

New Jersey Drinking Water Quality Institute Treatment Subcommittee

Recommendation on Cyanotoxin Treatment Options in Drinking Water

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January 13, 2025

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Executive Summary

This document presents the Treatment Subcommittee's evaluation of available methods of mitigating and treating cyanotoxins in drinking water. The Treatment Subcommittee reviewed the current literature and conducted outreach to drinking water systems across the United States to review treatment options for the removal of cyanotoxins, their efficiency, reliability, and viability for large-scale water treatment. In addition, the Treatment Subcommittee reviewed other cyanotoxin mitigation strategies implemented by other states.

Cyanotoxins can be produced by cyanobacteria in surface water bodies, such as lakes, reservoirs, and rivers, that are utilized as drinking water sources by water systems. As a result, the Treatment Subcommittee considered algal bloom prevention and mitigation strategies for cyanotoxin management in source waters. Treatment methods for removing cyanotoxins that have entered the drinking water treatment plant were also evaluated. Effective strategies varied based on whether intracellular and/or extracellular cyanotoxins were the main concern.

The Treatment Subcommittee advises that water systems manage cyanotoxins by carefully considering a multi-barrier approach that is uniquely designed and optimized to fit the characteristics of the system. Drinking water systems should have a Cyanotoxin Management Plan (CMP) that addresses prevention management, source water monitoring, and treatment optimization and considers both normal operating conditions and unusual or extreme conditions, such as drought and weather events.

The Treatment Subcommittee recommends that a treatment technique approach be considered by the New Jersey Department of Environmental Protection (NJDEP) to regulate cyanotoxins at drinking water systems. Furthermore, the Treatment Subcommittee recommends that the Department explore the impact of cyanotoxins to private wells and whether changes to the Private Well Testing Act (PWTa) could help address these impacts.

Section 1. Background

The Treatment Subcommittee of the New Jersey Drinking Water Quality Institute (DWQI) is responsible for identifying available treatment technologies or methods for the removal of hazardous contaminants from drinking water. The Treatment Subcommittee has met several times over the course of its review to discuss and investigate the best available treatment options for cyanotoxins. The subcommittee has gathered and reviewed data from several sources, including the literature and direct contact with public drinking water systems, to identify widely accepted and well-performing strategies for mitigation and removal of cyanotoxins. This report is intended to present the Treatment Subcommittee's findings.

Currently, there are no enforceable federal drinking water standards for any cyanotoxin. The United States Environmental Protection Agency (USEPA) released 10-day Drinking Water Health Advisory (HA) values for two cyanotoxins in 2015: microcystins and cylindrospermopsin. These HA values describe the concentrations of a contaminant in drinking water below which adverse health effects are not anticipated to occur over a specific period of exposure. Unlike a regulatory standard, USEPA's HAs are non-enforceable recommendations and are intended to provide guidance for public drinking water systems and health agencies in the event of contamination. For the aforementioned cyanotoxins, USEPA considered a 10-day exposure period given the intermittent, and often short-term human exposure scenarios for cyanobacterial blooms in drinking water. USEPA developed 10-day HA values for two age groups: less than six years old and older than or equal to six years old. This determination was made because bottle fed infants and young children consume more water per body weight relative to older individuals, so their exposure may be higher when drinking water is contaminated with cyanotoxins (USEPA, 2015a; USEPA, 2015b). See Table 1 below for USEPA's HA values for microcystins and cylindrospermopsin. Concurrently, USEPA released Health Effects Support Documents, which reviewed published literature on the physio-bio-chemical properties, environmental synthesis and fate, occurrence and exposure, and health effects, for three cyanotoxins: cylindrospermopsin, microcystins, and anatoxin-a (USEPA, 2015c; USEPA, 2015d; USEPA, 2015e).

Table 1. USEPA's 10-Day HAs for Cyanotoxins.

Cyanotoxin	USEPA 10-Day HA (µg/L)	
	< 6 years of age	6 years of age and older
Cylindrospermopsin	0.7	3.0
Microcystins	0.3	1.6

From 2018-2020, USEPA required monitoring of nine cyanotoxins and one cyanotoxin group at public water systems under the fourth Unregulated Contaminant Rule (UCMR4). This requirement was for all public drinking water systems serving a population greater than 10,000 people, in addition to 800 representative smaller systems nationwide. Samples were analyzed using the methods and minimum reporting levels listed in Table 2 for 10 parameters. Of the systems required to sample cyanotoxins under UCMR4 in New Jersey (107 total systems), there were two detections from one sampling event within one surface water system. The highest measured level of cylindrospermopsin was 0.2235 µg/L, and the highest measured level of anatoxin-a was 13.22 µg/L. Total microcystins were not found to be present in any sample; microcystin congeners (i.e., microcystin-LA) and nodularin were only analyzed if the result of total microcystins were ≥ 0.3 µg/L. As part of UCMR4, only surface water, groundwater under the direct influence of surface water (known as GUDI), and mix-use systems were required to sample for cyanotoxins.

Table 2. Metrics used by USEPA to measure cyanotoxins during UCMR4.

Contaminant	CAS Registry Number	Minimum Reporting Level (µg/L)	Analytical Methods
total microcystin	N/A	0.3	USEPA 546 (ELISA)
microcystin-LA	96180-79-9	0.008	USEPA 544
microcystin-LF	154037-70-4	0.006	USEPA 544
microcystin-LR	101043-37-2	0.02	USEPA 544
microcystin-LY	123304-10-9	0.009	USEPA 544
microcystin-RR	111755-37-4	0.006	USEPA 544
microcystin-YR	101064-48-6	0.02	USEPA 544
nodularin	118399-22-7	0.005	USEPA 544
anatoxin-a	64285-06-9	0.03	USEPA 545
cylindrospermopsin	143545-90-8	0.09	USEPA 545

In September 2017, the New Jersey Department of Environmental Protection's (NJDEP's) Division of Science and Research (DSR) released guidance values for microcystins, cylindrospermopsin, and anatoxin-a (NJDEP, 2017). In May 2021, NJDEP DSR recommended guidance values for saxitoxin (NJDEP, 2021a). Like USEPA, NJDEP DSR developed these guidance values to be protective of short-term (10-day) exposure. These guidance values are shown in Table 3, below.

Table 3. NJDEP DSR's 10-Day Drinking Water Guidance Values for Cyanotoxins.

Cyanotoxin	NJDEP Guidance Values (µg/L)	
	< 6 years of age	6 years of age and older
Cylindrospermopsin	0.2	1.0
Microcystins	0.07	0.3
Anatoxin-a	0.7	3.3
Saxitoxin	0.025	0.11

In April 2021, NJDEP released its 2021 *Cyanobacterial Harmful Algal Bloom (HAB) Freshwater Recreational Response Strategy* as a response protocol to algal blooms in freshwater, including those that are sources for drinking water. This is the third iteration of the strategy, first released in 2018 and previously amended in 2020 (NJDEP, 2021b). Algal blooms (i.e., phytoplanktonic overabundance events) pose critical threats to aquatic diversity and water quality targets, particularly when blooms are dominated by toxin-producing cyanobacteria.

In 2022, the DWQI's Health Effects Subcommittee completed their review of NJDEP DSR's guidance values for microcystins, cylindrospermopsin, anatoxin-a, and saxitoxin. The Subcommittee concurred that NJDEP's guidance values were protective for short-term exposure and supported the use of these values in drinking water for the four cyanotoxins. (Gleason, 2022).

Several states have adopted regulations for managing cyanotoxins in drinking water. The Ohio Environmental Protection Agency (OHEPA) requires routine monitoring for microcystins in finished water, with a requirement for water systems to notify their consecutive systems if microcystins exceed 0.3 µg/L

(OHEPA, 2022). The Oregon Health Authority (OHA) requires systems that utilize surface water as their source to test for microcystins and cylindrospermopsin and notify the public if levels exceed USEPA's health advisory levels (OHA, 2023). Rhode Island has established maximum contaminant levels (MCLs) for four cyanotoxins: 0.3 µg/L for microcystin, 20 µg/L for anatoxin-a, 1 µg/L for cylindrospermopsin, and 0.2 µg/L for saxitoxin (Rhode Island Department of Health, 2024).

The World Health Organization (WHO) recommended a provisional short-term exposure (no greater than two weeks) guidance value of 3 µg/L for total cylindrospermopsin and 1 µg/L for total microcystins. They have also established a guidance value of 3 µg/L for acute exposure for saxitoxins. A guidance value for anatoxins was not established by WHO. (WHO, 2022)

Cyanotoxins are uniquely challenging contaminants to treat. As outlined in this report, it is important to consider cyanotoxin contamination at different stages of its occurrence to manage both cyanobacterial growth and cyanotoxin production using a multi-barrier approach to treatment. For the purpose of this report, "source water" refers to sources of drinking water, such as lakes, rivers, or reservoirs with intakes, as well as any waters in the related drainage area that have an appreciable impact on water quality. Water systems should consult with the appropriate regulatory agencies prior to implementing the prevention and mitigation strategies discussed in this report.

