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STUDY OF THE FORMATION AND CONTROL OF DISINFECTION BY-PRODUCTS ORIGINATING FROM A SURFACE WATER SUPPLY ON THE VOLCANIC ISLAND OF GUAM

by

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B.S.Env.E., University of Central Florida, 2013

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ABSTRACT

Three oxidants have been evaluated for use as alternative chemical pretreatments for Fena Lake, a surface water that supplies the U.S. Navy's Public Water System (PWS) on the volcanic island of Guam. The study consisted of two investigative components. The first and primary component included a bench-scale evaluation to study the effects of different pre-oxidant chemicals on the formation of chlorinated disinfection by-products (DBPs). The second and ancillary component included a series of water treatment and distribution system management studies that analyzed DBP formation within the treatment plant and water distribution system. The goal of this research was to reduce total trihalomethane (TTHM) and the five haloacetic acid (HAA5) formations in the PWS.

In the primary component of the research, raw surface water from Fena Lake was collected by U.S. Navy personnel and shipped to University of Central Florida (UCF) laboratories for experimentation. Bench-scale tests that simulated the coagulation, flocculation, sedimentation and filtration (CSF) that comprises the Navy Water Treatment Plant (NWTP) were used to evaluate the use of two alternative pre-oxidants, potassium permanganate ($KMnO_4$) and chlorine dioxide (ClO_2) in lieu of gaseous chlorine (Cl_2). The research assessed DBP formation by comparing several pretreatment scenarios, namely: (1) no pretreatment, (2) chlorine pretreatment, and (3) alternative oxidant pretreatment. $KMnO_4$ pretreatment resulted in the lowest percent reduction of TTHMs and HAA5 relative to chlorine pretreatment, at 5.7% and 22.7%, respectively; however, this amount was still a reduction from the results demonstrated for the chlorine pretreatment condition. Without using a pre-oxidant, TTHM and HAA5 formation were reduced by 22.8% and

37.3%, respectively, relative to chlorine pretreatment. Chlorine dioxide demonstrated the greatest TTHM and HAA5 reduction relative to chlorine pretreatment at 34.4% and 53.3%, respectively.

The second component of research consisted of a series of studies that evaluated distribution system operations and management alternatives to identify opportunities that could achieve DBP reduction within the PWS. Three concerns that were addressed were the NWTP's compliance with the U.S. Environmental Protection Agency's (USEPA's) Stage 2 Disinfectants/Disinfection By-Products (D/DBP) Rule, variable hydraulic detention times within a small subdivision in the distribution system, and severe weather. It was determined that: (1) A decision based on in-plant studies to cease prechlorination at the NWTP resulted in a decrease in TTHMs and HAA5s throughout the distribution system by 62% and 75%, respectively; (2) A fluoride tracer study led to the discovery of a valved pipeline responsible for elevated DBPs because of excessive water age that when exercised and managed resolved intermittent DBP spikes in the PWS; and (3) when the NWTP's ballasted floc clarifier (BFC) was operated in-series prior to the conventional CSF process during severe weather conditions the TTHM and HAA5 were below 39 ug/L and 29 ug/L, respectively, proving BFC in-series is a practical option for the plant during severe weather.

This thesis is dedicated to the LaBerge family: Chris, Patricia, Craig, and Jenny

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LIST OF EQUATIONS

LIST OF ABBREVIATIONS

ACS	American Chemical Society
AEL	Advanced Environmental Laboratories, Inc.
alum	aluminum sulfate
B1285	Building 1285
BFC	ballasted floc clarifier
BrO_3^-	bromate
°C	degree(s) Celsius
$CaCO_3$	calcium carbonate
$Ca(OCl)_2$	calcium hypochlorite
CCl_3COOH	trichloroacetic acid
CECE	Civil, Environmental, and Construction Engineering
$CHBrCl_2$	bromodichloromethane
$CHBr_2Cl$	dibromochloromethane
$CHBr_3$	bromoform
$CHCl_2COOH$	dichloroacetic acid
$CHCl_3$	chloroform
$CH_2BrCOOH$	monobromoacetic acid
$CHBr_2COOH$	dibromoacetic acid
$CH_2ClCOOH$	monochloroacetic acid
Cl^-	chloride ion
Cl_2	chlorine
ClO_2	chlorine dioxide
ClO_2^-	chlorite
ClO_3^-	chlorate
CSF	coagulation, flocculation, sedimentation and filtration
Ct	product of chlorine residual concentration and contact time
D/DBP	disinfectants/disinfection by-products
DBPs	disinfection byproducts
DOC	dissolved organic carbon
EDA	ethylenediamine
EDTA	ethylenediaminetetraacetic acid
FAC	free available chlorine
Fe	iron
FP	formation potential
ft	feet
g	grams

g/L	grams per liter
GAC	granular activated carbon
GC	gas chromatography
HAAs	haloacetic acids
HAA5	five haloacetic acids
HOBr	hypobromous acid
HOCl	hypochlorous acid
IDSE	initial distribution system evaluation
$KMnO_4$	potassium permanganate
L	liter
lbs	pounds
LCL/LWL	lower control limit/lower warning limit
LRAA	locational running annual average
MCL	maximum contaminant level
mg/L	milligrams per liter
MG/MGD	million gallons/million gallons per day
mL	milliliter
Mn	manganese
MRDL	maximum residual disinfectant level
MRDLG	maximum residual disinfectant level goal
MTBE	methyl tertiary-butyl ether
NA	not applicable
Na_2SO_3	sodium sulfite
NaOCl	sodium hypochlorite
NAVFAC	Naval Facilities Engineering Command
NF	nanofiltration
NH_2Cl	chloramine
NH_4^+	ammonium
NH_4Cl	ammonium chloride
NOM	natural organic matter
NTU	nephelometric turbidity unit
NWTP	Navy Water Treatment Plant
O_3	ozone
OCl^-	hypochlorite ion
OH^-	hydroxide
PLC	programmable logic controller

PWS	public water system
RAA	running annual average
RO	reverse osmosis
RPD	relative percent difference
rpm	revolutions per minute
S^{2-}	sulfide
SDWA	Safe Drinking Water Act
SG	specific gravity
SM	standard methods
THMs	trihalomethanes
TOC	total organic carbon
TTHMs	total trihalomethanes
UCF	University of Central Florida
UCL/UWL	upper control limit/upper warning limit
USEPA	United States Environmental Protection Agency
UV	ultraviolet
WTP	water treatment plant
µg/L	micrograms per liter

1. INTRODUCTION AND MOTIVATION FOR THE RESEARCH

Disinfection of drinking water inactivates pathogenic bacteria and viruses and has effectively controlled biological waterborne disease outbreaks where employed. However, disinfectants react with natural organic matter (NOM) and inorganics present in source water and distribution systems to form regulated and non-regulated disinfection by-products (DBPs), including several that are known carcinogens, and many others whose toxicity are unknown (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2005). The United States Environmental Protection Agency (USEPA) requires community water systems to comply with the Safe Drinking Water Act's (SDWA's) Stage 2 Disinfectants and Disinfection By-Product (D/DBP) Rule to improve public health protection by limiting the consumer's exposure to regulated DBPs. According the USEPA (2006), the Stage 2 D/DBP rule builds upon earlier DBP rules by tightening compliance monitoring requirements for DBPs, including total trihalomethanes (TTHM) and five haloacetic acids (HAA5).

The U.S. Navy owns and operates its Navy Water Treatment Plant (NWTP) on the volcanic island of Guam located in the Marianas Islands. The NWTP is a conventional treatment plant that treats surface water from Fena Lake, Almagosa Spring, and Bona Spring using a coagulation, flocculation, sedimentation, and filtration (CSF) process. A review of water quality data by Brown and Caldwell (2014) demonstrated that numerous locations within the U.S. Navy's public water system (PWS) regularly exceeded the maximum contaminant levels (MCLs) for DBPs between 2009 and 2012.

In 2013 the Naval Facilities Engineering Command (NAVFAC) requested that the University of Central Florida (UCF) help the U.S. Navy's by conducting research to better understanding DBP formation chemistry within the Guam PWS. The Navy directed the University to work with its retained professional engineering firms to study alternative means to reduce DBP levels throughout the Navy's PWS on the island of Guam.

The primary motivation behind the research reported herein was to evaluate the alternative oxidants, potassium permanganate ($KMnO_4$) and chlorine dioxide (ClO_2), for use in treating Fena Lake in lieu of gaseous chlorine (Cl_2) pretreatment as a means to avoid the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) in the Navy's PWS. The second component of research assessed system operations and management alternatives to reduce DBP formation at the NWTP and throughout the water distribution system. This was achieved through a series of studies performed in Guam that addressed three concerns: (1) the NWTP's compliance with the Stage 2 D/DBP, (2) variable hydraulic detention times within a small subdivision in the distribution system registering increased levels of DBPs, and (3) impacts of severe weather conditions and subsequent effects on the NWTP. UCF was to evaluate alternative means to achieve measurable reductions in DBPs throughout the Navy PWS and provide recommend solutions in order that the Navy can achieve compliance with the D/DBP Rule. UCF was also tasked to evaluate interim solutions that may include changes to operational methods, implementation of treatment process changes, and/or other improvements that will achieve full compliance with Stage 2 D/DBP Rules.

2. EXISTING FACILITY AND SYSTEM LAYOUT

This chapter provides an overview of the Navy's raw water sources, NWTP configuration, operations, and water distribution system located on the island of Guam, as these descriptions relate to aspects of the facilities that are pertinent to DBP concerns.

Raw Water Sources

The U.S. Navy's PWS on the volcanic island of Guam is located in the western Pacific Ocean. The Fena Valley watershed of the Naval Magazine, a secure military compound, provides water to most naval facilities, in addition to some civilian communities. To supplement the primary water sources, the northern distribution system also has groundwater wells (Brown and Caldwell, 2014).

The raw water sources for the NWTP include Fena Valley Reservoir (Fena Lake), Almagosa Spring, and Bona Spring. Fena Lake is located in an inactive volcano crater and has a storage capacity of 2.1 billion gallons. The drainage area above the dam is six square miles of moderately to steeply sloped lands, heavy in jungle growth and covered with a variety of grasses (Boyle Engineering Corporation, 2001). Water from these southern volcanic areas of Guam tend to be soft, low in alkalinity, low in soluble minerals, and high in organics. Fena Lake supplies approximately 63% (8 million gallons per day (MGD)) to the Navy's water system (Boyle Engineering Corporation, 2001). Raw water from Fena Lake is typically withdrawn through a constructed screen house complex at a 12-foot (ft) depth, however the intake structure can be utilized at depths of up to 50 feet.

