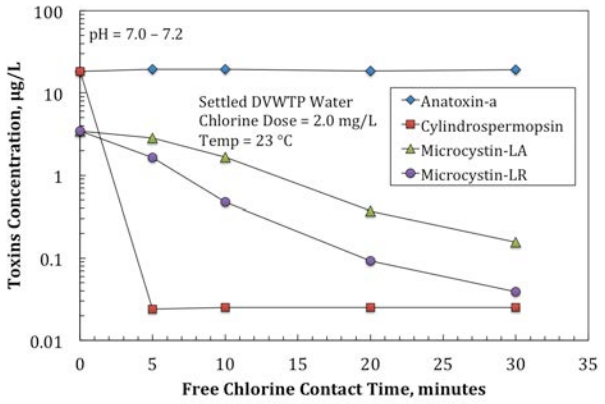

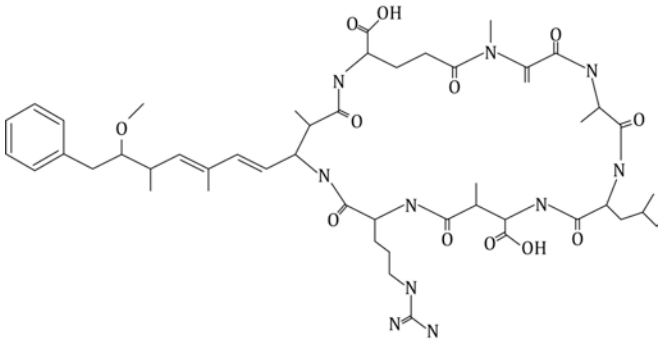

Bench-Scale Evaluation of the Potential Destruction of Cyanotoxins with Treatment Technologies Applied to South Bay Aqueduct Water

Technical Report

Prepared for

Zone 7 Water Agency

Alameda County Water District

Santa Clara Valley Water District

WQTS
Water Quality & Treatment Solutions, Inc.
An environmental engineering and science consulting company

October 5, 2015

BENCH-SCALE EVALUATION OF THE POTENTIAL DESTRUCTION OF CYANOTOXINS WITH TREATMENT TECHNOLOGIES APPLIED TO SOUTH BAY AQUEDUCT WATER

TECHNICAL REPORT

PREPARED FOR:

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EXECUTIVE SUMMARY

BACKGROUND

Cyanobacteria, formerly known as blue-green algae, are photosynthetic bacteria that are naturally present in lakes, streams, and most fresh water bodies. Under the right combination of environmental and ecological conditions, cyanobacteria can multiply into massive blooms. Many cyanobacteria produce trace chemicals that are toxic at low concentrations. These chemicals are commonly referred to as cyanotoxins, or algal toxins. The World Health Organization (WHO) has a provisional guidance value of 1 µg/L for total microcystin-LR, which is one of the most common types of cyanotoxins.[1] Cyanobacterial blooms have occurred in US water supplies for decades, but their occurrence has largely been limited to recreational waters. However, in 2014, a massive bloom in Lake Erie generated elevated levels of cyanotoxins that resulted in the breakthrough of 2.5 µg/L of microcystins into the City of Toledo's drinking water. Since this level exceeded the WHO's provisional guidance level of 1 µg/L, the City issued a "do not drink or boil" order for the tap water of half a million consumers. This event highlighted the vulnerability of drinking water to cyanotoxins.

Neither the USEPA nor the State of California currently has drinking water limits for cyanotoxins, and water utilities are not required to monitor for them in their water supplies. However, in response to the bloom in Lake Erie and its effect on the City of Toledo's drinking water, and after reviewing the available science, in 2015, the USEPA established health advisories (HAs) for two cyanotoxins: microcystin and cylindrospermopsin. The USEPA developed two 10-day HA levels for each toxin: one for infants younger than 6 years old, and one for individuals 6 years and older. The infant HA for microcystin was set at 0.3 µg/L, while that for cylindrospermopsin was set at 0.7 µg/L. Both levels are lower than the WHO guidance of 1 µg/L.

This study included a comprehensive bench-scale testing effort aimed at evaluating the efficiency of five different treatment technologies for the destruction or removal of cyanotoxins from South Bay Aqueduct (SBA) water. The study was funded jointly by the three SBA water users: Zone 7 Water Agency (Zone 7), Alameda County Water District (ACWD), and Santa Clara Valley Water District (SCVWD).

TESTING DESCRIPTION & RESULTS

Three water samples were collected and used in this study: A raw SBA sample collected from the influent to ACWD's WTP 2, a settled water sample from Zone 7's Del Valle Water Treatment Plant (DVWTP), and a settled water sample from SCVWD's Penitentia WTP. Each sample was spiked with approximately 10 µg/L of each of four cyanotoxins: 1) microcystin-LR, 2) microcystin-LA, 3) cylindrospermopsin, and 4) anatoxin-a. The raw SBA water sample was used for pre-ozonation testing and for PAC adsorption testing. The settled DVWTP water sample was used for chlorine and chloramine testing. The settled Penitentia WTP water sample was used for intermediate ozone

1 World Health Organization. *Guidelines for Drinking-Water Quality. 3rd Ed., Incorporating the first and second addenda, Volume 1, Recommendations*, Geneva (2008)

testing. Ozone, chlorine, chloramine, or PAC was added to each water sample at different doses, and some under different pH conditions. Cyanotoxin samples were then collected and analyzed using the LC/MS-MS method and the ELISA method calibrated to microcystin-LR.

CONCLUSIONS

The following table presents a summary classification of the effectiveness of each treatment technology against each type of cyanotoxin tested. A full circle indicates that the treatment technology is excellent at destroying or removing the toxin to below the HA levels, while an open circle indicates that it is ineffective against the toxin. A ¾-full circle suggests that the technology is could destroy the toxin to below the HA level, but may require a longer contact time or a higher dose than typically used. A half-full circle indicates that the technology is moderately effective, and needs to be supplemented by another technology in order to destroy the toxin to below the HA level.

Summary Classification of the Effectiveness of Each Treatment Technology for the Removal of the Cyanotoxins Evaluated in this Study

Technology	Microcystins	Cylindrospermopsin	Anatoxin-a
Ozone	●	●	●
Free chlorine	◕	●	○
PAC Adsorption	◒	◒	◒
Chloramine	○	○	○

● Excellent ◕ Good ◒ Moderate ○ Ineffective

"Excellent" = the technology can reliably reduce the toxin to below the HA level.
"Very good" = the technology is could destroy the toxin to below the HA level, but may require a longer contact time or a higher dose than typically used.
"Moderate" = the technology is moderately effective, and needs to be supplemented by another technology in order to destroy the toxin to below the HA level.
"Ineffective" = the technology did not reduce the toxins by any measurable amount under the conditions evaluated in this study.

As shown in above, the following is a synopsis of the findings of this study:

1. *Typical ozone doses used at SBA plants, whether on raw water or settled water, are highly effective at destroying all three types of toxins tested in this study.*
2. *Chlorine is highly effective at destroying cylindrospermopsin and virtually ineffective against anatoxin-a. Chlorine can destroy microcystins below the HA level, but requires longer contact time*

and can be assisted by a low(er) water pH compared to its effectiveness against cylindrospermopsin.

3. *Adsorption of the three types of toxins on Hydrodarco B (HDB) PAC was moderate. Effective control of toxins to below the HA levels requires coupling of PAC with another treatment technology.*
4. *Chloramine is ineffective against the types of toxins tested.*

Finally, one remaining challenge to the application of preozonation to SBA water within the context of cyanotoxins treatment is to develop an understanding of the ozone dose required to lyse the cyanobacterial cells that may be present in the raw water before the ozone can destroy the toxins that may be released from the inside of the cells. This study was not able to quantify this dose.

1.1 – BACKGROUND

Cyanobacteria, formerly known as blue-green algae, are photosynthetic bacteria that are naturally present in lakes, streams, and most fresh water bodies. They share key properties with algae in that they possess *chlorophyll-a* and produce oxygen during photosynthesis. However, they differ from algae in that they do not have a membrane-bound nucleus (i.e., they are prokaryotes while algae are eukaryotes). Nonetheless, due to their similarity to algae, their blooms have long been referred to as algal blooms, and for the purpose of this report, will be referred to interchangeably as cyanobacteria or algae.

Under the right combination of environmental and ecological conditions, cyanobacteria can multiply into massive blooms that extend for miles. The adjacent photograph shows a bloom in Lake St. Claire, which is part of the Great Lakes system between the US and Canada. The southern shoreline dominated by the algae bloom in the photograph is approximately 25 miles long.

http://eoimages.gsfc.nasa.gov

Figure 1.1 – Algae Bloom in Lake St. Claire (the Great Lakes)

Many cyanobacteria produce trace chemicals that are toxic at low concentrations. These chemicals are commonly referred to as cyanotoxins, or algal toxins. The World Health Organization (WHO) has a provisional guidance value of 1 µg/L for total microcystin-LR, which is one of the most common types of cyanotoxins.[2] Cyanobacterial blooms have occurred in US water supplies for decades, but their occurrence has largely been limited to recreational waters. However, in 2014, a massive bloom in Lake Erie generated elevated levels of cyanotoxins that resulted in the breakthrough of 2.5 µg/L of microcystins into the City of Toledo's drinking water. Since this level exceeded the WHO's provisional guidance level of 1 µg/L, the City issued a "do not drink or boil" order for the tap water of half a million consumers. This event highlighted the vulnerability of drinking water to cyanotoxins.

1.2 – REGULATORY REQUIREMENTS

Neither the USEPA nor the State of California currently has drinking water limits for cyanotoxins, and water utilities are not required to monitor for them in their water supplies. However, in response to the bloom in Lake Erie and its effect on the City of Toledo's drinking water, and after reviewing the available science, in May 2015, the USEPA established health advisories (HAs) for two cyanotoxins: microcystin and cylindrospermopsin. In addition, the Ohio EPA issued HAs for two other toxins: anatoxin-a, and saxitoxins. Microcystin and cylindrospermopsin are more

2 World Health Organization. *Guidelines for Drinking-Water Quality. 3rd Ed., Incorporating the first and second addenda, Volume 1, Recommendations*, Geneva (2008)

commonly generated in freshwater cyanobacterial blooms. The USEPA developed two 10-day HA levels for each toxin: one for infants younger than 6 years old, and one for individuals 6 years and older. These levels are listed in Table 1.1. While the range in HA levels between those for infants < 6 years old and those for individuals ≥ 6 years old is 4 to 5 fold, it would be difficult for a water system to publicly justify accepting a value higher than the infant HA value, which in essence sets the goal for a water system at the infant HA values.

