WATER TREATMENT CONSIDERATIONS FOR CYANOTOXINS

IN CLEAR LAKE **SWRCB - DIVISION OF DRINKING WATER** **MAR 2018**

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, current research findings, and potentially installing additional treatment to address these noxious blooms.

At this time, only USEPA cyanotoxins with health advisories and Clear Lake associated cyanotoxins are addressed with an emphasis on total microcystins. 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.

Due to the documented presence of cyanotoxins 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
- Contact amy.little@waterboards.ca.gov for assistance in developing one

Document Contents:

Treatment References:

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

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 removal or reduction of cyanotoxins.

OPTION 1. AVOID TOXINS

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 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)

[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.

necessary for coagulants to operate optimally.

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 the issue.

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 whether or not 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 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(a) 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].

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

[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.

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 [Measuring cyanotoxins in Drinking Water Lab List]

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

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.

Researchers demonstrate *Toxin A* is typically found with a toxin distribution of 95% intracellular. Suppose you have a bloom dominated by *Toxin A* and are monitoring toxin concentrations at the intake with a recent value of 5 ug/L. Without collecting additional samples, operators may be able to implement treatment strategies immediately while confirming intracellular toxins are removed with processes like conventional coagulation, flocculation, sedimentation, and filtration with samples. At 90% efficiency, optimizing appropriate treatment processes potentially reduces the intake toxin level

to the following *5 ug/L * 0.95 * 0.90* = **0.73 ug/L.** There is some evidence that extracellular toxins may be more persistent in the environment[4].

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

Based on research in Australia[5], it was found that primary routes of exposure to cyanotoxins were during recreation, inhalation, and skin absorption.

TOXIN SPECIFIC TREATMENT APPROACHES

The information provided in this section focuses on Clear Lake utility needs. Literature and publications were reviewed and placed into either a toxin section or a unit processes section. Research and knowledge on this topic is expanding rapidly. Consider reading the general references and references cited directly. You are encouraged to partner with other utilities, relevant agencies, consultants, researchers, and other water industry partners in your research. The Division recommends considering all treatment adjustments on a case-by-case basis until treatment research is further developed and consensus is established.

ANATOXIN-A

An alkaloid toxin; a neurotoxin; associated with dog deaths

Charge: neutral

Molecular Weight: 165.2 g/mol

Solubility: 7.2 x 10^4 at 25°C

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

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

Henry's Law constant: 6.6X10^{-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]

[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.

WATER TREATMENT CONSIDERATIONS FOR CYANOTOXINS

IN CLEAR LAKE **SWRCB - DIVISION OF DRINKING WATER** **MAR 2018**

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.
- CYN (article abstract DOES NOT reference CYN, only T&O compounds) competition demonstrated for sites on powder activated carbon[11]

[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.

- 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).

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

[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.

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

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

Pre-Oxidants: it is critical to either avoid lysis (recommended path) or completely inactivate the toxin molecule.

Ozone: Little or no cell lysis is demonstrated up to ozone dosages of less than 3 mg/L[23]. Ad hoc Clear Lake water treatment plant evaluations demonstrated ozone lysis can occur at 2.7 mg/L. 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

---

[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.

[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.

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).

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).

Pre-chlorination can promote better aggregation, improving algae and turbidity removal, yet can cause algal cell lysis[24] and increase concentration of cyanotoxins and dissolved organic substances[25], potentially contributing to disinfection product formation[26]. Brookes et al. (2008) found cell lysis to rapidly occur with chlorine. Pre-chlorination during blooms is heavily discouraged.

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).

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). 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 call for anionic or cationic aids. Also, aluminum sulfate can be a more efficient flocculating agent than iron salts (Pietsch et al., 2002). 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.

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)

[24] Chen JJ and Yeh, HH, 2005. Mechanisms of Potassium Permanganate on Algae Removal. *Water Res.*, 39:18:4420.
[25] 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.
[26] 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.

Filtration (UF Membrane): physically removes cells with little toxin release (Gijsbertsen-Abrahamse et al., 2006). 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)

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 [27]. 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).

Post-disinfection - chlorine: CT tables can assist with determining dosage necessary to reduce toxin concentrations.

RESOURCES

The bulk of the material contained in this draft factsheet is based on concepts introduced in the references below. An update of resources is maintained at our DDW HABs website.

Manual of Water Supply Practices – M57, 1st Edition, Algae: Source to Treatment

Other additional references:

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[28]

Future references to incorporate include:

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

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

[27] 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.

[28] 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.

WATER TREATMENT CONSIDERATIONS FOR CYANOTOXINS

IN CLEAR LAKE **SWRCB - DIVISION OF DRINKING WATER** **MAR 2018**

This document was assembled with the goal to provide additional references to treating water in Clear Lake, CA. In 2017, several water treatment plants experienced unprecedented water quality challenges, including turbidity breakthrough at the 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 at ***amy.little@waterboards.ca.gov***

SAMPLING

Work directly with your laboratory to understand the limits of the method selected and all sampling protocols.

Laboratory List/Sampling Guidance:

- Drinking Water laboratory list
- Source Water laboratory list

EXPAND THIS SECTION….

[CYN] Monitoring: Screening tools available include ELISA kits from Abraxis and Beacon with a detection range of 0.05 – 2 ug/L.

Methods available to confirm screening: LC/MS, LC/MS/MS, HPLC-PDA

TREATMENT EFFICIENCY TABLES BY TOXIN AND TREATMENT

Excerpt TABLE from Arnette Verna J. (2009): *See Table 6 in attached object below.*

Adobe Acrobat Document