Section 2. Algal Bloom Prevention in Source Water

While the scope of this report is limited to *prevention* and *treatment*, it is critical that water systems develop source water *monitoring* strategies to anticipate blooms. Systems should develop a monitoring strategy specific to their watershed and source water bodies and outline this strategy in their Cyanobacteria Management Plan (CMP). Monitoring strategies are most successful when systems have a detailed knowledge and understanding of the watershed, major sources of nutrient pollution, and bloom history within their watersheds.

Tools for cyanobacteria monitoring range from relatively low-cost methods that can continuously measure indicators of bloom risk to more resource-intensive but precise methods that can identify species and potential toxicity. Low-cost monitoring methods such as visual inspection by informed staff, fixed cameras and drones, Secchi disks, and turbidimeters can provide first warnings signals but can easily miss blooms that form below the surface. Measuring levels of chlorophyll- α (i.e., cyanobacterial pigment), phycocyanin (i.e., algal pigment proteins), and adenosine triphosphate (i.e., biologically produced energy compound; commonly referred to as ATP) can serve as more reliable indicators of phytoplanktonic activity. These lower-cost techniques can be deployed continuously when conditions make blooms possible. Suspected blooms should be monitored more intensively, using methods such as cell enumeration (by microscope or automated program) or gene sequencing (Almuhtaram et al., 2021). Remote sensing that measures phycocyanin by plane or satellite can supplement monitoring programs and provide last resort warnings as blooms develop. Flyover measurements from NJDEP are performed seasonally and are available at https://njdep.rutgers.edu/aircraft_phyco. Satellite data from USEPA is available through the Cyanobacteria Assessment Network Application (CyAN app) and can be accessed online. In general, systems are encouraged to invest in some form of phycocyanin measurement and to work with hydrologists and ecologists to assess their vulnerability.

Cyanobacteria may not produce toxins even at high cell densities or, conversely, may produce high toxin concentrations at modest cell densities; for this reason, no absolute threshold is defined to demarcate

when cyanobacteria growth produces cyanotoxins at levels which may pose a risk to human health. Any indicator of bloom formation should be rapidly followed up with continuous cyanotoxin testing for as long as bloom conditions endure.

Nutrient Management

Nutrient management is considered the first line of defense against harmful algal blooms (HABs) in source water. Nutrient management refers to the targeted reduction of nutrients, especially nitrogen (N) and phosphorus (P), entering the source water system from the watershed. Primary producers, such as phytoplankton, often exist at populations limited by the availability of N and P. Excessive anthropogenic inputs from point and nonpoint sources can lead to an overabundance of phytoplankton in aquatic ecosystems.

Systems striving to reduce their risk of HABs should also understand the difference between external and internal nutrient loading. External nutrient loading refers to nutrient pollution from inflows, often a result of both point and nonpoint pollution sources in the entire watershed. Internal nutrient loading refers to the release of nutrients that are temporarily fixed in sediments that are released by physical, chemical, or biological processes. Sediment disturbance and anoxia (i.e., low oxygen concentrations) are typically the most important drivers of internal nutrient loading. Even lakes with ostensibly low nutrient concentrations may experience blooms driven by pulses of these internal nutrients.

Inputs of P are of particular concern for cyanobacteria blooms, as many cyanobacteria species are capable of fixing N from atmospheric sources. While elevated N inputs have been shown to increase the magnitude of cyanobacterial dominance, experiments have demonstrated that P loading is generally the most important factor in bloom formation (Bogard et al., 2020; Molot et al., 2021). Significant progress has been made towards the reduction of P inputs from point sources, but nonpoint contributions remain significant compared to preindustrial baselines. Watershed management is complex, and nutrient management strategies can result in little to no change to the intensity of cyanobacterial blooms (Reinl et al., 2021). Nevertheless, an absolute reduction in P will likely realize water quality goals in the long term. Fastner et al., (2016), proposed a target range of 20-50 $\mu\text{g/L}$ for total P to control cyanobacterial blooms.

What follows are treatment techniques in which P inputs can be reduced at the watershed- and waterbody-scale.

Wastewater Treatment Plant Retrofitting and Diversion

Retrofitting a wastewater treatment plant refers to the addition of treatment steps to control the release of bioavailable P in secondary effluents. Tertiary treatment techniques to reduce P and N in these effluents include biological nutrient removal, membrane bioreactors, and filtration through filter beds or membranes. Wastewater treatment plants can also invest in capabilities to divert nutrient-rich effluents to waterbodies that are not utilized as drinking water sources (Fastner et al., 2016). It is important to note that alterations to wastewater treatment plant processes fall outside the control of public drinking water systems.

Waterbody Inflow Treatment

In cases where P inputs are too widespread to effectively control, P stripping treatments can be performed at the waterbody inflow. Inflow treatment involves dedicated facilities that utilize flocculants like alum to remove P from the water, with dosing procedures altered to account for the difference between inflow and whole-waterbody treatment. More advanced facilities can also

apply additional treatments such as post-flocculation and filtration (Fastner et al., 2016; Pilgrim & Brezonik, 2005).

Wetland Restoration

A reduction in excess nutrient inputs can be achieved through the restoration of existing wetlands or through the construction and operation of a treatment wetland. Subsurface flow constructed wetlands are commonly utilized by small treatment facilities to effectively control suspended solids, but their impacts on P are less consistent. Filter media, such as sands and soils, should be assessed based on P binding capacity. Filter media can be installed in a way that allows for periodic replacement (Vohla et al., 2011).

Floating Wetlands

Constructed floating wetlands consist of emergent vegetation planted on a buoyant structure in the source waterbody. Floating wetlands suppress algal establishment by acting as natural filters, removing nutrients from the water column with their roots, and by preventing the establishment of colonial algal mats at the surface. Substrates can be selected based on their ability to bind P to provide additional nutrient reductions (Pavlineri et al., 2017; Shen et al., 2022).

Riparian Buffers

Riparian vegetation, or vegetated buffer strips, can be planted between agricultural lands and surface waters to provide additional protection from excess nutrient inputs. Riparian buffers retain P through sedimentation and plant uptake, thus slowing P loading into the buffered waterbody. P exists in dissolved and particulate forms, and some riparian buffers have been shown to increase dissolved P, especially when vegetative buffers are established on converted agricultural land. Riparian buffers intended to reduce P inputs can prevent remobilization of P by amending soil with lime, introducing alum or a similar P fixative, tilling, or removing above-ground vegetation (Roberts et al., 2012). Bioretention basins provide similar nutrient reduction and can be designed for site-specific targets.

Waterfowl Deterrence

Waterfowl have been found to degrade water quality when populations become too large. Nutrient loading via feces can become a substantial source of external P inputs, with one study finding that waterfowl were responsible for 70% of all P entering the studied system externally (Manny et al., 1994). Waterfowl deterrents can range from predator silhouette cutouts to coordinated capture but must conform to species-specific game laws (Reyns et al., 2018).

Sediment Modification

Reducing external nutrient loading into a waterbody is critical in suppressing the emergence of HABs, but waterbodies may still experience eutrophication due to internal nutrient loading. Historic nutrient inputs and aquatic conditions may lead to the resuspension of nutrients previously trapped in sediments. Anoxic conditions at the sediment-surface can drive the release of P and ferrous iron, which are critical to cyanobacterial growth (Molot et al., 2014). Sediment removal and capping treatments, described below, address internal nutrient loading through the modification of source waterbody sediments.

Sediment Removal

Physical removal of P-rich sediments, or dredging, can reduce the internal nutrient loading for eutrophic systems. Dredging is typically cost-prohibitive, disrupts water quality in the short term,

and disturbs benthic habitats. Nevertheless, dredging has been shown to improve long-term ecological health in eutrophic systems without significant external nutrient loading (Reddy et al., 2007; Zhang et al., 2010).

Sediment Capping

Sediment capping involves the addition of an artificial barrier, either physical or chemical, between the sediment and the water to reduce the internal nutrient loading of a waterbody. Nutrient loading by resuspension, gas emission, or bioturbation can be controlled in this way. Fine-grained materials such as sand or clay can provide a physical barrier, whereas compounds like calcites or zeolites also draw down P from the water column (Hupfer & Hilt, 2008; Zamparas & Zacharias, 2014); see Section 3 for more information regarding compounds targeting P. A novel sediment capping treatment approach, modified local soil remediation, is in development, which involves flocculating and sinking algal blooms using chitosan-modified soils, capping sediments, and establishing macrophyte communities to permanently reduce the risk of HABs (Pan et al., 2019).

Physical Modification

Physical modifications prevent the growth of HABs by altering the hydrological and chemical features of waterbodies, especially stratified lakes and reservoirs. Cyanobacteria are particularly advantaged in stratified bodies owing to their vertical motility (Walsby et al., 1991). Mixing will therefore shift phytoplankton communities away from cyanobacteria-dominance if it is sufficiently strong to overcome this vertical motility advantage (Visser et al., 2016). Hydrological modification also includes techniques that address conditions in the hypolimnion (i.e., bottom layer of a stratified lake), such as high P concentrations or anoxia. Anoxic conditions facilitate the release of sediment-bound nutrients (especially P and ferrous iron) and thus accelerate bloom formation (Molot et al., 2014). While mixing is less effective for shallow, non-stratifying waterbodies, these systems can also be modified to prevent the development of anoxic conditions. Below are several hydrological modifications for the long-term prevention of cyanobacteria blooms.