The Almagosa Spring supply is from the Upper Dobo, Lower Dobo, and Chepek springs and supplies approximately 22% (2.9 MGD) to the water system. Bona Spring discharges from two springs within limestone caverns supplying approximately 15% (1.9 MGD) to the water system (Boyle Engineering Corporation, 2001). Raw water from the reservoir and the springs is pumped to, and treated by, the U.S. Navy's conventional surface water treatment plant. Springflow is highly dependent upon rainfall, and the yield from both springs may vary from 0.5 MGD throughout the dry season to 3 MGD during the wet season. A series of low limestone formation hills act as natural water storage reservoirs permitting recharge to the springs (Boyle Engineering Corporation, 2001).

NWTP Process Unit Operations

The NWTP is a conventional surface water treatment plant that treats the combination of Fena Lake water, Almagosa Spring, and Bona Spring. The water treatment plant is designed to produce 13.5 MGD of potable water. According to the U.S. Navy, the water treatment production varies from 10.5 MGD to 12.5 MGD during the wet and dry seasons, respectively. The raw water sources and key unit operations of the Navy's PWS are depicted in Figure 2.1.

A chlorine chemical feed point is located at the Fena Lake Pump Station's Building 1285 (B1285). The water is processed through conventional water treatment which includes coagulation, flocculation, and sedimentation. The Navy uses aluminum sulfate (alum) as the coagulant, adds lime for pH adjustment and polymer (as needed) for enhanced coagulation during the rapid mix phase of the process. There is a chlorine chemical feed location at the rapid mix location. The coagulation, flocculation, and sedimentation process is operated as a combined-unit operation as the Navy operates two clarifiers: a conventional CSF solids-contact process as previously described and a ballasted floc clarifier (BFC). These two clarifiers can be operated either in parallel or series configuration, depending on season, demand, and water quality (e.g. turbidity levels entering plant).

After the clarification process, there is a chlorine chemical feed point prior to filtration. The water is filtered through six dual-media, anthracite-sand filters, followed by post-filter fluoridation, and disinfection with ultraviolet (UV) and sodium hypochlorite. The finished water continues to a rectangular, dual-compartment, 1.06-million-gallon (MG), baffled clearwell to achieve contact time (Ct) requirements. Finished water is distributed between the Naval Magazine (0.72 MG), Maanot (0.59 MG), Apra Heights (0.5 MG) and Tupo (5.0 MG) reservoirs. From these primary finished water storage reservoirs, potable water is distributed to secondary reservoirs and throughout the Navy's water distribution system.

In January 2013 the U.S. Navy retained Brown & Caldwell (Honolulu, HI) and the UCF Civil, Environmental, and Construction Engineering (CECE) department to conduct research to investigate iron, manganese and DBP water quality issues within the Navy's Guam PWS. Early results showed that prechlorination significantly contributed to the formation of DBPs. Based on UCF's initial findings as reported in Hall (2014), the U.S. Navy ceased prechlorination at Fena Lake as well as at the rapid mix and post-filter chemical feed locations on August 28, 2013 (Hall, 2014). Additional discussion related to the significance of this decision and its impact on research activities is discussed herein.

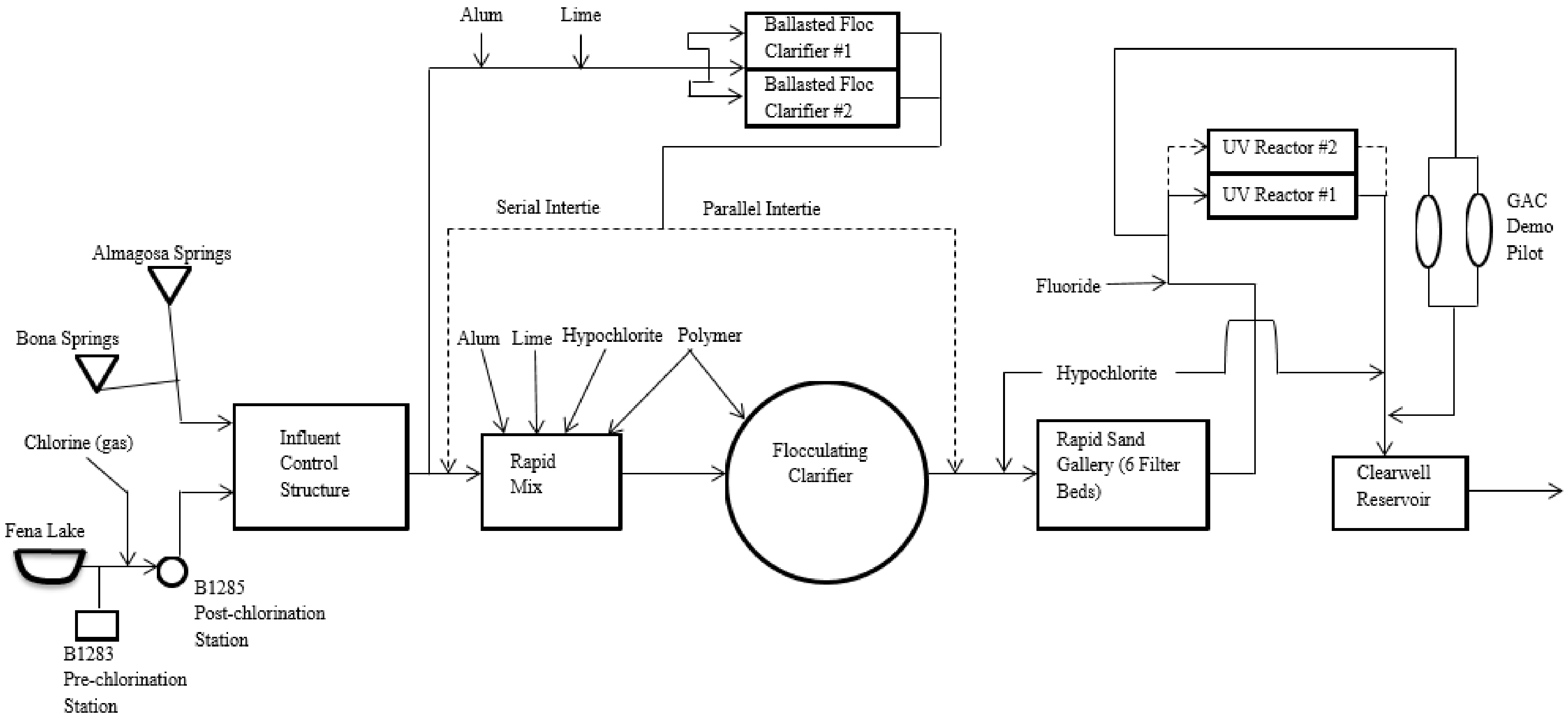


Figure 2.1
NWTP process flow diagram

3. LITERATURE REVIEW

Disinfection of potable water is one of the substantial public health advances over the past century and the practice of using chemicals for disinfection and oxidation is commonplace at water treatment plants (WTPs) throughout the world (Richardson, 2005). In order to protect potable water from disease-causing organisms, water purveyors often add the chemical chlorine as a disinfectant. When used as a disinfectant, chlorine reacts with naturally-occurring materials in the water to form by-products, such as TTHM and HAA5, which may pose health risks as these classes of chemicals are suspected carcinogens. Although many health effects are not completely understood, some health effects have been recognized to the extent that epidemiological risks can be quantified. Disinfection and oxidation by-products are a continuously changing concern for the drinking water community (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012).

Overview of Drinking Water Regulations Related to Disinfection By-Products (DBPs)

Due to concerns about the adverse health effects of chloroform, the USEPA promulgated the interim Trihalomethane Rule in 1979 (USEPA, 1979a). The four regulated THMs included chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). The MCL was established at 100 micrograms per liter (µg/L) for TTHMs (on a mass basis) measured as the running annual average (RAA) of four quarterly samples in the distribution system (USEPA, 1979a).

The Stage 1 D/DBP Rule reduced the TTHM MCL from 0.10 to 0.080 milligrams per liter (mg/L), and increased the number of regulated DBPs, as shown in Table 3.1 (USEPA, 1998). The rule was promulgated in 1998 and regulated additional contaminants that included HAA5, comprised of monochloroacetic acid ($CH_2ClCOOH$), dichloroacetic acid ($CHCl_2COOH$), trichloroacetic acid (CCl_3COOH), monobromoacetic acid ($CH_2BrCOOH$), and dibromoacetic acid ($CHBr_2COOH$). The Stage 1 D/DBP Rule also established maximum residual disinfectant levels (MRDLs), maximum residual disinfectant level goals (MRDLGs), and included a provision for surface water systems to meet DBP precursor removal requirements. Table 3.1 presents a summary of the key provisions of the Stage 1 D/DBP Rule, listing the type of DBP, its MCL, MRDL and MRDLG. Table 3.2 presents the mandatory DBP precursor (total organic carbon (TOC)) removal goals for varying TOC levels as a function of alkalinity as summarized in the Stage 1 D/DBP Rule. Compliance with the updated and revised MCLs began in January 2002 (USEPA, 1998).

Table 3.1

Stage 1 D/DBP Rule regulated contaminants (American Water Works Association, 2011)

Regulated Contaminant	MCL (mg/L)	By-product of	MRDL (mg/L)	MRDLG (mg/L)
TTHM	0.080	Chlorine	4.0 (as Cl_2)	4.0 (as Cl_2)
HAA5	0.060	Chlorine	4.0 (as Cl_2)	4.0 (as Cl_2)
Bromate (BrO_3^-)	0.010	Ozone	NA	NA
Chlorite (ClO_2^-)	1.0	Chlorine dioxide	0.8 (as ClO_2)	0.8 (as ClO_2)

NA = not applicable

Table 3.2

DBP precursor removal treatment technique requirements

Source water TOC (mg/L)	Source water alkalinity (mg/L as $CaCO_3$)		
	0-60	> 60 -120	> 120
> 2.0 to 4.0	35.0%	25.0%	15.0%
> 4.0 to 8.0	45.0%	35.0%	25.0%
> 8.0	50.0%	40.0%	30.0%

The Stage 2 D/DBP Rule was promulgated by the USEPA in January 2006 to further reduce the consumer's exposure to DBPs without compromising the control of microbial pathogens (USEPA, 2006). The Stage 2 D/DBP Rule requires water treatment utilities to complete an initial distribution system evaluation (IDSE). The IDSE is used to identify the locations throughout the system with the highest DBP concentrations and evaluate compliance via a locational running annual average (LRAA) (USEPA, 2006). Table 3.3 provides a summary of the difference in monitoring requirements between the Stage 1 and Stage 2 D/DBP Rule.

