

A LABORATORY SCALE ASSESSMENT OF THE EFFECT OF CHLORINE
DIOXIDE PRE-OXIDATION ON DISINFECTION BY-PRODUCT
FORMATION FOR TWO SURFACE WATER SUPPLIES

BY

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ABSTRACT

Chemical disinfection is the cornerstone of safe drinking water. However, the use of chemical disinfection results in the unintentional formation of disinfection by-products (DBPs), an outcome of reactions between the disinfectant and natural organic matter (NOM) present in the native (raw) water. DBPs are suspected carcinogens, and as such, have been regulated by the U.S. Environmental Protection Agency (USEPA) under the Safe Drinking Water Act (SDWA).

This document reports the results of a study that investigated the use of chlorine dioxide pre-oxidation for the reduction of DBP precursors, and subsequently, DBP formation potential (FP). To determine the effectiveness of the chlorine dioxide pre-oxidation process, two surface waters were studied: raw water from Lake Claire (Orlando, FL) and raw water from the East Maui Watershed (Makawao, HI). Lake Claire water contains approximately 11-12 mg/L of NOM and 35 mg/L as CaCO₃ of alkalinity, while the Maui source water typically ranges between 7-8 mg/L of NOM with 2-10 mg/L as CaCO₃ of alkalinity. Two chlorine dioxide doses were investigated (0.75 mg/L and 1.5 mg/L) and compared to a control to quantify the effectiveness of this advanced pre-treatment oxidation process. Water collected at each site was subject to the following treatment process: oxidation, coagulation, flocculation, sedimentation, ultrafiltration, and disinfection with free chlorine.

Disinfection by-product formation potential (DBPFP) analysis showed that ClO₂ pre-oxidation, in general, increased the 7-day DBPFP of the East Maui water, and decreased the 7-day DBPFP of the Lake Claire source water. For the Lake Claire water at the higher ClO₂ dose, total trihalomethanes (TTHM) were decreased by 37 percent and the five regulated haloacetic

acids (HAA₅) by 23 percent. For the East Maui source water at the higher ClO₂ dose, TTHM's were increased by 53 percent and HAA₅'s by 60 percent. Future research should determine the effect of alkalinity on DBPFP, which could be the reason why chlorine dioxide pre-oxidation caused one water source's DBPFP to decrease and the other to increase.

DEDICATION

For my parents, without your unconditional love and support I wouldn't be the strong and driven young woman I am today.

For my older brother Martin, thank you for being a great role model and friend.

For my younger siblings Claudia and Bernardo, I hope you both aspire to even greater heights in your chosen fields.

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LIST OF ACRONYMS

ACH	aluminum chlorohydrate coagulant
CECE	Civil, Environmental, and Construction Engineering
CU	color unit
DBPFP	disinfection by-product formation potential
DBPs	disinfection by-products
DI	deionized water
DOC	dissolved organic carbon
DOM	dissolved organic matter
EDTA	ethylenediaminetetraacetic acid
EEM	emission excitation matrix
EPA	Environmental Protection Agency
FL	Florida
FP	formation potential
GC	gas chromatography
GEMS	Girls Excelling in Math and Science
HAA	haloacetic acid
HAA ₅	haloacetic acids
HAN	haloacetonitriles
HI	Hawaii
I	industrial statistic
IC	ion chromatography

LRAA	locational running annual average
MCLG	maximum contaminant level goal
MCLs	maximum contaminant levels
MRDL	maximum residual disinfectant limit
MRDLG	maximum residual disinfectant limit goal
NOM	natural organic matter
NTU	nephelometric turbidity unit
PPM	parts per million volume
PPMV	parts per million volume
RPM	revolutions per minute
SDWA	Safe Drinking Water Act
SUVA	specific ultraviolet absorbance
THM	trihalomethane
TOC	total organic carbon
TTHM	total trihalomethanes
UCF	University of Central Florida
USEPA	United States Environmental Protection Agency
UV ₂₅₄	ultraviolet absorbance at 254 nanometers
WTP	water treatment plant

INTRODUCTION

Chlorination, because of its effectiveness and affordability as compared to other disinfection methods, is the most widely used chemical disinfection method in the production of safe drinking water. However, it has been shown that free chlorine can react with natural organic matter (NOM) to form disinfection by-products (DBPs) (Crittenden, et al., 2012). DBPs are suspected carcinogens (Richardson, et al., 2007), and as such, are regulated by the Environmental Protection Agency (EPA) through the Safe Drinking Water Act (SDWA) (USEPA, 2012). Thus, noncompliance with these existing regulations can occur when water sources rich in NOM are disinfected with chlorine.

Surface water sources, such as rivers and lakes, contain varying quantities of NOM. Consequently, the use of chlorine as a disinfectant at utilities employing surface water sources resulted in DBP formation. As a result, oxidation processes have been researched due to its ability to break up NOM molecules as a means to reduce DBP formation potential. This study aims to determine the effectiveness of chlorine dioxide pre-oxidation as a means of reducing the DBP formation potential of two surface water supplies.

Water from Hawaii (HI) and Florida (FL) was collected and used to evaluate the effectiveness of chlorine dioxide pre-oxidation at reducing DBP precursors (e.g., NOM). The Hawaii water source is the Waikamoi Rain Forest, near Makawao, on the island of Maui. The Florida water source is Lake Claire, located on the University of Central Florida (UCF) main campus in Orlando. The effectiveness of chlorine dioxide pre-oxidation at removing DBP precursor will be quantified relative to experimental controls.

LITERATURE REVIEW

DBPs are formed when water containing NOM is disinfected to protect consumers against water borne disease. The major chemical disinfectants employed by water purveyors today include chlorine, chloramine, ozone, and chlorine dioxide. As previously stated, chlorine remains the most widely used disinfectant in the drinking water community today. Regulatory agencies today have embraced stricter mandates designed to provide a balance between the use of disinfectants and the unintentional formation of DBPs. For this reason, it is imperative to find solutions for controlling DBP formation in distribution systems, without compromising the level of disinfection required for the production of safe drinking water.

U.S. EPA Regulations

In 1996 Congress amended the SDWA which required the U.S. EPA to establish new maximum contaminant levels (MCLs) for two major groups of chlorinated DBPs: total trihalomethanes (TTHMs) and five haloacetic acids (HAA₅). These regulated DBPs are suspected carcinogens which exhibit a chronic toxicity (Richardson, et al., 2007). In 2006, the Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 Rule) was implemented which placed stricter standards on DBP levels in potable distribution systems. This rule established the following: the TTHM MCL at 0.08 mg/L (as a sum of chloroform, bromoform, bromodichloromethane, and dibromochloromethane concentrations); the HAA₅ MCL was at 0.06 mg/L (as a sum of monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, and dibromoacetic acid concentrations); the bromate MCL at 0.01 mg/L; and the chlorite MCL at 1.0 mg/L (USEPA, 2010).

In addition, the maximum residual disinfectant limit (MRDL) for a distribution system was set at 4.0 mg/L for chlorine and chloramines, and 0.8 mg/L for chlorine dioxide. According to the rule, the secondary disinfectant residual must not drop below 0.2 mg/L at the farthest point in the distribution system. The Stage 2 Rule also introduced locational running annual average (LRAA) sampling for the determination of compliance with DBP standards (USEPA, 2010). The LRAA requires the selection of several sampling sites throughout the distribution system which are expected to have the highest concentrations of DBPs. Quarterly DBP samples are taken at each of the selected sites. To be in compliance with the Stage 2 Rule, the running annual average for each of the sampling sites must be below the MCL set by the EPA. A summary of the Stage 2 Rule is presented in Table 1.

Table 1: Regulated Contaminants and Disinfectants

Regulated Contaminants	Stage 2 DBPR	
	MCL (mg/L)	MCLG (mg/L)
TTHM	0.08	
Chloroform		0.07
Bromodichloromethane		0
Dibromochloromethane		0.06
Bromoform		0
HAA5	0.06	
Monochloroacetic acid		0.07
Dichloroacetic acid		0
Trichloroacetic acid		0.2
Bromoacetic acid		-
Dibromoacetic acid		-
Chlorite	1	0.8
Regulated Disinfectants	MRDL (mg/L)	MRDLG (mg/L)
Chlorine	4.0 as Cl ₂	4
Chlorine Dioxide	0.8	0.8

*(Adapted from USEPA, 2010)

Chlorine Disinfection and DBP Formation

Proper disinfection is accomplished by maintaining a disinfectant residual for a specific amount of time. The EPA has developed Ct values for this purpose, where C represents the disinfectant residual concentration and t represents the contact time. The Ct product required for achieving a given level of disinfection for several pathogens under specific conditions (pH, temperature, and type of disinfectant used) has been tabularized (Crittenden, et al., 2012; FDEP, 2010). Water purveyors, given a specific level of disinfection required by the EPA, must meet the tabularized Ct value to be in compliance. Primary disinfection, which is defined by the Ct product, is applied at the plant. Its main function is to inactivate the pathogens present in the water through contact time from the point of dosing to the point of entry to the distribution system. Secondary disinfection is the additional disinfectant dose applied to maintain a residual – between 0.2 mg/L and 4.0 mg/L – to prevent exposure to pathogens from the point of entry to the distribution system to the point of discharge at the consumer’s tap.

DBP formation is dependent on many factors, including: the type and concentration of disinfectant, the NOM concentration, the temperature and pH of the water, the contact time, and the bromide concentration (Crittenden, et al., 2012). Typically, the use of free chlorine as both a primary and secondary disinfectant leads to higher levels of regulated DBPs in NOM rich waters. DBP formation potential in water can generally be described as a direct relationship – an increase in NOM concentration or disinfectant dose can increase the quantity of DBPs formed. Higher water temperatures also typically promote the formation of DBPs. THM formation is favored at alkaline pH levels while acidic pH levels are ideal for HAA formation. Kim et al. (2002) showed the highest regulated DBP formation potential at pH 7 due to the formation of

both THMs and HAAs. Contact time between the disinfectant and NOM is a key factor in DBP formation. The higher the contact time between the constituents, the more DBPs will be formed. Therefore, regardless of pH, the more time the NOM and disinfectant have to react, the more DBPs are produced. Typically, as the concentration of bromide in water increases, the quantity of brominated DBPs also increases.

Identified DBP Control Methods

There are several approaches to controlling DBPs. Identified DBP control methods include: (i) reduction of disinfectant dose and residual, (ii) distribution system management, (iii) use of alternative primary and/or secondary disinfectant, (iv) reduction of NOM concentrations, and (v) removal of pre-formed DBPs. Changing the type of disinfectant is the most common method for controlling DBPs.

Chloramine is the most common substitute for free chlorine as a secondary disinfectant because chloramine has been shown to produce less regulated DBPs (Bougeard et al., 2010). Disinfection with chloramines entails mixing free chlorine and ammonia, and using the monochloramine produced as the disinfectant. Chloramines are less powerful than free chlorine, but they produce a stable and long lasting disinfectant residual. Although, in general, chloramines produce less regulated DBPs, they can produce unregulated DBPs, such as haloacetonitriles (HAN) and iodo-THMs (Bougeard et al., 2010). Unregulated chloramine DBPs, which could be more toxic than regulated chlorine DBPs, will likely be regulated in the near future (Bougeard, et al., 2010). Therefore, this study will focus on evaluating the effectiveness of chlorine dioxide as an alternative primary oxidant to reduce DBP precursors prior to chlorine disinfection.

Chlorine Dioxide Oxidation

Chlorine dioxide is a strong oxidant that is commonly used to reduce taste, odor, and color in water (Crittenden, et al., 2012). It has been shown that it can also reduce DBP formation potentials by altering the molecular structure of NOM (Yang et al., 2013, pp. 1477-1485). Chlorine dioxide is very effective at inactivating chlorine-resistant pathogens such as *Cryptosporidium parvum* and *Giardia lamblia* (Shi et al., 2013). Due to its disinfectant properties, chlorine dioxide reacts with the initial demand in the water thus reducing subsequent chlorine decay. Chlorine dioxide oxidation may lead to a decrease in the free chlorine dose – and subsequently a decrease in DBP formation potential - by reducing the initial chlorine demand (Shi et al., 2013). Chlorine dioxide has been shown to decrease DBP formation by 6 percent to 45 percent (Yang et al., 2013, pp. 5856-5864).

The main downside to chlorine dioxide pre-oxidation is the fact that it increases the formation of chlorite and chlorate ions in the water (Yang et al., 2013, pp. 1477-1485). Of the two ions, chlorite is regulated because it poses health risks to young children (USEPA, 2012). Due to this, chlorine dioxide dosages are limited by their subsequent formation of chlorite, which generally means a dose of no more than 2 mg/L (Yang et al., 2013, pp. 1477-1485). In the presence of bromide in the water, chlorine dioxide will also produce brominated DBPs (Yang et al., 2013, pp. 1477-1485).

MATERIALS & METHODS

As more surface water sources are employed for drinking water purposes, treatment strategies for the control of regulated DBPs is essential. This study aims to elucidate the effectiveness of chlorine dioxide pre-oxidation as a DBP control strategy for two surface water sources. The first source, Lake Claire, is situated on the northwest sector and is the largest stormwater retention pond on UCF property. The second source, the Waikamoi Rain Forest, is located on the east region of the Island of Maui on the slopes of Mount Haleakala.

Between June 2014 and July 2014, two experimental evaluations were performed per water source. Each experimental run was analyzed for regulated DBPs, chlorine residual, and chlorite concentration. Several additional water quality parameters were also monitored, and included: pH, temperature, turbidity, color, UV_{254} , chlorate concentration, DOC, chloride, bromide, and sulfate.

Sample Collection

Lake Claire is located on UCF's campus and is used for limited recreational activities. The lake has elevated NOM (11-12 mg/L) and contains 35 mg/L as $CaCO_3$ of alkalinity. For the experimental runs, 20 gallons of Lake Claire water was placed in an opaque plastic drum. The container was rinsed three times with Lake Claire water to reduce contamination, and collected in June of 2014. The 20 gallon drum was then taken to UCF's environmental engineering laboratory and stored inside a 4°C walk-in cooler until analysis were performed.

The East Maui watershed, fed by the Waikamoi Rainforest Reserve, is the source water for several water treatment plants in the Upcountry region. The Olinda Water Treatment Plant (WTP) draws its water from the highest elevation of this watershed. At this draw point, the

source water has the highest quantity of organic acids and the lowest quantity of alkalinity present. For this study, the UCF drinking water research group coordinated with County of Maui Department of Water Supply officials to obtain a 20 gallon sample of Olinda raw water. An opaque plastic 20 gallon drum was shipped to the Olinda WTP in July of 2014. The plant operators rinsed the container three times with raw water, collected the raw water sample, and shipped the drum back to the Environmental Engineering labs at UCF. The drum was then stored inside a 4°C walk-in cooler.

Reagents and Standards

Chlorine dioxide was generated on site using an Evoqua Water Technologies chlorine dioxide generator (Millennium III™ Chlorine Dioxide System, 181 Thorn Hill Road, Warrendale, PA 15086). A sample of aluminum chlorohydrate (ACH) was obtained from the Olinda WTP, and was used as the coagulant in this study. The THM and HAA quenching reagents, ammonium chloride and sodium sulfite, were made at the UCF Environmental Engineering labs. Ethylenediaminetetraacetic (EDTA) acid was used to quench the chlorite and chlorate samples. For disinfection, a stock solution of sodium hypochlorite was used. The anions monitored in this study were chloride, bromide, and sulfate. Table 2 summarizes the reagents and standards employed in this study.

Table 2: Experimental Reagents and Standards

Reagents		Standards
<ul style="list-style-type: none"> • Deionized Water (DI) 	<ul style="list-style-type: none"> • Lime Calcium Oxide Slurry (1.17, 8.79, and 17.7%) 	<ul style="list-style-type: none"> • pH
<ul style="list-style-type: none"> • Sodium Hypochlorite Stock 	<ul style="list-style-type: none"> • 100 g/L Sodium Sulfite, Na₂SO₃ 	<ul style="list-style-type: none"> • DOC
<ul style="list-style-type: none"> • Chlorine Dioxide 	<ul style="list-style-type: none"> • 50 g/L Ammonium Chloride, NH₄Cl 	<ul style="list-style-type: none"> • Color
<ul style="list-style-type: none"> • Aluminum Chlorohydrate coagulant 	<ul style="list-style-type: none"> • DPD Free Chlorine Reagent Powder Pillows 	<ul style="list-style-type: none"> • Turbidity
<ul style="list-style-type: none"> • Ethylenediaminetetraacetic Acid (EDTA) 		<ul style="list-style-type: none"> • Organic Free Water • Anions

Experimental Set-Up and Procedure

Two replicate runs were conducted per water source to study the effect of chlorine dioxide pre-oxidation on DBP formation potential. The Lake Claire experimental runs were conducted at the end of June 2014, while the Maui experimental runs were conducted mid-July 2014. In both cases, each run consisted of a control and two chlorine dioxide dosages as shown on Figure 1. The control experiment was used as a baseline for quantifying effect of chlorine dioxide pre-oxidation on DBP formation potential. The two chlorine dioxide dosages used in this study were 0.75 mg/L and 1.5 mg/L. Higher dosages were not pursued due to exceedances of EPA’s chlorite MCL that would be experienced. During each run, sample replicates of the control, dose 1, and dose 2 were taken to test the precision of the laboratory measurements obtained. For both water sources, the DBPFP and chlorine residual samples were stored at room temperature in a dark cabinet. An equipment & materials list and a detailed experimental procedure has been included in Appendix A and B, respectively.

