanobacterium *Microcystis Aeruginosa*. Water *Research*, 33: 15:3253-3262; Chow, CWk et al. 1998. The Effect of Ferric Chloride Flocculation on Cyanobacteria Cells. *Water Research*, 32:3:808-814.

[18] Pietsch, J, et al., 2002. Relevance of Intra- and Extracellular Cyanotoxins for Drinking Water Treatment. *Acta Hydrochim. Hydrobiol.*, 30:1:7-15.

[19] (Reference 1) Hoehn RC, Barnes DB, Thompson BC. Algae as source of trihalomethane precursors. *JAWWA* 1980, 72(6):344-350. (Reference 2) El-Dib MA, Ali RK. Mixed algal population and *Scenedesmus* sp. As trihalomethane precursors. *Bull Environ Contamin Toxicol* 1994, 52: 712-717.

[20] Edzwald JK, Paralkar A. Algae, coagulations and ozonataion. In: Klute R, Hahn H, eds. *Chemical Water and Wastewater Treatment (5th Gothenburg Symposium);* 2: 263-279. Berlin/New York: Springer Verlag 1992.

[21] Duguet JP, Bruchet A, Mallevialle J. Geosmin and 2-methylisoborneol removal using ozone or ozone/hydrogen peroxide coupling. *Proc 9th Ozone World Cong, IOA, New York, June* 1989; 1(18): 709-719.

[22] Edzwald JK, Paralkar A. Algae, coagulations and ozonataion. In: Klute R, Hahn H, eds. *Chemical Water and Wastewater Treatment (5th Gothenburg Symposium);* 2: 263-279. Berlin/New York: Springer Verlag 1992.

Recycling Backwash at WTP: this may represent a source of dissolved cyanotoxins; consider reducing this operation.

Ultrasound: There are conflicting reports on the effectiveness of ultrasound in controlling algal blooms in lakes. The frequency and energy density can have various results. This treatment can likely disrupt other biota, if present.

Pre-Oxidants: it is critical to either avoid lysis (recommended path) or completely inactivate the toxin molecule.
Ozone: Many factors (e.g. condition of the cell, bloom composition, dosage and pH) likely contribute to a successful ozone operation in the presence of cyanobacteria. Little or no cell lysis is demonstrated up to ozone dosages of less than 3 mg/L[23]. An ad hoc Clear Lake water treatment plant evaluation demonstrated ozone lysis can occur at 2.7 mg/L. However, cell damage was reported to cause cell damage at a low dosages near 0.5 mg/L (Coral et al., 2013). Dose of 1 mg/L have been shown to lyse cells and the dosages may not be enough to destroy the toxin (Pietsch et al., 2002; Schmidt et al., 2002; Hoeger et al., 2002; Hoeger et al., 2005). At a dosage of 1 mg/L ozone with 30 minutes of contact time, there was a significant reduction in MC (Himburg et al., 1999). Toxin inactivation is dependent on [DOC] and is incomplete if an ozone residual could not be maintained (Newcombe, 2002). NOM can interfere with ozone performance in reducing toxins (Shawwa and Smith, 2001). For 10 ug/L of MC, destruction was possible at 0.5 mg/L O_3 and 9 minutes of contact time (Hoeger et al., 2002). [NOM] and increasing pH can interfere with performance (Hoeger et al., 2002). Ozone was more effective on *Microcystis aeruginosa* compared to *Oscillatoria* sp. And *Lyngbya* sp. (Wert et al., 2013).

Potassium Permanganate: Lysing of cells can occur at low dosages (0.7 mg/L) with no effects on the [MC] (Pietsch et al., 2002). A concentration of 1.25 mg/L was effective in high DOM (6.7 mg/L) water for removal of MC-LR, MC-RR, MC-YR, although a contact time of 1 hour was needed (Rodriguez et al., 2007a). Carus's webinar (@ 30 min) depicts potassium permanganate as an effective treatment (<5 mg/L dosage from Fan (2014)); BBE webinar depicts potential cell lysis at higher dosages. An EPA webinar (near 29 min) compares potassium permanganate dosages (1, 2.5, and 5 mg/L) with and without PAC. The EPA webinar indicates 1.) There is a potential for extra-cellular release when applying potassium permanganate and 2.) if toxin is suspected to be released, consider interrupting potassium permanganate application and applying (or increasing) PAC. J.R. Laszakovits and A.A. MacKay (2019)[24] found (1) TOC/DOM can compete for permanganate and (2) the permanganate reaction with MC depends on temperature.