Table 3.3
Stage 1 vs. Stage 2 D/DBP Rule TTHM and HAA5 monitoring requirements

Elements	Stage 1 D/DBP Rule	Stage 2 D/DBP Rule
Consecutive system	Must monitor if the system provides any type of disinfection other than UV. No monitoring requirement if only the wholesale system provides treatment.	Must monitor if the system provides water treated with any type of disinfectant other than UV.
Number of samples	Based on population served, source water type and number of plants.	Based only on population served and source water type.
Sample locations	Locations representing maximum residence time in the distribution system. Larger system may include locations of average residence time.	Locations of highest TTHM and HAA5 averages as determined during the IDSE.
Determination of MCL compliance	Based on RAA or the average of four consecutive quarters of samples taken in the distribution system for TTHM and HAA5.	Based on LRAA or the average of four consecutive quarters of samples taken at each specific sampling location within the distribution system for TTHM and HAA5.
Monitoring frequency	System must conduct monitoring every quarter.	System must conduct monitoring every 90 days.

DBP Formation

The chemical by-products of the DBPs themselves are of particular interest in water treatment. DBPs are formed when disinfectants react with species naturally present in the water, particularly NOM and inorganic species. Some of this NOM is highly reactive with a wide range of oxidants. The reaction products include reduced forms of the oxidants (e.g., chloride, hydroxide, and chlorite when using chlorine, ozone, and chlorine dioxide, respectively) and oxidized forms of the organic or inorganic reactants (e.g., bromate), as presented in Figure 3.1 (American Water Works Association, 2011).

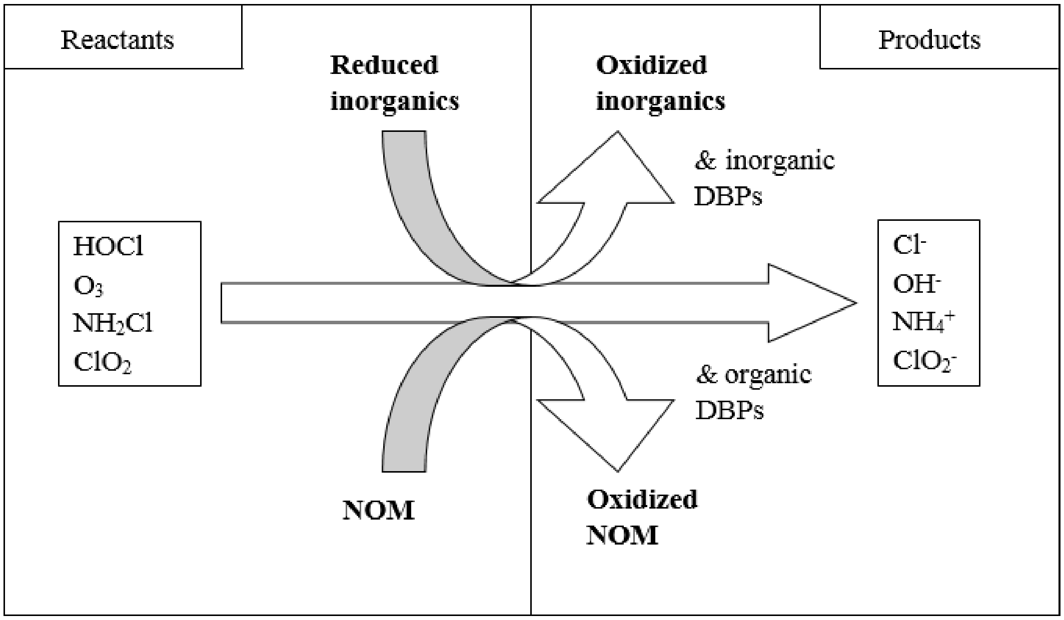


Figure 3.1
Schematic illustration of reactions of various oxidants with NOM and reduced inorganic substances (adapted from American Water Works Association, 2011)

The sites of disinfectant (oxidant) attack on NOM are often carbon-carbon double bonds and reduced heteroatoms (e.g., nitrogen and sulfur). The organic by-products formed are more highly oxidized, often containing more oxygen atoms. As the extent of the reaction increases, organic matter becomes more fragmented, and the specific by-products are simpler in structure (American Water Works Association, 2011).

Several of the disinfectants are capable of producing by-products that have halogen atoms (i.e., chlorine, bromine, and iodine) incorporated into their structure. Aqueous chlorine and bromine do this to the greatest extent, followed by chloramines and ozone. Aqueous chlorine, chloramines, and ozone are capable of oxidizing naturally occurring bromide to form active bromine (i.e., hypobromous acid (HOBr) or bromamines). The latter will react with NOM to form brominated organic compounds (e.g., bromoform and dibromoacetic acid) and, in the presence of free chlorine, mixed bromochloro-organics. The same is true with respect to the formation of iodinated DBPs in the presence of iodide, although iodinated DBPs tend to be found only in chloraminated waters (American Water Works Association, 2011).

Formation potentials (FPs) are an analysis of the capability of DBPs to form in water under controlled conditions. The analysis is conducted with predefined conditions to produce the maximum target DBP concentrations (Crittenden et al., 2012).

There are many factors that influence the formation of DBPs. Among them are contact time, temperature, pH, precursor type and concentration, disinfectant type and concentration, the ratio of oxidant to precursor, and concentrations of bromide and nitrogen (Connell, 1996).

Disinfectants (Oxidants) and their By-Products

Although hundreds of specific compounds have been identified as DBPs, only chlorination and chlorine dioxide by-products will be addressed in detail because they were the focus of this research. Potassium permanganate is introduced as a pre-oxidant, but does not produce by-products.

Chlorine

Chlorine is the most commonly used oxidant and disinfectant in water treatment practice. Chlorine is available in gaseous form (as Cl_2), as a concentrated aqueous solution (sodium hypochlorite, NaOCl, i.e., bleach), or as a solid (calcium hypochlorite, $Ca(OCl)_2$), or it can be electrolytically generated on-site (American Water Works Association, 2011). When water is dosed with chlorine gas, the chlorine quickly disproportionates to form hypochlorous acid (HOCl) and the chloride ion (Cl^-), as presented in Equation 3-1. Hypochlorous acid is a weak acid ($pK_a = 7.6$ at 25°C) that can transfer a proton to form the hypochlorite ion (OCl^-), as shown in Equation 3-2 (American Water Works Association, 2011).

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (3\text{-}1)$$

$$HOCl = H^+ + OCl^- \qquad (3\text{-}2)$$

The sum of Cl_2, HOCl, and OCl^- is frequently referred to as free available chlorine (FAC), and the concentrations of each species and their sum are most often expressed in the units of mg/L as Cl_2. If chlorine is added to water as liquid sodium hypochlorite, the following reactions occur:

$$NaOCl \rightarrow Na^+ + OCl^- \qquad (3\text{-}3)$$

$$OCl^- + H_2O = HOCl + OH^- \qquad (3\text{-}4)$$

The relative distribution of HOCl and OCl^- that results from the addition of sodium hypochlorite will be determined by pH, temperature, and the total chlorine concentration. Chlorine gas produces an acidic reaction which lowers the pH of the solution, whereas sodium hypochlorite is a base which will raise the pH of the water. The alkalinity of the water will impact the amount of change in the pH. The change of pH is likely to be fairly small due to low doses of chlorine are often used. Hypochlorous acid and the hypochlorite ion are both strong oxidizing agents, but HOCl is the stronger of the two. Hence, in general, oxidation reactions of chlorine are usually more effective at low pH values "unless the reactant exhibits pH-dependent behavior as in the case of phenol" (American Water Works Association, 2011).

The chlorination by-products include a wide range of halogenated and non-halogenated organic compounds. THMs and HAAs are end products of the reaction of chlorine with organic matter. There are four types of THMs and nine types of HAAs. According to the American Water Works Association (2011), waters with low bromide levels will produce the fully chlorine-substituted forms as the predominate species (e.g., chloroform and di- and trichloroacetic acid). Waters with high levels of bromide are likely to contain elevated levels of the bromide-containing analogues (e.g., bromoform and dibromoacetic acid) following chlorination. Waters with moderate levels of bromide will contain the mixed bromo/chloro analogues (e.g., bromodichloromethane and bromodichloroacetic acid) (American Water Works Association, 2011).

Given THMs volatility, chemical stability, and high halogen-carbon ratio, this class of compounds could be easily analyzed and were the first by-products to be found in finished drinking waters (Rook, 1974) (Bellar & Lichtenberg, 1974). The discovery of HAAs in chlorinated drinking water systems (Miller & Uden, 1983) and subsequent occurrence studies followed far behind the developed knowledge of THM studies by several years.

Chlorine Dioxide

Chlorine dioxide is unstable at high concentrations, and can explode on exposure to heat, light electrical sparks, or shocks. Chlorine dioxide is not shipped in bulk, but is generated on-site instead. Aqueous solutions are usually prepared from the gaseous chlorine dioxide generated, as chlorine dioxide is highly soluble in water. It does not hydrolyze in water as chlorine does and remains in its molecular form as ClO_2; however, chlorine dioxide is much more volatile than chlorine (Singer & Reckhow, 2011).

Chlorine dioxide typically reacts with most reducing agents (e.g., taste and odor compounds, NOM) through a one-electron transfer, as shown in Equation 3-5, to form oxidized organics such as aldehydes, ketones, and acids. At high pH values or in the presence of light or at elevated temperatures, chlorine dioxide disproportionates to form both chlorite (ClO_2-) and chlorate (ClO_3-), both of which are undesirable in drinking water, as presented in Equation 3-6 (Singer & Reckhow, 2011). The concentration of chlorite amounts for 50 to 70 percent of the chlorine dioxide consumed. Given this formation rate, “the formation of chlorite limits the chlorine dioxide dose that can be applied during drinking water treatment unless chlorite removal technologies are implemented downstream, since the MCL for chlorite is 1 mg/L” (Crittenden et al., 2012).

$$ClO_2 + e^- \rightarrow ClO_2^- \quad (3\text{-}5)$$

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \quad (3\text{-}6)$$

In relation to the use of chlorine dioxide, there are two sources of chlorite and chlorate. The first source is the generation process of chlorine dioxide in which residual chlorite may persist in the product solution if exceptionally high concentrations of sodium chlorite are used in the generator and are then injected into the process stream with the chlorine dioxide (Crittenden et al., 2012). The second source of chlorite and chlorate is formation as a by-product of the chlorine dioxide disinfection and oxidation reactions.