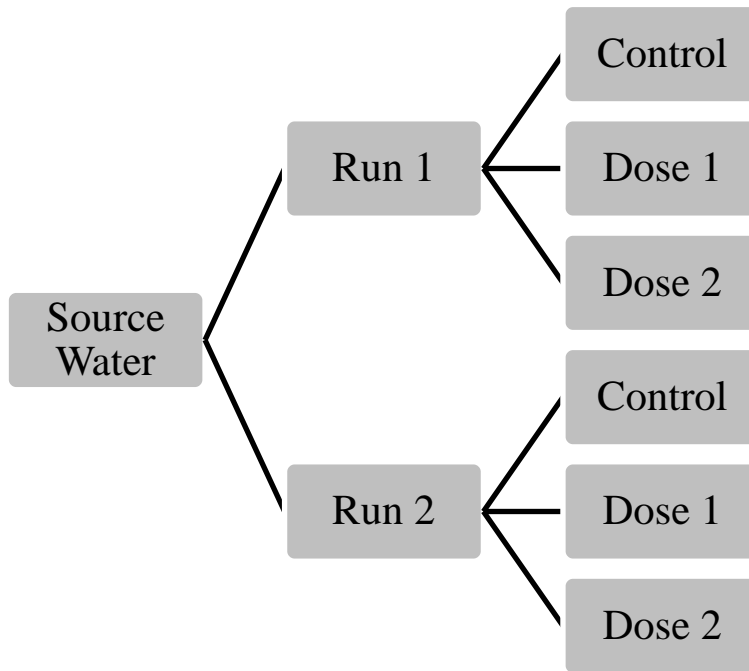
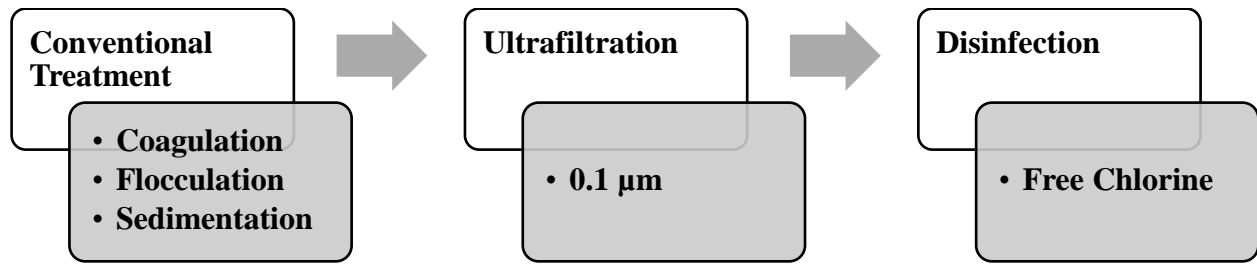


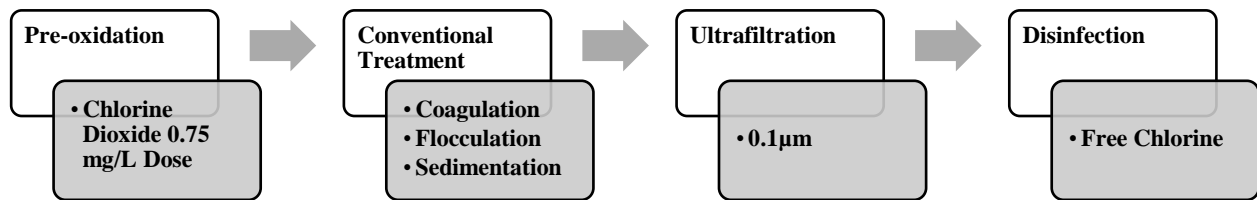
Figure 1: Chlorine Dioxide Testing Matrix

Lake Claire (FL):

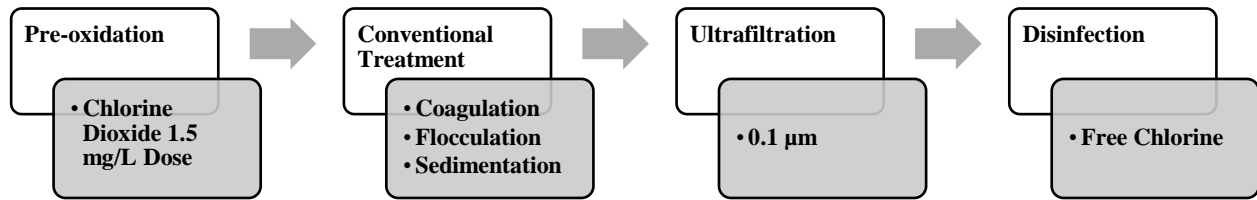
The chlorine dioxide pre-oxidation was conducted in a jar tester at 200 RPM for an hour to mimic pipe flow from the point of dose to the point of entry to a WTP. To simulate conventional treatment for this study, a jar tester was also used with the following testing sequence: coagulation for 15 seconds at 300 RPM, flocculation for 25 minutes at 25 RPM, and sedimentation for 45 minutes at 0 RPM. The control, dose 1, and dose 2 experiments were coagulated with 40, 33, and 42 PPM_v of ACH, respectively. The samples were then filtered through a 0.1 µm membrane filter and disinfected with 8.0 mg/L of sodium hypochlorite. Figure 2a-c contains a schematic summary of the experimental procedure.



(a) Lake Claire Control



(b) Lake Claire Chlorine Dioxide Dose 1



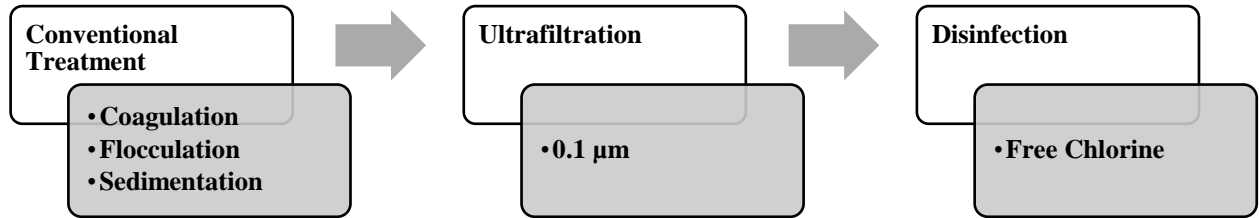
(c) Lake Claire Chlorine Dioxide Dose 2

Figure 2a-c: Lake Claire Experimental Procedure Flow Schematic

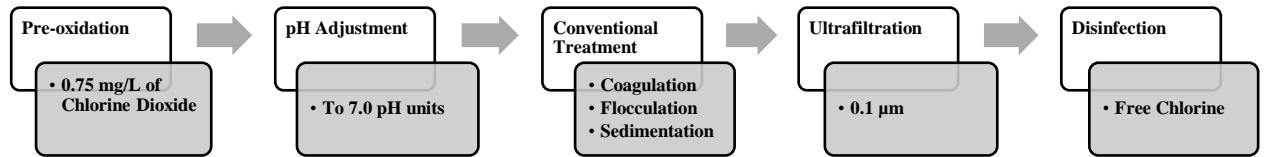
East Maui (HI):

The chlorine dioxide pre-oxidation was conducted in a jar tester at 200 RPM for an hour to simulate pipe flow from the point of dose to the point of entry to a WTP. The samples dosed with chlorine dioxide were then pH adjusted to 7.0 pH units. To simulate conventional treatment for this study, a jar tester was also used with the following testing sequence: coagulation for 15 seconds at 300 RPM, flocculation for 25 minutes at 25 RPM, and sedimentation for 45 minutes at 0 RPM. The control, dose 1, and dose 2 experiments were coagulated with 19.1 PPM_v of ACH. The samples were then filtered through a 0.1 µm membrane

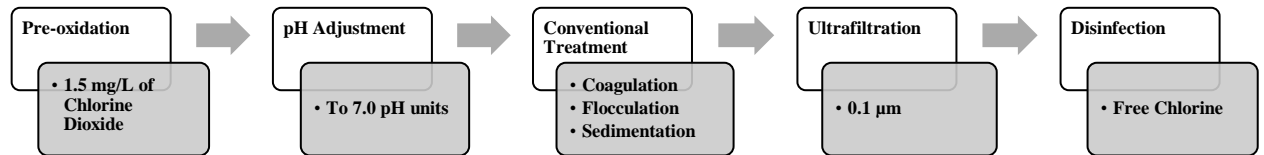
filter and disinfected with 4.0 mg/L of sodium hypochlorite. Figure 3a-c contains a schematic summary of the experimental procedure for the Maui water source.



(a) Maui Control



(b) Maui Chlorine Dioxide Dose 1



(c) Maui Chlorine Dioxide Dose 2

Figure 3a-c: Maui Experimental Procedure Flow Schematic

Analytical Methods

Regardless of water source, water quality data was collected at the same locations in the treatment process train. As shown on Figure 4, water quality data for the control experiments were taken from the raw, settled, filtered, and disinfected water. Figure 5 shows the water quality sample points for the chlorine dioxide experiments.

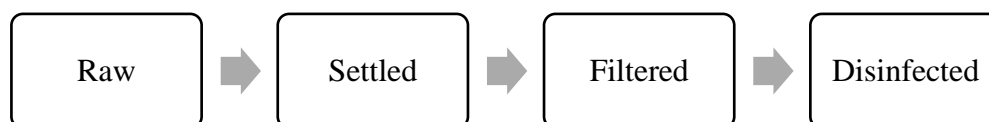


Figure 4: Control Experiments Water Quality Sample Points

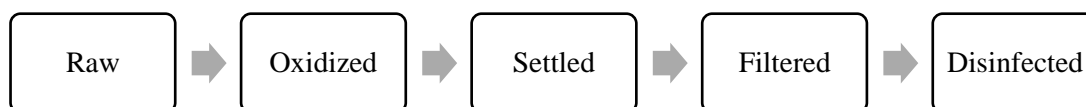


Figure 5: Chlorine Dioxide Experiments Water Quality Sample Points

The water quality parameters that were monitored at each sample point were previously identified in Table 3. Samples were filtered through a 0.1 μ membrane filter prior to being analyzed for color and UV₂₅₄. A Shimadzu RF-1501 spectrofluorophotometer was used for the fluorescence analysis. An emission excitation matrix (EEM) Diagram can be used to determine the type of organics in a sample based on the location of the peaks, as shown on Figure 6. Chlorine residual measurements were performed for the Lake Claire water for the following holding times: 96 hr, and 168 hr. For the Maui water, chlorine residual measurements were taken at 6 hr, 24 hr, 48 hr, 96 hr, and 168 hr. An third party laboratory, AEL, Inc., was partnered with for the DBP analysis. Two TTHM formation potential holding times were used, 96 hr and 168 hr. For the HAA formation potential, only a 168 hr holding time was used. Samples analyzed

were done in accordance with the Standard Methods for the Examination of Water and Wastewater (Eaton & Franson, 2005).

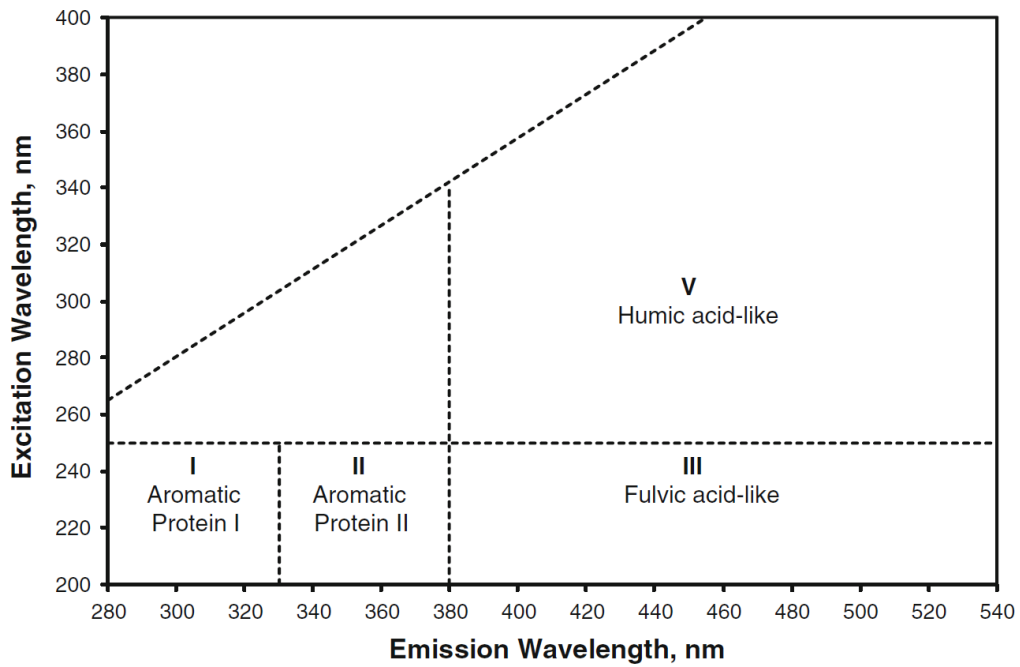


Figure 6: EEM Diagram Peak Characterization

Table 3: Water Quality Monitoring Matrix

Water Quality Parameter	Raw	Oxidized	Settled	Filtered	Disinfected
pH	✓	✓	✓	✓	
Temperature	✓	✓	✓	✓	
Turbidity	✓	✓	✓	✓	
Color	✓	✓		✓	
UV ₂₅₄	✓	✓		✓	
DOC	✓	✓		✓	
SUVA	✓	✓		✓	
Anions (Cl ⁻ , Br ⁻ , SO ₄ ⁻²)	✓	✓		✓	
Fluorescence Spectroscopy	✓	✓			✓
Chlorine Residual					✓
DBPs					✓

RESULTS

Lake Claire Results

A decrease in DBPFP was seen when the lake water was oxidized with 1.5 mg/L of chlorine dioxide. TTHM's decreased and HAA₅'s increased when the 0.75 mg/L chlorine dioxide dose was used. Although DBP formation potential was above EPA's MCL for all cases, chlorite concentrations were below the MCL (Figure 7). After a seven day incubation time, the chlorine residual in the water samples were all between 1.5 mg/L and 3.5 mg/L (Figure 8). Samples analyzed for bromide were found to be below the equipment's detection limit (less than 0.2 mg/L).