Mechanical Mixing

Mechanical mixing disrupts the vertical migration of cyanobacteria by destabilizing stratified bodies and entraining cyanobacteria in turbulent flow. Additionally, mixing in deep waterbodies can reduce light availability for positively buoyant phytoplankton, which appears to disadvantage cyanobacteria (Mitrovic et al., 2003; Visser et al., 2016). Mechanical mixing devices include axial flow pumps (low velocity) and direct drive mixers (high velocity), which drive warm water down across the thermocline (i.e., the thermal boundary in a stratified body) to induce destratification. Surface mixers can be used to suppress cyanobacteria growth without destratification and can be applied to smaller, shallower systems (Visser et al., 2016). Mixing systems are limited by the range of influence (i.e., the area that falls within the zone of mixing), and improperly designed, which can resuspend sediments and worsen water quality (Slavin et al., 2022).

Aeration

Aeration systems can alter the structure of the water column as well as the dissolved oxygen content at the sediment-water interface. Whether the system contributes to mixing or thermocline erosion depends on the specifications of the instruments installed. Common aeration systems include airlift aerators, Speece cones, and bubble-plume diffusers (Singleton & Little, 2006). Aeration may not achieve desired P reduction goals if organic matter sedimentation rates

remain high enough to deplete hypolimnetic dissolved oxygen (Gächter & Wherli, 1998). Aeration can also prevent cyanobacterial dominance in shallow, non-stratified bodies (Wang et al., 2021).

Hypolimnetic Withdrawal

Stratified waterbodies with significant internal nutrient loading from sediments may benefit from hypolimnetic withdrawal. Structures draw water directly from the nutrient-rich hypolimnion, decreasing P concentrations and reducing the extent of anoxia (Nürnberg, 2019); however, hypolimnetic withdrawal can potentially weaken stratification such that hypolimnetic temperatures increase, with a commensurate increase in microbial productivity and a short-term worsening of water quality (Dunalska et al., 2014). Compared to other hydrological interventions, hypolimnetic withdrawal is relatively low-cost to install and operate (Anderson et al., 2014).

Flushing

Flushing refers to the intentional increase in water throughput to minimize cyanobacterial residence times. Cyanobacterial blooms are rare in lotic (i.e., flowing water) systems, except when discharge rates are reduced by drought (Bowling & Baker, 1996). Cyanobacteria growth and mortality rates can be modeled to determine appropriate flow rates for a given waterbody (Verspagen et al., 2006). Water diversions to impacted systems can also serve as an emergency mitigation strategy.

Curtain Weirs

Physical barriers can be employed to divert nutrient-rich water away from the epilimnion (i.e., upper layer of a stratified lake), lowering the growth potential for cyanobacteria. Curtain weirs allow for passive redirection of nutrients and are most appropriate for deep waterbodies with high external loading from inflows. Further, this inflow diversion can potentially induce artificial mixing under the right circumstances. Modeling can guide decisions about installation depth and location, as well as predict hydrological impacts (Dutta & Das, 2020).

Biological Control

Cyanobacteria blooms represent an ecological imbalance that favors primary producers. Biological control measures involve alterations to the ecosystem, such as supplanting cyanobacteria with less harmful primary producers or introducing additional consumers to restrict phytoplanktonic growth. Biological control measures can be hard to predict, owing to the complexity of ecological interactions, and may even exacerbate cyanobacterial dominance. Nevertheless, such measures can successfully augment other preventative strategies so long as they are properly planned and monitored.

Macrophyte Establishment

Macrophytes (i.e., aquatic plants) compete with phytoplankton for nutrients, provide shelter for zooplankton, and stabilize nutrient-rich sediments (Triest et al., 2016). Macrophyte establishment often relies on an ecosystem-level regime shift and an extended clear-water phase, which may be difficult to induce and sustain. Maintenance of a clear water state can depend heavily on nutrient inputs and other ecological factors. When successfully implemented, macrophyte establishment provides low-cost, long-term preventative treatment (De Backer et al., 2014). Seasonal dieback of macrophytes, especially non-native species, can sometimes lead to internal nutrient loading that drives seasonal cyanobacteria growth. Weed harvesting represents a relatively low-cost method of drawing legacy nutrients out of the waterbody, and more beneficial macrophytes can be planted to gradually replace the harvested species (Gibbs et al., 2022).

Zooplankton Addition

Zooplankton addition can increase grazing pressure on cyanobacteria and suppress blooms. Cyanobacteria deter grazing through their large size, production of toxins, and aggregation in colonies or filaments (Urrutia-Cordero et al., 2015). Zooplankton research has focused primarily on the response of rotifers (i.e., wheel animalcules), copepods (i.e., small crustaceans), and cladocerans (i.e., water fleas) to cyanobacterial dominance, with the latter group containing the genus *Daphnia* (Nandini & Sarma, 2023). Large-bodied *Daphnia* have demonstrated an ability to control various cyanobacterial taxa, especially *Microcystis*, but this control method may depend on zooplankton-eating fish removal (Chislock et al., 2013; Urrutia-Cordero et al., 2015).

Fish Removal

The removal of benthic-feeding and zooplankton-eating fish (e.g., carp) can control cyanobacterial growth by indirectly enhancing zooplanktonic abundance, especially larger zooplankton taxa which are better suited to cyanobacterial control. Benthic-feeding fish resuspend sediment-bound nutrients through bioturbation, so their removal can also control cyanobacterial growth through nutrient limitation. Fish removal experiments have succeeded in controlling blooms, but conditions can revert to cyanobacterial dominance in the long term absent other interventions (Triest et al., 2016).

Piscivorous Fish Addition

Top-down ecological control of zooplankton-eating species can be achieved by supplementing or introducing piscivorous (i.e., fish-eating) species. Piscivore addition experiments are more inconsistent, with indirect impacts on plankton-eating and planktonic species often developing in unexpected ways. In some cases, cyanobacterial dominance is exacerbated (Triest et al., 2016). Piscivore addition may be more successful when combined with zooplankton addition to control ecological cascading effects.

Section 3. Algal Bloom Mitigation in Source Water

Clarifying Agents

Clarifying agents promote the removal or aggregation of particles as either a mitigative or preventative strategy depending on their use. Clarifying agents are a diverse class of compounds which can be used to precipitate nutrients from the water column (i.e., turn dissolved substance into a solid), aggregate cells (i.e., bind cells together), or induce cell lysis (i.e., bursting of the cell membrane). In many cases, these compounds perform multiple functions, and the utility of a given compound can change depending on environmental conditions. Coagulant clarifying agents alter chemical charges or structures, and in this context are deployed to render nutrients less bioavailable. Flocculant clarifying agents physically aggregate cells and can be used in conjunction with a ballast material to sink and sequester biomass in the sediment layer, or they can enhance flotation for removing biomass at the surface (Lürling et al., 2020). Nutrient inactivators target nutrients and render them less bioavailable; they are discussed alongside clarifying agents in this report due to their ability to improve water quality. The clarifying agents discussed below treat cyanobacteria blooms by addressing point and nonpoint nutrient pollution, either directly or indirectly through the aggregation and removal of cell biomass.

Aluminum-based Compounds

Aluminum-based compounds are among the most used clarifying agents, and their primary application is for nutrient removal. Aluminum (Al) salts react with alkalinity in the water to form solid $\text{Al}(\text{OH})_3$ flocs with high P affinity, which allows these compounds to rapidly strip P from the water column. As a secondary function, these flocs also trap cyanobacterial cells and cause cell lysis from extended contact. Aluminum treatments in waterbodies with neutral pH and adequate buffering capacity can be applied with relatively minor ecological consequences (Jančula & Maršálek, 2011; Kibuye et al., 2021a). Common aluminum compounds include aluminum sulfate (alum) and polyaluminum chloride (PACl). The effective pH range for alum is estimated between 6 and 8, whereas PACl is effective between 5 to 8. All aluminum compounds lower the pH of waterbodies post-application; however, for PACl this effect is weaker. Aluminum can produce toxic cations at $\text{pH} < 5.5$ and toxic anions at $\text{pH} > 8.5$; there has been observed negative ecological and physiological effects across pH ranges on nontarget fish and zooplankton (Lürling et al., 2020). Aluminum-based compound application can dramatically reduce P concentrations within hours, and some waterbodies see overall lasting P reductions for years (Huser et al., 2016). A comparative study of cell flocculants found PACl to be highly effective at high ($>1500 \mu\text{g}$ chlorophyll- α /L) concentrations without significant impacts on other water quality parameters (Liu et al., 2022).