The primary application of chlorine dioxide has been for taste and odor control, although it is also an effective oxidant for reduced iron and manganese and is a primary disinfectant. One of the principal advantages of chlorine dioxide is that it does not react with ammonia. Hence, much lower doses of chlorine dioxide are required for most oxidative applications compared to chlorine dosage requirements. Another advantage is that chlorine dioxide does not enter into substitution reactions with NOM to the same degree that free chlorine does and, accordingly, does not form trihalomethanes, haloacetic acids, or most other commonly observed halogenated disinfection by-products that result from chlorination, at least not to any appreciable extent. Chlorine dioxide reacts only very slowly with bromide. Hence, brominated by-products, either organic or inorganic are not a concern following treatment with chlorine dioxide (Singer & Reckhow, 2011).

Potassium Permanganate

Potassium permanganate is an alternative to chlorine for oxidation at water treatment plants, and according to Crittenden and coworkers (2012) has proven effective for the control of iron (Fe), manganese (Mn), and sulfide (S^{2-}). Potassium permanganate forms less THMs and HAAs than chlorine when used as a pre-oxidant and is not known to produce regulated by-products. However, $KMnO_4$ is a weak disinfectant, so additional chemical disinfection is often needed and may result in DBP formation (Crittenden et al., 2012).

Conventional Chemical Oxidation

Oxidation is the reaction between two chemicals in which an exchange of electrons between one chemical and the chemical being oxidized takes place (Connell, 1996). Oxidation is often used in municipal drinking water treatment to treat aesthetic qualities such as color, taste, and odor that affect the consumer perception and acceptance of a water (Crittenden et al., 2012).

The three oxidants evaluated in this research (chlorine, potassium permanganate, and chlorine dioxide), and their corresponding applications, are summarized in Table 3.4. The forms and application methods of chlorine, chlorine dioxide, and potassium permanganate are described in Table 3.5. Additional oxidants that are often used in water treatment include, but are not limited to, ozone, monochloramine, and hydrogen peroxide. The oxidants are often added at the beginning (e.g. pre-oxidation) or end (e.g. disinfection) of the water treatment process; however, oxidants can also be added at various intermediate points (Crittenden et al., 2005).

Table 3.4

Oxidants and their application in water treatment (adapted from Crittenden et al., 2005)

Purpose	Oxidants	Applications
Oxidation of reduced inorganic species	Chlorine, permanganate, chlorine dioxide	Convert soluble metals such as Fe (II) and Mn (II) to insoluble forms; oxidize odorous sulfide; destroy metal organic complexes
Oxidation of organics	Permanganate, chlorine dioxide	Destroy taste-and odor-causing compounds; destroy toxic organics [e.g., pesticides, benzene, trichloroethene, methyl tertiary-butyl ether (MTBE)]; eliminate color; reduce natural organic matter and disinfection by-product precursors
Biocidal agents	Chlorine	Control nuisance growths such as algae in pretreatment basin or reservoirs; as primary disinfectants to meet Ct[a] regulations

[a] Ct = product of chlorine residual concentration (mg/L) and contact time (min).

Table 3.5
Common oxidants, forms, and application methods (adapted from Crittenden et al., 2005)

Oxidant	Forms	Application Methods
Chlorine, free	Chlorine gas, sodium hypochlorite solution	Gas eductors and spray jets
Chlorine dioxide	Chlorine dioxide gas produced on-site using 25 percent sodium chlorite solution reacted with gaseous chlorine, aqueous chlorine, or acid	Gas eductors
Permanganate	Available in bulk as granules	Added as dry chemical using feeder or as concentrated solution (no more than 5% by weight)

Control of Disinfection By-Products

There are numerous approaches to control DBP concentrations. Many efforts have focused on changing the type of the disinfectant. Reducing the disinfectant use to minimize DBP formation has proved to be effective; however, doing so has direct implications for increasing the risk of illness from microbial contamination. Other alternatives to control DBP concentrations have been done by changing from free chlorine to ozone or UV primary disinfection and from free chlorine to chloramination for secondary disinfection. Potassium permanganate pretreatment was found to reduce the formation potential of chloroform. As the amount of permanganate consumption increased, chloroform reduction increased as well (Colthurst & Singer, 1982). Permanganate addition and chloramination was found to reduce DBPs below 20 µg/L in a study (Nnadi, Hernandez, & Fulkerson, 2004). A study on the formation of DBPs after pre-oxidation with chlorine dioxide resulted in a 45% reduction in THM formation potentials (Yang et al., 2013).

However, if the use of alternative disinfectants is not viable, as would be in the case of coastal estuarine environments, then another method is to minimize DBP formation by removing organic precursor material prior to the point of disinfection is evaluated. Consequently, optimizing the coagulation process for removal of both TOC and particles (turbidity) becomes an effective strategy as has been demonstrated by enhanced coagulation experiences in the drinking water community (Matilainen, Vepsäläinen, & Sillanpää, 2010) (USEPA, 1999).

Removing DBPs after their formation is most appropriate for control of biodegradable by-products and possibly for removal of highly volatile DBPs such as chloroform (American Water Works Association, 2011). Results from a study showed that air stripping greatly reduced the required amount of disinfectant and removed THMs (Nnadi et al., 2004). Results from an additional study showed a high efficacy of chlorite removal on granular activated carbon (GAC) filters (Ranieri & Swietlik, 2010).

Removing DBPs after their formation is limited and can be costly if membranes are required (Duranceau & Taylor, 2010). The removal of DBP precursors or dissolved organic carbon (DOC) by reverse osmosis (RO) or nanofiltration (NF) has been studied extensively (Jones & Taylor, 1992; Taylor, Mulford, Barrett, Duranceau, & Smith, 1989; Taylor, Mulford, Duranceau, & Barrett, 1989). Nanofiltration membranes have been shown to control THM formation potential in highly organic (>10 mg/L DOC) potable water sources (Taylor et al., 1986). These efforts have often been necessitated by inadequate efficiency of DBP removal using conventional coagulation and softening treatment processes (Duranceau & Taylor, 2010).

4. MATERIALS & METHODS

This chapter initially describes the experimental plan, testing locations, tests, materials, chemicals, and procedures used to conduct the bench-scale evaluation of the alternative pre-oxidants study. Additionally, the experimental plan for the treatment and distribution system operations and management alternatives analysis component of work is described. This second component of research consisted of a series of studies designed to identify opportunities that could achieve DBP reduction within the PWS. The methods and procedures used in both components work were developed to aid UCF research activities in support of the overall study. This chapter also provides a description of the methods used to obtain existing database information, third-party sources, laboratory procedures and field activities, or compiled from computerized databases (should they exist).

Bench-Scale Evaluation of Alternative Pre-oxidants and Impacts on DBP Formation

Overview of the Experimental Plan

Raw surface water from Fena Lake was collected by the U.S. Navy and shipped to UCF laboratories for evaluation and analysis. Bench-scale jar tests that simulated the conventional NWTP were used to evaluate several pretreatment scenarios, namely 1) no pretreatment, 2) chlorine pretreatment 3) potassium permanganate pretreatment, and 4) chlorine dioxide pretreatment. Assessing the DBPs formed in each of these scenarios would aid in the understanding of DBP formation within the U.S. Navy's PWS on Guam.

A schematic that presents an illustrative overview of the bench-scale study experimental design is presented in Figure 4.1. In this plan, Fena Lake raw water was first disinfected with 1) no pretreatment, 2) chlorine (NaClO), 3) potassium permanganate, and 4) chlorine dioxide. Then, the water was disinfected at the rapid mix (for the chlorine dose condition only) followed by coagulation, flocculation, sedimentation, filtration, and chlorine disinfection at the clearwell. TTHM and HAA5 formation potential samples, in addition to chlorine residual samples, were collected and incubated at 30°C to represent the distribution system. Water quality was taken throughout the bench-scale experiments. Detailed descriptions of these procedures are provided in the remainder of this section.