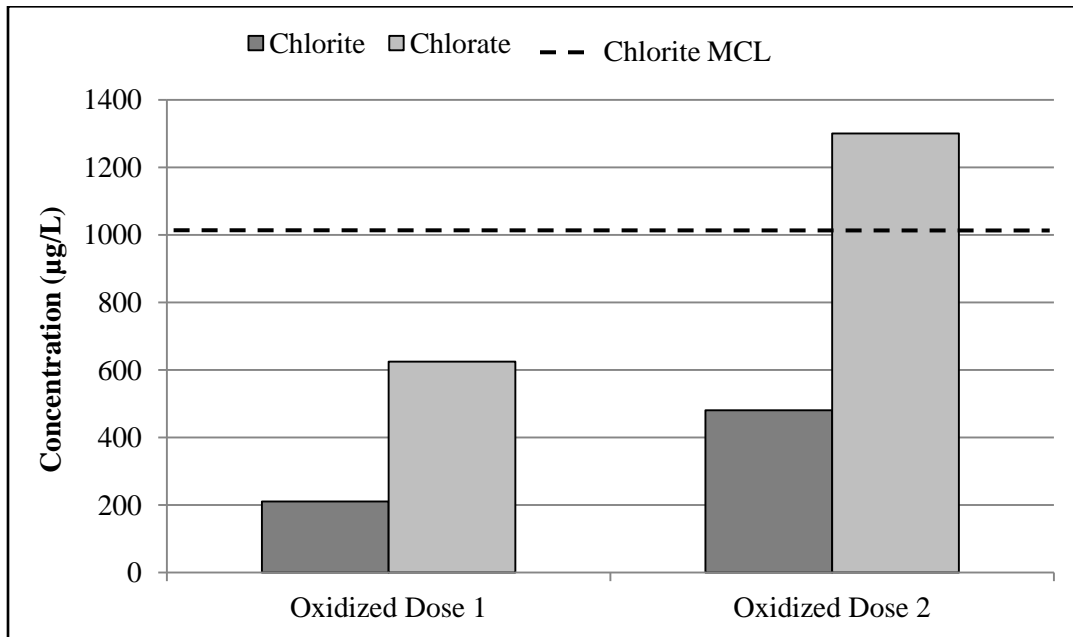


Figure 7: Average Chlorite and Chlorate Concentrations

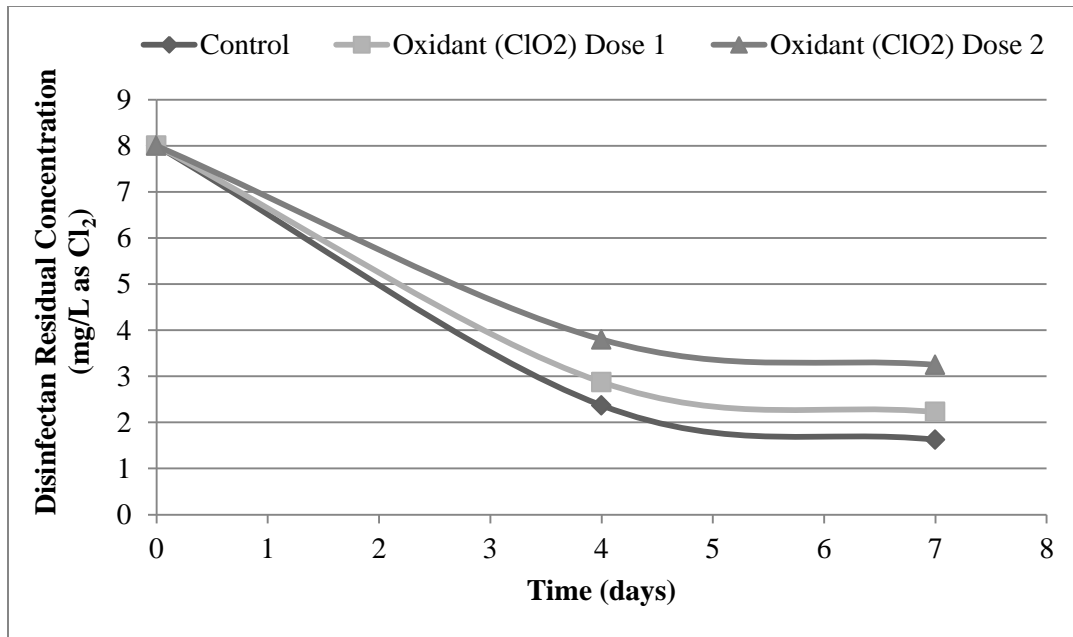


Figure 8: Average Chlorine Residual Concentration Decay with Time

Effect of Dose on Water Quality

As before noted, three ClO₂ doses were studied - 0 mg/L ClO₂ (control), 0.75 mg/L ClO₂ (Dose 1), and 1.5 mg/L ClO₂ (Dose 2). The water quality data gathered during both runs was averaged and is presented on Table 4. Variations in the filtered (final) temperature and pH were relatively small for all ClO₂ dosages. A 23% (Dose 1) and 39% (Dose 2) reduction in turbidity was seen when ClO₂ was applied to the water.

The final color, DOC, UV₂₅₄, and SUVA for Dose 1 did not decrease with respect to the control as expected. For the Dose 1 experiments, color and UV₂₅₄ remained the same, DOC increased slightly, and SUVA decreased slightly. Conversely, relative to the control experiment, pre-oxidation with 1.5 mg/L of ClO₂ decreased the final color, DOC, UV₂₅₄, and SUVA of the filtered water. Specifically, color was reduced by approximately 67%, DOC by around 33%, UV₂₅₄ by about 41%, and SUVA by roughly 12%.

Table 4: Lake Claire (FL) Water Quality Summary

Water Quality Parameter	ClO ₂ Dose	<u>Treatment Train Sample Point</u>			
		Raw	Oxidized	Settled	Filtered
pH	Control		-	7.21±0.44	7.33±1.84
	Dose 1	7.23±0.51	7.22±1.21	6.69±1.40	6.83±1.52
	Dose 2		6.66±1.52	6.12±1.46	6.80±4.13
Temperature (°C)	Control		-	22.5±3.81	22.4±1.91
	Dose 1	22.5±4.45	22.5±4.45	22.5±4.45	22.4±1.27
	Dose 2		22.5±5.08	22.4±3.81	22.4±0.64
Turbidity (NTU)	Control		-	0.310±0.38	0.123±0.92
	Dose 1	0.97±0.76	0.890±1.27	0.365±0.32	0.095±0.57
	Dose 2		0.893±0.22	0.328±0.22	0.075±0.44
Color (CU)	Control		-	-	0.003±0.00
	Dose 1	0.03±0.00	0.0273±0.00	-	0.003±0.00
	Dose 2		0.0245±0.01	-	0.001±0.00
DOC (PPM)	Control		-	-	5.82±1.26
	Dose 1	11.8±0.20	11.6±0.72	-	6.08±4.89
	Dose 2		11.4±0.81	-	3.91±3.04
UV ₂₅₄ (cm ⁻¹)	Control		-	-	0.111±0.03
	Dose 1	0.354±0.01	0.342±0.01	-	0.111±0.03
	Dose 2		0.332±0.02	-	0.066±0.11
SUVA (L/mg-m)	Control		-	-	1.91±0.02
	Dose 1	3.00±0.06	2.95±0.29	-	1.82±0.94
	Dose 2		2.91±0.38	-	1.68±1.62

Effect of Dose on Formation Potential

Using the averaged 7-day TTHM and HAA₅ formation potential obtained, the effect of ClO₂ dose on DBP formation potential was assessed. As shown on Figure 9 and 10, a 1.5 mg/L dose of ClO₂ decreased the 7-day TTHM concentration by 37% and the 7-day HAA₅ concentration by 23%. Conversely, at a dose of 0.75 mg/L of ClO₂, the 7-day TTHM concentration decreased by 8% and the HAA₅ concentration increased by 7%. This increase in HAA₅ concentration for Dose 1 could be correlated with the increased DOC content seen in Table 4.

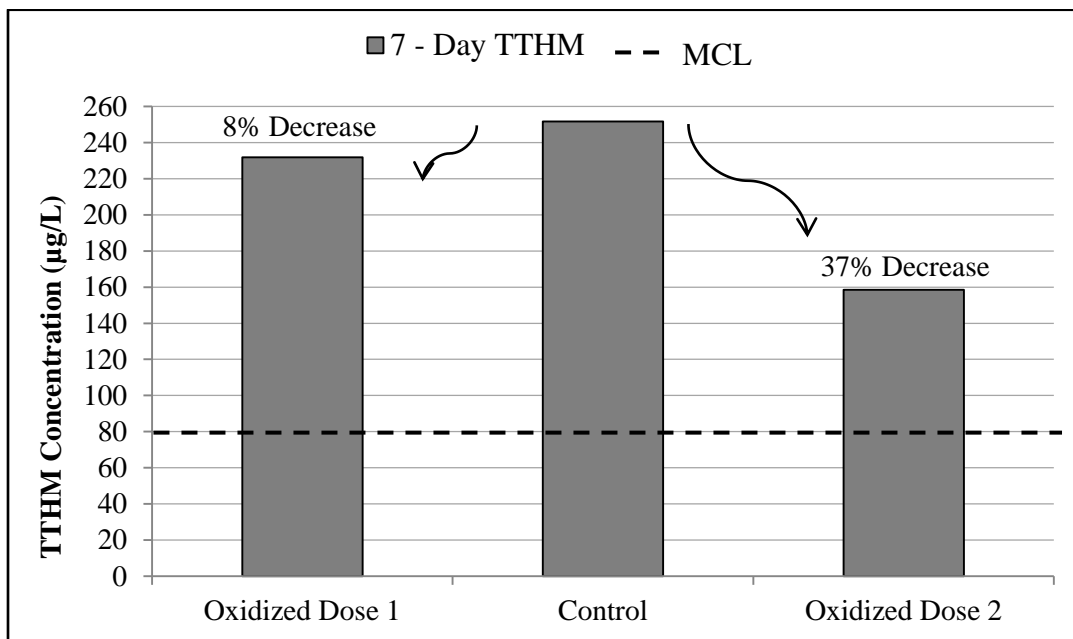


Figure 9: Average Seven-day TTHM Formation Potential

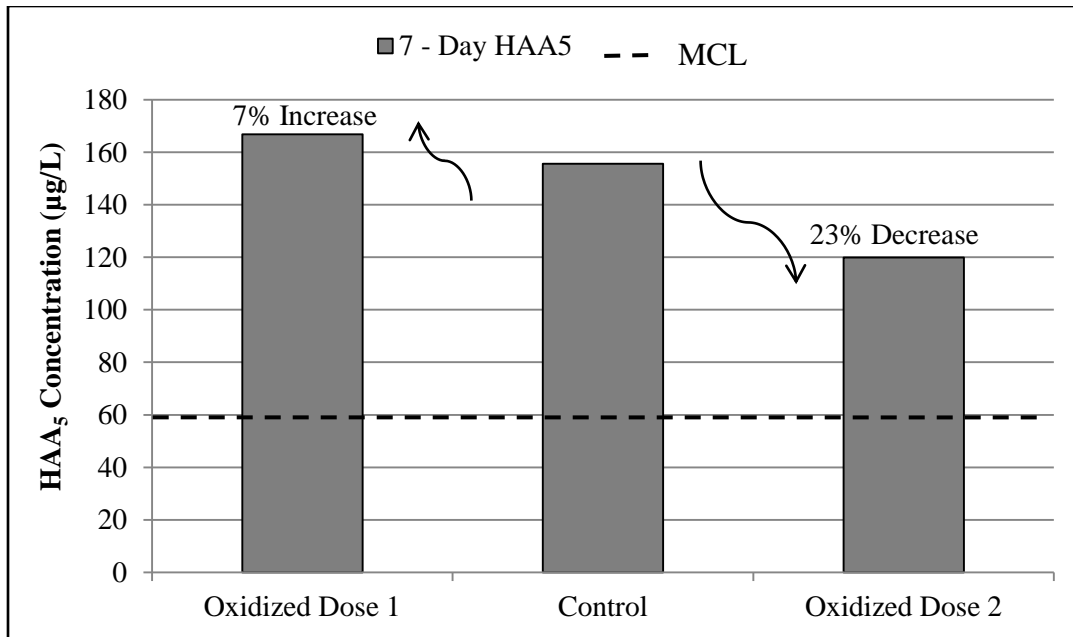


Figure 10: Average Seven-day HAA₅ Formation Potential

Spectrofluorometer Results

Emission excitation matrix (EEM) diagrams were generated to monitor the changes in dissolved organic matter (DOM) characteristics. These EEM diagrams are a three-dimensional contour plot made using Minitab, based on the fluorescence intensity of the water sample analyzed at certain wavelengths. Figures 11 through 14 show the EEM diagrams for the raw water, and chlorinated samples for all ClO₂ doses. Based on Figure 6 and the generated diagrams, it can be concluded that the raw water's DOC is mostly comprised of fulvic acid-like compounds and some humic acid-like compounds. A reduction in the fluorescence intensities detected (spread and maximum peak value) in the chlorinated samples (Figure 12 through 14), with respect to the raw water EEM diagram, can be correlated back to the reduction in DOC and DBPs seen in Table 4 and Figures 9 & 10. Appendix C contains the generated EEM diagrams for the Lake Claire experiments.