Table 1.1 – 10-Day Health Advisory (HA) Levels Set by the USEPA for Microcystin and Cylindrospermopsin, and by the Ohio EPA for Anatoxin-a and Saxitoxins

Toxin	"Do Not Drink" for Infants Younger than 6 years old and Sensitive Populations(1)	"Do Not Drink" for Individuals 6 years and older
Microcystin(2)	0.3 µg/L	1.6 µg/L
Cylindrospermopsin(2)	0.7 µg/L	3 µg/L
Anatoxin-a(3)	20 µg/L	20 µg/L
Saxitoxins(3)	0.2 µg/L	0.2 µg/L

(1) These include pregnant women, nursing mothers, those receiving dialysis treatment, the elderly, and immune-compromised individuals.
(2) USEPA HA levels
(3) Ohio EPA HA levels

HAs are different from Maximum Contaminant Levels (MCLs) in that they are not enforceable standards, and a water system is not required to monitor for chemicals that have HAs. The USEPA has HAs for a number of chemicals that do not have drinking water standards. The challenge for a water system is to decide whether to monitor for chemicals with HAs, how frequently to monitor for them, and what to do if the HAs are exceeded in its drinking water when all drinking water standards are met. However, for cyanotoxins, considering the acute health effect of the toxins of concern, and the fact that the cyanobacterial blooms are highly visible, it is important for a water agency to have plans in place that include measures to minimize the occurrence of cyanobacterial blooms in the water source, and to have treatment barriers that would destroy or remove potential toxins from the water and prevent them from entering the drinking water system. In addition, it is important to note that cyanotoxins were listed in the USEPA's draft Contaminant Candidate List 4 (CCL4) published in February 2015 and cyanotoxins are likely to be included in the Unregulated Contaminant Monitoring Rule 4 (UCMR4) anticipated to be published during the later part of 2015.

The Zone 7 Water Agency (Zone 7), Alameda County Water District (ACWD), and Santa Clara Valley Water District (SCVWD) rely on the same water source, the South Bay Aqueduct (SBA), which conveys water from the Sacramento-San Joaquin Delta through Alameda and Santa Clara Counties. The three agencies pooled resources and jointly funded a study to evaluate the efficiency of their treatment systems at destroying cyanotoxins if a cyanobacterial bloom were to occur in the Delta or

the SBA. Blooms could also occur in Dyer Reservoir, Patterson Reservoir, or Lake Del Valle, all of which are storage reservoirs along the SBA. This technical report documents the study and its results.

1.3 – STUDY OBJECTIVE

This study aimed at quantifying the efficiency of five (5) treatment barriers employed at the water treatment plants of the three SBA agencies: Zone 7, ACWD, and SCVWD against four (4) potential cyanotoxins. The five treatment technologies evaluated include the following:

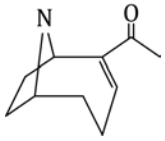
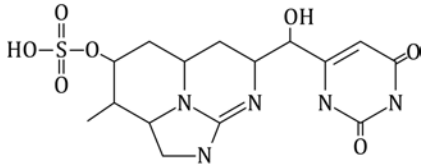
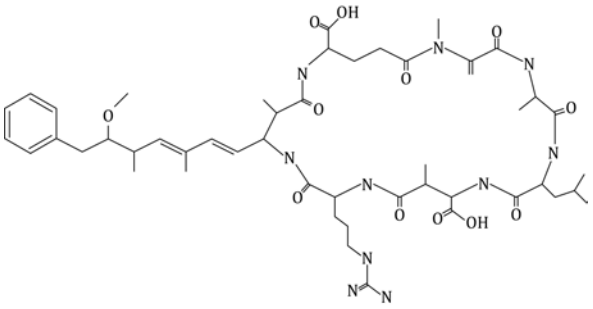
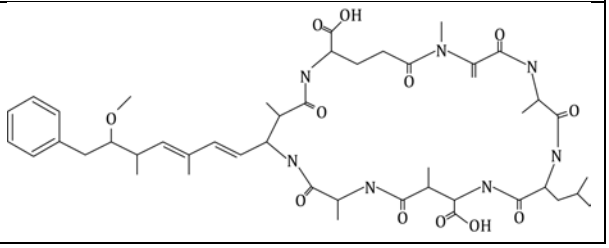
1. *Ozone applied to raw water (i.e., preozonation)*
2. *Ozone applied to settled water (i.e., intermediate ozonation)*
3. *Chlorine*
4. *Chloramine*
5. *Powdered Activated Carbon (PAC) adsorption*

The four cyanotoxins used in this study are listed in Table 1.2, along with their chemical formula, type of toxicity, and molecular structure. Microcystin and anatoxin-a have been identified in California freshwater bodies, and are the State's most commonly detected algal toxins.[3] Microcystins are the most numerous of the algal toxin compounds as there are more than 100 congeners (forms) of this compound. Microcystin LR and LA were used in this study because their adsorbability onto activated carbon has been found to differ (Newcombe et al. 2002).[4] Cylindrospermopsin is a toxin produced by *Cylindrospermopsis*, one of the more common genera of cyanobacteria found in California.

3 *Draft Voluntary Statewide Guidance for Blue-Green Algae Blooms, Blue Green Algae Work Group of the SWRCB, CDPH and OEHHA (July 2010)*

4 *Newcombe, G. 2002. Removal of Algal Toxins from Drinking Water Using Ozone and GAC. Water Research Foundation, Denver CO.*

Table 1.2 – The Four Cyanotoxins Evaluated in this Study

Toxin	General Information	Molecular Structure
Anatoxin-a	Formula: $C_{10}H_{15}NO$ Toxicity: Neurotoxin	
Cylindrospermopsin	Formula: $C_{15}H_{21}N_5O_7S$ Toxicity: Liver & Kidney	
Microcystin-LR	Formula: $C_{49}H_{74}N_{10}O_{12}$ Toxicity: Liver (hepatotoxin)	
Microcystin-LA	Formula: $C_{46}H_{67}N_7O_{12}$ Toxicity: Liver (hepatotoxin)	

The SBA was constructed between 1960 and 1965 as the first Delta water delivery system under the State Water Project (SWP). The SBA begins at Bethany Reservoir with a pumping plant that lifts the water 566 feet before it flows by gravity through a combination of open channels, pipes, and tunnels that traverse Alameda County and part of Santa Clara County before ending in the Santa Clara Terminal Reservoir located at SCVWD's Penitencia WTP. This section presents brief information about each of the SBA agencies, and describes its main water treatment plant that was the focus of this study.

2.1 – ZONE 7 WATER AGENCY

The Zone 7 Water Agency treats SBA water at two surface water treatment plants: The Patterson Pass Water Treatment Plant (PPWTP) and the Del Valle Water Treatment Plant (DVWTP). The focus of this study was on the DVWTP whose process flow schematic is shown in Figure 2.1. The DVWTP is a 40-MGD conventional filtration plant that uses chlorine to meet its *Giardia* and virus disinfection requirements through the filters and a filter overflow structure before ammonia is added to convert the chlorine to chloramine in the treated water. While DVWTP does not have a permanent PAC feed system, Zone 7 has the ability to lease a PAC feed system for use at the plant, which it has done in past years when experiencing taste-and-odor (T&O) episodes in the SBA.

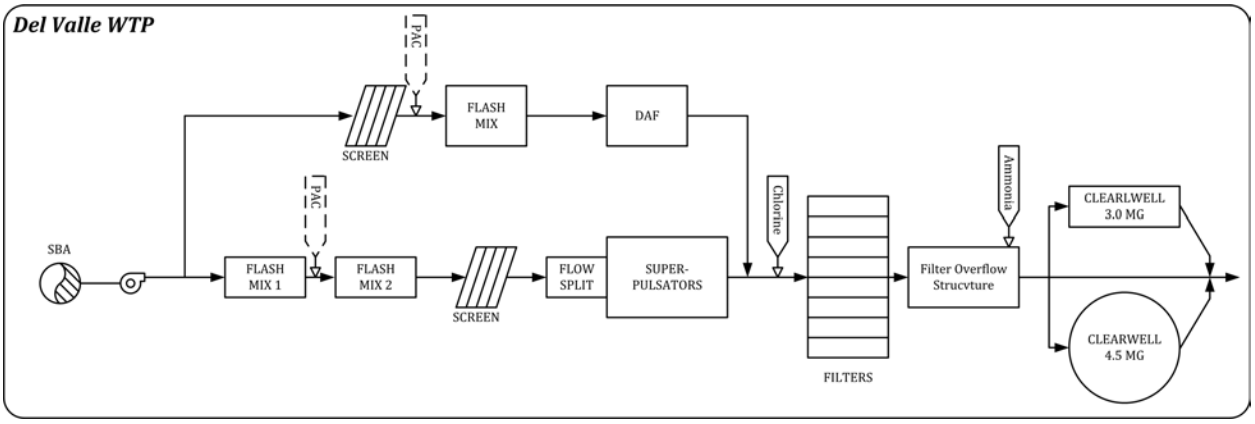


Figure 2.1 – Process flow diagram of Zone 7's DVWTP showing the locations of the chemical additions relevant to Cyanotoxins removal or destruction

For the DVWTP, the three potential technologies for cyanotoxins control are 1) adsorption on PAC, 2) destruction with free chlorine, and 3) destruction with chloramine.

2.2 – ALAMEDA COUNTY WATER DISTRICT

ACWD owns and operates two surface water treatment plants named Mission San Jose WTP (MSJWTP) and WTP 2. MSJWTP was built as a 10 MGD conventional filtration plant, which was then converted to a membrane filtration plant. MSJWTP is currently planned for decommissioning. WTP 2 is a 28 MGD conventional filtration plant with preozonation. Figure 2.2 shows a schematic process flow diagram of the plant showing the chemicals relevant to cyanotoxins destruction. CO_2 is added to the raw water on a continuous basis to stabilize the water pH before it enters the ozone contactor. Low doses of chlorine and ammonia can be added to the ozone contactor influent to suppress bromate formation when the bromide level in the raw water is elevated. At the design flow of 28 MGD, the average hydraulic retention time through the ozone contactors is 12 minutes. After preozonation, coagulation, flocculation, sedimentation, and biological filtration, chlorine is added to the influent of the clearwell, which has a volume of 73,000 gallons. Ammonia is added at the clearwell outlet to convert the free chlorine to chloramine.

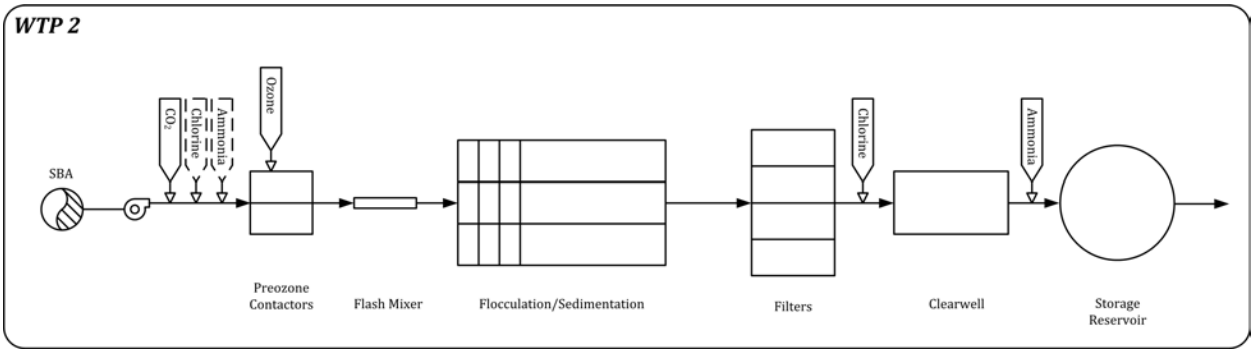


Figure 2.2 – Process flow diagram of ACWD's WTP2 showing the locations of the chemical additions relevant to Cyanotoxins removal or destruction

At a flowrate of 20 MGD (e.g., typical summer rate), the average free chlorine contact time through the clearwell is calculated at approximately 5 minutes. At a flowrate of 10 MGD, this average free chlorine contact time increases to 10 minutes.