Chitosan

Chitosan is an organic polymer derived from chitin (i.e., the polymer that strengthens the exoskeletons of crustaceans, insects, and the cell wall of fungi) that operates as a coagulant for cyanobacterial cells. In contrast to aluminum-based compounds, chitosan is biodegradable and nontoxic despite inducing cell lysis in cyanobacteria (Lürling et al., 2020). Chitosan is often deployed with a ballast material to sink flocculated algae. It is the preferred flocculant for the emerging modified local soil restoration technique, where a natural coagulant is combined with local soil as ballast to sink algal biomass and promote submerged macrophytes (Pan et al., 2011). Chitosan is ineffective at high pH, with a peak in efficacy around 8 (Lürling et al., 2017). Modified chitosan compounds are being developed to enhance efficacy across a range of conditions (Li et al., 2023). In a comparative study of cell flocculants, chitosan was shown to perform best at lower ($<200 \mu\text{g}$ chlorophyll- α /L) concentrations (Liu et al., 2022).

Lanthanum-modified Bentonite (LMB)

Lanthanum-modified bentonite (LMB) is a modified clay with high P affinity. Unlike chitosan and aluminum-based compounds, LMB does not form flocs but instead acts solely as a P-fixative that sinks P to the sediment. LMB is particularly effective at sequestering P due to the stability of the resultant mineralized phosphate compound (LaPO_4) across a range of pH and redox conditions, including anoxic conditions. LMB has been shown to be effective across a wide range of waterbody sizes and conditions, and no negative health or ecological effects have been reported (Copetti et al., 2016).

Calcium-based Compounds

Calcium (typically in the chemical form of CaCO_3) in the form of lime (i.e., a rock) or calcite (i.e., a mineral) acts as a P-fixative that precipitates and binds with P for transport to the sediment; research has shown that lime-based fixation can increase the P sedimentation rate in a full-scale waterbody (Dittrich et al., 2011). While calcium-based treatments can effectively remove available P, redissolution occurs post-application and multiple treatments are often required to

see appreciable results. Further, repeated calcium additions increase pH and may impact ecological assemblages (Kibuye et al., 2021a).

Iron-based Compounds

Iron-based compounds include iron chloride (FeCl_3), iron sulfate (FeSO_4), and polymeric ferric sulfate (PFS). While iron-based compounds are primarily deployed as P-fixatives, these compounds can also flocculate cyanobacterial cells (Jiang et al., 1993; Kibuye et al., 2021a). Iron is naturally occurring in aquatic systems and increases primary productivity at low concentrations. At high concentrations, iron induces oxidative stress and can lyse cells. Iron-based compounds rapidly bind dissolved P and improve water quality, but this interaction is redox-sensitive; anoxic conditions will depress P-binding and generate ferrous iron (Fe^{2+}), an important component of cyanobacterial growth (Molot et al., 2014; Kibuye et al., 2021b). Ecological impacts related to oxidative stress appear limited to macrophytes and other primary producers (Kibuye et al., 2021b). In a study comparing compounds for cell flocculation, iron chloride was the most effective at high ($>1500 \mu\text{g chlorophyll-}\alpha/\text{L}$) concentrations but was comparable to PACl and lowered pH considerably (Liu et al., 2022).

Algaecides

Algaecides are compounds designed to stop algal bloom growth by damaging cells and increasing mortality. While algaecide application rapidly reduces cell counts during active cyanobacterial blooms, the destruction of these cells releases intracellular toxins (see Section 5 for more information). Toxins within cyanobacterial cells often greatly exceed extracellular toxin (see Section 6 for more information) counts during active blooms, meaning algacidal treatments may exacerbate water quality crises. Algaecides can be chemical, biological, or mechanical in nature, with variable impacts on targeted blooms, non-target species, and the toxins released by cell death. Critically, algaecide treatments address individual bloom events without altering the environmental drivers of cyanobacterial dominance and should therefore be viewed as a last resort. Below is a summary of chemicals, biological agents, and devices that attack cyanobacteria organisms directly.

Copper-based Algaecides

Copper-based compounds inhibit critical cellular functions in phytoplankton and induce cell lysis. Copper is commonly applied as copper sulfate (CuSO_4), but many modified compounds have been developed to extend its utility across a range of environmental conditions. Copper's toxicity is not limited to cyanobacteria, and mortality has been documented in nontarget algae, zooplankton, and vertebrates post-application (Kibuye et al., 2021b). Nontarget effects and the release of intracellular cyanotoxins mean that the timing and dosage of copper application are particularly important. Copper algaecides should be applied at low doses early on in bloom formation to minimize harm to nontargets (Tsai, 2016). Dosing decisions can be tailored to minimize cyanotoxin release, although populations may rebound without repeated applications. Accumulation of copper in sediments of treated bodies poses variable risks depending on site characteristics (Crafton et al., 2021).

Peroxide-based Algaecides

Peroxide-based algaecides act as oxidants, inducing cellular stress and mortality. Peroxide-based algaecides operate selectively against cyanobacteria compared to eukaryotic algae, and peroxide breaks down into oxygen and water, leaving no residuals. Hydrogen peroxide (H_2O_2) is the most common peroxide-based algaecide; however, sodium percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, also

referred to as sodium carbonate peroxyhydrate) operate similarly. High counts of green algae may minimize the efficacy of peroxide-based algaecides, as these algae have natural defense mechanisms against reactive oxygen species (Kibuye et al., 2021b). Peroxide-based algaecides induce lysis and thus release intracellular toxins, but these toxins can themselves be oxidized by the treatment. Hydrogen peroxide is capable of comparable bloom control compared to copper-based algaecides, with the additional benefit of degrading released toxins and leaving no residuals (Kansole & Lin, 2017). Peroxide-based algaecides are limited by light availability, as ultraviolet radiation is needed to accelerate the generation of reactive oxygen species. Alternatives like sodium percarbonate are able to function in low-light environments (Xu et al., 2021). Consideration should be given to light conditions at the time or depth of application. Treatment is most effective at the onset of bloom formation (Kibuye et al., 2021b).

Biological Algaecides

Biological algaecides refer to bacterial, fungal, and other biotic agents that arrest cyanobacterial growth directly. This emergent field of cyanobacterial control is diverse, with a vast array of candidate organisms using different mechanisms of control and many species-specific interactions. For this reason, this report provides only a general outline of existing biological algaecides with case studies provided for each biological category: 1) bacterial, 2) fungal, and 3) viral (see Appendix for more information). These control techniques often boast high target specificity, meaning their efficacy will depend on the homogeneity of the cyanobacterial bloom. Further, some biological agents are capable of degrading cyanotoxins (Kormas & Lympelopoulou, 2013). More research is needed before this form of cyanobacterial control can be practically implemented.

Straw Decomposition

Barley and rice straws exhibit algacidal properties as they decay, though the mechanism itself is not fully understood. The decomposition of these straws is believed to release chemicals that are toxic to cyanobacteria, but potential nontarget effects are unknown. Straw treatments do not yield immediate results; while one experiment showed cyanobacterial declines 12 days post-application, most applications do not see appreciable progress for two to six months. Effective straw decomposition may not take place in low oxygen systems, and the selectivity of straw's algacidal properties is uncertain. While straw decomposition has the potential to provide low-cost, long-term algacidal treatment, research is needed to clarify the mechanisms, ecological impacts, and appropriate dosing (Kibuye et al., 2021b).

Sonication

Sonication, or ultrasonication, is an emerging treatment technique that uses ultrasonic frequencies to rupture the gas vacuoles of cyanobacterial cells. The process, known as acoustic cavitation, degrades photosynthetic structures in the cell and disrupts their buoyancy, causing them to sink to the sediment layer. Sonication is highly selective, as only cyanobacteria with gas vacuoles are targeted; however, some cyanobacteria species lack gas vacuoles and are thus resistant to the technique (Rajasekhar et al., 2012). Sonication device parameters, namely frequency, power, and exposure time, can be optimized for efficient removal and the minimization of extracellular cyanotoxins, although more research on optimization is required before standard prescriptions become available. Field testing has been limited, and the effective range of these devices is still indeterminate. Studies have also demonstrated strong nontarget

effects on zooplankton and fish, highlighting the risk of implementing this technology in the field before it is fully understood (Kibuye et al., 2021b).

Physical Structures

When preventative and mitigative actions fail to control cyanobacterial blooms, physical safeguards can be employed to minimize harm to critical areas. Barriers like booms and curtains or bubble curtains can help contain cyanobacteria to areas where treatment application may be more effective (Asaeda et al. 1997; Asaeda et al., 2001). Shading structures may also be installed to dampen cyanobacterial growth in select areas and can work synergistically with other mitigative treatments (Chen et al., 2009).

Lotic System Treatments

Most of the treatment processes discussed above were designed for and studied in lentic (i.e., still water) systems. Systems facing cyanobacterial blooms in lotic (i.e., free moving) waters face additional challenges, as rivers occupy greater areas and often run through multiple jurisdictions. Preventative treatments for lentic systems are typically not applicable to lotic systems, and chemical treatment processes are rendered impractical by the size and flow rate of affected areas. Algal bloom formation in rivers typically occurs from late winter to early spring, as opposed to lentic algal bloom formation which occurs most frequently from summer to early autumn. While lotic algal blooms have similar nutrient and light requirements, hydrodynamic conditions such as water level variation have an outsized impact on the likelihood of bloom formation. Low and steady water levels upstream of a given river reach were found to be strong predictors of algal bloom risk (Xia et al., 2020). Therefore, water level management represents one of the few tools available for combating lotic algal blooms. Monitoring key nutrients like P during the seasonal peak for lotic algal blooms is also recommended, along with controls for any pollution point sources that may be contributing to nutrient loading during the seasonal peak or periods of low water levels.