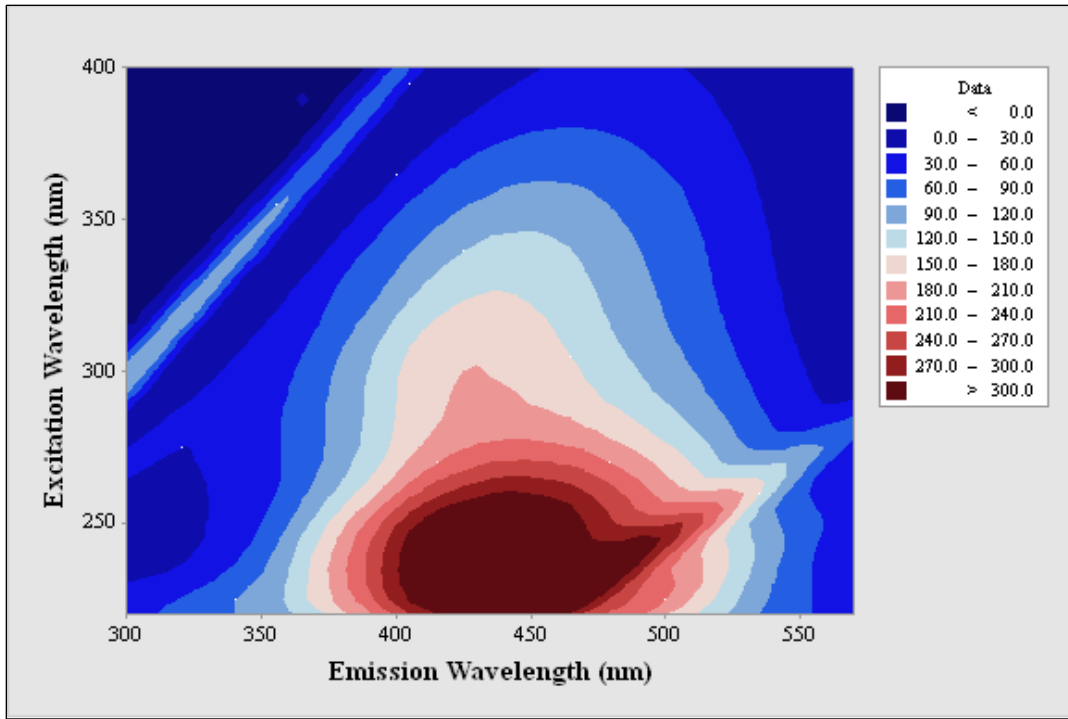


Figure 11: Raw Water EEM Diagram

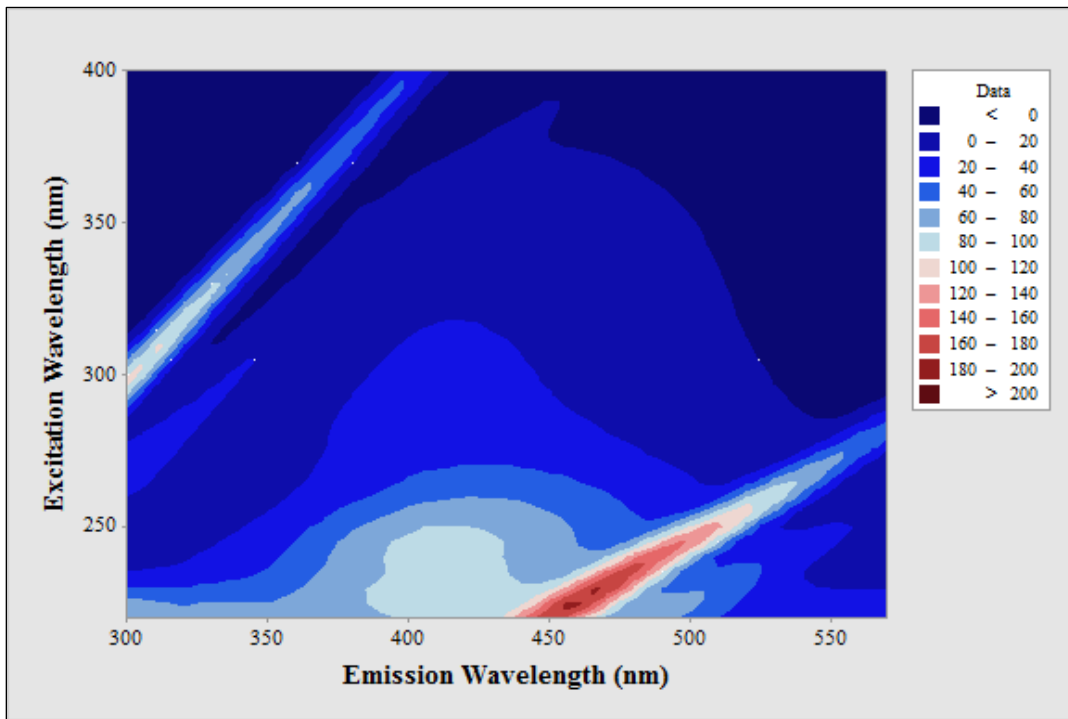


Figure 12: Control Chlorinated EEM Diagram

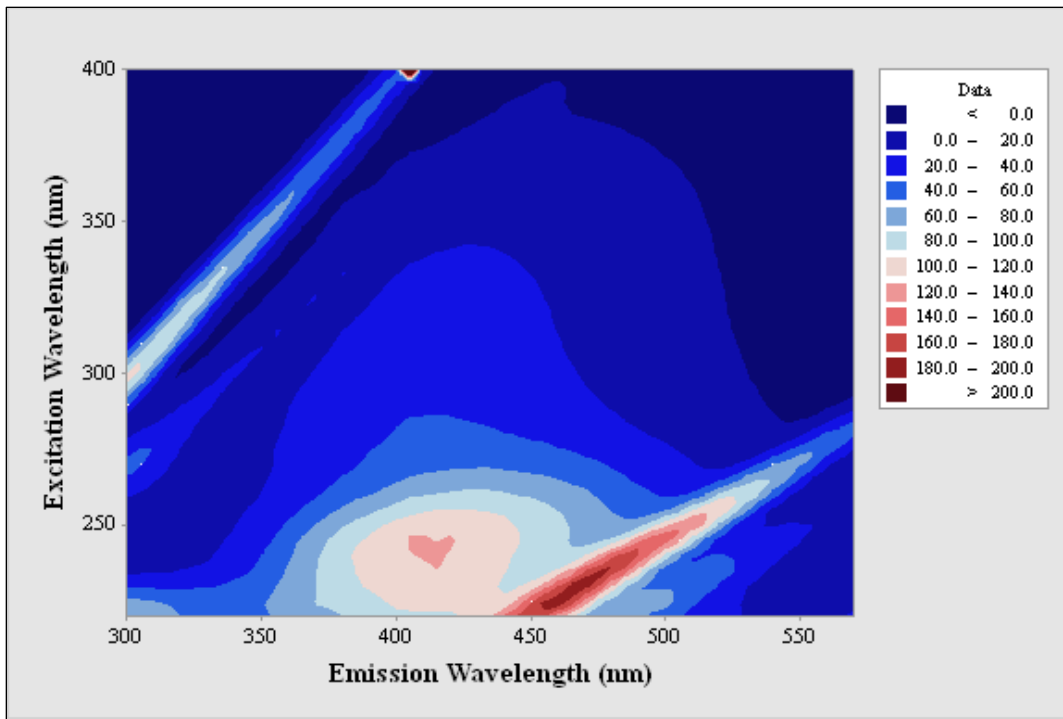


Figure 13: ClO₂ Dose 1 Chlorinated EEM Diagram

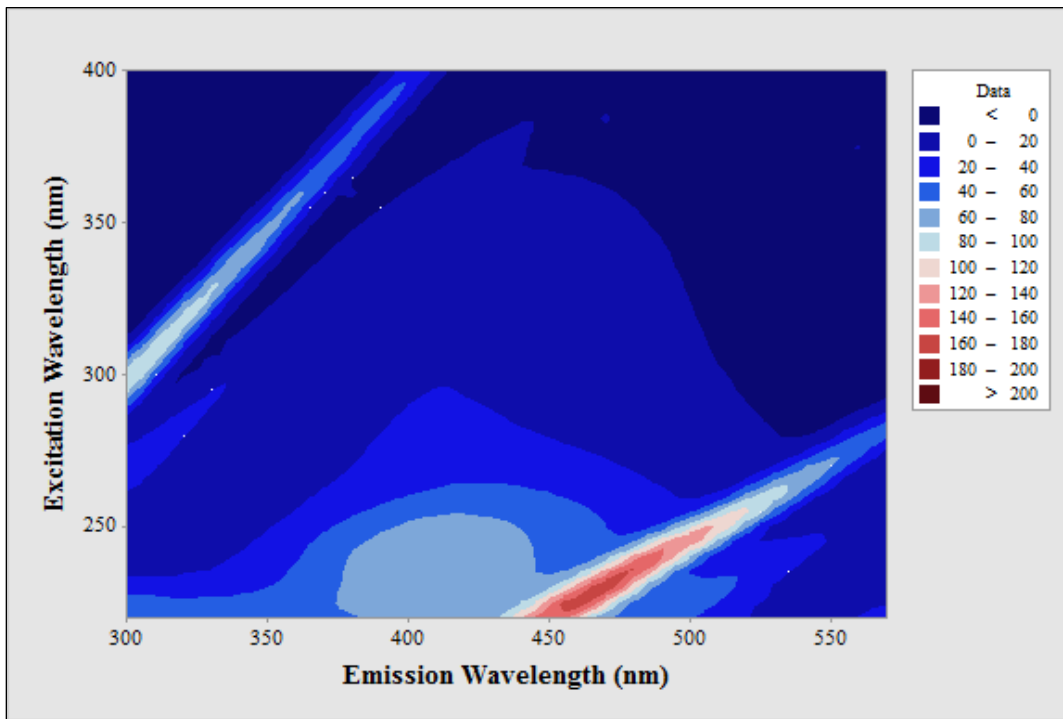


Figure 14: ClO₂ Dose 2 Chlorinated EEM Diagram

Maui Results

Chlorine dioxide pre-oxidation showed an increase in DBPFP for the Maui water source. Under both ClO_2 doses, TTHM concentrations and HAA_5 concentrations after a 7-day holding time were increased significantly. Figure 15 presents the chlorite and chlorate data gathered, with the chlorite level being well below the 1 mg/L EPA MCL. Chlorine residual decay was monitored for this experimental water source. After a seven day holding time, the chlorine residual in the water samples were between 0.7 mg/L and 1.4 mg/L (Figure 16). Samples analyzed for bromide were found to be below the equipment's detection limit (less than 0.2 mg/L).

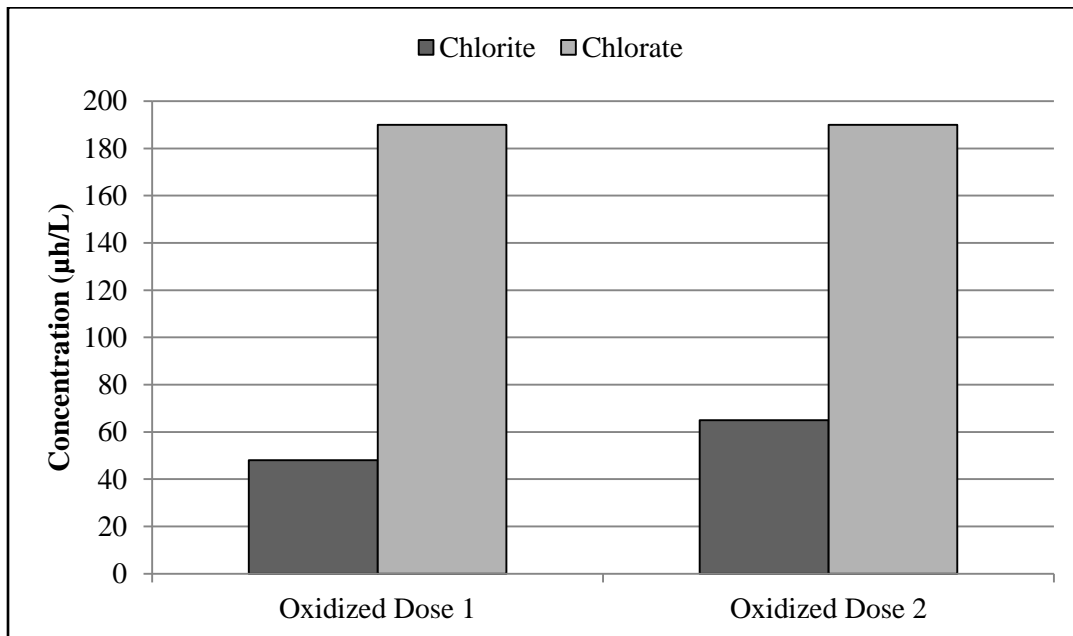


Figure 15: Average Chlorite and Chlorate Concentrations

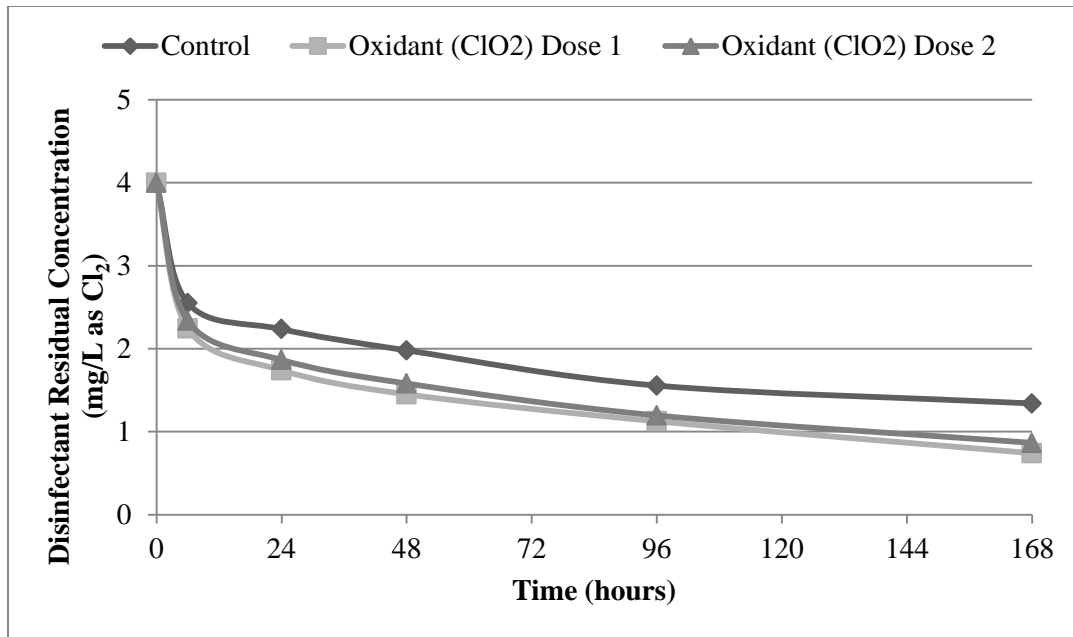


Figure 16: Average Chlorine Residual Concentration Decay with Time

Effect of Dose on Water Quality

For the Maui experiments, the same ClO₂ doses were investigated - 0 mg/L ClO₂ (control), 0.75 mg/L ClO₂ (Dose 1), and 1.5 mg/L ClO₂ (Dose 2). Table 5 contains the averaged values for the various water quality parameters monitored. While the temperature for the filtered samples remained the same for all doses studied, the pH for each of the doses varied slightly. The most notable difference in pH was seen between Dose 1, at 5.39, and Dose 2, at 6.13.

Notably, Dose 1 saw only a small decrease in filtered turbidity and color, in contrast with a considerable increase in DOC and UV₂₅₄ of 40% and 44%, respectively. Furthermore, relative to the control experiment, Dose 2 exhibited an increase in turbidity, color, DOC, and UV₂₅₄. While Dose 2 increased DOC content only by approximately 18%, an equal increase in UV₂₅₄ was seen between Dose 1 and Dose 2. The calculated SUVA values for each of the doses were 1.69 (control), 1.78 (Dose 1), and 2.05 (Dose 2).

Table 5: East Maui (HI) Water Quality Summary

Water Quality Parameter	ClO ₂ Dose	<u>Treatment Train Sample Point</u>			
		Raw	Oxidized	Settled	Filtered
pH	Control		-	5.39±1.52	5.45±0.89
	Dose 1	5.65	3.51±0.19	5.88±1.21	5.39±5.91
	Dose 2		3.24±0.13	6.07±0.10	6.13±0.19
Temperature (°C)	Control		-	23.2±3.49	22.9±1.27
	Dose 1	22.7	22.7±0.64	23.4±3.18	22.9±0.32
	Dose 2		22.7±0.64	23.4±1.91	22.9±2.22
Turbidity (NTU)	Control		-	0.310±0.25	0.065±0.06
	Dose 1	2.53	2.60±0.70	0.355±0.25	0.060±0.0
	Dose 2		2.59±1.08	0.465±0.57	0.090±0.13
Color (CU)	Control		-	-	0.0015±0.01
	Dose 1	0.043	0.029±0.02	-	0.0013±0.00
	Dose 2		0.022±0.03	-	0.0018±0.00
DOC (PPM)	Control		-	-	2.32±0.29
	Dose 1	7.21	7.19±3.12	-	3.24±8.28
	Dose 2		6.65±0.49	-	2.73±1.77
UV ₂₅₄ (cm ⁻¹)	Control		-	-	0.039±0.00
	Dose 1	0.320	0.281±0.06	-	0.056±0.04
	Dose 2		0.252±0.11	-	0.056±0.03
SUVA (L/mg-m)	Control		-	-	1.69±0.35
	Dose 1	4.44	3.92±2.58	-	1.78±3.38
	Dose 2		3.78±1.90	-	2.05±2.37

*The Raw water quality was only measured once due to water quantity limitations

Effect of Dose on Formation Potential

The effect of ClO₂ dose on DBP formation potential was evaluated using the averaged 7-day DBPFP data analyzed. As shown on Figure 17 and 18, Dose 1 and Dose 2 caused a substantial increase in both categories of regulated DBPs. Dose 1 increased the 7-day TTHM concentration by 49% and the 7-day HAA₅ concentration by 50%. Similarly, Dose 2 increased the 7-day TTHM concentration by 53% and the HAA₅ concentration by 60%. The increases in DBPFP may be directly related to the increased DOC content and UV₂₅₄ readings shown on Table 5 for the Dose 1 & 2 samples.

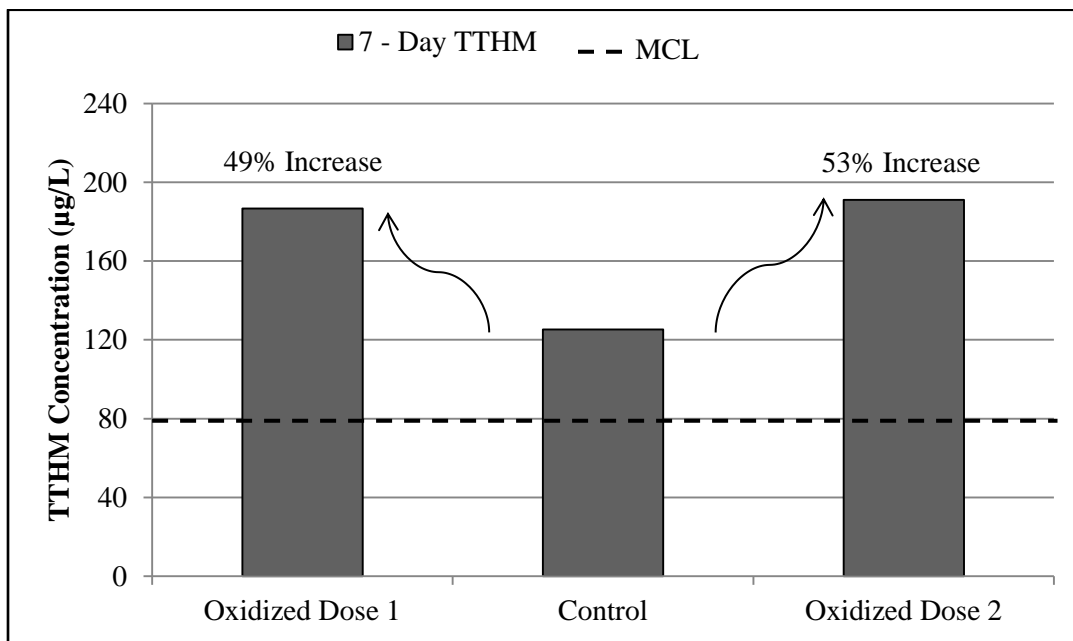


Figure 17: Average Seven-day TTHM Formation Potential

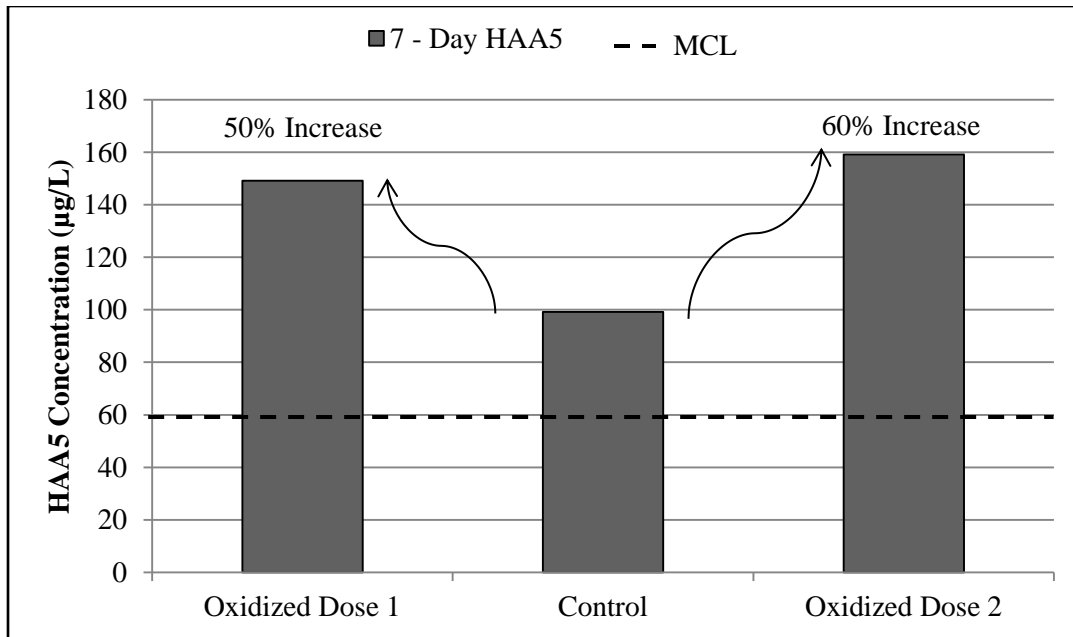


Figure 18: Average Seven-day HAA₅ Formation Potential

Spectrofluorometer Results

To monitor the changes in DOM characteristics, EEM diagrams were generated for the raw water, filtered water, and chlorinated water samples. The excitation and emission wavelength ranges used were 220 nm to 400 nm and 300 nm to 570 nm. Figures 19 through 22 show the EEM diagrams for the raw water, and chlorinated samples for all ClO₂ doses. Based on Figure 6 and the generated diagrams, it can be concluded that the raw water’s DOC is mostly comprised of fulvic acid-like compounds. Although a reduction in the fluorescence intensities detected (spread and maximum peak value) in the chlorinated sample can be seen (Figure 20 through 22), the ClO₂ samples had higher filtered DOC content and DBPFP. Appendix D contains the generated EEM diagrams for the Maui experiments.