For ACWD's WTP 2, the three potential technologies for cyanotoxins control are 1) destruction with preozone, 2) destruction with free chlorine, and 3) destruction with chloramine.

2.3 – SANTA CLARA VALLEY WATER DISTRICT

SCVWD owns and operates three surface water treatment plants: The Penitencia WTP (42 MGD), the Rinconada WTP (80 MGD), and the Santa Teresa WTP (100 MGD). All three plants are conventional filtration WTPs with chlorine disinfection and chloramine in the distribution system. However, the Penitencia WTP and Santa Teresa WTP include intermediate ozonation, while the Rinconada WTP is currently being retrofitted with preozonation. Since SCVWD is the only SBA

agency with intermediate ozonation, settled water from the Penitencia WTP was used for testing toxins destruction with intermediate ozonation.

Figure 2.3 shows a process flow schematic of the Penitencia WTP. The plant includes a PAC feed system that SCVWD can use when needed. SCVWD has a hydrogen peroxide (H_2O_2) feed system that can feed H_2O_2 to the influent of the intermediate ozone contactor, if needed, to improve T&O control. At the design flow of 40 MGD, the average hydraulic retention time through the ozone contactors is 10 minutes. Chlorine is added at the influent to the 3.2-MG clearwell and ammonia is added at the outlet of the clearwell to convert the residual chlorine to chloramine. At the plant's full capacity of 42 MGD, the average chlorine contact time through the clearwell is estimated at 100 minutes. At half the design capacity, the average contact time increases to about 3.3 hours.

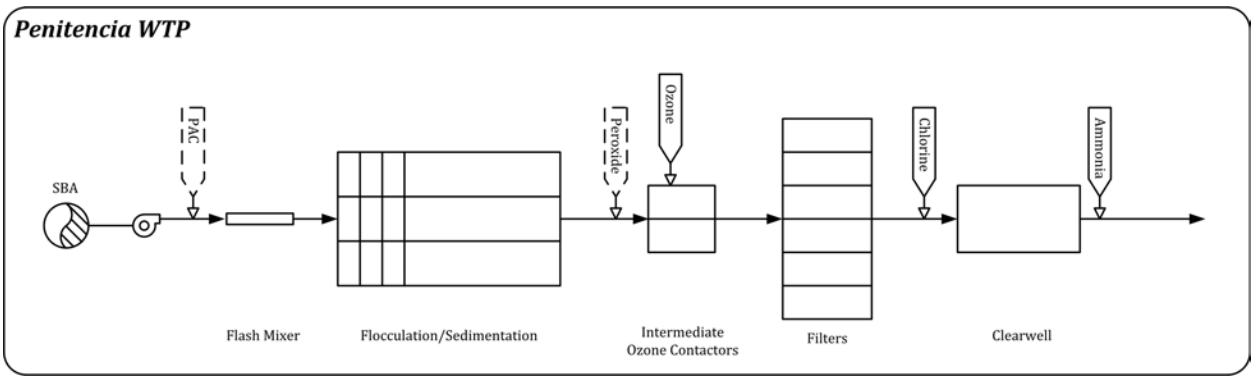


Figure 2.3 – Process flow diagram of SCVWD's Penitencia WTP showing the locations of the chemical additions relevant to Cyanotoxins removal or destruction

For SCVWD's Penitencia WTP, the four potential technologies for cyanotoxins control are 1) removal with PAC, 2) destruction with intermediate ozone, 3) destruction with free chlorine, and 4) destruction with chloramine.

2.4 – SUMMARY

In summary, all three agencies utilize several technologies that have the potential to destroy or remove cyanotoxins from the water. Table 2.1 presents a summary of these technologies for each of the three plants discussed in this section. Zone 7's DVWTP has chlorine and chloramine contact before the water is served to the retail agencies. Zone 7 also has the ability to temporarily add PAC at the DVWTP. ACWD's WTP 2 includes preozonation, and has free chlorine and chloramine contact times before the water enters the distribution system. SCVWD's Penitencia WTP includes an optional PAC addition, intermediate ozonation, as well as free chlorine and chloramine contact before the water is served into the system.

Table 2.1 – Summary of potential Cyanotoxins treatment technologies employed at each of the three WTPs evaluated in this study

Technology	Zone 7 Water Agency (DVWTP)	Alameda County Water District (WTP2)	Santa Clara Valley Water District (Penitencia WTP)
Preozone		✓	
Intermediate Ozone			✓
Chlorine	✓	✓	✓
Chloramine	✓	✓	✓
PAC Adsorption	✓		✓

All bench-scale testing was conducted at WQTS' laboratory in Los Angeles, California. A raw SBA water sample was collected from the influent of ACWD's WTP2 and used in preozone testing and PAC adsorption testing. A settled water sample was collected from Zone 7's DVWTP and used in chlorine and chloramine testing. Finally, a settled water sample was collected from SCVWD's Penitencia WTP and used for intermediate ozone testing. All three water samples were filtered through a 1-µm filter paper before testing for the purpose of removing particulate matter that may have interfered with the analytical methods employed in the study. The selection of the large size of 1–µm paper ensured that the filtration step did not alter the dissolved constituents of the water, especially the dissolved organic matter, which is expected to have direct bearing on the results of the study.

3.1 – MATERIALS

Stocks of each of the four cyanotoxins were purchased from two suppliers: Cayman Chemical (Ann Arbor, MI) and Enzo Life Sciences, Inc. (Farmingdale, NY). The 100-µg microcystin LA and LR stocks obtained from Cayman Chemical were stored in methanol and ethanol, respectively, while the 100-µg cylindrospermopsin stock was a dry powder. The toxins obtained from Enzo Life Sciences, Inc. were all dry powder, including a 1-mg anatoxin-a stock. During preliminary ozone testing, and after consultation with Dr. Carrie Guo of the Metropolitan Water District of Southern California, it was determined that the liquid stocks cannot be used for testing because methanol, and possibly ethanol, added a high ozone demand to the water. Therefore, all ozone testing in this study was conducted using powder stocks of toxins. Some of the methanol and ethanol stocks were used in the chlorine and chloramine testing since preliminary testing showed no impact on the chlorine or chloramine demand of the water. Hydrodarco B PAC was used in this study (Norit Americas, Inc.). A slurry of the PAC was prepared and allowed to wet for 24 hours before it was used in the testing.

During the course of the project, several attempts were made to obtain algae stocks from California recreational lakes that were experiencing toxic algae blooms. The intent was to take aliquots from these blooms and add them to the SBA water sample used in the study. However, as shown later in this report, the levels in the recreational lake samples, including those inside the algae cells, were not high enough to allow their use in this study.

3.2 – EXPERIMENTAL METHODS

All testing was conducted in a batch mode in which the water was spiked with the four toxins at a target of 10 µg/L each, separated into glass bottles as needed for each test, and then the chemical was added to the bottle at the target dose. Samples were then collected from each bottle at predetermined times and poured into the analytical bottles provided by Eurofins Eaton Analytical (EEA) Laboratories (Monrovia, CA). For the PAC testing, the samples were filtered through 0.45 µm filter paper directly into the analytical bottles.

A bench-scale ozone generator was used to generate a high concentration ozone stock solution in distilled water (approximately 30 mg/L). Aliquots of this stock ozone solution were then spiked into 150-mL of test water samples. Chlorine solutions were prepared from a commercial hypochlorite solution (Spectrum Chemicals, Gardena, CA). For chloramine testing, it was important not to add the chlorine and ammonia sequentially because it would run the risk of exposing the toxins to free chlorine. Therefore, a preformed monochloramine solution was prepared in distilled water that was adjusted to pH 9.5 with sodium hydroxide. The monochloramine concentration was verified before its use.

3.3 – ANALYTICAL METHODS

All toxins samples were analyzed by EEA Laboratories using two methods: Liquid chromatography coupled with tandem Mass Spectrometry (LC/MS-MS) and Enzyme Linked Immunosorbent Assay (ELISA) calibrated for microcystin-LR. The LC/MS-MS method quantifies individual toxins, while the ELISA method quantifies the total microcystins only. There are dozens of microcystin "congeners", where a congener refers to a unique variation on the microcystin molecule. For example, the microcystin-LR and microcystin-LA used in this study are two congeners of microcystin. It is noted that when USEPA released the HAs in June 2015 the Agency recommended that utilities use the ELISA method for monitoring total microcystins in raw and treated water, and not the LC/MS-MS method. The rationale is that the LC/MS-MS method does not yet identify all the microcystin congeners, whereas the ELISA method does. However, since the ELISA method is an indirect measurement of the concentration of the microcystins, there is uncertainty in the water community about its accuracy under all conditions. It is also important to note that, while the ELISA method is supposed to quantify all microcystins, it is usually calibrated to one of them (for example, the one used by EEA for this study was calibrated to MC-LR). While it also picks up MC-LA, it is not a 1:1 relationship. In other words, a 1µg/L of MC-LA may be quantified by the ELISA method used at only 0.6 µg/L.

All ozone residual measurements were made using the Indigo Method (Standard Method 4500-O3 B). Free and total chlorine concentrations were measured using the DPD Method on a HACH DR890 instrument (HACH Co., Fort Collins, CO). Monochloramine was measured using the monochlor-F method on the HACH DR890 instrument.

SECTION 4.0 – TESTING RESULTS

The water samples used in this study were collected from three locations: SBA raw water was collected from the influent to ACWD's WTP2, settled water collected from Zone 7's DVWTP, and settled water collected from SCVWD's Penitencia WTP. The dates the three samples were collected, and their general chemical qualities, are presented in Table 4.1. Raw SBA water was used for preozonation testing and for PAC adsorption testing. The TOC of the SBA water was relatively high at 6.2 mg/L. On the other hand, its inorganic quality was typical, including bromide of 0.22 mg/L, pH of 8.46, alkalinity of 79 mg/L as $CaCO_3$, and a conductivity of 539 µS/cm.

Settled DVWTP water was used for chlorine and chloramine testing. At the time of sampling, the DVWTP was operating with a high ferric chloride dose (>50 mg/L), which explains the low TOC of 1.92 mg/L, as well as the low pH of 6.04 and low alkalinity of 20 mg/L as $CaCO_3$. Settled Penitencia WTP water was used for intermediate ozonation testing. The settled water from the plant had a moderate TOC of 3.64 mg/L, as well as moderate pH of 7.46 and alkalinity of 68 mg/L as $CaCO_3$. The hardness of the Penitencia WTP water was measured at 168 mg/L as $CaCO_3$ compared to that measured in the raw SBA water (86 mg/L as $CaCO_3$) or settled DVWTP water (90 mg/L as $CaCO_3$). This was likely due to the difference in the Lake Del Valle blend into the SBA between the sampling dates. It is noted that all water samples were filtered through 1-µm filter paper before they were used in the testing in order to eliminate any potential effect of particulate matter on the analytical methods employed in the study. With the choice of the large-size filter paper, the filtration step did not have any effect on the dissolved constituents of each water sample.