Summary of Preventative Treatments

Preventative treatments can only be recommended on a case-by-case basis, but the goal for source waterbody managers should be nutrient reduction and the establishment of a macrophyte-dominated, clear water ecological state.

When prevention fails, the selection of appropriate clarifying or algaecide agents depends on source waterbody characteristics. The primary characteristics to consider are depth (including whether the waterbody stratifies), whether nutrient loading is primarily external or internal, and whether blooms occur seasonally or perennially. Lüring et al., (2020), describe a decision-making process based on these characteristics that can help waterbody managers decide which strategy for cyanobacterial control makes sense for their system. Secondary decisions regarding specific compounds can be made by considering the effective pH and alkalinity ranges along with other functional limitations. Research suggests that algaecides should only be deployed early in the bloom formation process, and peroxide-based algaecides are recommended in these cases. Chitosan should be a first resort cell flocculant given its ecological safety, but at high cell concentrations (or when cost is prohibitive) an aluminum-based compound such as PACl is recommended. LMB is recommended as a P-fixative, although aluminum-based compounds can likewise be substituted if cost renders LMB impractical.

Section 4. Intracellular Cyanotoxins within the Treatment Plant

Once a cyanobacteria bloom has developed, drinking water treatment plants should prioritize the removal of intact cells. Most cyanotoxins are produced and stored within the cell cytoplasm and are released upon cell death. Cells subjected to sufficient environmental or chemical stressors will rupture, a process referred to as lysis, releasing these toxic compounds into the water. While most modern treatment plants can remove cyanobacterial cells without altering their treatment methods, it is crucial that these methods minimize cell lysis to avoid overwhelming downstream treatment barriers with cyanotoxins. What follows is an assessment of common treatment technologies and their ability to safely remove intracellular cyanotoxins.

Alternate Sources, Blending, and Intake Depths

If alternative sources of water are available, systems could consider temporarily switching to or blending with non-impacted sources for the duration of the bloom to prevent treatment system contamination. Cyanobacteria bloom duration can vary significantly owing to their complex ecology, but a system with high confidence in their source water treatment and a viable alternative water source may avoid the need for in-plant treatment entirely in this way.

Treatment plants with multiple raw water intakes should consider switching or blending intakes according to conditions. Cyanobacteria typically aggregate closer to the surface owing to their buoyancy, although the diel vertical migration exhibited by many species may justify alternating between shallow and deep intakes during the night and day, respectively. Depth-integrated sampling across multiple times of day can help inform optimal intake selection.

Pre-Treatment Oxidation

In the event of a toxic cyanobacteria bloom, systems should consider stopping pre-treatment oxidation as oxidants, such as chlorine, will lyse cells upon contact. While oxidation is also capable of degrading cyanotoxins, pre-treatment oxidation doses are unlikely to degrade more toxins than they release (Ma et al., 2012). In contrast, potassium permanganate (KMnO₄) has demonstrated an ability to remove extracellular cyanotoxins without inducing cell lysis when applied at concentrations below 3 mg/L (Fan et al., 2013). Where pre-treatment oxidation is necessary for other water quality objectives, permanganate at low concentrations is recommended.

Coagulation, Flocculation, and Sedimentation

The coagulation, flocculation, and sedimentation stages of treatment provide the best opportunities for the efficient removal of intracellular cyanotoxins without risk of cell lysis. Dissolved air flotation (DAF) is particularly effective, as the flotation of sludge allows for rapid removal of cyanobacterial cells owing to their natural buoyancy (Teixeira & Rosa, 2006). While the replacement of existing infrastructure with DAF is capital-intensive, facilities chronically impacted by cyanobacteria blooms may benefit from this investment in the long-term as climate change makes blooms more frequent and intense (Paerl & Paul, 2012).

Systems can optimize the physical removal of cyanobacteria by selecting an effective coagulant and adjusting dosage according to the dominant cyanobacterium and certain water quality parameters.

Alum, iron chloride, and PACl are generally effective coagulants for the aggregation of cyanobacterial cells. Compared to alum, PACl reduces pH 50% less and its equivalent dose is 26% lower; however, PACl has a narrower range of optimal pH (De Julio et al., 2010). Appropriate dosing can depend on several factors, as coagulants will function differently based on cell morphology, species characteristics, and the stage of bloom development (Newcombe et al., 2021). Optimization based on turbidity was found to result in optimal cyanobacterial removal when raw water measured above 10 NTU (Newcombe et al., 2021). While some coagulants function best under low pH conditions, cell lysis is a concern at pH above 6 (Qian et al., 2014). Given the numerous variables that may influence coagulation, jar testing can be a reliable way to find the optimum coagulant dose during an active bloom.

Enhanced or optimized coagulation refers to improvements to the standard coagulation process, especially for the removal of natural organic matter to help reduce the formation of disinfection byproducts. Recent innovations in enhanced coagulation include the use of pre-oxidation, ballasted flocculation, and magnetic additives (Cui et al., 2020). Research indicates that low concentrations of pre-treatment oxidants, such as permanganate, can assist the coagulation process, but also carry risk of cell lysis and therefore is not recommended for all systems (Wang et al., 2012; Cui et al., 2020; see Appendix for more information). Ballasted sedimentation involves the addition of a dense ballast material, such as microsand, to accelerate the rate of sedimentation. Experiments have shown that ballasted sedimentation removes cyanobacterial cells at rates comparable to DAF, making this a viable alternative for treatment plants that rely on conventional sedimentation (González-Galvis et al., 2022).

Magnetic powder can improve aggregation and combine with an externally applied magnetic field for efficient, accelerated removal (Cui et al., 2020). Magnetic nanoparticles were successfully combined with polyferric chloride to form a composite capable of improved coagulation efficiency through the adsorption of cells by magnetite (Jiang et al., 2010).

Ultrasonic radiation, or ultrasound, represents a novel approach in enhancing coagulation during cyanobacterial blooms. Like in the sonication source water treatment previously discussed, ultrasonic transducers can be installed to selectively damage the cyanobacteria's gas vacuoles. High frequencies damage cells without inducing lysis by removing the buoyancy-generating gas vacuoles and controlling bacterial growth (Huang et al., 2021).

Coagulation, flocculation, and sedimentation techniques will remove most cyanobacteria cells, but even the highest removal rates during bloom events can translate to significant cell counts reaching the pre-filtration stage. For this reason, any pre-filtration oxidation should either cease or be adjusted upward to effectively oxidize both cyanobacteria cells and the intracellular toxins released.

The high cyanobacteria removal rate of the coagulation, flocculation, and sedimentation stage means that cyanotoxins will quickly become highly concentrated in sludge. Cyanobacteria cells in sludge will typically degrade and release their intracellular toxins, necessitating frequent sludge removal. There have been documented instances of cyanobacteria proliferating within the sludge or supernatant itself, with one experiment showing over 80% of cells remaining viable for seven days after coagulation (Pestana et al., 2016). This ability is dependent on species, water quality, temperature, and the biological and chemical interactions within the sludge, meaning it is exceedingly difficult to predict. Cyanobacteria that remain viable in sludge can delay peak cyanotoxin pulses by days or even weeks, creating a substantial window of uncertainty. One study found that even low cell counts at a plant intake (< 1000 cells/mL) resulted in sludge and backwash cell counts of over 100,000 cells/mL (Almuharam et al., 2018). This means that even when cell counts remain below bloom event thresholds, toxin release from accumulated cells can still

pose a serious threat to drinking water quality. Systems recycling backwash or other residuals to the head of the plant should suspend this operation to whatever extent is feasible.

Membranes

Low-pressure membrane filtration, referring to either micro- or ultrafiltration, provides an effective barrier against intracellular cyanotoxins as pore sizes are significantly smaller than cyanobacterial cells. In the event of an active bloom, the accumulation of cell material may increase transmembrane pressure sufficiently to lyse cells, so backwashing frequencies should be adjusted accordingly. Microfilters may prove more difficult to backwash during active blooms, but the prior addition of coagulant can mitigate the increased effects of transmembrane pressure (Hiskia et al., 2020). Nanofiltration and reverse osmosis membranes will be rapidly clogged by cyanobacterial cells; while these membranes are effective for cyanotoxin removal, they should not be relied on for bulk intracellular removal (Merel et al., 2013).

Filtration

For most conventional treatment plants, filtration represents the final barrier against intracellular cyanotoxins. Standard sand-anthracite filtration is sufficient for cell removal, but only if the above pre-filtration steps are optimized to remove the bulk of cells. Cells accumulating on and within filter media will eventually lyse from either shear stress or natural decomposition and will typically release cyanotoxins after 24-48 hours of retention. Shortening filter run times and increasing backwash frequency can reduce the risk of toxin release. For some species, severe blooms reaching sand-anthracite filters demonstrated an ability to breakthrough into finished water, emphasizing the need for effective pre-filtration treatment and close monitoring of in-filter turbidity (Zamyadi et al., 2013).