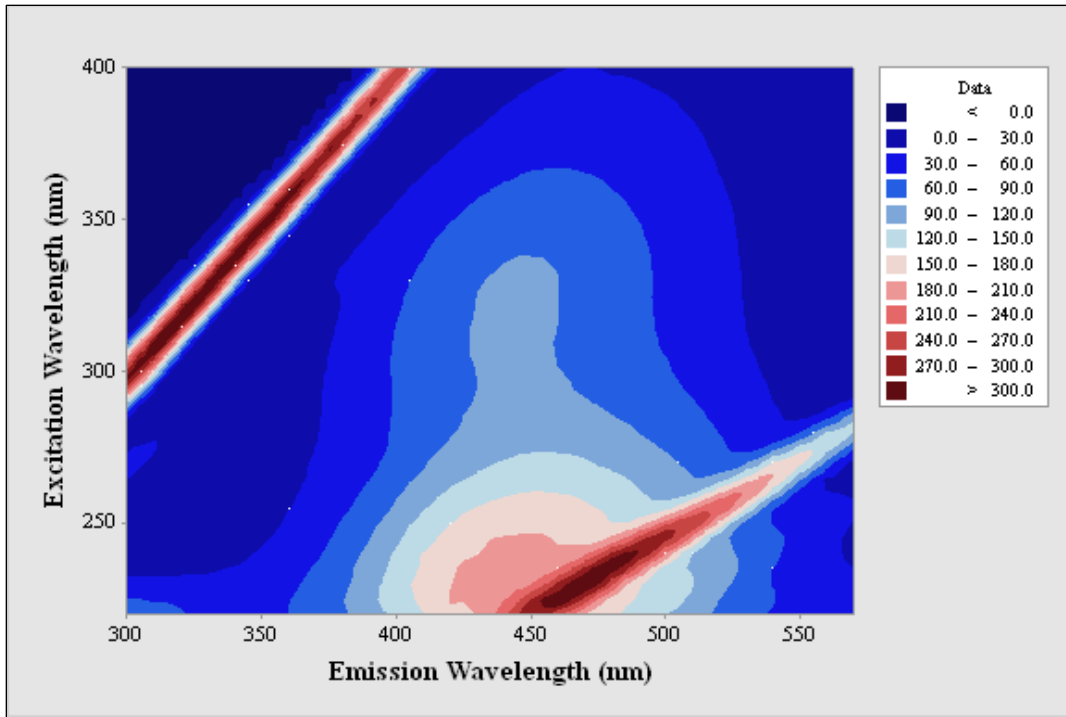


Figure 19: Raw Water EEM Diagram

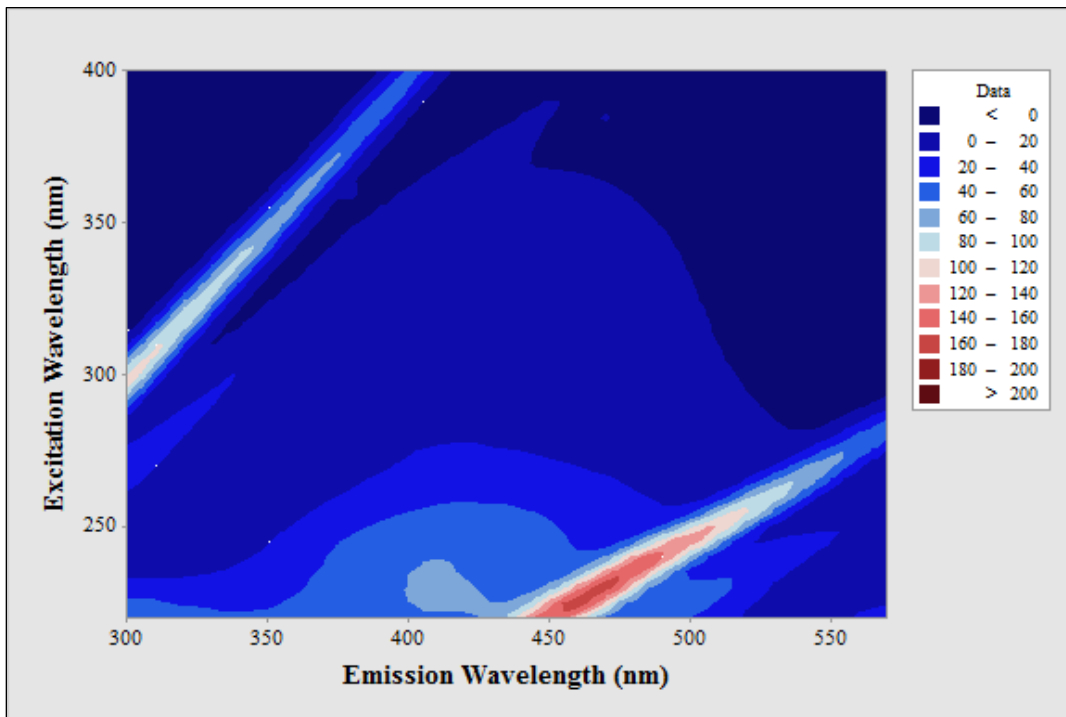


Figure 20: Control Chlorinated EEM Diagram

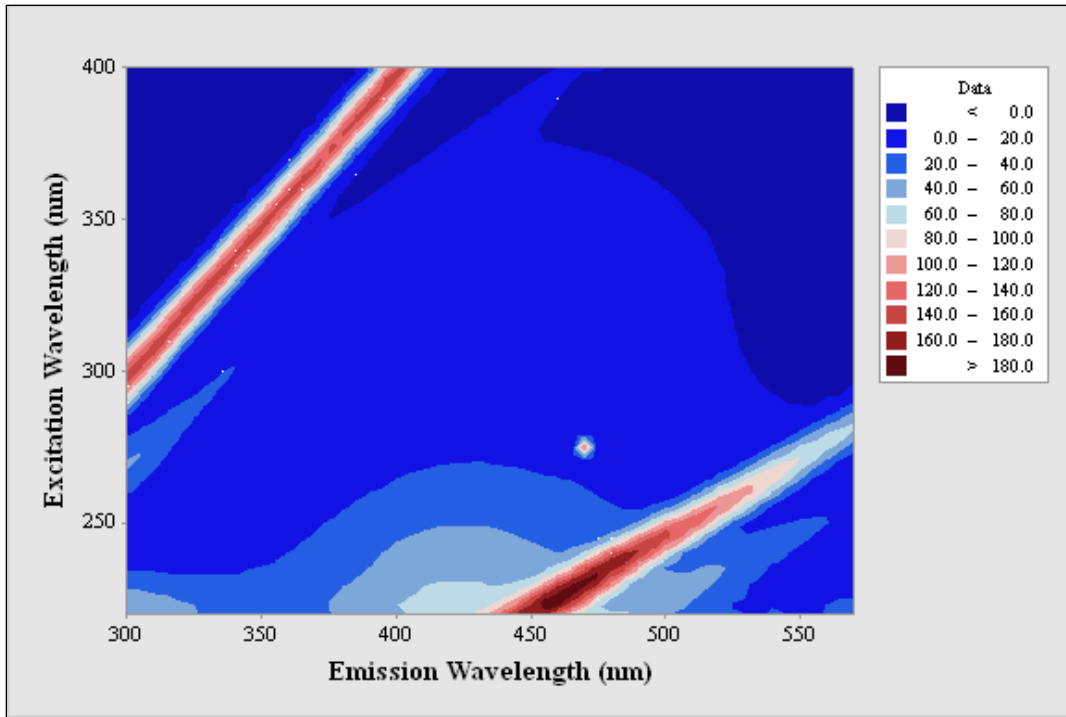


Figure 21: ClO₂ Dose 1 Chlorinated EEM Diagram

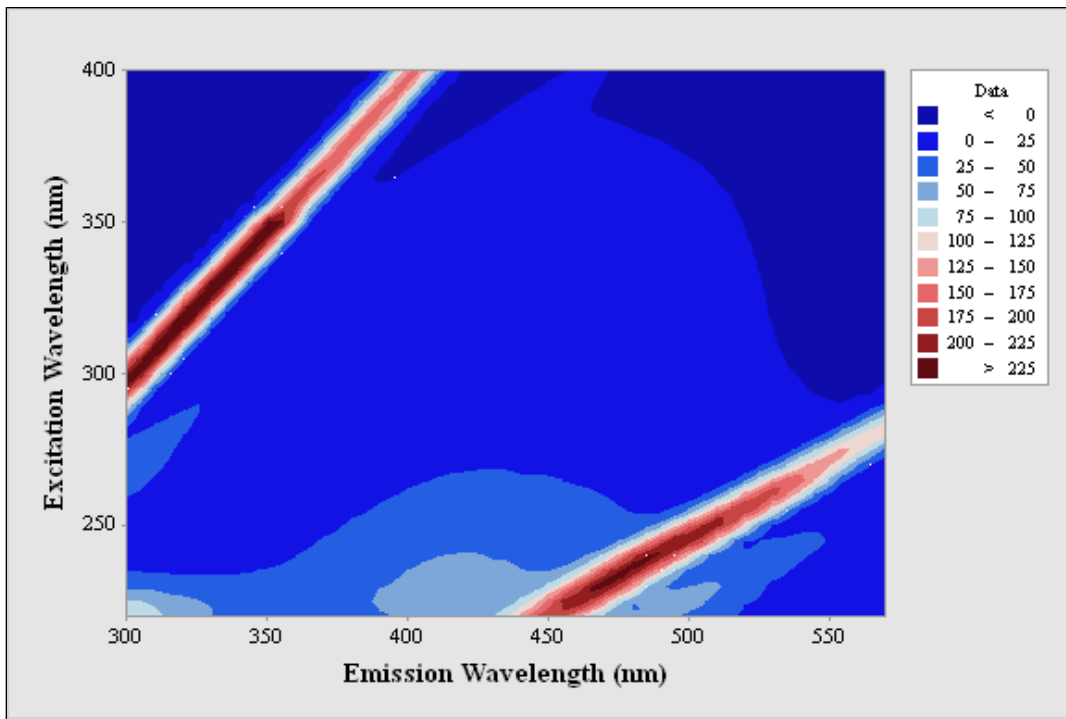


Figure 22: ClO₂ Dose 2 Chlorinated EEM Diagram

Statistical Analysis of Laboratory Data

A statistical analysis was performed using the water quality data collected in the study to establish a mean and 95 percent confidence interval for the experimental results. The results of this analysis are reported in Table 4 (Lake Claire) and Table 5 (East Maui).

A paired T-test was performed to evaluate the 7-day DBPFP data at a specific confidence level, and determine $t_{\text{calculated}}$ and t_{critical} . Using the paired T-test method, if $|t_{\text{calculated}}| > t_{\text{critical}}$, then the means are significantly different at a specified level of confidence. Table 6 displays the $t_{\text{calculated}}$ and t_{critical} values calculated during the analysis.

Table 6: Paired T-test Results Summary

Lake Claire			
7-day TTHM	$t_{\text{calculated}}$	t_{critical}	Confidence Level (%)
Control vs. Dose 1	0.867	0.727	70
Control vs. Dose 2	4.47	3.08	90
7-day HAA ₅	$t_{\text{calculated}}$	t_{critical}	Confidence Level (%)
Control vs. Dose 1	4.14	3.08	90
Control vs. Dose 2	3.41	3.08	90
East Maui			
7-day TTHM	$t_{\text{calculated}}$	t_{critical}	Confidence Level (%)
Control vs. Dose 1	3.88	3.08	90
Control vs. Dose 2	7.05	3.08	90
7-day HAA ₅	$t_{\text{calculated}}$	t_{critical}	Confidence Level (%)
Control vs. Dose 1	34.13	3.08	90
Control vs. Dose 2	58.52	3.08	90

The analysis found that for Lake Claire the change in the 7-day TTHM for Dose 2 and the change in the 7-day HAA₅ for Dose 1 & Dose 2 (when compared to the control) were significantly different at a 90% confidence level. The change observed in the 7-day TTHM for Dose 1 when compared to the control was significantly different at a confidence level of 70%. For the East Maui data the change in DBPFP between the control and pre-oxidized samples, for both TTHM and HAA₅, was significantly different at a 90% confidence level.

Results Summary

This study found that pre-treatment of surface water using ClO₂ could increase or decrease DBP formation in water depending on water source and type. Specifically, Lake Claire water dosed with 1.5 mg/L of ClO₂ reduced TTHM by 37% and HAA₅ by 23%, whereas East Maui water at the same oxidant dose increased TTHM by 53% and HAA₅ by 60%. It is suspected that for the East Maui water, ClO₂ reacted with the large organic molecules, breaking them down into several smaller ones. Subsequently, these smaller organic molecules were not effectively removed by conventional treatment and ultrafiltration. The increase in DBPFP observed in the East Maui experiments could be linked to the higher filtered DOC concentration in the dosed samples, when compared to the control. Table 7 summarizes the chlorine dioxide pre-oxidation experimental findings.

Table 7: Chlorine Dioxide Pre-Oxidation Experiment Summary

Source Water	ClO ₂ Dose	DOC (PPM)	SUVA (L/mg-m)	7-Day TTHM (µg/L)	7-Day HAA ₅ (µg/L)
Lake Claire					
Run 1	Control	5.92	1.91	265	157
	Dose 1	5.70	1.90	222	166
	Dose 2	3.67	1.55	151	111
Run 2	Control	5.72	1.91	238	154
	Dose 1	6.47	1.75	241	168
	Dose 2	4.14	1.81	166	129
East Maui Watershed					
Run 1	Control	2.34	1.66	126	96
	Dose 1	3.89	1.52	171	144
	Dose 2	2.87	1.86	182	157
Run 2	Control	2.30	1.72	125	103
	Dose 1	2.59	2.05	202	154
	Dose 2	2.59	2.24	200	162

CONCLUSIONS

The purpose of this study was to quantify the effectiveness of chlorine dioxide pre-oxidation as a control strategy for DBPFP of two surface water supplies. Lake Claire raw water, located in Orlando, FL, and Olinda WTP raw water, located in Maui, HI, were the two surface waters investigated in this case study. A 0.75 mg/L dose of ClO_2 and a 1.5 mg/L dose of ClO_2 were used to oxidize the water, to prevent the violation of EPA's chlorite MCL. A conventional treatment process (coagulation, flocculation, sedimentation), followed by ultrafiltration was employed for this study.

While the organic content, as measured by DOC, for the Lake Claire raw water was higher than the Maui water, both raw waters had high SUVA values. These SUVA values for both surface waters, at 3.00 L/mg-m and 4.44 L/mg-m respectively, show that the raw water DOC is mostly made up of hydrophobic, aromatic organic compounds. This is further supported by the EEM diagrams, which showed that both surface water sources were high in humic and fulvic organic acids. Although the DOC, SUVA, and EEM data was similar for the source waters, chlorine dioxide pre-oxidation treatment produced different 7-day DBPFP.

A ClO_2 dose of 0.75 mg/L resulted in an increase in HAA_5 and a decrease in TTHM formation potential for Lake Claire. The Lake Claire overall DBPFP was reduced when the raw water was oxidized with 1.5 mg/L of ClO_2 . Conversely, both ClO_2 doses caused a notable increase in the overall DBPFP for the Maui water.

One of the key differences between these two surface water sources was their alkalinity level (FL ~ 35 mg/L as CaCO_3 , HI ~ 6 mg/L as CaCO_3). Future studies should determine the effect of alkalinity on this treatment process to assess its effect on DBPFP. The results could

potentially explain why Lake Claire's DBPFP decreased, while East Maui Watershed's increased.