Table 4.1 – Quality of the Water Samples Used in this Study

Parameter	Unit	SBA Raw	Del Valle WTP Settled Water	Penitencia WTP Settled Water
Sampling Date	--	4/29/15	4/27/15	5/27/15
TOC	mg/L	6.2	1.92	3.64
UV-254 (filtered)	cm^{-1}	0.170	0.039	0.052
Bromide	mg/L	0.22	0.22	0.361
pH	--	8.46	6.04	7.46
Alkalinity	mg/L $CaCO_3$	79	20	68
Hardness, Total	mg/L $CaCO_3$	86	90	168
Conductivity	µS/cm	539	586	750
Turbidity	NTU	5.1	0.7	0.8
Anatoxin-a	µg/L	<0.02	<0.02	<0.02
Cylindrospermopsin	µg/L	<0.05	<0.05	<0.05
Microcystin-LR	µg/L	<0.1	<0.1	<0.1
Microcystin-LA	µg/L	<0.1	<0.1	<0.1

4.1 – DESTRUCTION WITH PREOZONATION

The destruction of algal toxins with raw water ozonation (i.e., preozonation) was evaluated under typical operating conditions at ACWD's WTP2. ACWD uses carbon dioxide, CO_2, to neutralize the wide fluctuations in raw water pH caused by diurnal algal activity in the SBA. Since the pH typically fluctuates between 7.5 and 9.5, ACWD varies the CO_2 dose to maintain a pH of approximately 7.2 entering the ozone contactor. This was the primary pH condition used in the preozonation testing.

To maintain bromate control, ACWD adds low doses of chlorine and ammonia to form chloramine in the water entering the ozone contactor. The chloramine concentration is typically 1.0 mg/L. As part of this study, the effect of chloramine addition for bromate control on the destruction of algal toxins at pH 7.2 was evaluated.

As an alternative to prechloramine addition, ACWD can also achieve bromate control by increasing the CO_2 dose to lower the pH to approximately 6.5. Therefore, the destruction of algal toxins with preozonation at pH 6.5 was also evaluated.

Figure 4.1 shows a plot of the ozone residual vs ozone dose applied to raw SBA water at pH 7.2 with a contact time of 2 minutes. The plot shows that the 2-minute demand of the water was 3 mg/L, with a linearly higher residual present in the water with increasing ozone dose above 3 mg/L. Figure 4.2 shows a plot of the rate of ozone decay in raw SBA water at the two pH values of 7.2 and 6.5. The ozone dose was 3 mg/L and no prechloramine was added. While the residual value at 2 minutes was at or below 0.05 mg/L, the ozone residual at 30 seconds and 1 minute were measurably higher. This emphasizes the point that, while the 2-minute ozone residual was virtually zero at a dose of 3 mg/L, the algal toxins did get exposed to ozone between ozone addition and ozone reaching a non-detectable residual value.

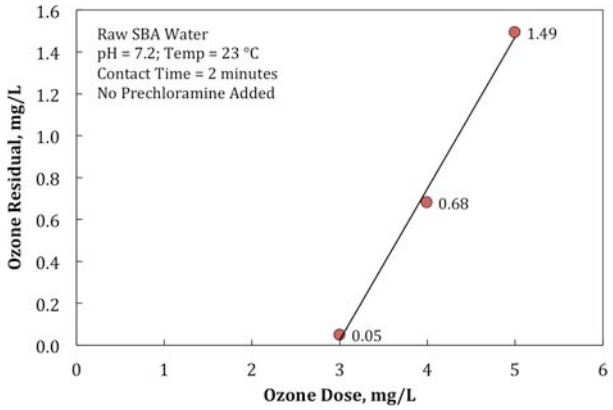


Figure 4.1 – 2-minute ozone demand in raw SBA water at pH 7.2

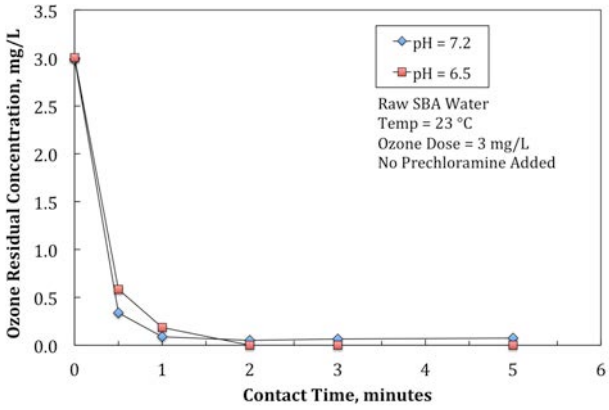


Figure 4.2 – Decay of ozone in raw SBA water at pH values of 7.2 and 6.5

Figures 4.3 and 4.4 show profiles of the spiked toxins in SBA water exposed to various ozone doses for a contact time of 10 minutes. Figure 4.3 shows the results at pH 7.2, and Figure 4.4 shows the results at pH 6.5. For the two microcystins (i.e., LR & LA), an ozone dose of 1 mg/L was sufficient to reduce their concentrations at pH 7.2 from as high as 22 µg/L to well below 0.5 µg/L (>97.8% destruction). A dose of 2 mg/L ozone was required to completely destroy anatoxin-a and cylindrospermopsin. Figure 4.4 shows very similar destruction profiles at pH 6.5 compared to those at pH 7.2 in Figure 4.3. It is noted that ozone doses of only 1 and 3 mg/L were evaluated at pH 6.5, while ozone doses of 1, 2, and 3 mg/L were evaluated at pH 7.2.

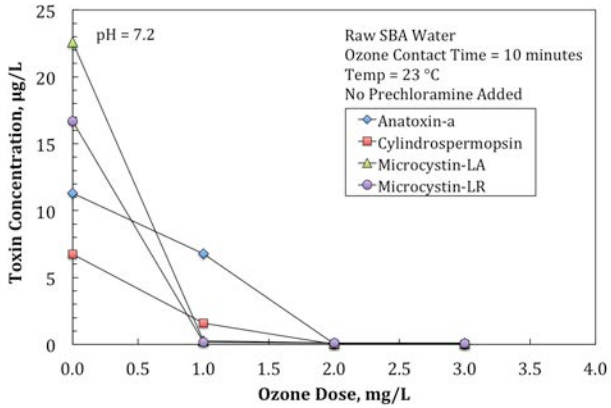


Figure 4.3 – Impact of ozone dose on toxins destruction in raw SBA water at pH 7.2

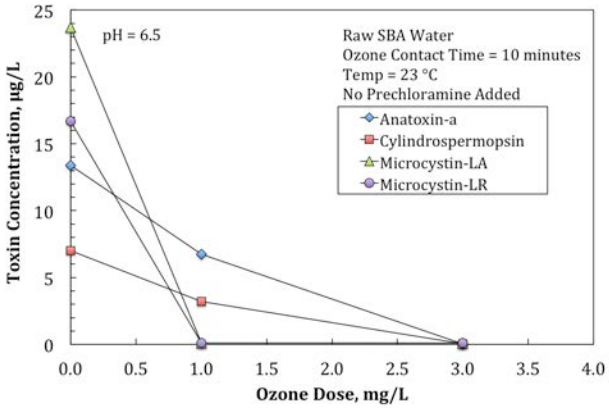


Figure 4.4 – Impact of ozone dose on toxins destruction in raw SBA water at pH 6.5

Figure 4.5 presents the results of the ELISA method analysis and compares them to the infant HA level of 0.3 µg/L. The data are presented for all pH and prechloramination conditions evaluated. The testing results show that a preozone dose greater than 1 mg/L destroyed the microcystins from an influent of approximately 20 µg/L to below the infant HA level of 0.3 µg/L regardless of water pH (between 6.5 and 7.2) and prechloramine dose (between 0 and 1 mg/L). Similarly, Figure 4.6 compares the cylindrospermopsin levels to the infant HA level of 0.7 µg/L. The results show that a dose of 1.5 or 2 mg/L destroys this toxin from its spiked level of approximately 7 µg/L to well below the infant HA level of 0.7 µg/L.

In summary, the preozonation results show that a conservative preozone dose of 2 mg/L is sufficient to reduce all four toxins from a high of 25 µg/L to non-detectable levels, and achieve compliance with the new HA levels issued by the US EPA.

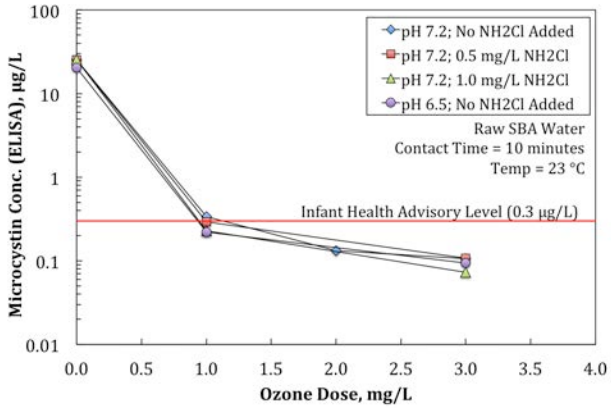


Figure 4.5 – Impact of ozone dose, pH, and prechloramine dose on microcystin levels as measured by the ELISA method

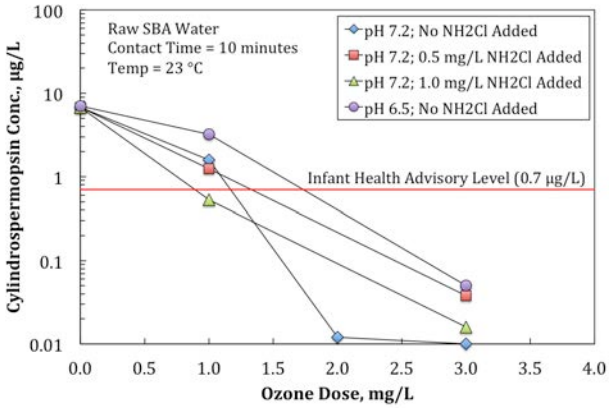


Figure 4.6 – Impact of ozone dose, pH, and prechloramine dose on the destruction of cylindrospermopsin with preozonation

4.2 – DESTRUCTION WITH INTERMEDIATE OZONATION

Intermediate ozonation testing was conducted on settled water from SCVWD's Penitencia WTP. The settled water was filtered through a 1–µm filter paper to remove suspended matter that may interfere with the analytical method used (e.g., ozone analysis, toxins analysis, etc.). Testing was conducted at two pH conditions (6.5 and 7.5), and the impact of H_2O_2 addition on the destruction of algal toxins was evaluated.

Figure 4.7 compares the rate of ozone decay in settled Penitencia WTP water compared to raw SBA water. While a dose of 3 mg/L added to raw water dissipated to <0.05 mg/L in 2 minutes, a dose of 2 mg/L applied to settled water did not decay to <0.05 mg/L until after 5 minutes of contact time. The full decay profile in settled water was only conducted with a dose of 2 mg/L and a pH of 6.5. However, Figure 4.8 shows a comparison between the 2-minute ozone residual values measured under the three intermediate ozonation conditions evaluated (i.e., pH and H_2O_2 addition). At a pH of 6.5, without H_2O_2 addition, the residual ozone remaining in the water after two minutes of contact time was still relatively high (0.62 mg/L). However, at the same pH of 6.5, with the addition of 0.5 mg/L H_2O_2, the ozone residual dissipated to 0.09 mg/L within two minutes of contact time. At pH 7.5 without H_2O_2 addition, the ozone residual dissipated to 0.08 mg/L within two minutes of contact time. These observations confirm the known fact that ozone decay is accelerated at higher pH and/or with the addition of H_2O_2.