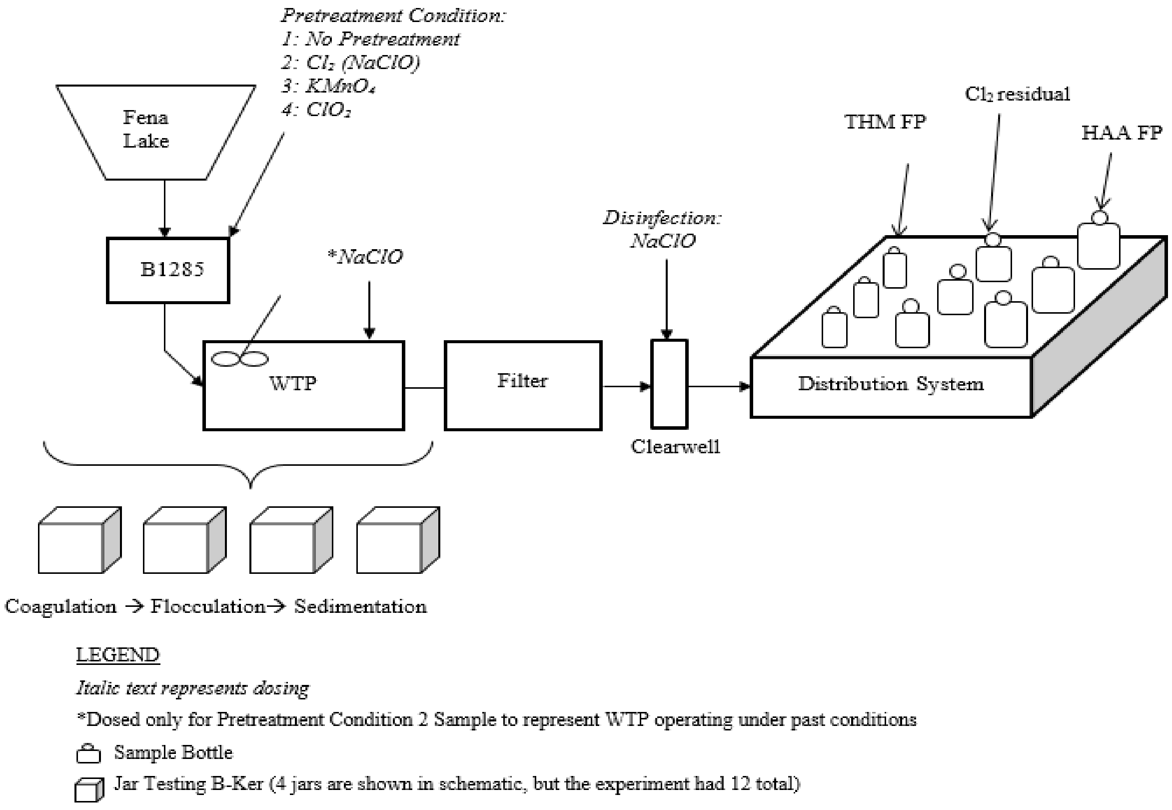


Figure 4.1
UCF bench-scale disinfection by-product study layout

Sample Collection

Raw water samples were collected from various depths of Fena Lake by the U.S. Navy and shipped to UCF drinking water laboratories for experimentation between October 2013 and August 2014. Sampling depths were determined by the NWTP and mimicked the full-scale system (usually drawn at 12-foot depth). The water samples were collected in 1-L plastic amber bottles and were shipped on ice for preservation until received at UCF. Samples were then stored in 4°C until the experiments took place. Samples were collected and stored in accordance with *Standard Methods for the Examination of Water and Wastewater* 1060 B. Collection of Samples and 1060 C. Sample Storage and Preservation (American Public Health Association, American Water Works Association, & Water Environment Federation, 2005) in addition to the *Handbook for Analytical Quality Control in Water and Wastewater Laboratories* (USEPA, 1979b).

Tests, Methods, Equipment, and Preservation

Table 4.1 provides a list of test locations, methods, detection levels, preservation techniques, and holding times required for the tests used during this research. Analyses were conducted in the field and in the laboratory. The method reference and the equipment used for each test is listed in Table 4.1 for reference. The preservation technique describes how the samples were preserved for the specified test, unless the test had to be analyzed immediately (in which case the sample was not preserved for later analysis). The holding time is the time in which the specified test can be analyzed in; for example, the pH test should only be conducted within 0.25 hours holding time, after which the sample should no longer be tested for pH, according to the method provided.

Table 4.1
Summary of analytical testing methods used for characterization of water samples

Test	Test location	Method/ equipment description	Method detection level	Preservation technique	Holding time
.pH	UCF lab/field	SM: 4500-H^+ B Electrometric Method/ HQ40d Portable pH, Conductivity, and Temperature Meter	0.01 pH Units	Analyze immediately	0.25 hours
Chlorine Dioxide (ClO_2)	UCF lab	HACH Method 8138: Chlorine Dioxide Direct Reading Method/ HACH Spectrophotometer DR5000	5 mg/L ClO_2	Analyze immediately	0.25 hours
Chlorine (Cl_2), free	UCF lab	HACH Method 8021:Chlorine, Free DPD Method/ HACH Spectrophotometer DR5000	0.02 mg/L Cl_2	Analyze immediately	0.25 hours
Chlorate	AEL	EPA Method 300.1:Determination of Inorganic Anions in Drinking Water by Ion Chromatography/ Ion chromatograph	0.003 mg/L	50 mg/L EDA	28 days
Chlorite	AEL	EPA Method 300.1/ Ion chromatograph	0.01 mg/L	50 mg/L EDA; cool, 4 °C in the dark	14 days
Conductivity	UCF lab/field	SM:2510 B Laboratory Method/ HQ40d Portable pH, Conductivity, and Temperature Meter	0.01 µS/cm	Analyze immediately	0.25 hours
HAA5	AEL	SM:5710C/ Agilent 6890N Network Gas Chromatograph	3 µg/L	Analyze immediately; or cool, 4ºC in the dark	14 days
Temperature	UCF lab/field	SM: 2550 B: Laboratory Method/ HQ40d Portable pH, Conductivity, and Temperature Meter	0.01 °C	Analyze immediately	0.25 hours
TOC	UCF lab	SM: 5310C: Persulfate-Ultraviolet Oxidation Method/ Tekmarr-Dohrmann Phoenix 8000: The UV-Persulfate TOC Analyzer	0.1 mg/L	Cool, 4ºC in the dark	28 days
TTHM	UCF lab	SM: 6232 B: Liquid-Liquid Extraction Gas Chromatographic Method/ Agilent 6890N Network Gas Chromatograph	1 µg/L	Analyze immediately; or cool, 4ºC in the dark	14 days
Turbidity	UCF lab/field	SM: 2130 B: Nephelometric Method/ HACH 2100q Portable Turbidimeter	0.01 NTU	Analyze immediately; or cool, 4ºC in the dark	48 hours
UV-254	UCF lab	SM: 5910 B: Ultraviolet Absorption Method/ DR5000	0.01 cm^{-1}	Analyze immediately; or cool, 4ºC in the dark	48 hours

SM = Standard Methods AEL = Advanced Environmental Laboratories , Inc. EDA = ethylenediamine

Chemicals and Reagents

Table 4.2 provides a list and a brief description of the chemicals used in the UCF bench-scale component of work.

Table 4.2
Summary of chemicals used in DBP bench-scale experiments

Chemical	Description
Aluminum sulfate (alum)	Coagulant, SG = 1.34, dry weight = 48.5%
Ammonium chloride	ACS grade – used for HAA analysis
Chlorine dioxide	1700 mg/L stock concentration
DPD free chlorine reagent	Powder pillows – used for chlorine residual analysis
EDTA	Used for chlorite and chlorate sample preservation
Hexane	ACS grade – used for THM analysis
pH buffer solutions	4, 7, and 10 pH buffer solutions
Potassium permanganate	ACS grade – solid
Sodium hydroxide	ACS grade – solid, 97.8% used for pH adjustment
Sodium hypochlorite stock	ACS grade – liquid, used for chlorine dosing
Sodium sulfite	ACS grade – used for THM analysis
THM calibration standard mix	100,000 mg/L stock concentration – 4-8047 Supelco

ACS = American Chemical Society
EDTA = ethylenediaminetetraacetic acid
SG = specific gravity

Preparation of Potassium Permanganate

A solution of potassium permanganate was prepared by diluting one gram of potassium permanganate crystals in a 100-milliliter (mL) volumetric flask of distilled water. The volumetric flask was covered with parafilm and mixed thoroughly. A secondary stock solution was prepared in order to be able to dose small volumes of Fena Lake water by diluting one-mL of the primary potassium permanganate stock solution in 100-mL of distilled water. 10-mL of the secondary stock solution was equal to one-mg/L potassium permanganate.

Preparation of Chlorine Dioxide

In order to produce chlorine dioxide chemical for use in experimentation, a Siemens AC-10 chlorine dioxide generator was installed by Evoqua (2650 Tallevast; Sarasota, FL) at UCF's drinking water laboratory which was used to evaluate Fena Lake's chlorine dioxide demand at the bench-scale. The generator works on the basis of the acid/chlorite process and generates chlorine dioxide as an aqueous solution. Dilute hydrochloric acid (9%) and dilute sodium chlorite (7.5%) are used as starting components for the generation of chlorine dioxide (Siemens Water Technologies).

In the chlorine dioxide bench-scale unit, reagents are fed from carboys to the reaction tank with a peristaltic pump where a solution with approximately 20-grams (g) ClO_2 per liter (L) is generated. This solution is flushed with water into the preparation tank after a defined reaction time. This generates a defined chlorine dioxide solution with less than 2.5 grams per liter (g/L). The preparation tank is in connection with the intermediate tank. From the intermediate tank the solution is taken by the metering pumps. The exact addition of both starting components is monitored by electronic flow sensors. The chlorine dioxide solution was pumped from the generator into 125-mL amber bottles, capped, and stored in a refrigerator. The initial concentration of the chlorine dioxide solution was measured immediately after collection using the Chlorine Dioxide Direct Reading Method 8138.

Figure 4.2
Siemens AC-10 chlorine dioxide generator

In the event of deviation, the control unit automatically activates an alarm. If there is insufficient operating water available for dilution, the system switches to a stop mode. Vapors produced during the solution flow within the tanks are safely removed in the absorption unit that is installed within the generator equipment. The system is controlled by programmable logic controller (PLC) in combination with an operating and observation panel with a sealed keypad. In addition, the unit is placed within a locked laboratory with limited access by key-card only.

Fena Lake Dosing in Jar Testing Unit

Bulk water from Fena Lake was mixed in a 5-gallon bucket to allow for a homogenous sample. The initial water quality parameters (conductivity, pH, temperature, turbidity, and TOC) were recorded. The sample water was then transferred to two six-paddle programmable jar testers that were used to conduct this study. Each apparatus included six stainless-steel, one-inch x three-inch paddles spaced six inches apart, simultaneous variable speed adjustment for paddle rotation from 1 to 300 revolutions per minute (rpm), powder-coated steel uni-frame chassis, built-in illuminator, anti-glare curtain, and dust cover. The paddles were adjusted to the maximum depth of nine inches during each experiment. Twelve two-L square acrylic B-KER2® testing jars, equipped with sampling ports, were used to contain the water samples for each jar testing unit.