APPENDIX A: EQUIPMENT & MATERIALS LIST

Equipment

- Chlorine Dioxide Generator
- Stir Plate
- White Plastic Containers with spout
- pH meter
- Turbidity meter
- Spectrophotometer
- Shimadzu RF-1501 Spectrofluorophotometer
- TOC analyzer
- Jar testing machine with 6, two liter jars
- 20-200 μL , 200-1000 μL and 1-5 ml Eppendorfs
- Vacuum pump
- IC
- GC
- Fume hood

Materials

- Eppendorf disposable tips
- Kim wipes
- Parafilm
- Labels
- TOC vials with foil and caps – 84
- 0.45, 0.2, 0.1 micron filters
- Erlenmeyer flask with side tube (labeled) – 3
- Filtering cups (labeled) - 3
- 500 mL Erlenmeyer flasks with wide mouth - 12
- Beakers
- Graduated Cylinder
- Plastic transfer pipets
- 10 mL cuvette
- UV254 vial
- Volumetric Flask
- Turbidity vial
- 1 L Amber bottles and caps
- 60 mL Amber bottle and caps - 20
- 250 mL Amber bottle and caps - 9
- 125 mL Amber bottle and caps - 20
- 3000 mL beaker - 2
- 1000 mL graduated cylinder – 3 (labels: Raw, ClO₂ Dose 1, ClO₂ Dose 2)
- Stir bars (small, medium, large)
- Magnetic pick-up bar
- Wooden platform for coagulant dosing
- Septas for coagulant dosing
- Scissors
- Gloves

APPENDIX B: DETAILED EXPERIMENTAL PROCEDURE

Coagulant Dose Determination:

1. Determine the volume adjusted plant coagulant dose, and a dose higher and one lower than the plant dose
2. Set up the jar testing equipment and input the jar testing sequence
 - a. 300 RPM for 15 sec
 - b. 15 RPM for 25 min
 - c. 0 RPM for 45 min
3. Transfer 13.5 L of raw water into the white plastic container to bring the temperature to ambient and place drum of water back in cooler
4. Clean jars and fill jars 1 through 6 with 2 L of raw water sample using the graduation on the jars
5. Using an Eppendorf, apply ClO₂ Dose 1 to jars 1-3 and ClO₂ Dose 2 to jars 4-6
6. While the reaction is taking place, align the wooden beam with the septas for coagulant dosing. For jars 1-3, coagulant doses are: plant volume adjusted, higher than plant, lower than plant. Repeat for jars 4-6
7. Use Eppendorf to measure out each jar's coagulant dose and pour on respective septas. Record the coagulant dose for each jar and the chlorine dioxide dose it received
8. At the end of the chlorine dioxide reaction time, dose the water (using the wooden bar) and turn on the jar testers simultaneously, observe coagulation, write notes and take pictures

9. While the jar testing sequence is running its course, place a 500 mL Erlenmeyer flask and a piece of parafilm next to each jar, with a label indicating the jar number, coagulant dose, and ClO₂ dose
10. Once the jar testing sequence is over, waste a small amount of water from each jar and withdraw ~500mL of coagulated water from the jars (making sure not to get settled particles) and parafilm the top of the flask
11. Run turbidity, UV254, pH, and temperature on each of the flasks and record
12. Clean jar testing equipment and glassware used
13. Determine the best coagulant dose for ClO₂ dose 1 and 2 based on the water quality results

Prep-work for experimental runs:

1. Prepare the TOC standards and the quenching reagents for the experiment
2. Speak to lab manager to reserve jar testing equipment and space in lab for experiment
3. Write labels for all samples
4. Gather DBPFP amber bottles and caps that will be used
5. Find an empty incubation cabinet for DBPFP samples in lab
6. Calibrate probes needed (pH, etc)
7. Check to make sure all needed equipment is in stock (kimwipes, Eppendorfs tips, etc)
8. Clean any glassware that will be needed (1000 mL beakers, big graduated cylinders, etc)
9. Set out and separate cleaned glassware that will be used for experiment (waste beaker, 1000 mL beaker, Erlenmeyer flask, etc)

10. Store water in cooler
11. Make space for DBPFP samples in cooler
12. Prepare and store a batch of chlorine dioxide

Experiment Run:

1. Take water drum out of cooler and transfer 13.5 L of raw water into the white plastic container. Set out to bring up to room temperature. If necessary use water bath
2. Wipe down all counter space which will be used for experiment and set down paper towels
3. Using a cart, bring all needed equipment from 440 to 438 and set up filtering station, calibrate pH probe, turn on Spectrophotometer, create color standard curve, calibrate turbidity meter
4. Once water is at room temperature, rinse six 2 L jars from the jar tester with a little bit of the raw water from the white plastic container
5. Add 2 L of raw water into jars 1 through 6 using jar gradations
6. Label the jars 1 and 2 “Control”, 3-4 “ClO₂ Dose 1”, and 5-6 “ClO₂ Dose 2”
7. Fill a 500 mL Erlenmeyer flask with raw water and label it for raw water quality testing. Parafilm the tops. Set Aside
8. Set up the jar testing machine for 200 RPM continuously for 1 hour and lower stir bars
9. Using two Eppendorfs and the ClO₂ stock, apply Dose 1 and Dose 2 to the respective jars, and simultaneously turn the jar tester on and set a 1 hour timer
10. While the reaction is taking place, align the wooden beam with the septas. Using an Eppendorf pour the plant volume adjusted coagulant dose on the septas for jar 1 and 2,

the optimal coagulant dose for ClO₂ dose 1 on the septas for jar 3 and 4, and the optimal coagulant dose for ClO₂ dose 2 on the septas for jar 5 and 6

11. Record the coagulant dose for each jar and the ClO₂ dose it received
12. At the end of the chlorine dioxide reaction time, turn off jar tester and withdraw 500 mL of oxidized water from jars 3-6 into labeled Erlenmeyer flasks.
13. Dose the water (using the wooden bar) with ACH and turn on the jar testers simultaneously, observe coagulation, write notes and take pictures
14. Label twelve 500 mL flask as “Control – Settled” (4), “Dose 1 – Settled” (4), and “Dose 2 – Settled” (4).
15. Run turbidity, pH and temperature for the “Raw WQ”, “Oxidized ClO₂ Dose 1 WQ”, and “Oxidized ClO₂ Dose 2 WQ” flasks. Be conservative with the water
16. Once the jar testing is over, waste a little bit of water from each jar into a waste beaker
17. Withdraw 1500 - 2000 mL of water from jars 1&2 combined, 3&4 combined, and 5&6 combined into labeled Erlenmeyer flasks, “Control-Settled WQ”, “ClO₂ Dose 1-Settled WQ”, and “ClO₂ Dose 2-Settled WQ”, parafilm the top and set aside for water quality.
18. Using a filtering station, filter 1000 mL of control-settled, dose 1-settled, and dose 2-settled water. Monitor filtering process to refill filter cup or change filters. (Take picture of set up)
 - a. Pour first 500 mL of finished 0.1 μm filtered water into an Erlenmeyer flask and label “Control-Filtered WQ”, parafilm, and set aside.
 - b. Repeat process for each sample (dose 1 and dose 2)

- c. Pour 1 L of finished water into a labeled 2 L beaker (maintain beaker covered with a piece of foil and record exact volume of water in it using a graduated cylinder)
 - d. Rinse filtering set ups with DI three times and remove excess water with kimwipe or air
19. Set up labeled DBPFP amber bottles, uncapped, on counter.
 20. Place the labeled 2 L beaker with “Control-Filtered” water on a stir plate, add a medium-large stir bar and turn on power
 21. Using a pH probe, record the temperature and starting pH of the water in the beaker
 22. Using an Eppendorf, record the time and add the chlorine dose to the water and let it mix for a few seconds
 23. Fill amber bottles to the top and cap, check for bubbles and dry. Place them in the incubation cabinet
 24. Repeat steps 19-23 with the ClO₂ Dose 1 –Filtered and ClO₂ Dose 2 – Filtered water.
 25. Run turbidity, pH and temperature for the “Control-Settled WQ”, “ClO₂ Dose 1-Settled WQ”, and “ClO₂ Dose 2-Settled WQ”, “Control-Filtered WQ”, “ClO₂ Dose 1-Filtered WQ”, and “ClO₂ Dose 2-Filtered WQ”. Be conservative with the water
 26. Run color and UV254 for all water quality samples
 27. Fill and label DOC vials for required WQ sample points.
 28. Quench DBPFP samples as needed with quenching reagents.
 - a. Record chlorine residual
 - b. Ship DBPFP samples for analysis

Clean-up

1. Turn off all equipment (Spec, pH meter, stir plates, etc)
2. Pack up equipment that goes in cases and place everything on cart and return to 440 to its proper place.
3. Take all used/dirty glassware to 440 and wash and let to dry for next run.