Pre-chlorination can promote better aggregation, improving algae and turbidity removal, yet can cause algal cell lysis[25] and increase concentration of cyanotoxins and dissolved organic substances[26], potentially contributing to disinfection product formation[27]. Cyanobacteria can have different sensitivity during chlorine oxidation (X. He et al., 2016). Brookes et al. (2008) and Fan (2014) found cell lysis to rapidly occur with chlorine. Pre-chlorination during blooms is heavily discouraged.

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[23] Edzwald JK, Paralkar A. Algae, coagulations and ozonataion. In: Klute R, Hahn H, eds. *Chemical Water and Wastewater Treatment (5th Gothenburg Symposium);* 2: 263-279. Berlin/New York: Springer Verlag 1992.

[24] Laszakovits, JR and MacKay, AA, 2019. *Removal of cyanotoxins by potassium permanganate; Incorporating competition from natural water constituents.* Water Res., 155: 86-95.

[25] Chen JJ and Yeh, HH, 2005. Mechanisms of Potassium Permanganate on Algae Removal. *Water Res.*, 39:18:4420.

[26] Plummer, JD and Edzwald, JK, 2001. Effect of Ozone on Algae as Precursors for Trihalomethane and Haloacetic Acid. Envir. Sci & Technol., 35:18:3661; Lam, AKY, Prepas, EE, Spink, D, and Hrudey, SE, 1995. Chemical Control of Hepatotoxic Phytoplankton Blooms: Implications for Human Health. *Water Res.*, 29:8:1845.

[27] Henderson, R, Parsons, SA, and B. Jefferson, 2008. Impact of Algal Properties and Preoxidation on Solid-Liquid Separation of Algae. *Water Res.,* 42:8:1827.

Micro-straining: 10-100% diatom reduction, 45%-75% cyanobacteria reduction, and 50-60% chlorophyceae reduction[28].

Dissolved Air Flotation: Cell removal is likely very effective but dissolved toxin removal is not likely (Yoo et al., 1995, Hrudley et al., 1999, Ribau Teixeira & Rosa, 2006b).

Mixing: Cyanobacteria cells can remain intact despite high velocity gradients generated during mixing (Lam et al., 1995).

Coagulation/Flocculations and sedimentation: Cyanobacteria removals vary from 62% to 98.9% (Jian et al., 1993; Vlaski et al., 1996; Jiang and Graham, 1998; Driakes et al., 2001). Neutralize charge in water to maximize efficiency. Enhanced coagulation can be effective (cationic polymer addition to inorganic coagulant; additional removal of NOM as measured using TOC) (Mouchet, P. and V. Bonnélye, 1998). Coagulation inhibition observed while using poly-aluminum chloride (Takaara et al., 2007, 2010; Sano et al., 2011). Flocs are light in weight and likely need coagulant aids for flocculation process (Bernhardt and Clasen, 1994). Different cases likely call for anionic or cationic aids. Also, aluminum sulfate can be a more efficient flocculating agent than iron salts (Pietsch et al., 2002). Sludge blanket (95-98% removal with powdered anionic polyelectrolyte) is favorable over static settling (90% removal). Acid addition can be beneficial and potentially reduce coagulant dosage. Increase flocculation times were beneficial. There have been cases of cyanotoxins released during flocculation/filtration stages of treatment (e.g. hydraulic stress) (Pietsch et al., 2002).

Sludge accumulation: many processes accumulate cells, including clarifiers, filters, membranes and others. It is imperative to monitor how often sludge is removed from these unit processes to ensure extra-cellular toxins are not released (Drikas et al., 2001; Pietsch et al., 2002).

Clarification: cells can release cyanotoxins with the first 48 hours (Pietsch et al., 2002) – keep sludge cleared out on a more frequent basis.