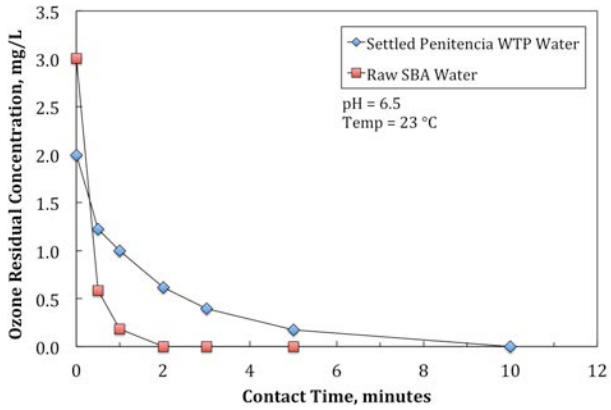


Figure 4.7– Differences in rate of ozone decay between raw and settled SBA water

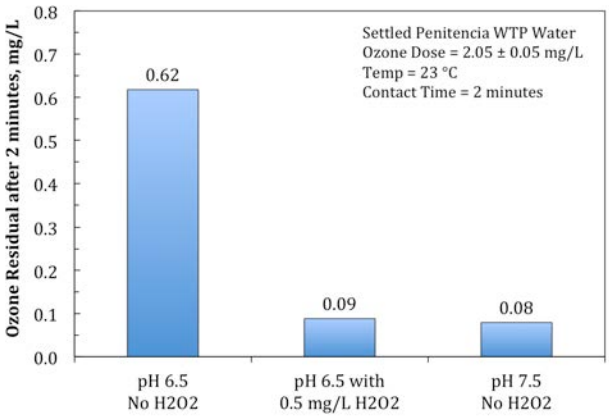


Figure 4.8 – Impact of pH and hydrogen peroxide addition on the 2-minute ozone residual

Figures 4.9 and 4.10 show the destruction of all four toxins at pH 6.5 without H_2O_2 addition and with the addition of 0.5 mg/L H_2O_2, respectively. There are noticeable differences in toxins destruction at an ozone dose of 0.5 mg/L where the addition of 0.5 mg/L H_2O_2 appears to hinder the ozone's ability to destroy anatoxin-a and cylindrospermopsin. This is likely due to the rapid loss of ozone with the addition of hydrogen peroxide. However, all four toxins are reduced to <0.3 µg/L at an ozone dose of 1.0 mg/L and higher, regardless of whether or not 0.5 mg/L H_2O_2 is added to the water upstream of ozone addition.

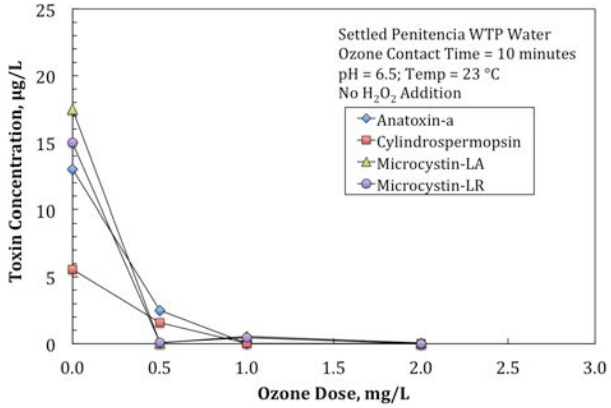


Figure 4.9 – Toxins destruction as a function of intermediate ozone dose at pH 6.5 and no H_2O_2 addition

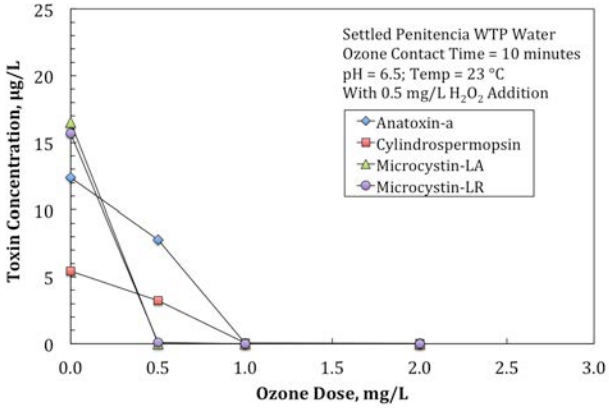


Figure 4.10 – Toxins destruction as a function of intermediate ozone dose at pH 6.5 and the addition of 0.5 mg/L H_2O_2

Similarly, Figure 4.11 shows the destruction of all four toxins with intermediate ozonation at pH 7.5 without H_2O_2 addition. At a dose of 1.0 mg/L and higher, all toxins are reduced to very low levels. Figure 4.12 presents the results from the most recalcitrant toxin, anatoxin-a. The toxin concentration is plotted on a log-scale to highlight the concentrations reached at high(er) ozone

doses. The plot shows the addition of 1.0 mg/L ozone destroyed anatoxin-a from approximately 12 µg/L to less than 0.1 µg/L under all three combinations of pH and H_2O_2 evaluated.

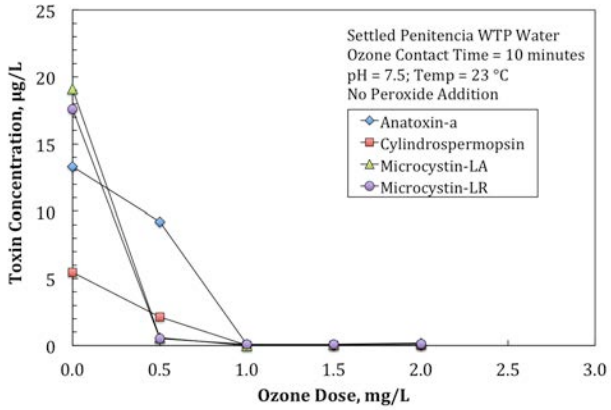


Figure 4.11 – Toxins destruction as a function of intermediate ozone dose at pH 7.5 and no H_2O_2 addition

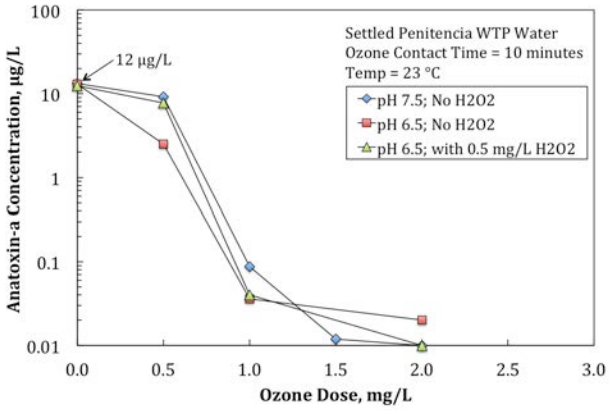


Figure 4.12 – Impact of intermediate ozone dose on the destruction of anatoxin-a under all pH and H_2O_2 conditions evaluated

Finally, Figures 4.13 and 4.14 show the levels of microcystins (measured using the ELISA method) and cylindrospermopsin achieved under all conditions and compares them to their respective infant HA levels of 0.3 µg/L and 0.7 µg/L, respectively. The results clearly demonstrate that intermediate ozonation at a dose of 1.0 mg/L or higher met the HA levels with a significant safety margin under all conditions tested.

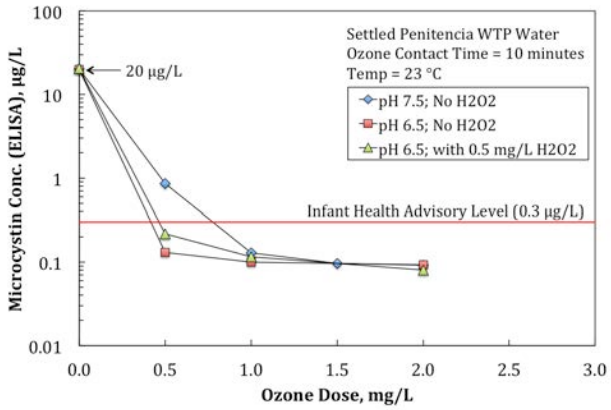


Figure 4.13 – Impact of intermediate ozone dose on the destruction of microcystins as measured by the ELISA method

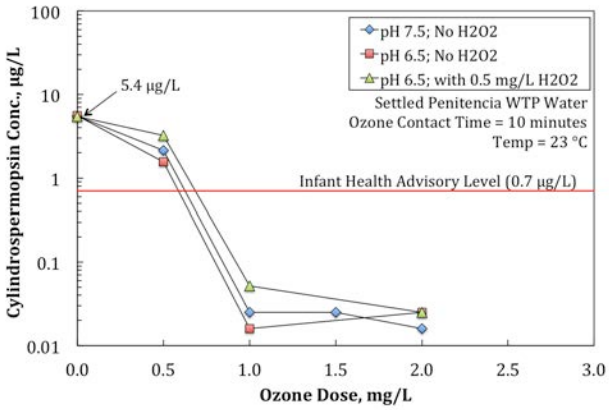


Figure 4.14 – Impact of intermediate ozone dose on the destruction of cylindrospermopsin

4.3 – DESTRUCTION WITH CHLORINE

The destruction of all four toxins with free chlorine was evaluated using settled water from DVWTP that had been filtered through a 1-µm filter paper to remove suspended material that might interfere with the analytical methods. With the high ferric chloride dose applied at DVWTP, the settled water pH can be as low as 6.0. Therefore, for the purpose of this study, the destruction of oxidants with chlorine was evaluated at two pH values: 6.0 and 7.0. During the test, the pH drifted slightly upwards resulting in a range of 6.0 to 6.2 and 7.0 to 7.2. The maximum contact time evaluated was only 30 minutes since all SBA agencies maintain chloramine in their distribution systems.

Figures 4.15 and 4.16 present information on the chlorine demand of the test water sample. When dosed with approximately 2 mg/L, the chlorine residual decreased to approximately 1.5 mg/L within the 30 minute contact period as shown in Figure 4.15. Figure 4.16 shows the 30-minute residual after the addition of three different chlorine doses: 1, 2, and 3 mg/L at the two pH values evaluated. The profile shows that the 30-minute chlorine demand is approximately 0.75 mg/L with no difference between the two pH values.

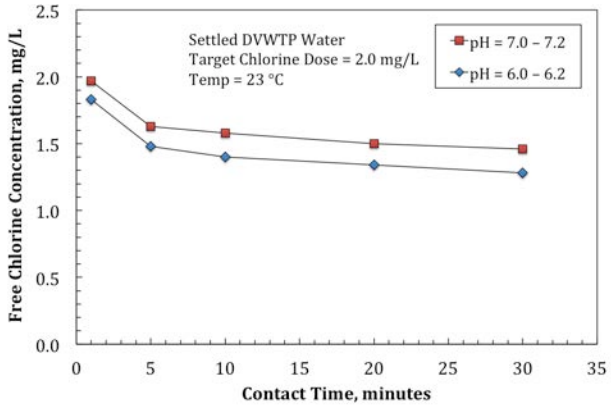


Figure 4.15 – Rate of decay of 2 mg/L chlorine added to DVWTP settled water at two pH levels

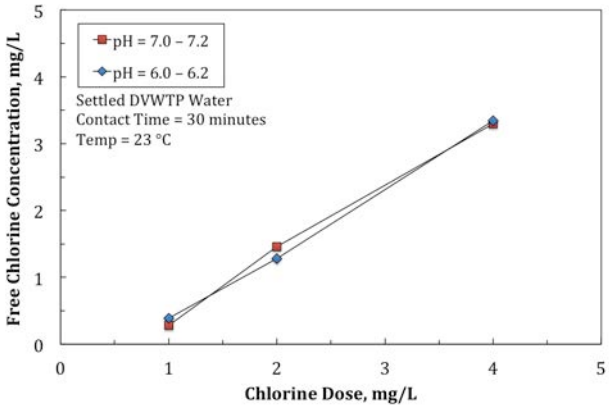


Figure 4.16 – Free chlorine residual concentration after 30 minutes of chlorine addition to DVWTP settled water

Figures 4.17 and 4.18 show the destruction of toxins at pH 7.0 to 7.2. Figure 4.17 is a plot of the toxins concentration after 30 minutes of exposure to different chlorine doses, while Figure 4.18 is a plot of the rate of toxins destruction over time after exposure to a chlorine dose of 2 mg/L. The results show a wide range of impact of chlorine on the four toxins evaluated. While cylindrospermopsin was rapidly destroyed with a chlorine dose of only 1 mg/L, anatoxin-a was completely unaffected by chlorine up to a dose of 4 mg/L. As for the two microcystins, while they were also completely destroyed by the chlorine doses applied, their rate of destruction was significantly slower than that of cylindrospermopsin as shown in Figure 4.18. It is noted that the toxins concentration in Figure 4.18 is shown on a log-scale.