APPENDIX C: LAKE CLAIRE FLUORESCENCE SPECTROSCOPY DATA

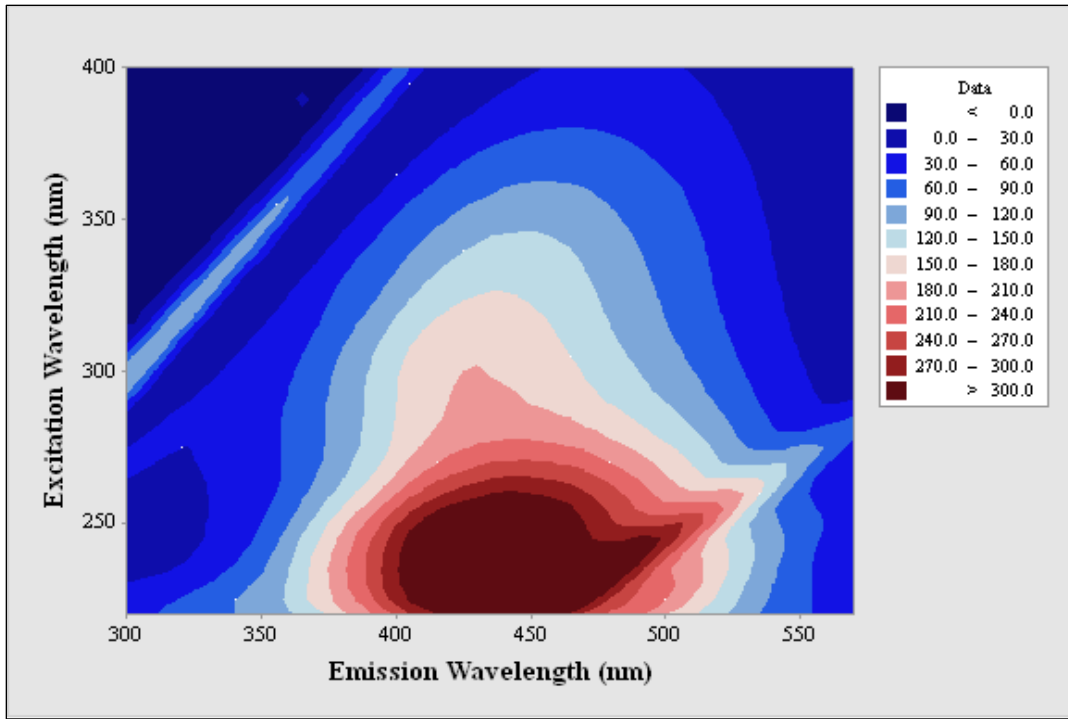


Figure C.1: Raw Water EEM Diagram

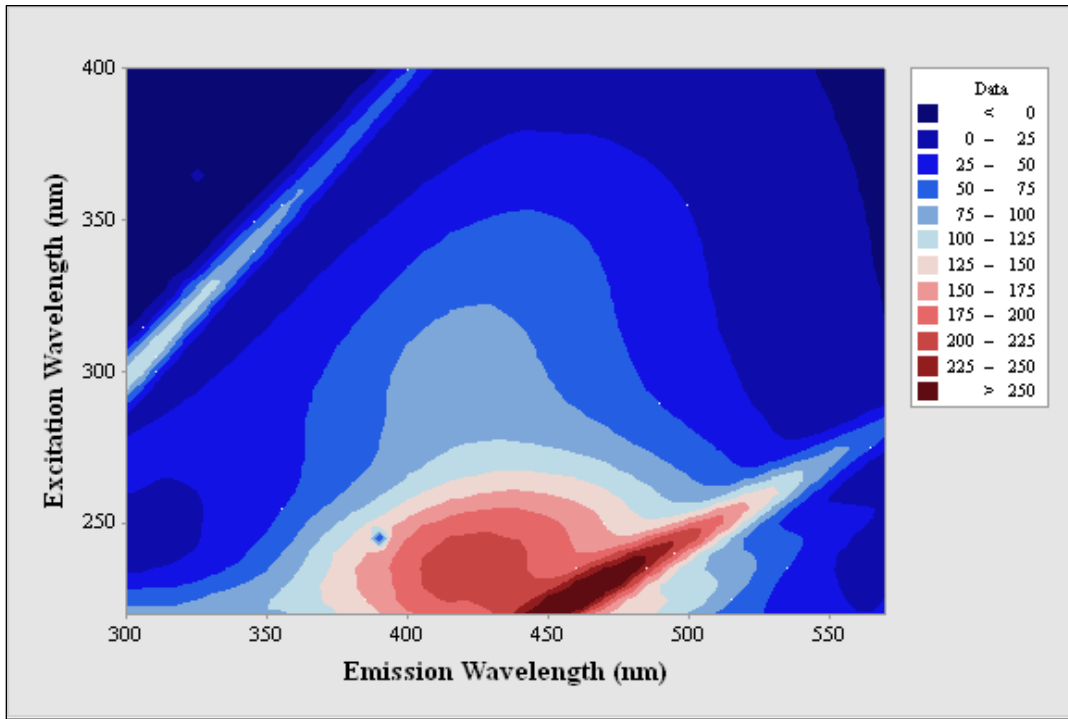


Figure C.2: Control Finished Water EEM Diagram

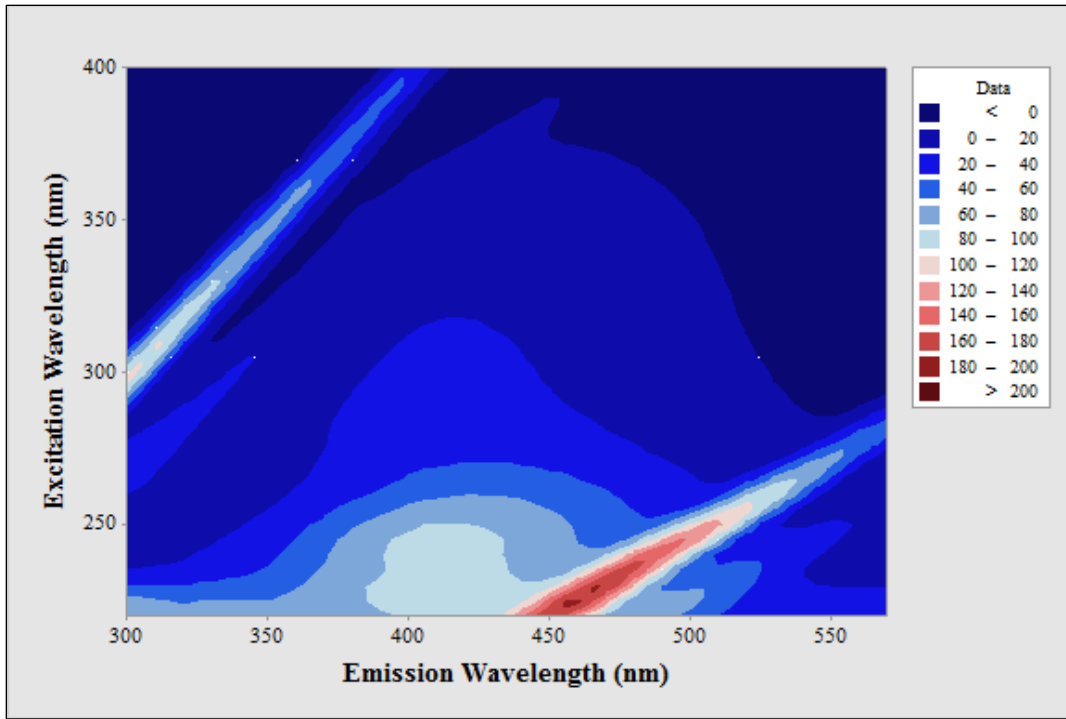


Figure C.3: Control Chlorinated Water EEM Diagram

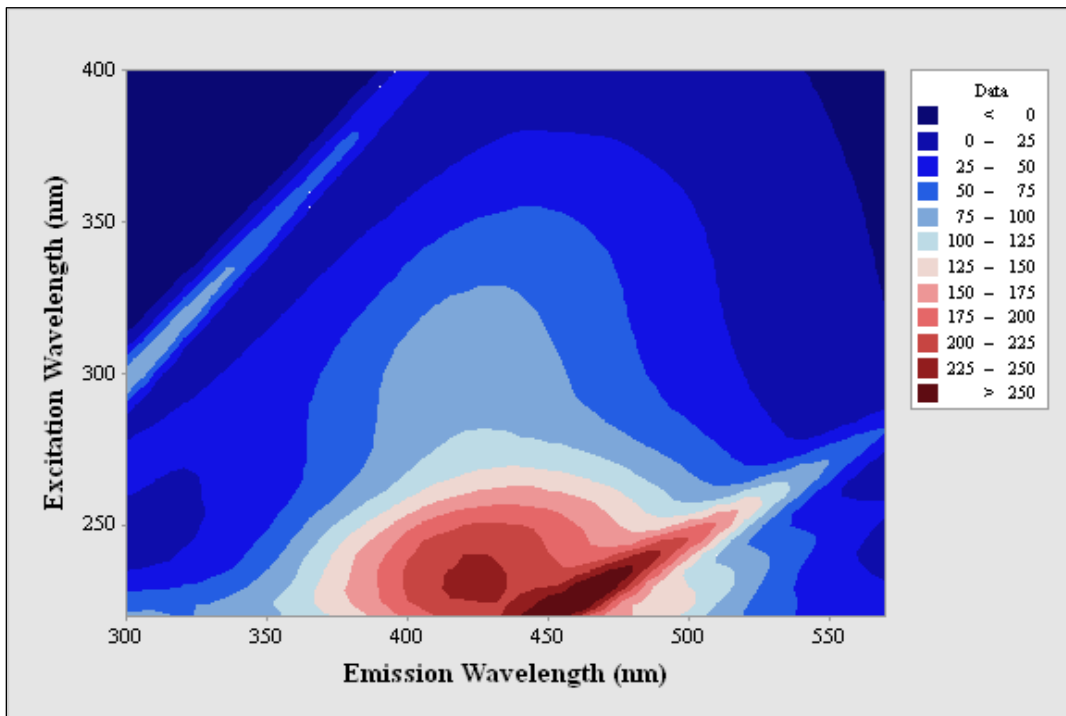


Figure C.4: ClO₂ Dose 1 Finished Water EEM Diagram

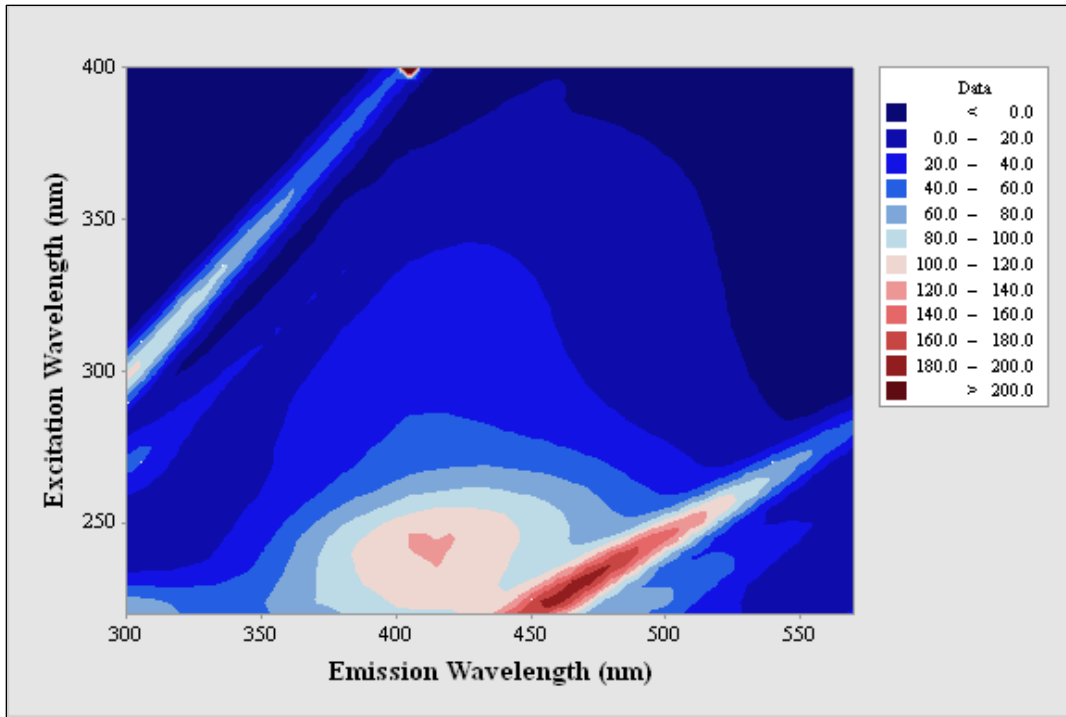


Figure C.5: ClO₂ Dose 1 Chlorinated Water EEM Diagram

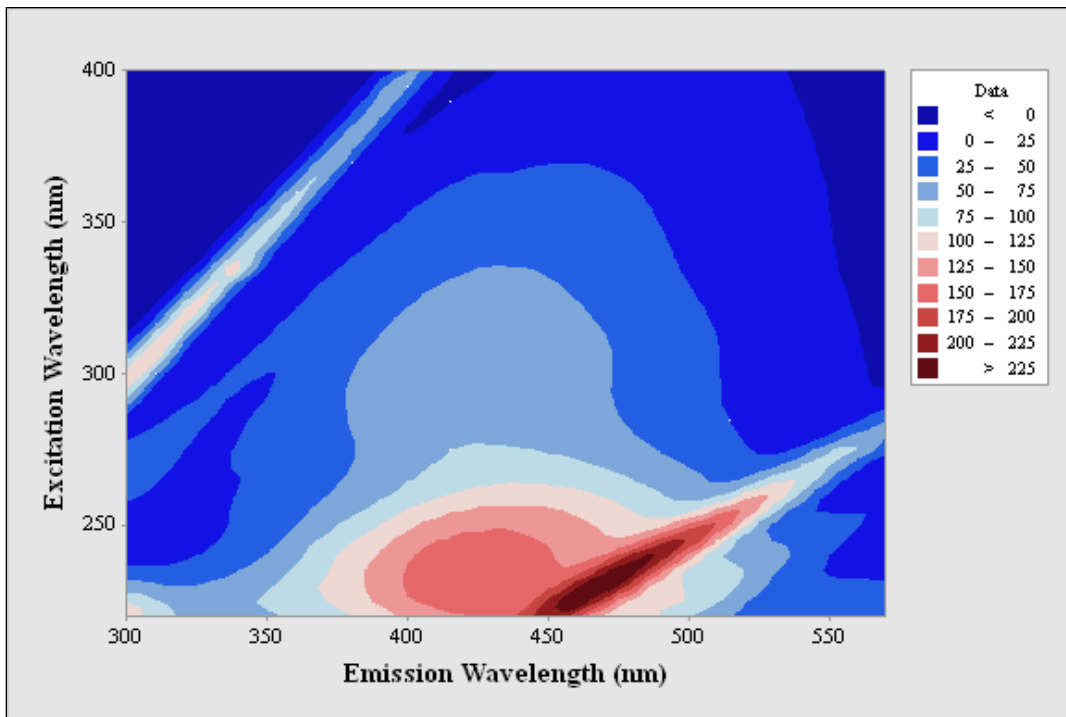


Figure C.6: ClO₂ Dose 2 Finished Water EEM Diagram

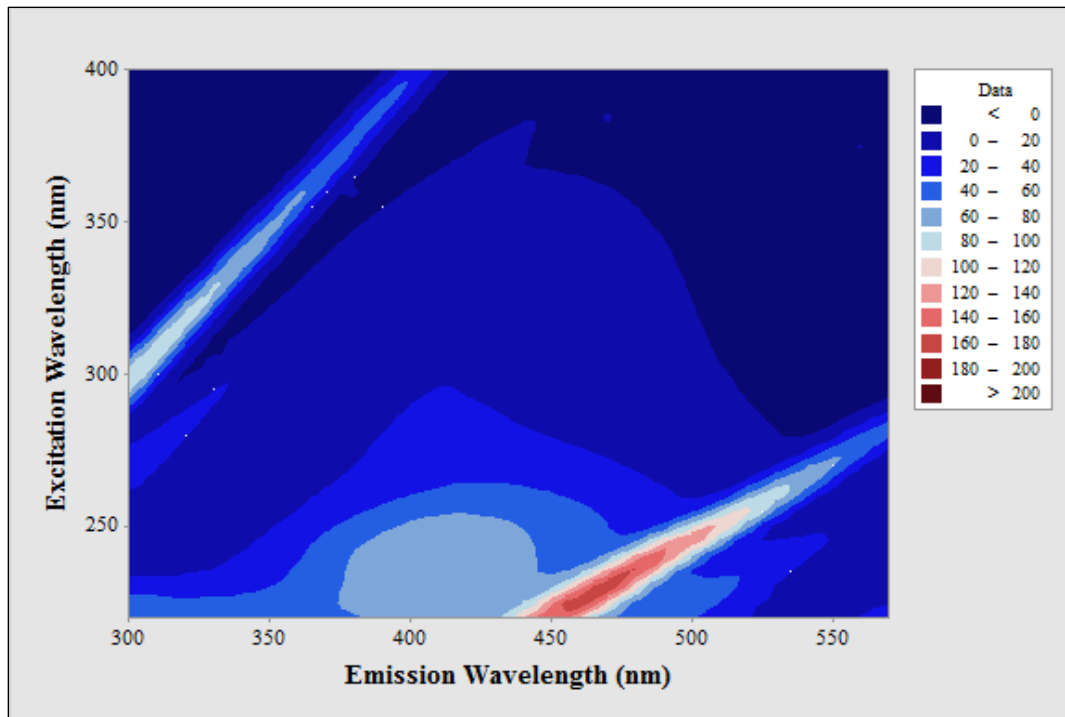


Figure C.7: ClO₂ Dose 2 Chlorinated Water EEM Diagram

APPENDIX D: MAUI FLUORESCENCE SPECTROSCOPY DATA

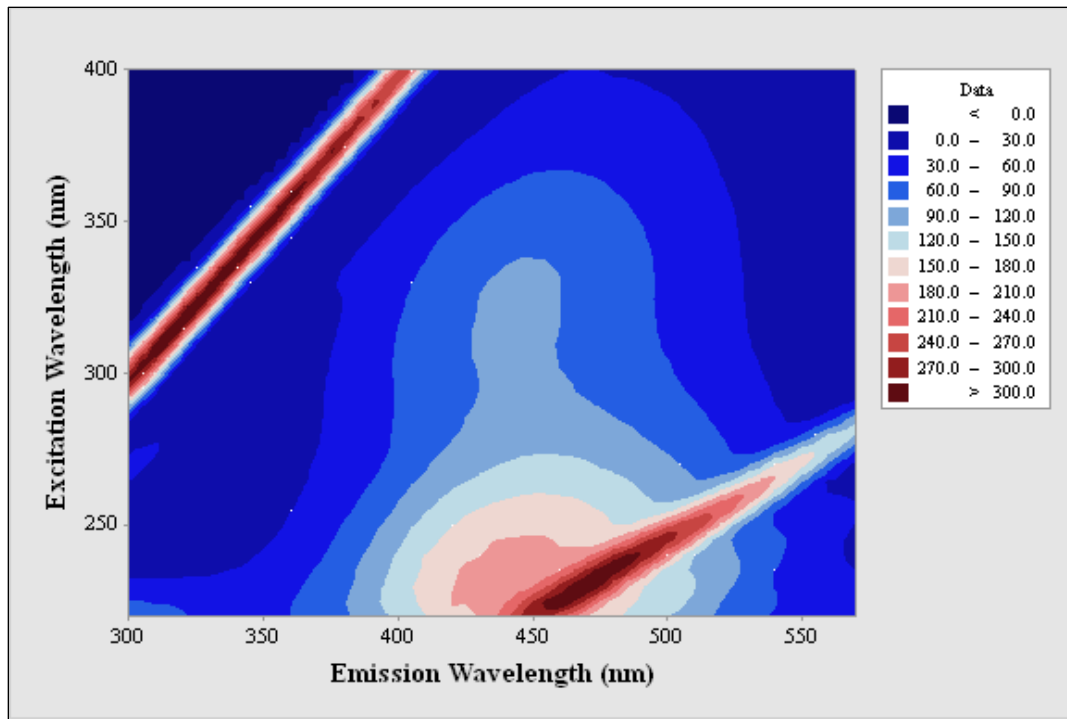


Figure D.1: Raw Water EEM Diagram

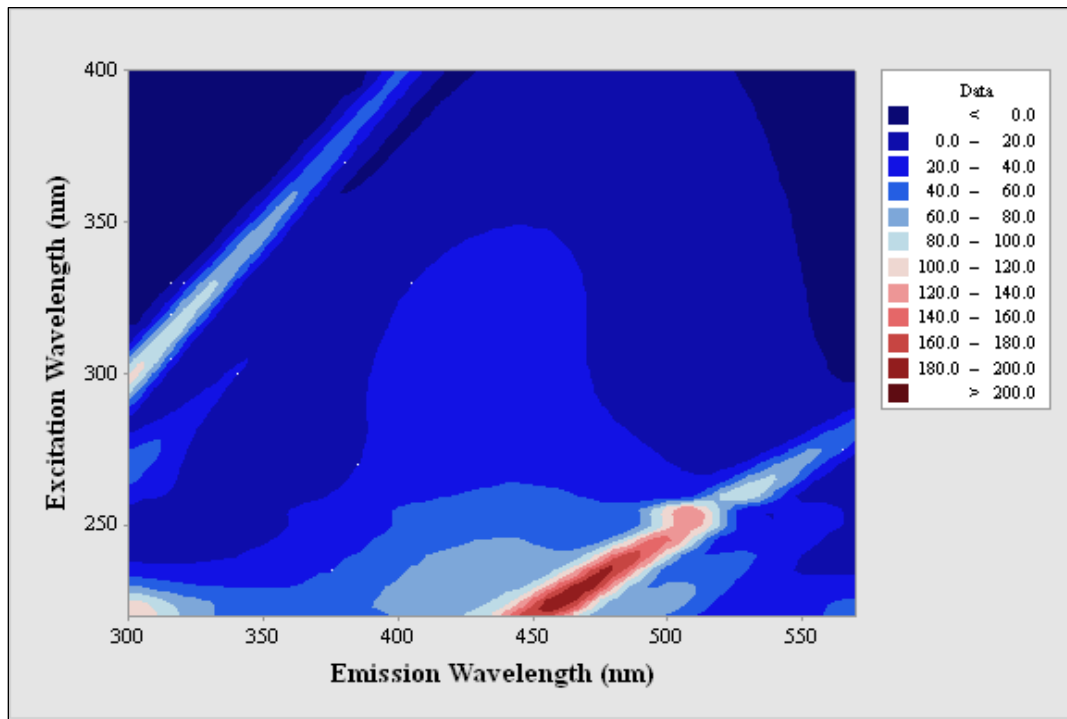


Figure D.2: Control Finished Water EEM Diagram

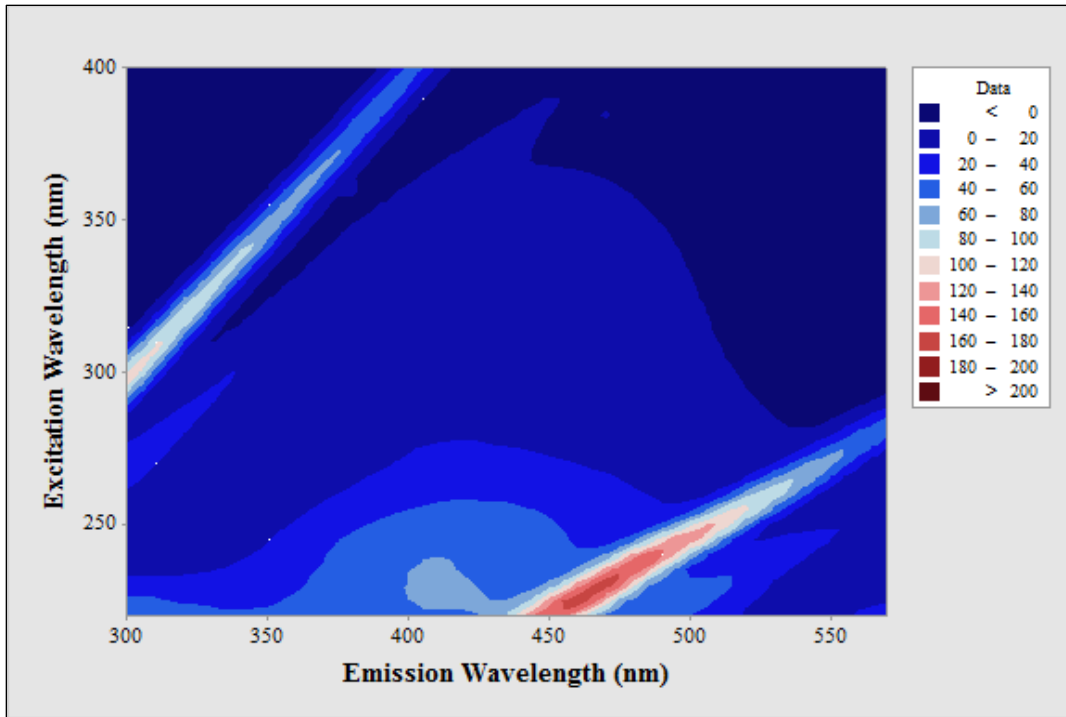


Figure D.3: Control Chlorinated Water EEM Diagram

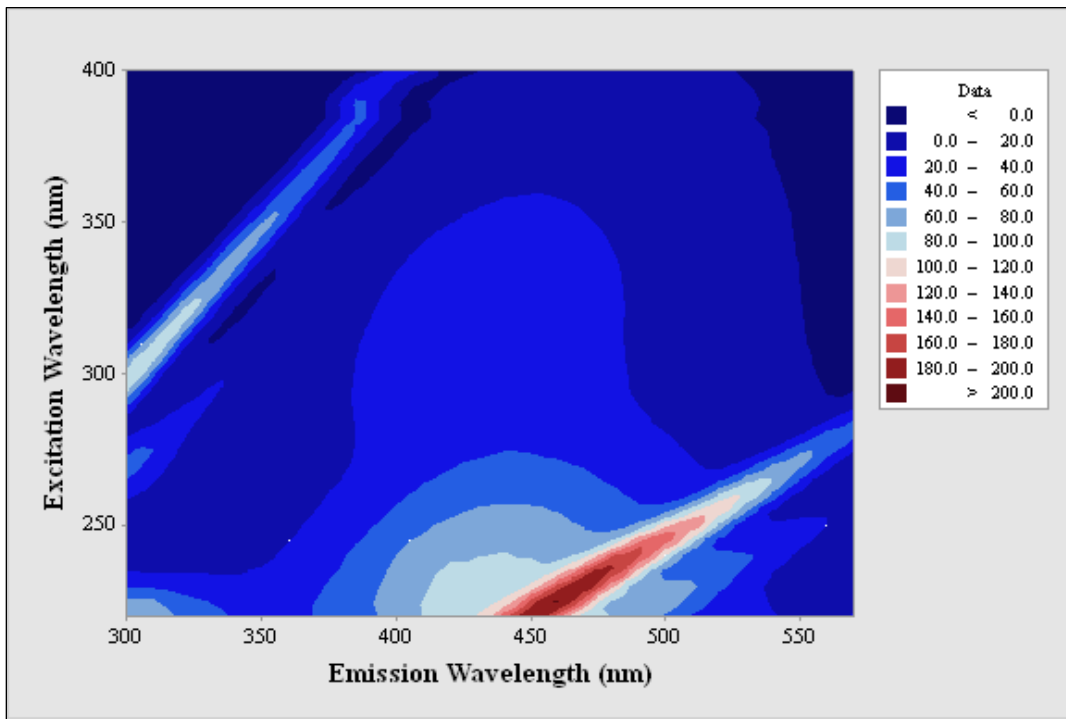


Figure D.4: ClO₂ Dose 1 Finished Water EEM Diagram

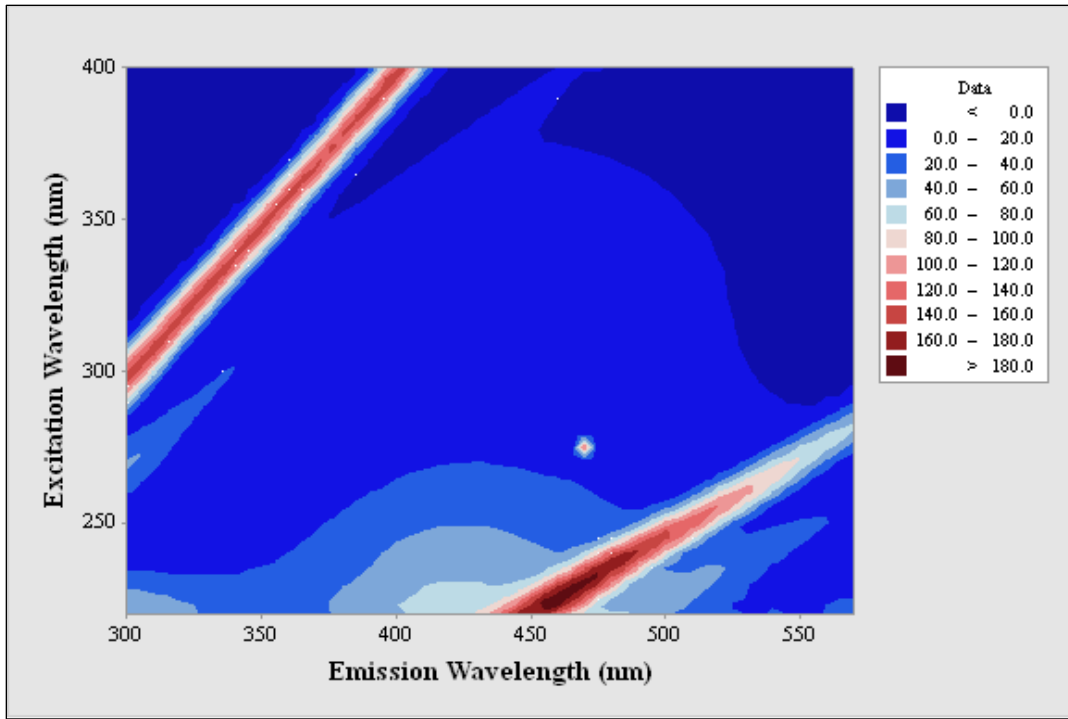


Figure D.5: ClO₂ Dose 1 Chlorinated Water EEM Diagram

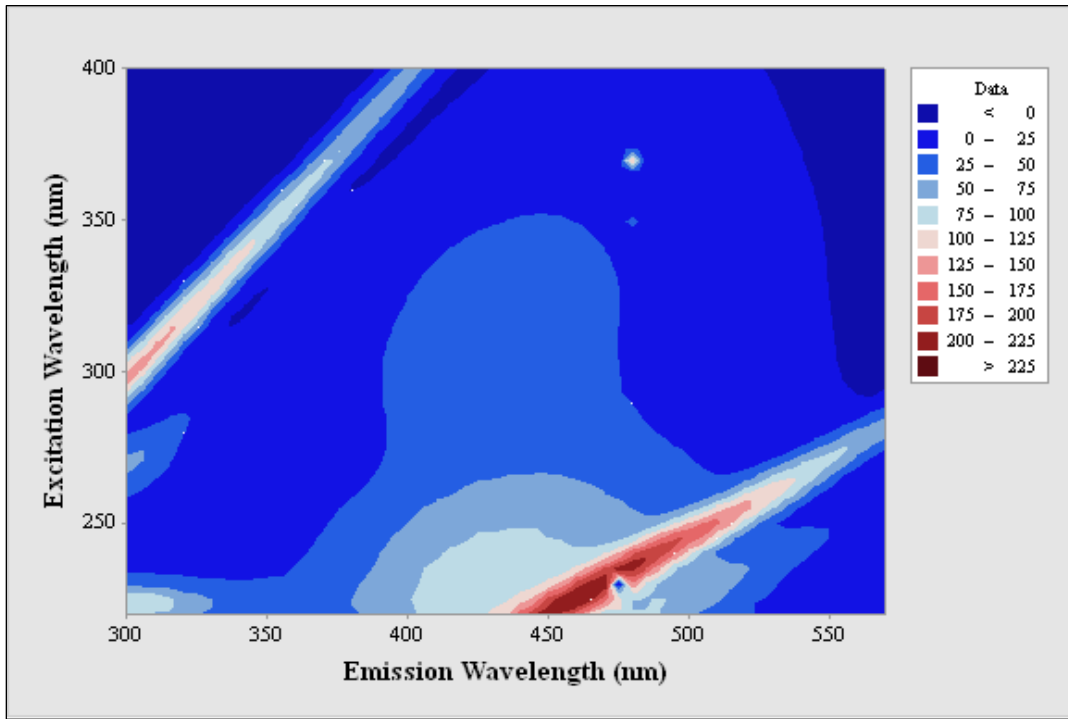


Figure D.6: ClO₂ Dose 2 Finished Water EEM Diagram

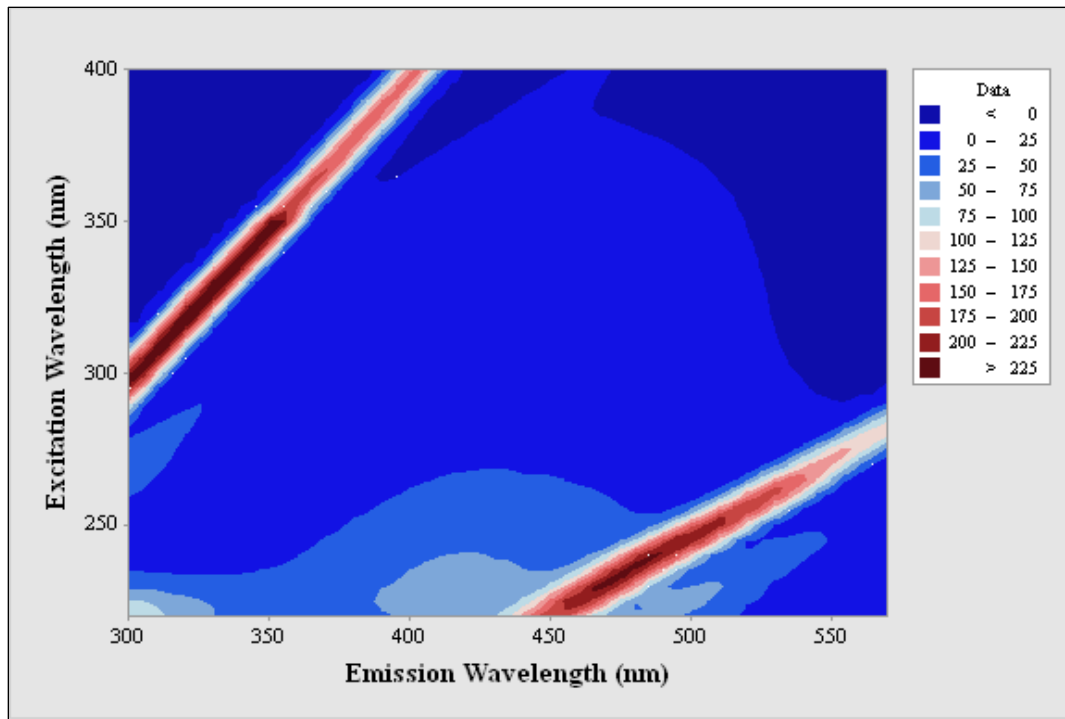


Figure D.7: ClO₂ Dose 2 Chlorinated Water EEM Diagram

REFERENCES

- Alam, M. Z., Cantwell, R. E., Hofmann, R., Andrews, R. C., Rand, J. L., Gagnon, G. A., . . .
Andrews, S. A. (2008). Effect of ClO₂ Pretreatment on Subsequent Water Treatment Processes. *Journal of Environmental Engineering*, 134(6), 478-485.
- Ayyildiz, O., Ileri, B., & Sanik, S. (2009). Impacts of water organic load on chlorine dioxide disinfection efficacy. *Journal of Hazardous Materials*, 168, 1092-1097.
- Bougeard, C. M., Goslan, E. H., Jefferson, B., & Parsons, S. A. (2010). Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine. *Water Research*, 44(3), 729-740.
- Brown and Caldwell. (2011). *Organic Carbon Reduction Study*. Wailuku, HI: Engineering Report Prepared for the County of Maui Department of Water Supply.
- Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J., Tchobanoglous, G., & Borchardt, J. H. (2012). *MWH's Water Treatment Principles and Design* (3rd ed.). Hoboken, New Jersey: John Wiley & Sons, Inc.
- Cumming, A., Duranceau, S. J., & Rodriguez, A. (2013). *Olinda Water Ozone Treatment Assessment for Color and DBP Reduction Final Report*. Orlando: University of Central Florida.
- Duan, J., Cao, X., Chen, C., Shi, D., Li, G., & Mulcahy, D. (2012). Effects of Ca(OH)₂ assisted aluminum sulfate coagulation on the removal of humic acid and the formation potentials of tri-halomethanes and haloacetic acids in chlorination. *Journal of Environmental Sciences*, 24(9), 1609-1615.

- Eaton, A. D., & Franson, M. A. (2005). *Standard Methods for the Examination of Water & Wastewater*. American Public Health Association.
- Edzwald, J. K. (Ed.). (2011). *AWWA Water Quality & Treatment: A Handbook on Drinking Water* (6th ed.). New York: McGraw-Hill.
- Farley, C. G., Gentzler, R., & Flythe, C. W. (March 2012). What Happens When Chloramines and Chlorine Meet? *AWWA Opflow*, 38(3), 22-26.
- FDEP. (2010). *Chapter 62-555 Permitting, Construction, Operation, and Maintenance of Public Water Systems*. Tallahassee: FDEP.
- Gebbie, P. (2005). A Dummy's Guide to Coagulants. *Annual Water Industry Engineers and Operators' Conference* (pp. 75-83). Schweppes Centre - Bendigo: Annual Water Industry Engineers and Operators' Conference.
- Guo, W., Shan, Y., & Yang, X. (2014). Factors affecting the formation of iodo-trihalomethanes during oxidation with chlorine dioxide. *Journal of Hazardous Materials*, 264, 91-97.