HydroxIde injection: In Xiamen, China, cyanobacteria cells were inactivated (and cells remained intact) with a hydroxide dosage of 1 µg/L with 20 seconds of contact time. “Oxidation can alter the surface characteristics and charge of cyanobacteria, which then enhances the effectiveness of coagulation and flocculation for their subsequent removal (Fan et al., 2013).” The treatment included plasma reactors with power supplies and cooling units, gas/liquid injectors, gas/liquid mixers, filters, and pumps.[29]

Filtration (Rapid Rate Filtration): It is likely intact cells (> 1 µm in size) are reduced provided filters are properly maintained and filters are ripened (Ryan Hanley, 2012). Dissolved MC is not expected to be removed by this process. Biodegradation: this has only been demonstrated in natural waters but shows promise as a potential method of toxin removal. Pre-oxidants operating upstream of filter beds: increases in extra-cellular toxins at this stage could be potentially attributed to a pre-oxidant rupturing cell membranes trapped in a filter bed (Schmidt et al., 2002). Backwash Operations: critical to monitor filters during blooms to reduce ‘hydraulic effects of transport’ (Pietsch et al., 2002). Cells can lyse just after 24 to 48 hours on filter beds (Lepisto et al., 1994; Chorus and Bartram, 1999).

Filtration (Slow Sand): Recommend reading Verna J. Arnette’s Masters of Science thesis work (2009)

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[28] P. Mouchet & V. Bonnélye, 1998. Solving algae problems: French expertise and world-wide applications. *J Water SRT*, vol 47, No.3, pp. 125-141.

[29] Bai, M., Zheng, Q., Zheng, W., Li, H., Lin, S., Huang, L. and Z. Zhang, 2019. *OH Inactivation of Cyanobacteria Blooms and Degradation of Toxins in Drinking Water Treatment Systems*. Water Research, 154: 144-152.

Filtration (UF Membrane): physically removes cells with little toxin release (Gijsbertsen-Abrahamse et al., 2006) but not likely reduce extra-cellular cyanotoxins. Microcystin adsorption can occur on the membrane for polyethersulfone type (Lee and Walker, 2006). The addition of PAC in the membrane feed water may improve cyanotoxin removal. Recommend reading Verna J. Arnette's Masters of Science thesis work (2009) and X. He et al. (2016).

Granular Activated Carbon (GAC)/Powdered Activated Carbon (PAC): GAC and PAC can be very effective for MC reduction. For MC reduction, wood based carbons are more effective than coal based (Donati et al., 1994; Mohamed et al., 1999; Huang et al., 2007) and coconut based (Lee and Walker, 2006). Wood based typically have higher mesopore (20 to 500 nm) volume and low micropore volume. Low levels of cyanotoxins can be reduced in the presence of NOM. PAC dosages of up to 20 mg/L performed the best when compared to pre-oxidant additions, achieving a >90% reduction in toxins (Schmidt et al., 2002). PAC can reduce MC from 20 – 80% for a dose of approximately 10 mg/L of PAC (Ho et al., 2011). (PAC does not remove intact cells and associated toxins.) Mesopore adsorption of MC by GAC and PAC can take up to 15 and 60 minutes of contact time, respectively [30]. Biologically active GAC filters are getting mixed results.

Pumps: a centrifugal pump did not appear to lyse cells or release toxins when applied to a membrane (Gijsbertsen-Abrahamse et al., 2006).

Advanced Oxidation Process – hydrogen peroxide and UV: no further toxin degradation (of MC-RR) was observed at a maximum H_2O_2 dosage of 1 mmol/L and optimum UV light intensity was 3.66 mW/cm^2 (Qiano et al., 2005). X. He, et al. (2016) states "…whether UV/H_2O_2 is indeed capable of successfully inactivating cyanobacteria needs further investigation."

Biofiltration: A. Thees, et al, (2019) demonstrated Lake Erie contained naturally occurring and robust bacteria that could reduce MC-LR concentrations (between 0.9 and 19 ug/L/day). It's important to consider WQ thresholds to ensure a healthy biological community and testing is in place to ensure no pathogenic bacteria are present.