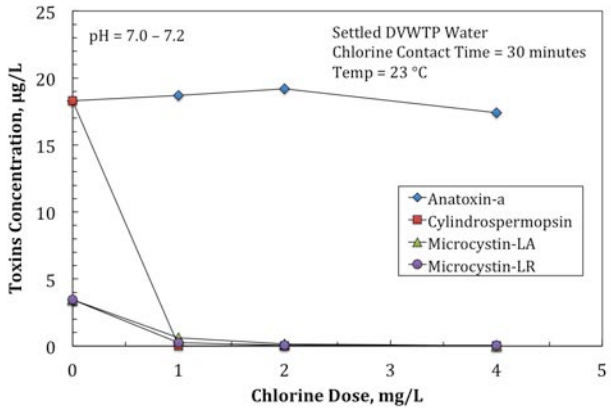


Figure 4.17 – Impact of chlorine dose on toxins destruction after 30 minutes of contact time at pH 7.1 ± 0.1

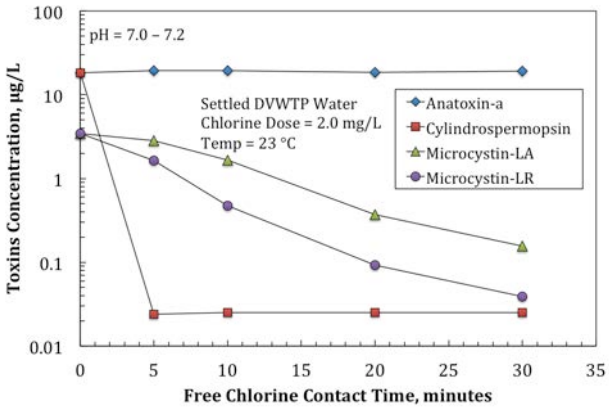


Figure 4.18 – Rate of toxins destruction after the addition of 2 mg/L chlorine to DVWTP settled water at pH 7.1 ± 0.1

Figures 4.19 and 4.20 show the same profiles of toxins destruction as Figures 4.17 and 4.18, but at pH 6.0 to 6.2. The high rate of cylindrospermopsin destruction with chlorine at pH 6.0 to 6.2 and the complete resistance of anatoxin-a to destruction with chlorine are identical to those experienced at pH 7.0 to 7.2. The two microcystins were also fully destroyed by all chlorine doses as shown in Figure 4.19. However, comparing their profiles in Figure 4.20 to those in Figure 4.18 shows that the rate of microcystin destruction is slower at higher pH values. Considering that the concentration of hypochlorous acid, HOCl, increases with decreasing pH while that of OCl^- decreases, this observation suggests that HOCl, and not OCl^-, might be the free chlorine species that reacts with the microcystins. If this hypothesis is correct, then the rate of destruction of microcystins with chlorine at pH above 8.0 or 8.5 will be significantly reduced since the HOCl concentration at those pH values is only a small fraction of the free available chlorine.

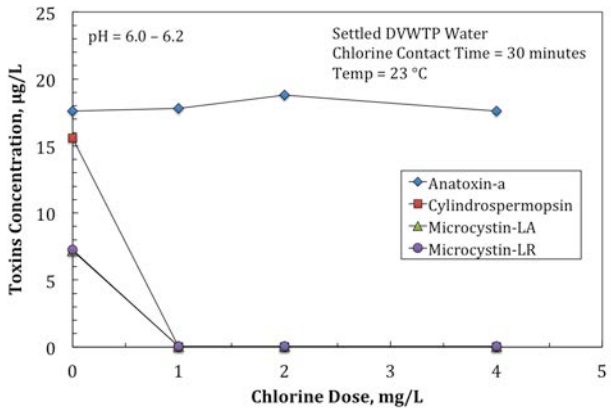


Figure 4.19 – Impact of chlorine dose on toxins destruction after 30 minutes of contact time at pH 6.1 ± 0.1

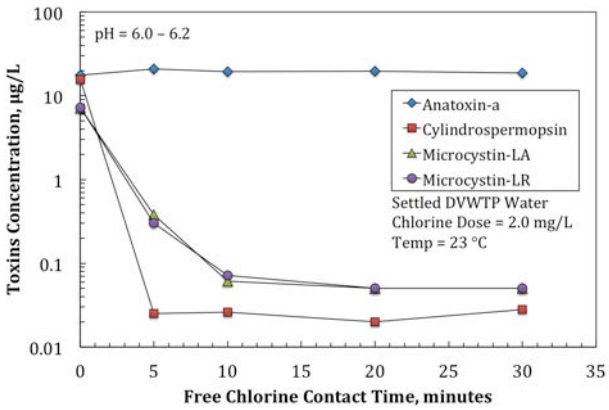


Figure 4.20 – Rate of toxins destruction after the addition of 2 mg/L chlorine to DVWTP settled water at pH 6.1 ± 0.1

Figures 4.21 through 4.24 focus on the microcystin levels measured using the ELISA method and the level of cylindrospermopsin in comparison to their respective infant HA levels. While the microcystins were destroyed to below the infant HA of 0.3 µg/L at the chlorine doses and contact times evaluated, Figures 4.21 and 4.22 again clearly show that their destruction with chlorine is less efficient at higher pH. This was not the case for cylindrospermopsin, which was destroyed to below its infant HA level of 0.7 µg/L with a chlorine dose of 1 mg/L and a contact time of only 5 minutes, and was not impacted by pH (within the range evaluated).

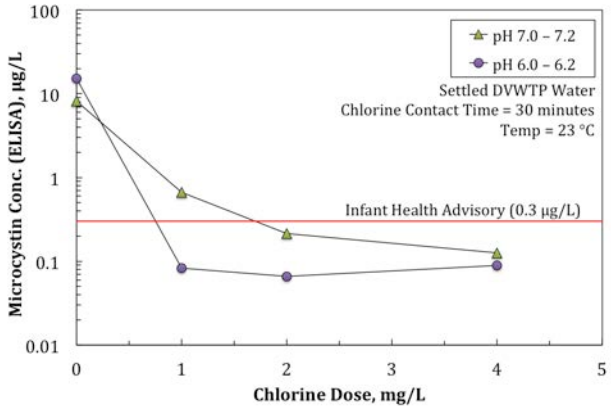


Figure 4.21 – Impact of chlorine dose on microcystins destruction (ELISA method) after 30 minutes of contact time

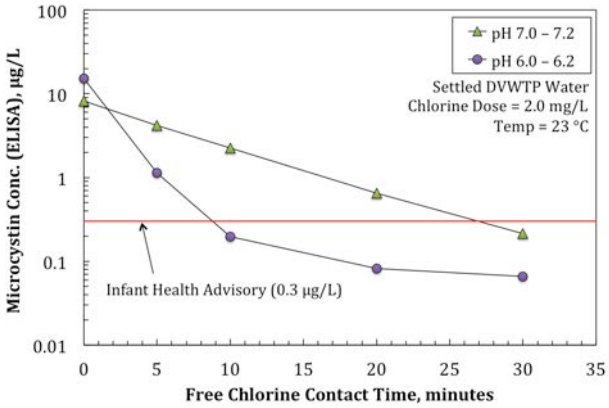


Figure 4.22 – Rate of microcystins destruction (ELISA method) after the addition of 2 mg/L chlorine to DVWTP settled water

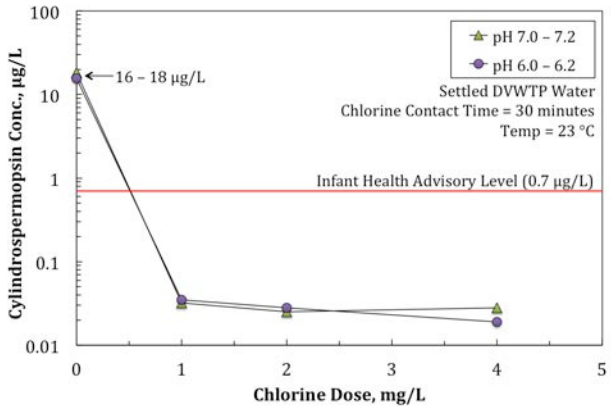


Figure 4.23 – Impact of chlorine dose on cylindrospermopsin destruction after 30 minutes of contact time

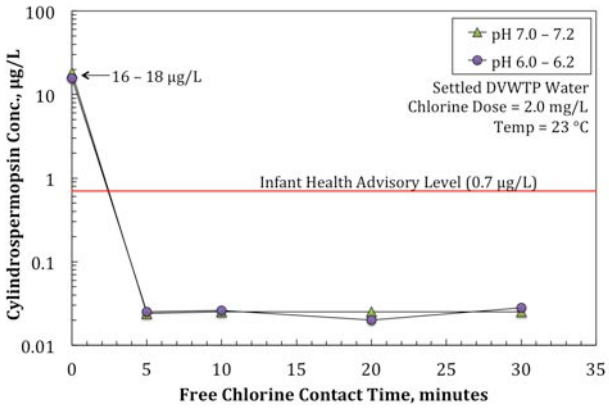


Figure 4.24 – Rate of cylindrospermopsin destruction after the addition of 2 mg/L chlorine to DVWTP settled water

4.4 – DESTRUCTION WITH CHLORAMINE

The destruction of algal toxins with chloramine was evaluated using settled DVWTP water that had been filtered through a 1–µm filter paper to remove suspended material. Since the majority of chloramine contact is at finished water pH, all chloramine testing was conducted at pH 8.5. Figures 4.25 and 4.26 show that the chloramine was completely stable in the water up to 2 hours of contact time during which no measurable chloramine decay was observed.