Section 5. Extracellular Cyanotoxins within the Treatment Plant

Extracellular cyanotoxins are primarily released as cyanobacterial cells undergo lysis. Cyanobacterial lysis can be catalyzed by several factors, including the physio-chemical properties of raw water undergoing treatment. Coupled with the additional challenges faced when trying to monitor extracellular cyanotoxins (i.e., monitoring based not on a visible algal bloom), it is widely recommended that intracellular cyanotoxin (i.e., cyanobacterial) treatment be a priority mechanism for treatment plants to protect finished drinking water from cyanotoxins (Kull et. al 2006; Almuhtaram et. al 2018). Given the difficulty of controlling cyanobacterial growth in raw water, coupled with the need for a preventative measure in case of cyanobacterial lysis within the treatment plant itself, there are numerous recommended pathways of treatment to degrade cyanotoxins. These treatments are typically more expensive than treatment for intracellular toxins (i.e., intact bacterial cells) because of the physical-chemical reactions necessary for treatment (USEPA, 2016). Different treatment techniques are separated into three broad categories based on their properties: 1) physical removal, 2) biological degradation, and 3) chemical degradation (Westrick et al., 2010). The next sections will outline conventional treatment techniques within each category, and the benefits and limitations associated with each.

Physical Removal

The physical removal of cyanotoxins from drinking water is based on keeping the molecular integrity intact while separating it from the finished water. Most commonly, physical removal of cyanotoxins is achieved by using activated carbon as an adsorption media; membrane filtration is also a technique (Westrick et al., 2010).

Activated Carbon

Activated carbon can be manufactured using a variety of carbon-rich materials to achieve a desired level of quality. Through carbonization, the starting material becomes extra porous and electro-charged, making it able to adsorb several different oppositely charged contaminants, removing them from the processed water. Activated carbon is typically created in one of two forms: granular (GAC) and powdered (PAC). The main differences in GAC and PAC are the costs associated with them; however, GAC is more widely used in water treatment than PAC since considerations of dosage, optimal contact time, pH, and carbon pore volume need to be determined when relying on PAC. Overall, the two biggest considerations when using activated carbon are its source material and mesopore size (National Research Council 1980; Albuquerque Júnior et al., 2008; USEPA, 2016; Abbas et al., 2020; Hiskia et al., 2020).

GAC is widely used in water treatment because it can either adsorb or filter many different contaminants. Most research on the effectiveness of GAC at adsorbing cyanotoxins has been focused on microcystin-LR and other microcystins, but it is generally agreed upon that GAC can be used to treat most cyanotoxins, with yields above 90% removal efficacy. In addition, GAC can be modified by changing source material to design treatment that is more effective based on a system's individual needs (Hiskia et al., 2020). The design of a GAC bed (i.e., as part of a sand bed or as a deep bed), required time to filter, and lifespan is highly dependent on system specifics (USEPA, 2016).

Membrane Separation

Main categories of membrane technologies include microfiltration, nanofiltration, reverse osmosis, and ultrafiltration. These technologies show potential for cyanotoxin removal at the lab-scale and small community scale, but increase with complexity and complications as the system it is used on grows. These complications, including the possibility of cell lysis, high energy costs, how the membrane material impacts its ability to remove certain toxins, and the formation of biofilm that impedes influx, makes membrane technology rather ineffective at the large-scale (Kumar et al., 2018). USEPA, (2016), acknowledges that membrane technology is rarely used in drinking water treatment due to unanswered questions about its effectiveness.

Biological Degradation

Biological degradation of cyanotoxins focuses on disrupting enzymatic, metabolic, and molecular pathways using a biofilm. While the degradation pathways themselves are still vaguely described in the literature, the common interpolation is that certain types of microorganisms have degradation genes (*mlr* + genes) that are triggered by high concentrations of cyanotoxin (produced by *mcy* genes).

The success of biological degradation is impaired by several variables that are either able or not able to be controlled in a treatment setting. Environmental factors such as temperature, pH, and the concentrations of metals and organic matter in the raw water are important considerations needed to keep degradation pathways intact. It is also important to consider the concentrations of degradation bacteria needed compared to cyanotoxin levels to maintain a steady reaction and keep treatment time low; making sure that degradation bacteria are present on the biofilm and can degrade the targeted cyanotoxin is the most important variable to consider (USEPA, 2016). Sand filtration is also inefficient against bacteria with high motility, and can lyse intact cells, thus increasing levels of cyanotoxins (Sorlini et al., 2018).

Biofiltration is the most effective means of using biological degradation in the water treatment process because it can be utilized by making already available techniques, such as sand beds and activated carbon, biologically active. Rapid and slow sand filtration, for example, uses microorganisms on the sand grains to transform and degrade contaminants remaining following sedimentation; however, further research is needed to fully explain the biological mechanisms behind sand filtration, including optimization of setup, the toxicity and mobility of by-products, and how adaptation and genetic expression of the degrading bacteria changes over time as they are exposed to concentrations of cyanotoxins mixed with other contaminants (Benner et al., 2013). Two other considerations with sand filtration are the land that is required for them, the possibility of clogging if intracellular blooms are dense, and need for regular cleaning and changing of the top layer of sand to prevent bacterial growth (USEPA, 2016; Hiskia et al., 2020).

Bio-activated carbon uses microorganismal growth on the surface of activated carbon to both degrade and adsorb cyanotoxins. The literature is unclear whether bio-activated carbon is beneficial or a hindrance to treatment performance, and more research is needed to determine its applicability (Hiskia et al., 2020).

Chemical Degradation

Utilizing oxidation reactions in water treatment comes with both benefits and drawbacks. While benefits include its ability to treat both organic and inorganic contaminants and to serve as a disinfectant, oxidation is known to be non-specific. As opposed to what is observed in physical removal techniques, oxidants broadly react with all types of impurities without regard to removing specific contaminants. Rather, the oxidation reaction transforms contaminants into reaction byproducts. These byproducts are difficult to predict, given the variability in how oxidants react with certain functional groups and in the presence of multi-variable levels of organic matrices, leading to unpredictable outcomes and information in gauging their potential toxicological profiles (von Guten, 2018).

USEPA, (2016), outlines common oxidants and their general efficacy in treating the four most prevalent cyanotoxins in the United States (Table 4). As demonstrated by the information presented, different oxidant reagents have different effects on each cyanotoxin; no one oxidant is necessarily effective at degrading all four cyanotoxins. This means that oxidation treatment should be used in conjunction with other treatment methods to assure full spectrum, multi-barrier treatment regarding a system’s specific needs (von Guten, 2018; Schneider & Bláha 2020).

Table 4. Effectiveness of cyanotoxin degradation per oxidant (USEPA, 2016, [Table 3-1]).

Oxidant	Anatoxin-a	Cylindrospermopsin	Microcystin	Saxitoxin
Chlorine	Not effective	Effective at low pH (between 6-8)	Effective in right conditions*	Somewhat effective
Chloramine	Not effective	Not effective	Not effective at normal doses	Inadequate information
Chlorine dioxide	Not effective at normal doses	Not effective	Not effective at normal doses	Inadequate information
Potassium permanganate	Effective	Data ranges from not effective to possibly effective	Effective in right conditions*	Not effective
Ozone	Effective	Effective	Very effective	Not effective

Oxidant	Anatoxin-a	Cylindrospermopsin	Microcystin	Saxitoxin
UV / advanced oxidation	Effective	Effective	Effective at high UV doses in right conditions*	Inadequate information

**"right conditions" defined as dependency on initial cyanotoxin concentration, pH, temperature, and presence of natural organic matter*

Advanced Oxidation

Advanced oxidation processes (AOPs) utilize the generation of hydroxyl radicals (-OH), which has a high redox potential and thus high reactivity, to react with organic contaminants (Glaze et al., 1987). In the drinking water treatment process, the most common AOPs implemented as described in the research is the utilization of an oxidant, such as hydrogen peroxide or ozone (O₃), in combination with photolysis (i.e., ultraviolet radiation) to catalyze hydroxyl generation and chemical reaction. Unlike when using hydrogen peroxide as an oxidant, ozone is a toxin when in the gaseous phase and precautions must be taken to achieve a safe working condition (Schneider & Bláha 2020). Research has shown that using both hydrogen peroxide and ozone in AOP increased the efficiency of microcystin degradation when used at a proper ratio (Loganathan, 2017; Svrcek & Smith 2004). The use of photolysis and hydrogen peroxide AOP has shown not to create toxic byproducts when used to treat microcystin-LR (Liu et al., 2016). Overall, the research shows that photolysis and hydrogen peroxide AOP is effective at treating microcystin (Qiao et al., 2005; He et al., 2015; Moon et al., 2017), cylindrospermopsin (He et al., 2013), anatoxin-a (Tak et al., 2018), and BMAA (Chen et al., 2018) toxins when proper dosage and considerations are taken. Treatment efficiency is impacted by water quality parameters, such as high pH, high dissolved oxygen, high organic and metal contents, and high turbidity (He et al., 2013; Loganathan, 2017; Schneider & Bláha 2020).