- Kim, J., Chung, Y., Shin, D., Kim, M., Lee, Y., Lim, Y., & Lee, D. (2002). Chlorination by-products in surface water treatment process. *Desalination*, 151(1), 1-9.
- Lamsal, R., Walsh, M. E., & Gagnon, G. A. (2011). Comparison of advanced oxidation processes for the removal of natural organic matter. *Water Research*, 45(10), 3263-3269.
- Matilainen, A., Vepsäläinen, M., & Sillanpää, M. (2010). Natural organic matter removal by coagulation during drinking water treatment: A review. *Advances in Colloid and Interface Science*, 159(2), 189-197.

- Mosteo, R., Miguel, N., Martin-Muniesa, S., Ormad, M. P., & Ovelleiro, J. L. (2009). Evaluation of trihalomethane formation potential in function of oxidation processes used during the drinking water production process. *Journal of Hazardous Materials*, 172(2), 661-666.
- Reckhow, D. A., & Singer, P. C. (1990). Chlorination By-products in Drinking Waters: From Formation Potentials to Finished Water Concentrations. *American Water Works Association*, 82(4), 173-180.
- Reynolds, T. D., & Richards, P. A. (1996). *Unit Operations and Processes in Environmental Engineering* (2nd ed.). Stamford, Connecticut: Cengage Learning.
- Richardson, S., Plewa, M. J., Wagner, E. D., Schoerly, R., & Demarini, D. M. (2007). Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water. A review and roadmap for research. *Mutation Research/Reviews in Mutation Research*, 636, 178-242.
- Sawyer, C. N., McCarty, P. L., & Parkin, G. F. (2003). *Chemistry for Environmental Engineering and Science*. New York : McGraw-Hill.
- Shi, Y., Ling, W., & Qiang, Z. (2013). A comparison of disinfection by-products formation during sequential or simultaneous disinfection of surface waters with chlorine dioxide and chlor(am)ine. *Environmental Technology*, 34, 1191-1198.
- Sorlini, S., Gialdini, F., Biasibetti, M., & Collivignarelli, C. (2014). Influence of drinking water treatments on chlorine dioxide consumption and chlorite/chlorate formation. *Water Research*, 54, 44-52.

- Swietlik, J., Raczyk-Stanislawiak, U., Bilozor, S., Ilecki, W., & Nawrocki, J. (2002). Effect of Oxidation with Chlorine Dioxide on the Adsorption of Natural Organic Matter on Granular Activated Carbon. *Polish Journal of Environmental Studies*, 11(4), 435-439.
- USEPA. (2010, August 15). *Comprehensive Disinfectant and Disinfection Byproducts Rules (Stage 1 and Stage 2): Quick Reference Guide*. Retrieved October 30, 2013, from EPA United States Environmental Protection Agency: http://www.epa.gov/ogwdw/mdbp/qrg_st1.pdf
- USEPA. (2012, March 6). *Water: Stage 1 Disinfectant and Disinfection Byproduct Rule*. Retrieved October 25, 2013, from EPA United States Environmental Protection Agency: <http://water.epa.gov/lawsregs/rulesregs/sdwa/stage1/factsheet.cfm>
- Xiao, F., Zhang, X., Zhai, H., Yang, M., & Lo, I. M. (2010). Effects of enhanced coagulation on polar halogenated disinfection byproducts in drinking water. *Separation and Purification Technology*, 76(1), 26-32.
- Xie, J., Wang, D., Leeuwen, J. v., Zhao, Y., Xing, L., & Chow, C. W. (2012). pH modeling for maximum dissolved organic matter removal by enhanced coagulation. *Journal of Environmental Sciences*, 24(2), 276-283.
- Yang, X., Guo, W., & Lee, W. (2013). Formation of disinfection byproducts upon chlorine dioxide preoxidation followed by chlorination or chloramination of natural organic matter. *Chemosphere*, 91(11), 1477-1485.
- Yang, X., Guo, W., Zhang, X., Chen, F., Ye, T., & Liu, W. (2013). Formation of disinfection byproducts after pre-oxidation with chlorine dioxide or ferrate. *Water Research*, 47(15), 5856-5864.