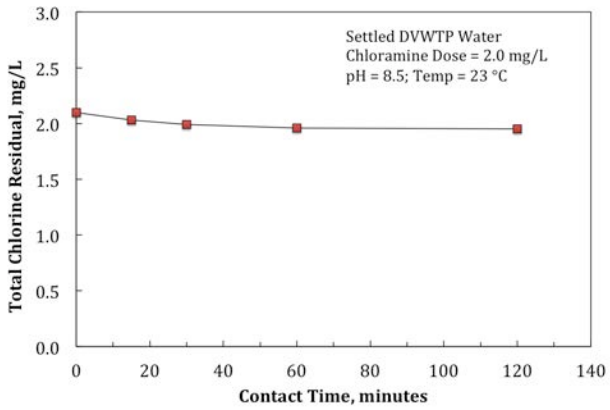


Figure 4.25 – Stability of 2 mg/L chloramine in settled DVWTP water

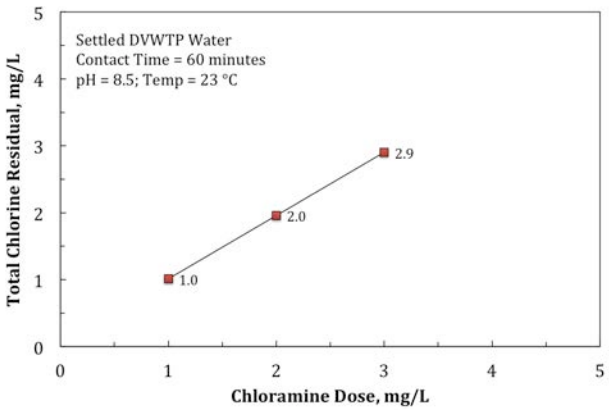


Figure 4.26 – Total chlorine residual 60 minutes after adding chloramine to settled DVWTP water

Figures 4.27 and 4.28 present results for the toxins destruction with chloramine doses up to 3 mg/L and chloramine contact times of up to 2 hours. The results show that chloramine had no effect on all four toxins when spiked in the water at levels ranging from 7 to 12 µg/L.

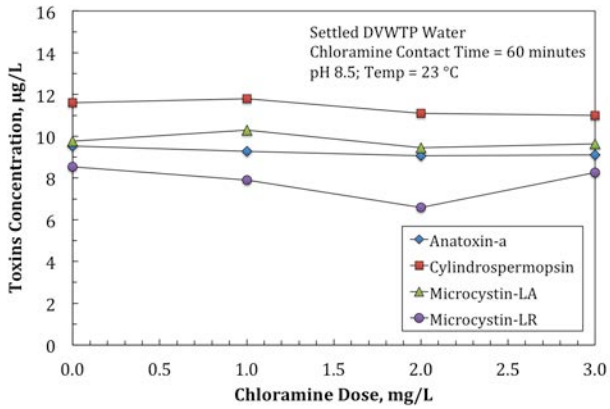


Figure 4.27 – Toxins destruction with chloramine added to settled DVWTP Water

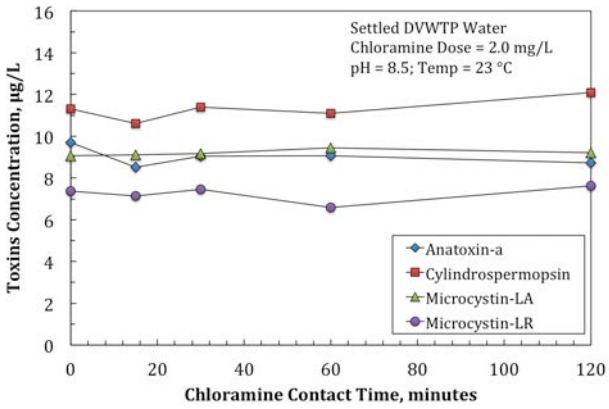


Figure 4.28 – Rate of toxins destruction with 2 mg/L chloramine added to settled DVWTP water

4.5 – REMOVAL WITH POWDERED ACTIVATED CARBON

The removal of algal toxins with PAC was evaluated using raw SBA water adjusted to two different pH values of 7.5 and 8.5. Figures 4.29 and 4.30 show the amount of toxins remaining in solution after 30 minutes of adsorption onto PAC doses of 10, 20, and 40 mg/L at the two pH levels. While the toxins did adsorb onto the added PAC, the removals achieved were relatively modest compared to the level of destruction achieved with ozone or chlorine as discussed earlier. Figures 4.31 and 4.32 present the same removal results but expressed in percent removed. At the high dose of 40 mg/L, as much as 95% removal of some toxins was achieved, which is a relatively high value for adsorption processes. However, with a starting concentration as high as 15 µg/L, a process that achieved 95% removal still leaves as much as 0.75 µg/L in the water.

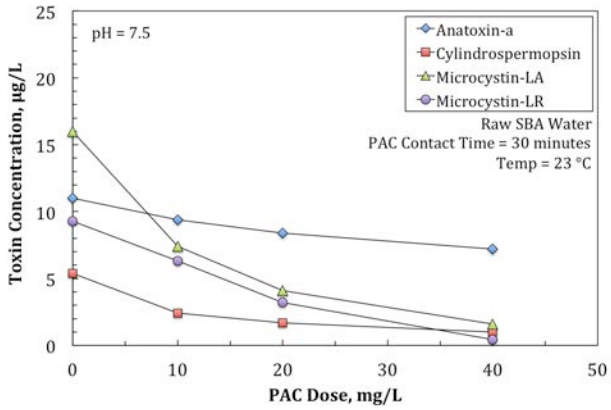


Figure 4.29 – Toxins removal with Norit HDB PAC at pH 7.5

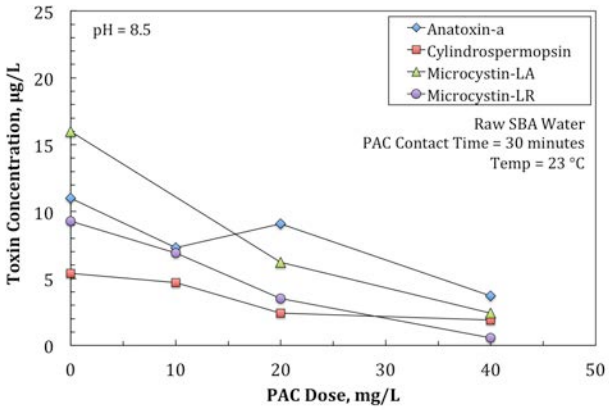


Figure 4.30 – Toxins removal with Norit HDB PAC at pH 8.5

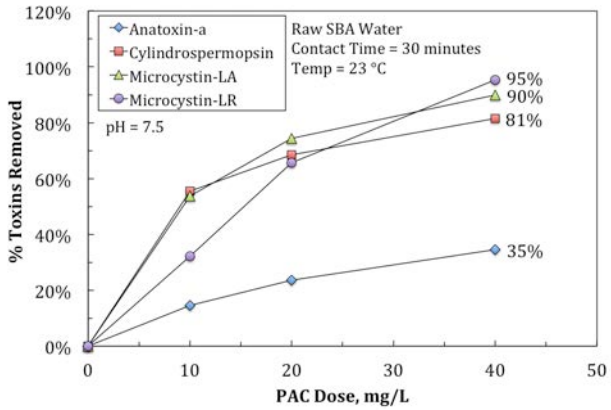


Figure 4.31 – Percent toxins removed with Norit HDB PAC at pH 7.5

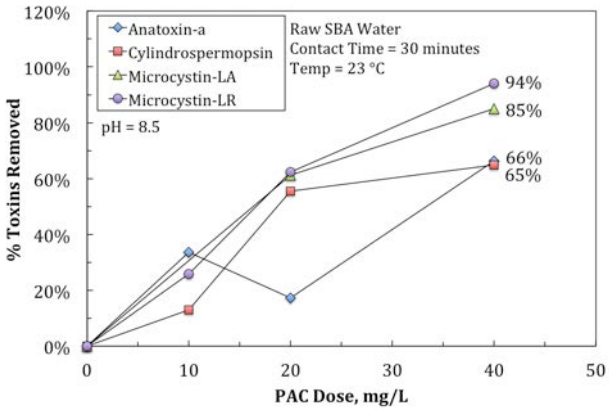


Figure 4.32 – Percent toxins removed with Norit HDB PAC at pH 8.5

Figures 4.33 and 4.34 compare the levels of microcystins, measured by the ELISA method, and those of cylindrospermopsin to their respective infant HA levels of 0.3 µg/L and 0.7 µg/L. Figure 4.33 shows that the addition of 40 mg/L PAC reduced microcystins from 16 µg/L to 1.5 µg/L and 2.2 µg/L at pH 8.5 and 7.5, respectively, which are still significantly higher than the infant HA level of 0.3 µg/L. Similarly, Figure 4.34 shows that the addition of 40 mg/L PAC reduced cylindrospermopsin from 5.4 µg/L to 1.0 µg/L and 1.9 µg/L at pH 8.5 and 7.5, respectively, which are significantly higher than the infant HA level of 0.7 µg/L.

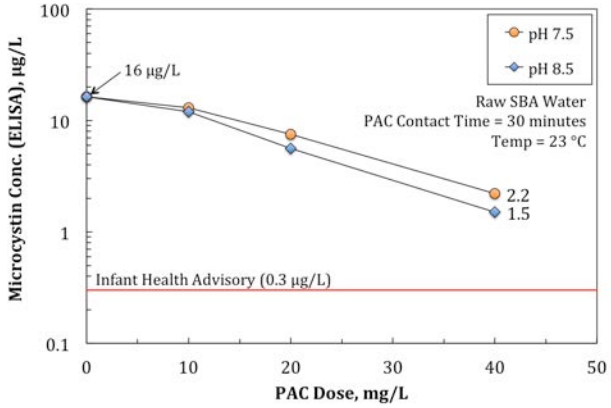


Figure 4.33 – Impact of Norit HDB PAC dose on microcystins removal (ELISA Method) after 30 minutes of contact time

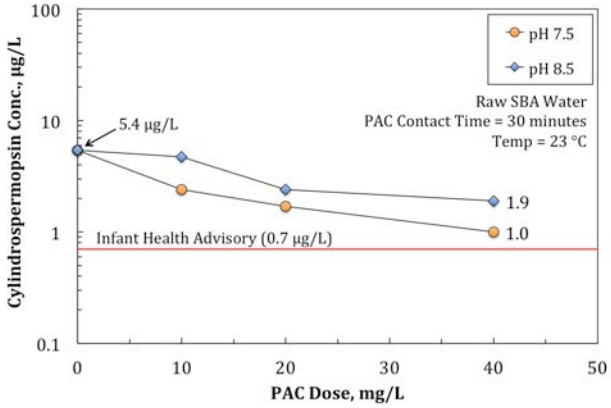


Figure 4.34 – Impact of Norit HDB PAC dose on cylindrospermopsin removal after 30 minutes of contact time

4.6 – INTRA-CELLULAR VS. EXTRA-CELLULAR TOXIN LEVELS

While all testing discussed earlier was conducted by spiking purchased toxins into water samples, concern is always expressed about naturally occurring toxins that are inside the cyanobacteria cells present in the raw water. When an oxidant is added to the raw water, it may lyse the cells and release the intra-cellular toxins into the water, thus causing an actual increase in the toxins concentration in the water. This will be an important consideration for how a utility responds to a potential cyanotoxin event in its source water. During this study, attempts were made at obtaining live algae samples that contained intra-cellular toxins to evaluate this issue.

Laboratory cultured samples of *anabaena sp.* and *microcystis aeruginosa* were purchased from Carolina Biological Supply Company (Burlington, NC). These algae are believed to be toxin producers. However, these cultured samples were found to contain no detectable toxins. At that time, we realized that we need to obtain natural algae samples that are producing toxins. In May 2015, a sample of surface algae was collected from a Bay area lake that was experiencing an algae bloom. The sample was analyzed, without dilution, for dissolved and total toxins. The only toxin present in the sample was microcystin-LA, and the levels measured are shown in Figure 4.35. A photograph of the green water is inserted in the graph to illustrate the high level of algae in the sample. The total intra-cellular toxin level was measured at 13.3 µg/L. While this is significantly higher than the microcystin HA value, it is well within the range of toxin levels evaluated during

bench-scale testing. If this level were released into the water after the algae cells are lysed, the preozonation testing results showed that an ozone dose of 2 mg/L should be sufficient to reduce this concentration to less than the infant HA level of 0.3 µg/L. The lysing dose will be in addition to the dose required to destroy the toxins themselves. However, the ozone dose required to lyse the cells and release the toxins is unknown at this time.