Section 6. Conclusion

Based on the above evaluation, the Treatment Subcommittee concludes that cyanotoxins can be reliably and feasibly managed and/or removed by drinking water systems to the accuracy of available approved analytical methods. Treatment should be optimized to fit the characteristics of a system, with particular consideration for:

- 1) Capabilities to mitigate or treat cyanotoxins in the source water and in the treatment plant,
- 2) Pathways for both intracellular and extracellular cyanotoxins, and
- 3) Strategies for both normal conditions and in anticipation and preparation of unusual or extreme conditions, such as drought and weather events.

The Treatment Subcommittee recommends that a treatment technique approach be considered. Furthermore, the Treatment Subcommittee recommends that drinking water systems have a Cyanotoxin Management Plan (CMP) that addresses prevention management, source water monitoring, and treatment optimization.

Public Review Draft

The Treatment Subcommittee acknowledges that prevention and mitigation are significant components to the management of potential HABs, and prevention and mitigation strategies should be uniquely designed to the natural and anthropogenic characteristics of individual watersheds. The Treatment Subcommittee advises that water systems manage cyanotoxins by carefully considering a multi-barrier approach that consists of establishing a robust watershed management plan and optimizing treatment plant technologies.

Furthermore, the Treatment Subcommittee recommends that the Department explore the impact of cyanotoxins to private wells and whether changes to the Private Well Testing Act (PWTa) could help address these impacts. In some instances, private wells may be affected by cyanotoxins if the source is ground water under the influence of surface water. Under the current PWTa testing framework, which requires testing at time of sale and every five years for rental properties, it would be extremely difficult to capture risk to cyanotoxins at private wells. In addition, there would not be a standard level for private wells under the PWTa if the Department utilizes a treatment technique approach.

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Appendix: Case Studies and Additional Information

Prevention

Wastewater Treatment Plant Retrofitting and Diversion

Lake Constance, Central Europe

Wastewater facilities upstream of a reservoir were retrofitted to recover P from outflows by the addition of flocculation and sand filtration treatment. These additions helped reduce lake water P concentrations from a maximum value of 87 mg/m³ to 13 mg/m³. (Müller, 2002).

Lake Washington, Washington, USA

Secondary sewage effluent was diverted away from a eutrophic lake over a 5-year period, resulting in annual P input reductions from a high of 204 kg/yr to a low of 43 kg/yr post-diversion. (Edmondson & Lehman, 1981).

Waterbody Inflow Treatment

Fish Lake and Tanners Lake, Minnesota, USA

Treatment facilities were constructed to mix alum into lake inflows, and detention ponds were used to settle floc before discharging to the lakes. 8 mg/L of aluminum was found to greatly reduce P concentrations long-term, from 50 µg/L to under 30 µg/L. (Pilgrim & Brezonik, 2005).

Wetland Restoration

Lake Apopka, Florida, USA

Wetlands upstream of a eutrophic lake were restored with the installation of a 2 km² treatment wetland alongside several other remediation strategies. The installation was highly effective at removing suspended solids and removed 30-67% of total P despite difficulties with hydrologic short-circuiting. (Coveney et al., 2002).

Floating Wetlands

Experimental Lakes, Greece

A pilot-scale study loaded constructed floating wetlands with agrochemicals and achieved average nutrient reductions between 27% and 83%, with duckweed and water hyacinth performing comparably. (Pavlidis et al., 2022).

Riparian Buffers

Multiple Watersheds, Japan, Indonesia, and India

A field monitoring study conducted in Japan and Indonesia quantified the impact of riparian buffer zones on water quality, finding the greatest improvements in buffer zones located along higher order streams where the gradient is low. (Anbumozhi et al., 2005).

Waterfowl Deterrence

Flanders, Belgium

Coordinated hunting (molt captures) and egg destruction targeting Canada geese was found to avoid water quality impairments and grasslands degradation, the cost of which would have exceeded control expenditures. (Reyns et al., 2018).

Sediment Removal

Lake Okeechobee, Florida, USA

Sediment samples from Lake Okeechobee were used in an experiment simulating various dredging depths, demonstrating that removing the top 30 cm of sediment can remove approximately 65% of sediment-bound P. (Reddy et al., 2007).

Sediment Capping

Lake Taihu, China

A three-year sediment capping experiment was conducted in a relatively shallow, eutrophic lake. A locally sourced soil low in calcium was used to cap sediments, leading to reductions in both N and P in the water column. (Sun et al., 2023).

Mechanical Mixing

Multiple Lakes, United States

Solar powered circulation devices were deployed in three reservoirs previously impacted by blooms at a density of approximately 0.15 km²/device. The devices operated for 6 years, during which the phytoplankton community shifted toward eukaryotic algae and diatoms and algaecide use for cyanobacteria suppression declined by 85%. (Hudnell et al., 2010).

Aeration

Lake Nieuwe Meer, Netherlands

Artificial mixing and aeration via bubble plumes maintained uniform temperature and oxygen distribution in a deep lake that typically stratified during summer. During the 2 years of bubble plume operation, *Microcystis* counts were significantly lower compared to preceding control years. (Visser et al., 1996).

Hypolimnetic Withdrawal

Walnut Canyon Reservoir, California

Water quality simulations were generated to investigate several treatment options for a stratifying lake with elevated nutrient levels in the hypolimnion. Hypolimnetic withdrawal was predicted to improve dissolved oxygen conditions and lower P concentrations without significant capital or operating costs, and these predictions were validated after implementation. (Anderson et al., 2014).

Flushing

Lower Darling River, Australia

A harmful algal bloom emerged in a weir pool in the Lower Darling River, which was downstream of a system of regulated lakes. Flow releases of 300 ML/day were sufficient to prevent blooms, and 3000 ML/day was sufficient to suppress the existing bloom within a week. (Mitrovic et al., 2011).

Curtain Weirs

Terauchi Dam Reservoir, Japan

Two vertical curtains were installed to divert warmer, nutrient-rich inflows downward. Algae grew on the inflow side of the curtain barriers before settling out, reducing nutrient concentrations and bloom occurrence downstream. (Asaeda et al., 2001).

Macrophyte Establishment

Guishui Lake, China

Three macrophyte species (*Lindernia rotundifolia*, *Hygrophila stricta*, and *Cryptocoryne crispata*) showed inhibitory effects on cyanobacteria, improved water quality, and decreased oxygen demand in microcosm experiments. (Wang et al., 2012).

Zooplankton Addition

Daphnia pulicaria, a species of zooplankton common in deep lakes, were tested for their ability to prey upon *Microcystis* and *Anabaena* cyanobacteria. Despite microcystin levels of 100 µg/L, the *Daphnia* suppressed cyanobacterial biomass by more than 80% compared to the control. (Chislock et al., 2013).

Fish Removal

Lake Ringsjön, Sweden

Cyprinids were removed from a eutrophic lake in 2005 to assess the long-term impacts on the lake's frequent cyanobacterial blooms. The proportion of large-bodied *Daphnia* species increased from 3% in 2005 to 58% by 2012, and early-summer cyanobacteria biomass was significantly reduced due to grazing pressure. (Ekvall et al., 2014).

Piscivorous Fish Addition

Lake Shirakaba, Japan

Rainbow trout fingerlings and large-bodied *Daphnia* were introduced into a small, shallow lake with recurring blooms. Small-bodied *Daphnia* and the planktivorous pond smelt were replaced by these introduced species, leading to reduced total phosphorus, decreased cyanobacteria bloom severity, and the expansion of submerged macrophytes. (Ha et al., 2013).

Clarifying Agents

Aluminum-based Compounds

Lake Barleber, Germany

A 6-week treatment of aluminum sulphate was applied to a large eutrophic lake at an equivalent of 5.7 mg Al³⁺/L (480 tons total). Halfway through the treatment, total phosphorus was reduced from its high point of 190 µg/L down to the detection limit of 3 µg/L and remained between 6-15 µg/L for nearly a decade. (Rönicke et al., 2021).

Chitosan

Lake Tai, China

Chitosan-modified soils were sprayed over a section of lake experiencing a cyanobacteria bloom, using 4 tons in the 0.1 km² bay. The bloom was removed within a day, secchi depth increased from 0 cm to 30 cm, total P and N were reduced by more than 86%, and after 4 months submerged macrophytes recovered. (Pan et al., 2011).

Lanthanum-modified Bentonite (LMB)

Multiple Lakes, Canada

Total Phosphorus (TP) was measured in a series of Canadian lakes before and after LMB application. One lake saw a reduction in TP from 0.25 mg/L pre-treatment to 0.10 mg/L in the years post-treatment, with several other lakes showing similar declines. (Nürnberg, 2017).

Calcium-based Compounds

Lake Luzin, Germany

The hypolimnion of a eutrophic lake was treated with calcium hydroxide ($\text{Ca}(\text{OH})_2$) combined with deep water aeration. Sedimentation of P increased significantly within a year of treatment. (Dittrich et al., 2011).

Iron-based Compounds

Maltański Reservoir, Poland

A shallow, eutrophic lake with P concentrations ranging from 0.17-0.73 mg/L experienced chronic cyanobacteria blooms. Iron sulphate treatments were applied 5-6 times per year, and while the first summer post-treatment still saw one cyanobacteria bloom, their occurrence declined significantly thereafter. (Gołdyn et al., 2014).