The jar testing beakers (jars) were filled with two liters of sample water. There were three jars per pre-oxidant condition; i.e. three jars for no pretreatment, chlorine pretreatment, potassium permanganate pretreatment, and chlorine dioxide pretreatment. There were twelve jars total, as presented in Figure 4.3**.**

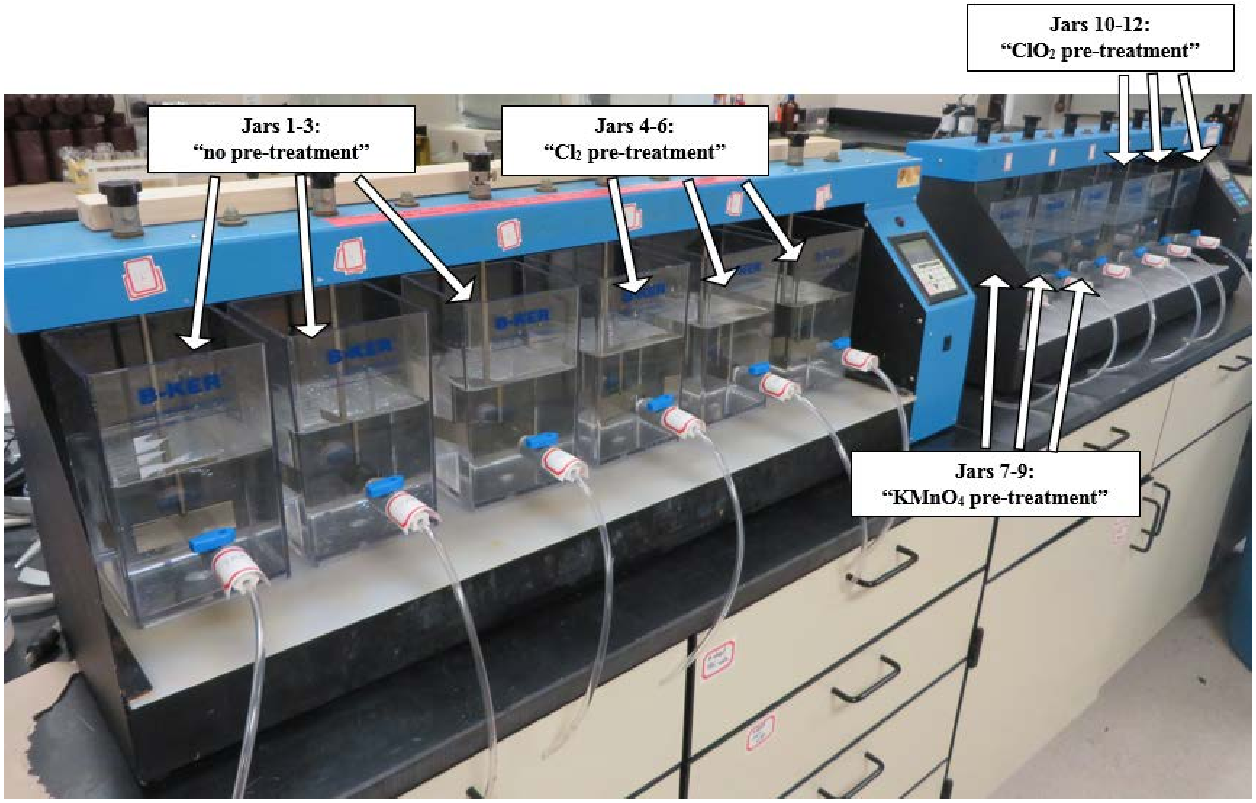


Figure 4.3
DBP jar testing equipment used for experimentation

Next, the jars were dosed for pretreatment using Equation 4-1, in which the oxidant dosing volume was the only unknown value and was solved for using the equation. Jars 1, 2, and 3 were not dosed with a pre-oxidant (to represent no pretreatment). Jars 4, 5, and 6 were dosed with 1.25 mg/L Cl_2. This chlorine dose concentration was calculated using Equation 4-2, in which the pounds (lbs) and flow operation data was provided by the NWTP to represent Fena Lake under previous operating conditions. Jars 7, 8, and 9 were dosed with 1.75 mg/L $KMnO_4$, which was established as the optimum potassium permanganate dose in a previous UCF study (UCF, 2013). Jars 10, 11, and 12 were dosed with 1.1 mg/L ClO_2, which was established as the optimum chlorine dioxide dose in a separate UCF study (UCF, 2014).

$$C_1V_1 = C_2V_2 \tag{4-1}$$

$C_1 = concentration\ of\ the\ oxidant\ stock\ solution\ \left(\frac{mg}{L}\right)$

$C_2 = target\ concentration\ of\ the\ sample\ \left(\frac{mg}{L}\right)$

$V_1,\ V_2 = oxidant\ dosing\ volume\ (mL), sample\ volume\ (mL)$

$$Lbs = Flow\ (MGD) \times Concentration\ \left(\frac{mg}{L}\right) \times 8.34 \tag{4-2}$$

The jar testing units were then covered and mixed at 120 rpm for two hours to simulate pipe flow. According to the plant operators, Fena Lake water takes approximately two hours to go from Building 1285 to the NWTP Fena Pipe influent location.

Coagulation, Flocculation, Sedimentation, and Filtration (CSF)

Once the jars were mixed for two hours, alum coagulant was added to each of the jars at the rapid mix. The laboratory at the NWTP in Guam, DZSP21, shipped alum that was used at the NWTP to the UCF laboratory for the bench-scale tests. The coagulant dose was based on daily plant operations data acquired from the NWTP and was between 35-40 mg/L. Also, Jars 4, 5, and 6 were dosed with 0.7 mg/L Cl_2 (hypochlorite) to represent the rapid mix location under previous chlorination conditions. This chlorine dose concentration was calculated using Equation 4-2, in which the pounds and flow operation data was provided by the NWTP to represent past operating prechlorination conditions. The different coagulation-flocculation phases were chosen by jar tests performed and consisted of a rapid mix at a speed of 150 rpm for three minutes and a slow agitation phase at the speed of 25 rpm for 15 minutes (Zogo, Bawa, Soclo, & Atchekpe, 2011). Then, the sample water settled for one hour to represent the sedimentation process.

After the sedimentation process was complete, samples were collected in multiple 1000-mL Erlenmeyer flasks for filtration. The samples were filtered through a 0.45-micron filter using a vacuum filter apparatus. The vacuum apparatus was cleaned and a new filter was used for each sample.

Dosing at the Clearwell

After the samples had been filtered, they were collected in 4-L glass amber bottles (four bottles total, one for each pretreatment condition). Each sample volume was dosed with bleach (hypochlorite) disinfectant to simulate primary disinfection at the clearwell. The "no pretreatment" sample was dosed with 3 mg/L Cl_2, which was determined from NWTP data (when the NWTP ceased prechlorination). The "chlorine pretreatment" sample was dosed with 2.5 mg/L Cl_2, also determined from NWTP data (when the NWTP used prechlorination). The "potassium permanganate pretreatment" and "chlorine dioxide pretreatment" samples were dosed with 3.75 and 3 mg/L Cl_2, respectively.

DBP Formation Potentials

THM and HAA samples were collected in 60-mL and 250-mL capped amber glass bottles, respectively, for formation potential testing. Chlorine residual samples were collected in 125-mL capped amber glass bottles. The chlorine residual, TTHM, and HAA5 samples were incubated at 30°C to represent the distribution system. There were chlorine residual, TTHM, and HAA5 sample bottles to represent each of the following times: clearwell (0-hour), 48-hour, and 168-hour. Chlorite and chlorate samples were collected from the water that had been pre-treated with chlorine dioxide in 125-mL glass amber bottles. The chlorite and chlorate samples were preserved with ethylenediaminetetraacetic acid (EDTA) and stored at 4°C in accordance with EPA Method 300 (Hautman, 1997). Table 4.3 provides a summary of the samples collected for residual chlorine, TTHM, HAA5, and TOC parameters.

Table 4.3
UCF bench-scale treatment DBP formation potential study

Location	Parameter	Comments
B1285 Post-Chlorination Station	Residual chlorine, TTHM, HAA5, TOC	Grab and Quench*. Take chlorine residual reading
Rapid Mix	Residual chlorine, TTHM, HAA5, TOC	Grab and Quench*. Take chlorine residual reading
Clearwell	Residual chlorine, TTHM, HAA5, TOC, Chlorite, Chlorate	Grab and Quench*. Take chlorine residual reading
Clearwell formation potential (bulk sample to be collected at the same time as the "grab and quench")		
Clearwell (2-Hours)	Residual chlorine, TTHM, HAA5	Quench* after 2 hours of incubation at 30°C. Take chlorine residual reading
Clearwell (4-Hours)	Residual chlorine, TTHM, HAA5	Quench* after 4 hours of incubation at 30°C. Take chlorine residual reading
Clearwell (8-Hours)	Residual chlorine, TTHM, HAA5	Quench* after 8 hours of incubation at 30°C. Take chlorine residual reading
Clearwell (24-Hours)	Residual chlorine, TTHM, HAA5	Quench* after 24 hours of incubation at 30°C. Take chlorine residual reading
Clearwell (48-Hours)	Residual chlorine, TTHM, HAA5	Quench* after 48 hours of incubation at 30°C. Take chlorine residual reading
Clearwell (96-Hours)	Residual chlorine, TTHM, HAA5	Quench* after 96 hours of incubation at 30°C. Take chlorine residual reading
Clearwell (168-Hours)	Residual chlorine, TTHM, HAA5	Quench* after 168 hours of incubation at 30°C. Take chlorine residual reading

*Quenched the TTHM and HAA5 samples only

The samples were then removed from the oven at the designated time and residual chlorine was measured; TTHM bottles were quenched with sodium sulfite (Na_2SO_3) and stored at 4°C in a refrigerator until analysis could be performed. In a similar fashion, the HAA5 bottles were quenched with ammonium chloride (NH_4Cl) and stored at 4°C until chemical analysis could be performed. The TTHM FP and HAA5 FP samples were collected and measured in UCF's drinking water laboratories in accordance with *Standard Methods for the Examination of Water and*

Wastewater 5710 B, Total Trihalomethane Formation Potential and 5710 D, Formation of Other Disinfection By-Products (American Public Health Association et al., 2005).

TTHMs were analyzed after the final 168-hour sample was quenched using gas chromatography (GC) analysis. TTHMs were analyzed in UCF's drinking water laboratories in accordance with the *Standard Methods for the Examination of Water and Wastewater* 6232 B, Liquid-Liquid Extraction Gas Chromatographic Method (American Public Health Association et al., 2005). TTHM's were analyzed at UCF; however, for purposes of time and schedule, the majority of HAA5s, chlorite, and chlorate analyses were performed at a certified laboratory in Orlando, FL.

The DBP formation potentials for these source waters were plotted in Excel, in which the specific DBP concentrations obtained by experimentation were graphed over time. The ultimate (7-day or 168-hour) TTHM formation was determined from experimental data to serve as a means of representation of distribution system conditions experienced within the U.S. Navy's PWS.

System Management Experimental Plan

Several in-plant studies were performed at the NWTP in addition to studies performed throughout the Navy's distribution system in Guam to evaluate the formation of DBPs under various conditions.