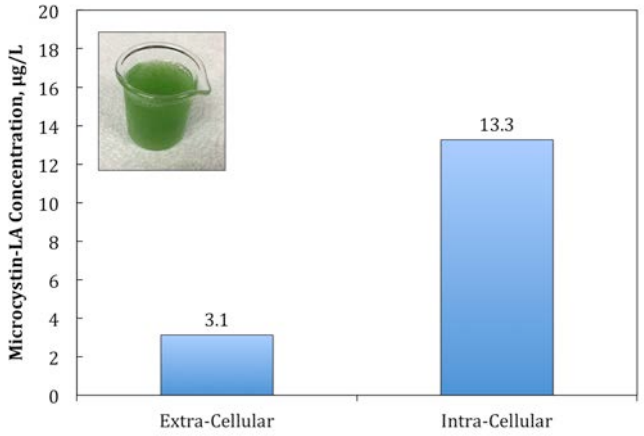


Figure 4.35 – Extra-cellular and intra-cellular levels of microcystin-LA measured in a Bay area recreational lake sample experiencing a severe algal bloom

4.7 – ELISA VS. LC/MS-MS METHOD

As discussed earlier, all samples were analyzed using the LC/MS-MS method and the ELISA method for microcystins. While the LC/MS-MS method quantifies individual microcystins, the ELISA method quantifies a molecular fragment common to all microcystins, and is therefore supposed to represent a measure of the concentration of total microcystins. However, as discussed earlier, the ELISA method is typical calibrated to one congener, in this case MC-LR. Experience suggests that it does not necessarily provide an accurate measurement for the other congeners (e.g., MC-LA). Nonetheless, the results collected in this study were used to compare the two analytical methods with the assumption that the ELISA method measures both MC-LA and MC-LR accurately. The comparison is shown in Figures 4.36 and 4.37. Each figure is plotted as the total MC values measured by the ELISA method vs. the sum of the MC-LA and MC-LR concentrations measured by the LC/MS-MS method. The diagonal line in each figure is the 1:1 line, which represents the "line of equal values" between the two methods.

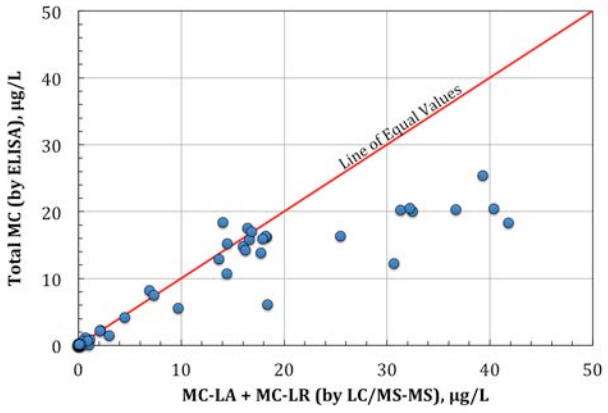


Figure 4.36 – Comparison of the microcystin results based on the two analytical methods employed (all data points included)

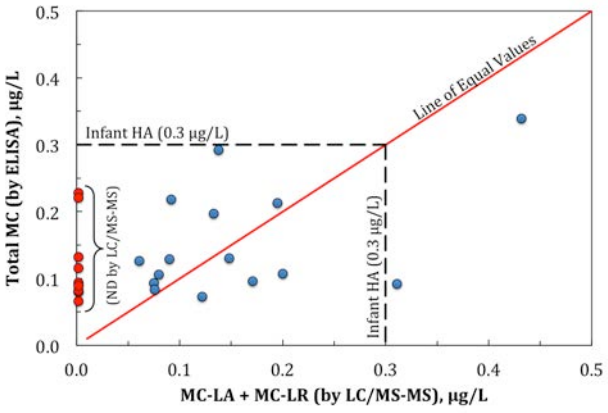


Figure 4.37 – Comparison of the microcystin results based on the two analytical methods employed (plot limited to <0.5 µg/L)

Figure 4.36 includes all the data collected in this study. The plot shows that the two methods compare well at low concentrations, but increasingly deviate from each other with increasing toxin concentration. It is unclear at this time whether this is due to analytical challenges or a result of fact that the ELISA method is calibrated to MC-LR and tends to under-estimate MC-LA. However, Figure 4.37 shows that, with the exception of one data-point, if one method measures the MC concentration below the HA of 0.3 µg/L, the other method measures it at < 0.3 µg/L as well.

SECTION 5.0 – SUMMARY & CONCLUSIONS

A comprehensive bench-scale testing effort was conducted to evaluate the efficiency of five different treatment technologies for the destruction or removal of cyanotoxins from South Bay Aqueduct (SBA) water. This study was funded jointly by the three SBA water users: Zone 7, ACWD, and SCVWD. The results can be used by each agency to assess the ability of its treatment plant(s) to treat the drinking water and protect public health in the event a cyanobacterial bloom were to occur in the water source and produce elevated levels of cyanotoxins.

5.1 – SUMMARY OF WORK CONDUCTED

Three water samples were collected and used in this study: a raw SBA sample collected from the influent to ACWD's WTP2, a settled water sample from Zone 7's DVWTP, and a settled water sample from SCVWD's Penitentia WTP. Each sample was spiked with approximately 10 µg/L of each of four cyanotoxins: 1) microcystin-LR, 2) microcystin-LA, 3) cylindrospermopsin, and 4) anatoxin-a. The raw SBA water sample was used for pre-ozonation testing and for PAC adsorption testing. The settled DVWTP water sample was used for chlorine and chloramine testing. The settled Penitentia WTP water sample was used for intermediate ozone testing. Ozone, chlorine, chloramine, or PAC was added to each water sample at different doses, and some under different pH conditions. Cyanotoxins samples were then collected and analyzed using the LC/MS-MS method and the ELISA method calibrated to microcystin-LR.

5.2 –OBSERVATIONS

The results of the study are detailed in this report. The following are observations made based on the results:

Preozonation

1. Ozone is highly effective at destroying all four toxins tested from raw SBA water. For the quality of the water sample used in the study, a preozone dose of 2 mg/L is sufficient to destroy the toxins from a potential raw water concentration of up to 25 µg/L down to below the HA levels.
2. Preozone testing was conducted at pH 7.2 and 6.5, and with or without the addition of a low prechloramine dose for bromate control. The efficiency of ozone destruction of the cyanotoxins was relatively the same under all conditions tested.

Intermediate Ozonation

1. Ozone is highly effective at destroying all four toxins tested from coagulated and settled SBA water. For the quality of the water sample used in this study, an intermediate ozone dose of 1 mg/L is sufficient to destroy the toxins from a potential raw water concentration of up to 17 µg/L down to below the HA levels.

2. Intermediate ozone testing was conducted at pH values of 6.5 and 7.5, and with or without the addition of hydrogen peroxide. The efficiency of ozone destruction of the cyanotoxins was relatively the same under all conditions tested.

Free Chlorine Testing

1. The chlorine testing results were mixed. Chlorine was virtually ineffective against anatoxin-a, but highly effective against cylindrospermopsin. While chlorine was effective at destroying the two microcystins, the rate of reaction was significantly slower than that with cylindrospermopsin, and the rate was affected by the pH of the water.
2. For the quality of the settled DVWTP water sample received, a chlorine dose of 1 mg/L was sufficient to destroy the cylindrospermopsin from a high of 16 to 18 µg/L down to less than 0.1 µg/L within 5 minutes of contact time. This level is well below the infant HA level of 0.7 µg/L.
3. For the quality of the settled DVWTP water sample received, at a pH of 7.5, a chlorine dose of 2 mg/L was sufficient to lower the microcystins from an average of 10 µg/L to below the infant HA level of 0.3 µg/L within a contact period of 30 minutes. Lowering the pH to 6.5 reduced the contact time required to 10 minutes.

Chloramine Testing

The testing showed that chloramine at a dose of up to 3 mg/L was virtually ineffective at destroying any of the four toxins tested for up to two hours of contact time.

PAC Testing

1. The adsorption of the four toxins onto the PAC used varied. Under some conditions, the adsorption of anatoxin-a was significantly lower than that of the other toxins.
2. While up to 95% removal was achieved with a PAC dose of 40 mg/L and a contact time of 30 minutes, this was not sufficient to reduce the spiked levels to below the infant HA levels for either microcystin or cylindrospermopsin.
3. Based on the results obtained, cyanotoxins removal with PAC adsorption can be characterized as "moderate" in that it was not able to meet the HA levels on its own under the conditions tested. However, if paired with another technology, it can greatly contribute to toxins removal.

5.3 – CONCLUSIONS

Table 5.1 presents a visual summary classification of the effectiveness of each treatment technology against each type of cyanotoxin tested. A full circle indicates that the treatment technology is excellent at destroying or removing the toxin, while an open circle indicates that it is ineffective against the toxin. A ¾-full circle suggests that the technology is good at destroying the toxin, but

may require a longer contact time or a higher dose that typically used. A half-full circle indicates that the technology is moderate in its effectiveness in that it achieved partial removal or destruction, but needs to be supplemented by another technology for effective treatment to be achieved.

Table 5.1 – Summary Classification of the Effectiveness of Each Treatment Technology at the Removal of the three types of Cyanotoxins Tested from Raw or Settled SBA Water

Technology	Microcystins	Cylindrospermopsin	Anatoxin-a
Ozone	●	●	●
Free chlorine	◕	●	○
PAC Adsorption	◒	◒	◒
Chloramine	○	○	○

● Excellent ◕ Good ◒ Moderate ○ Ineffective

"Excellent" = the technology can reliably reduce the toxin to below the HA level.

"Very good" = the technology is could destroy the toxin to below the HA level, but may require a longer contact time or a higher dose than typically used.

"Moderate" = the technology is moderately effective, and needs to be supplemented by another technology in order to destroy the toxin to below the HA level.

"Ineffective" = the technology did not reduce the toxins by any measurable amount under the conditions evaluated in this study.

As shown in Table 5.1, the following is a synopsis of the findings of this study:

1. *Typical ozone doses used at SBA plants, whether on raw water or settled water, are highly effective at destroying all three types of toxins tested in this study.*
2. *Chlorine is highly effective at destroying cylindrospermopsin and virtually ineffective against anatoxin-a. Chlorine can destroy microcystins to acceptable levels, but requires a longer contact time and can be assisted by a low(er) water pH compared to its effectiveness against cylindrospermopsin.*
3. *Adsorption of the three types of toxins on Hydrodarco B PAC was moderate. Effective control of toxins requires coupling of PAC with another treatment technology. It is also possible that other types of PAC may result in higher toxins removal than that achieved with Hydrodarco B PAC.*
4. *Chloramine is ineffective against the types of toxins tested.*

Finally, one remaining challenge to the application of preozonation to SBA water within the context of cyanotoxins treatment is to develop an understanding of the ozone dose required to lyse the cyanobacterial cells that may be present in the raw water before the ozone can destroy the toxins that may be released from the inside of the cells. This study was not able to quantify this dose.