Miscellaneous Cell Flocculants

Magnesium Hydroxide (Lama et al., 2016), organic polymer cationic starch, synthetic compounds such as cationic polyacrylamides and cationic polyamine, extracts derived from *Moringa oleifera* seeds (Lürling et al., 2020).

Miscellaneous Clarifying Agents

Solid-phase P sorbents (SPB) including clays, waste-products (e.g., red and black ochre) or soils, typically enriched with aluminum, iron, or lanthanum (Spears et al., 2013; Noyma et al., 2016). Biochar, a cheaper alternative to activated carbon, can be similarly modified to enhance P adsorption (Almanassra et al., 2021).

Algaecides

Copper-based Algaecides

Courtille Lake, France

A *Microcystis* bloom that resisted treatment by alum was dosed with 63 µg/L copper sulphate. The bloom was effectively controlled within 2 days, but after 2 months *Microcystis* reappeared. (van Hullebusch et al., 2002).

Peroxide-based Algaecides

Lake Koetshuis, the Netherlands

An in-situ experiment was conducted to illustrate both the selectivity and efficacy of peroxide. Peroxide dosed with a water harrow dispersal device eliminated 99% of cyanobacteria and microcystin within a few days, while non-target algae, zooplankton, and macrofauna were largely unaffected. (Matthijs et al., 2012).

Xiashan Reservoir, China

Sodium percarbonate (SPC) was applied to waterbody with an active filamentous cyanobacteria bloom. 3.0 mg/L of SPC was sufficient to suppress the bloom, and the peroxide remained effective at low light levels owing to interactions with the carbonate ions generated by SPC decomposition. (Xu et al., 2021).

Biological Algaecides

Bacterial Control

Bacillus cereus, a phytoplankton-lytic bacterium, was tested in a series of cultures and demonstrated an ability to lyse harmful cyanobacteria. (Shunyu et al., 2006).

Fungal Control

Trichaptum abietinum, a fungus strain, demonstrated an ability to prey upon several harmful cyanobacteria species. All algal cells were destroyed within 48 hours of co-incubation. (Jia et al., 2010).

Viral Control

Cyanophages, mostly belonging to the family *Myoviridae*, were found to infect *Microcystis* hosts. The average rate of infection for *Microcystis* cells varied widely, between 0.1 and 32%, and cyanophage populations were found to expand directly after cyanobacteria bloom formation. (Mankiewicz-Boczek et al., 2016).

Straw Decomposition

Derbyshire Reservoir, U.K.

50 g/m³ of decomposing barley straw was distributed over a disused water supply reservoir. Phytoplanktonic productivity and cyanobacterial dominance appeared to decline significantly, although the mechanism is unknown. (Everall & Lees, 1996).

Sonication

Canoe Brook Reservoir, New Jersey

Ultrasonic buoys were installed in a reservoir and operated for 5 months. During this period, taste and odor compounds linked to cyanobacteria were controlled, and the average alum dose used by the associated drinking water treatment plant was reduced by 22%, more than compensating for the cost of the ultrasonic treatment. (Schneider et al., 2015).

Miscellaneous Algaecides

Herbicides can also be used to control cyanobacterial blooms. However, herbicidal chemicals are nonselective, exhibiting high nontarget toxicity, and may persist in the ecosystem long after treatment. General herbicides include diuron, endothall, diquat, paraquat, atrazine, and simazine (Matthijs et al., 2016).

Quaternary ammonium compounds, commonly used in pool water, also show promise as algaecides with cyanobacteria-selective properties (Zhang et al., 2021).

Metal algaecides also include potassium- and silver-based compounds, although both lack a substantive body of research demonstrating efficacy.

Additional peroxide-based compounds include calcium peroxide (CaO₂), magnesium peroxide (MgO₂), and peracetic acid (C₂H₄O₃) (Sukeni & Kaplan, 2021). Other compounds which generate reactive oxygen species similar to peroxide-based compounds include phthalocyanines and titanium dioxide (TiO₂), though neither have been adequately tested in field studies (Jančula & Maršálek, 2011).

Many compounds isolated from biotics have shown algacidal properties, including *Ephedra equisetina* root extracts, anthraquinones, L-lysine, stilbenes (1,2-diphenylethylene congeners), alkaloid nostocarboline, isoquinoline alkaloids, and 2-methylacetoacetate. Such compounds are under investigation to determine feasibility, and most are price-prohibitive compared to more common treatments in the above section (Jančula & Maršálek, 2011; Matthijs et al., 2016).

Ozone is commonly used within treatment facilities, but emerging technologies delivering oxygen and ozone via micro- and nanobubbles have made deployment in source water feasible. These systems can

reduce anoxia in addition to controlling active blooms, but no field studies have been conducted to determine efficacy or practicality (Kibuye et al., 2021a).

Nanomaterials represent an emerging technology, with nanoparticles of zerovalent iron or silver highlighted as potential cyanobacteria-selective algaecides that, after lysing cells, generate flocculating byproducts to facilitate cell removal. Field studies and information on nontarget effects are limited but suggest high specificity and low environmental risk (Matthijs et al., 2016).

Ultraviolet light irradiation has been proposed for cyanobacterial control and has been implemented successfully in the field, but species show variable responses to this treatment and wider ecological impacts are poorly understood (Li et al., 2020).

Advanced Oxidation Processes

Eastern Qatar

Thirty-five drinking water samples were collected from public and private locations. Initial ELISA results show that all samples were below the 1 µg/L MC-LR recommendation set by WHO. Experimental design analyzed the impact of MC-LR degradation at varying ozone dosage, and the impact of degradation of constant ozone degradation at varying MC-LR concentrations. Hydrogen peroxide was used in combination with ozone at a fixed ratio of 0.25 throughout. The results showed that initial toxin concentration and organic content governed oxidant dosage. The results suggest that an ozone dosage of 0.75 mg/L would be sufficient to degrade MC-LR, since initial toxin concentrations were low. (Ponnusamy et. al 2019)

Drinking Water Treatment Plant Strategies

Veolia Water, Hackensack, New Jersey

The system utilizes pre-oxidation (via ozone), dissolved air flotation, chlorination, dual media filtration, and optional PAC addition as treatment pathways within their treatment plan. From samples collected in 2021 and 2022, all finished water results have shown treated levels below the NJDEP DSR's Guidance Values. Raw water samples showed microcystin levels between 0-0.05 µg/L, cylindrospermopsin between 0-0.09 µg/L, and anatoxin-a between 0-0.06 µg/L; finished water samples showed microcystin levels between 0-0.012 µg/L, and 0 µg/L for cylindrospermopsin and anatoxin-a. Capital costs for are estimated to have been around \$430,000 from strategy development (including predictive modeling, fishery survey, etc.), treatment implementation (including aeration system, vertical profiler, DAF sondes, etc.), and land management (including geese control, algaecide treatment, forestry management, etc.). System treatment capacity is 200 MGD.

NJWSA, Manasquan, New Jersey

Monitoring samples are collected daily (from the Manasquan River) and weekly (from the reservoir) during peak season. The system is redeveloping their source water mitigation strategy to better prevent HAB formation based on internal P loading. The system utilizes filtration, ozonation, coagulation, flocculation, and GAC as treatment pathways. The strategy is also altered annually based on weather and reservoir conditions. The system generally treats with small quantities of algaecide every other year, with a unit cost of \$6,000. Treatment firm capacity is 4 MGD.

Passaic Valley Water Commission, New Jersey

Monitoring samples are collected weekly during peak season. The system utilizes sand ballasted ACTIFLO[®] coagulation to remove bulk organic matter, phytoplankton, bacteria, etc. from raw water. This is followed

by ozonation, filtration, and chlorination for disinfection. The system determines the optimal ozone dose based on pH levels. Treatment firm capacity is 85 MGD, with average around 50 MGD; total capacity is 110 MGD.

City of Richland, Washington

The system is newly implementing sodium permanganate as a source water mitigation strategy. The capital cost estimated around \$30,000 for initial setup and tracking equipment. The system utilizes direct filtration strategies within their treatment plant. Treatment capacity is 36 MGD and 15 MGD for their two treatment plants, respectively.

Eugene Water and Electric Board, Oregon

The system utilizes coagulation, flocculation, rapid mix, sedimentation, rapid sand filtration, pre- and post-filtration pH adjustments, post-mixed oxidation, and PAC as treatment pathways.

Joint Water Commission, Oregon

The system has multiple points of monitoring at its reservoirs. The system utilizes coagulation, flocculation, rapid mix, sedimentation, rapid sand filtration, pre- and post- gas chlorination, caustic soda pH adjustment, and PAC and GAC as treatment pathways. Treatment capacity is 75 MGD.

Salem, Oregon

The system utilizes PAC and pre-ozonation for mitigation in their source water. In the treatment plant, the system utilizes coagulation, flocculation, and sedimentation, slow sand filtration, post-hypochlorination, soda ash pH adjustment, activated carbon, fluoridation, as treatment pathways.

Clackamas River Water, Oregon

The system utilizes coagulation, flocculation, and sedimentation, rapid sand filtration, hypochlorination, pre- and post- soda ash pH adjustment, activated carbon, fluoridation, as treatment pathways.