In-Plant DBP Analysis at the NWTP Clearwell and Distribution System Pre and Post-chlorine Shutoff

In-plant studies were performed at the NWTP and throughout the distribution system from May to September of 2013 regarding DBP formation before and after the Navy ceased prechlorination at

Fena Lake, the rapid mix chemical feed location, and the chemical feed location upstream of the filters. TTHM and HAA5 samples were collected from within the plant's clearwell and at four sample locations throughout the distribution system (McCool's, Madrid Circle, Plumeria St., and Portola St.) in capped 125-mL glass vials. The samples were then delivered to and analyzed at the DZSP21 laboratory in Guam. The clearwell DBP concentrations were to be used in comparison with TTHM and HAA5 concentrations at the clearwell from the previous year (September 2012) to analyze the DBPs with and without prechlorination operating under the same seasonal conditions. The samples collected within the distribution system were to be compared with historical plant data. The goal of this study was to investigate the extent of DBP formation throughout the distribution system caused by prechlorination that caused the Navy to violate the Stage 2 D/DBP Rule.

Fluoride Tracer Study

Laboratory staff at DZSP21 indicated that the NWTP's treated water required nine days to reach one residential unit in the Apra View Housing complex (a DBP monitoring sample location in the distribution system), while the housing unit across the street experienced a five-day travel time for the water to reach the home after leaving the NWTP. A fluoride tracer study was performed within the U.S. Navy's PWS originating at the NWTP in September of 2013 to quantify dispersion and determine the contact time for the disinfectant and confirm the nine-day detention time in the Apra View Housing complex.

BFC Study for Severe Weather Conditions

In October 2013, the NWTP plant operated the BFC in series with the conventional alum coagulation surface water treatment plant due to severe weather that occurred coincidentally with two earthquakes that caused a rise in raw water turbidity. DBP samples were taken throughout the distribution system in order to provide DBP formation conditions within the PWS distribution system while the BFC was online to provide another opportunity for system management.

Analytical Testing Locations

The research described in this document was in part conducted at primarily two locations: (1) on-site at the U.S. Naval Base on Guam from May to October 2013, and (2) at the UCF's Orlando campus location between October 2013 and August 2014. Samples were collected by the Navy at various depths of the Navy's Fena Lake Reservoir. Sampling depths were determined by the NWTP and mimicked the full-scale system (usually drawn at 12-ft depth). Samples were then shipped by the Navy to UCF.

Field and Laboratory Quality Control

Statistics and quality control analyses were calculated in accordance with the *Standard Methods for the Examination of Water and Wastewater* 1010 B. Statistics and 1020 B. Quality Control (American Public Health Association et al., 2005), respectively.

Relative percent difference (RPD) was used in replicate and duplicate analyses and was calculated using Equation 4-3. An acceptable range of RPD between the ranges of 90%-110%. If a value fell outside three times the standard deviations from the mean, it was considered an outlier and was removed from the results.

$$RPD = \frac{S-D}{(S+D)/2} \times 100\% \tag{4-3}$$

$S = sample\ result\ (mg/L)$

$D = duplicate\ sample\ result\ (mg/L)$

Accuracy

An accuracy chart was constructed from the average and standard deviation The percent recovery was calculated for each spiked TTHM sample processed through the GC using Equation 4-4. The percent recovery of each spike was plotted on an accuracy chart to assess the consistency of the GC analyzer accuracy.

$$\%\ Recovery = \frac{C_{sample+spike} - C_{sample}}{C_{spike}} \times 100\% \tag{4-4}$$

$C_{sample+spike} = the\ concentration\ of\ the\ spiked\ sample\ (mg/L)$

$C_{sample} = the\ concentration\ of\ the\ sample (mg/L)$

$C_{spike} = the\ concentration\ of\ the\ spike\ (mg/L)$

The accuracy chart also includes upper and lower warning levels (UWL and LWL, respectively) in addition to upper and lower control levels (UCL and LCL, respectively). The warning limits and control limits were defined to be plus or minus two and three standard deviations from the mean, respectively. The UCL and LCL were calculated using Equation 4-5. The UWL and LWL were calculated using Equation 4-6.

$$UCL = \mu + 3s \text{ and } LCL = \mu - 3s \tag{4-5}$$

$$UWL = \mu + 2s \text{ and } LWL = \mu - 2s \tag{4-6}$$

$\mu = the\ mean\ of\ the\ percent\ recovery\ values$

$s = the\ standard\ deviation\ of\ the\ percent\ recovery\ values$

Precision

A precision chart was constructed from the average and standard deviation values to monitor process variation. Upper warning limits and upper control limits are calculated for precision charts. The industrial statistic (I-statistic) was calculated using Equation 4-7 to create control charts for the precision of the THM analysis.

$$I = \frac{|\mathrm{S-D}|}{(S+D)} \tag{4-7}$$

$S = sample\ result\ (mg/L)$

$D = duplicate\ sample\ result\ (mg/L)$

Upper control limits (UCL) for precision charts were defined to be the average I-value plus three standard deviations and were calculated using Equation 4-8. Upper warning limits (UWL) for precision charts were defined as the average I-value plus two standard deviations of the industrial statistic values and were calculated using Equation 4-9.

$$UCL = I_{avg} + 3s \tag{4-8}$$

$$UWL = I_{avg} + 2s \tag{4-9}$$

$I_{avg} = the\ average\ of\ the\ industrial\ statistic\ values$

$s = the\ standard\ deviation\ of\ the\ industrial\ statistic\ values$

Data points that fell above the UCL or below the LCL were removed from the results. If any two points were successively exceeding the warning limits, the data was considered to be a control violation. The data was checked by analyzing another sample and corrected for bias or disregarded.

Many of the activities performed by UCF relied upon historical existing information and include the collection of new information. Consequently, UCF shall be entitled to rely upon the accuracy of data and information provided by Brown and Caldwell, the U.S. Navy, DZSP21 and others without independent review or evaluation; UCF will attempt to identify and point-out questionable or uncertain data, where appropriate. When reviewing third-party independent laboratory or other relevant data, UCF will exercise judgment on the applicability of the information based on experience and investigation. This may involve comparing more than one source of historical information, if available. Historical laboratory chain-of-custody forms, parameter quality control charts, and data reports and/or similar information will also be reviewed, if available. Quality control data associated with the water quality information provided on data sheets or noted in laboratory logs will be reviewed to ascertain quality care in reporting and analyzing data.

5. RESULTS & DISCUSSION

Alternative Pre-oxidant Study Results for DBP Removal

Historically, the NWTP implemented chlorination at four locations that included Fena Lake, the rapid mix basin, pre-filters and the clearwell prior to the distribution system point-of-entry. However, soon after research conducted by UCF and as reported by Hall (2013) commenced, prechlorination was ceased on August 28, 2013 at three of the historical locations: Fena Lake, the rapid-mix, and pre-filter locations. This was because Hall (2013) and colleagues at UCF had demonstrated (soon after commencing research on the Navy's water supply) that prechlorination was not required as background iron was in the oxidized form and manganese remained below the detection limit under normal Fena Lake operating conditions.

After prechlorination ceased, it was found that DBP levels had significantly decreased within the PWS. Consequently, as a stop-gap measure to comply with the D/DBP Rule, the evaluation of DBPs formed without a pre-oxidant (to represent the WTP's current conditions) was integrated into the testing plan in addition to the evaluation of DBPs formed when alternative pre-oxidants, potassium permanganate and chlorine dioxide, were used in treating Fena Lake in lieu of gaseous chlorine. Each of these four pre-oxidant conditions (no pretreatment, Cl_2 pretreatment, $KMnO_4$ pretreatment, and ClO_2 pretreatment) were simulated and resultant samples were treated with chlorine (simulating post chlorination at the clearwell) for primary disinfection.

A total of six experimental runs were performed at UCF, and are summarized in Table 5.1. The first three experiments evaluated TTHMs formed when chlorine, potassium permanganate, and no pre-oxidant were added at the Fena Lake pump station. Experiment 4, 5, and 6 evaluated TTHMS and HAA5s for the four pre-oxidant conditions (no pre-oxidant, Cl_2, $KMnO_4$, and ClO_2).

Table 5.1
Summary of DBP data collected by experiment event

Experiment #	Experiment date	Pre-oxidant							
		$KMnO_4$		Cl_2		ClO_2		No pre-oxidant	
		TTHM	HAA5	TTHM	HAA5	TTHM	HAA5	TTHM	HAA5
1	Oct. 2013	✓		✓				✓	
2	Oct. 2013	✓		✓				✓	
3	Jan. 2014	✓		✓				✓	
4	June 2014	✓	✓	✓	✓	✓	✓	✓	✓
5	July 2014	✓	✓	✓	✓	✓	✓	✓	✓
6	Aug. 2014	✓	✓	✓	✓	✓	✓	✓	✓

A summary of the TTHMs and HAA5 formations for the experiments conducted in these studies are presented in Figure 5.1. The average amount of TTHMs and HAA5 formed by using potassium permanganate, chlorine dioxide, and without using a pre-oxidant were compared to the TTHMs and HAA5 formed when the plant used prechlorination. The results show that without using a pre-oxidant at the Fena Lake pump station, TTHMs and HAA5 formation would be reduced by 22.8% and 37.3%, respectively, based on this specific set of experimental conditions. Potassium permanganate had the lowest percent reduction of TTHMs and HAA5, at 5.7% and 22.7%, respectively; however, this amount was still a reduction from the results demonstrated for the chlorine pretreatment condition. Chlorine dioxide demonstrated the greatest TTHM and HAA5 reduction at 34.4% and 53.3%, respectively.