Post-disinfection: CT tables can assist with determining dosage necessary to reduce toxin concentrations. AWWA assembled a comprehensive tool to assist with CT for cyanotoxins.

RESOURCES

The bulk of the material contained in this draft factsheet is based on concepts introduced in the listed references below. An update of resources is maintained at our DDW HABs website and tools to support public water systems.

Manual of Water Supply Practices – M57, AWWA, 1st Edition, Algae: Source to Treatment
EPA Guidance, Australian Document – lots of FAQs
Verna J. Arnette, 2009, Master's Thesis, University of Cincinnati
Toxic cyanobacterial breakthrough and accumulation in a drinking water plant[31]
Toxic cyanobacteria and drinking water - Impacts, detection, and treatment, *Harmful Algae* (He, X. et al., 2016)

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[30] Park, J., Jung, S., Choi, J., Kim, J., Hong, S., Lee, S., (2018), Mesoporous carbon for efficient removal of microcystin-LR in drinking water sources, Nak-Dong River, South Korea: Application to a field-scale drinking water treatment plant. *Chemosphere* V193, 883-891.

[31] Zamyadi, Arash, MacLeod, S. L., Fan, Y, McQuaid, N., Dorner, S., Sauvé, Sébastien, Prévost, M. (2012) Toxic cyanobacterial breakthrough and accumulation in a drinking water plant: A monitoring and treatment challenge. *Water Research* v46, 1511-1523.

Future references to incorporate include:

State of knowledge and concerns on cyanobacterial blooms and cyanotoxins (Merel, S. et al., 2013)

Toxic cyanobacteria and drinking water - Impacts, detection, and treatment, *Harmful Algae* (He, X. et al., 2016)

This document was assembled with the goal to provide additional references to those treating water in Clear Lake, CA. In 2017, several water treatment plants experienced unprecedented water quality challenges, including turbidity breakthrough at a water treatment plant, an increase in manganese and ammonia (3 mg/L) concentrations in source waters, and finally, a pink event in raw source waters.

Please, contact me to include your observations or request changes/more information on a topic. This was assembled with water treatment plants around Clear Lake in mind. Due to the incredible volume of journal articles available, at times, I relied upon a synthesis made by parties referenced in this section.

Send comments to amy.little@waterboards.ca.gov

LABORATORY LIST TO SUPPORT MONITORING EFFORTS

A Water Research Foundation Project #4647 conducted a comprehensive review (published 2019) for the various methods available to measure microcystins. Further, there are stakeholder recommendations on page 137 based on their findings. There is an overview on current laboratory methods available to measure toxins discussed in “Toxic cyanobacteria and drinking water - Impacts, detection, and treatment” (He, X. et al., 2016) and “Cyanotoxins: Which detection technique for an optimum risk assessment?” (Gaget, V. et al., 2017). It recommended “using both the ELISA and PP2aIA in parallel would provide a semi-quantitative concentration of microcystin and insight in into the relative toxicity of the water.” Also, referring to qPCR methods, “if there are a high number of cyanotoxin gene copies, then it is prudent to test for cyanotoxins…Although many proof-of-concept studies have been performed, no direct freshwater cyanotoxin biosensors are available.” (He, X., et al., 2016) “Results showed that there was generally a good correlation between the presence of potentially toxigenic cyanobacteria and the detection of the toxin by ELISA.” (Gaget, V et al., 2017).

Work directly with your laboratory and materials above to understand the limits of the method selected and all sampling protocols. Direct measurements using EPA Method 544 (microcystin and nodularin) includes three steps: sample preservation, concentration, and quantification and EPA Method 545 (cylindrospermopsin and anatoxin) includes two steps: sample preservation and quantification.

Laboratory List: Drinking Water laboratory list | Source Water laboratory list

EFFECTIVE TREATMENT TABLES (BY TOXIN AND TREATMENT)

- Comprehensive Table 6 from Arnette, Verna J. (2009)
- Table A2.5 from An Introduction to Drinking Water Contaminants, Treatment, and Management for Users of the National Environmental Standard for Sources of Human Drinking Water Prepared for the Ministry for the Environment by Chris Nokes, Environmental Science and Research Ltd (June 2008)