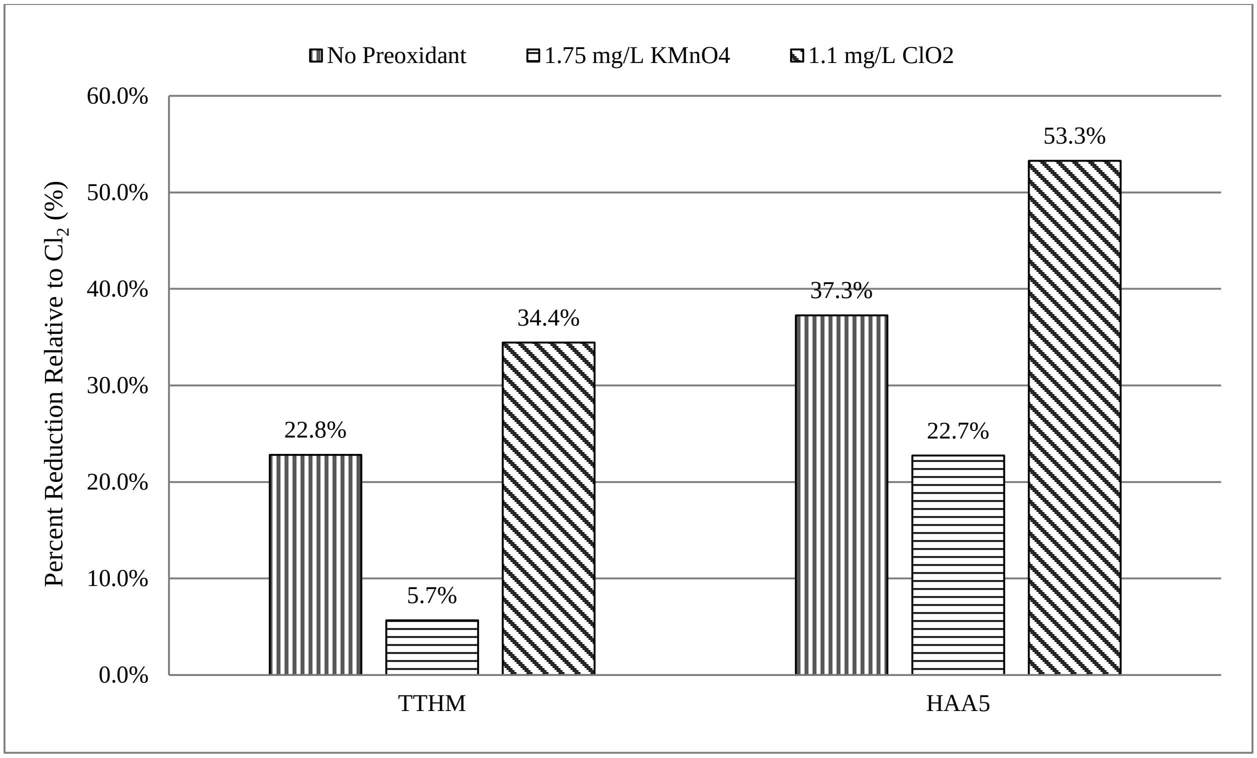
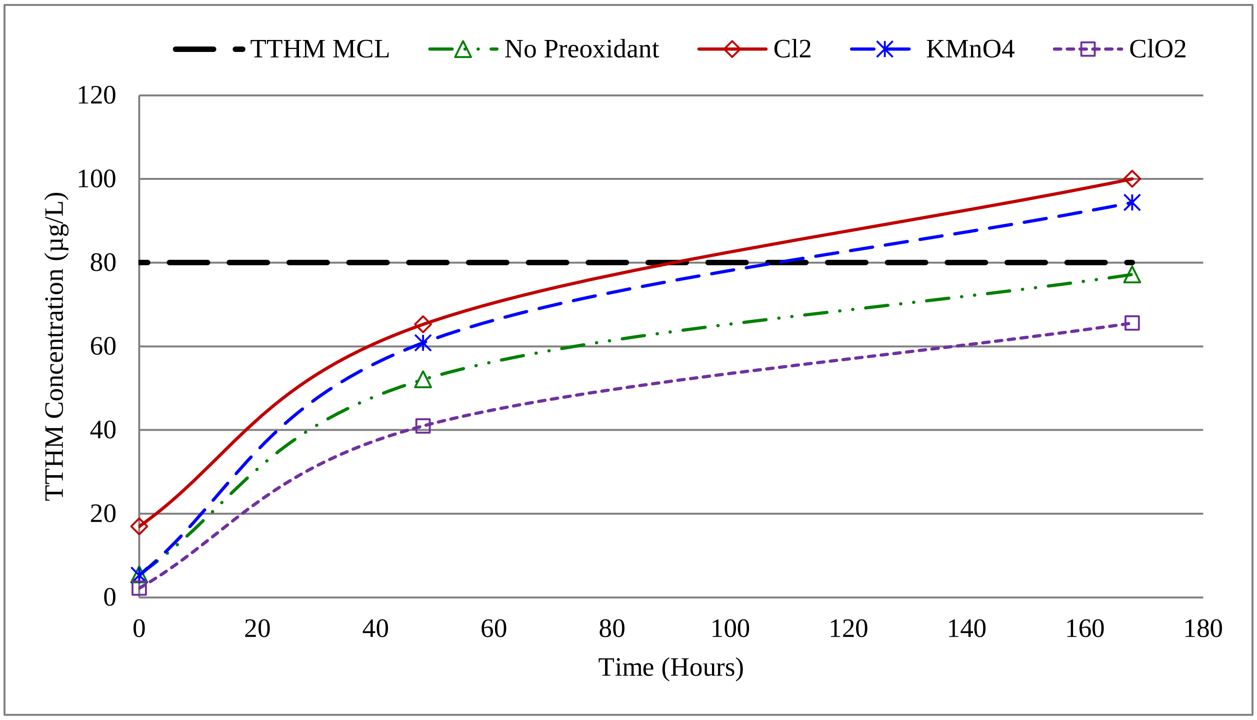


Figure 5.1
7-Day formation potential TTHM and HAA5 percent reduction relative to chlorine pretreatment for various pretreatment conditions

DBP Formation Potentials for Alternative Pre-oxidant Study

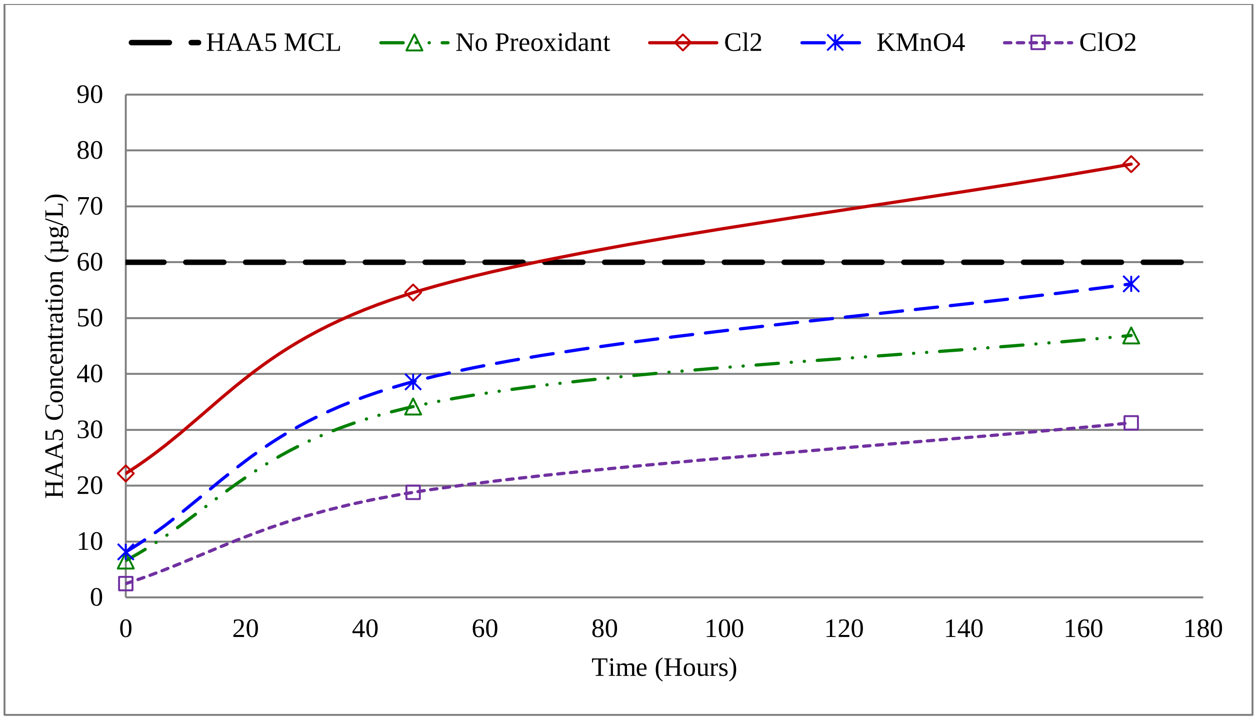
The DBP formation potentials for these source waters were determined by plotting the specific DBP concentrations obtained by experimentation against time. The TTHM and HAA5 formation potentials in Figure 5.2 and Figure 5.3, respectively, display the average results of the evaluation of four pre-oxidant conditions at Fena Lake: no pre-oxidant, chlorine pretreatment, potassium permanganate pretreatment, and chlorine dioxide pretreatment. These samples were taken from Fena Lake and treated by jar test simulations of the NWTP.

Results show that the greatest amount of TTHMs and HAAs were formed by the chlorine pre-oxidant dose, followed by potassium permanganate, no pre-oxidant condition, and chlorine dioxide, respectively. Chlorine dioxide and no pre-oxidant were the two conditions that did not exceed the regulated TTHM MCL of 80 µg/L after 168 hours of disinfectant contact time, as shown in Figure 5.2. As for the HAA5s, the results indicated that at the 168-hour mark the chlorine pre-oxidant condition was the one condition that would exceed the 60 µg/L HAA5 MCL, as shown in Figure 5.3.



Cl2 = 1.25 and 0.7 mg/L Cl_2 at B1285 and the rapid mix, respectively
KMnO4 = 1.75 mg/L $KMnO_4$ at B1285
ClO2 = 1.1 mg/L ClO_2 at B1285

Figure 5.2
TTHM formation potential for alternative pre-oxidant study



Cl2 = 1.25 and 0.7 mg/L Cl_2 at B1285 and the rapid mix, respectively
KMnO4 = 1.75 mg/L $KMnO_4$ at B1285
ClO2 = 1.1 mg/L ClO_2 at B1285

Figure 5.3
HAA5 formation potential for alternative pre-oxidant study

These results are comparable to those found in literature. While permanganate is a weaker disinfectant than chlorine, it is an acceptable oxidant that has been used for the control of iron, manganese, and sulfide (Crittenden et al., 2012). Potassium permanganate was found to form less TTHMs and HAA5s than chlorine. Chlorine dioxide, however, is a stronger oxidant and disinfectant. Chlorine dioxide produces two inorganic by-products when applied to natural waters: chlorite and chlorate. The Stage 1 D/DBP Rule set the MCL for chlorite in water at 1.0 mg/l (1,000 µg/L) and although no MCL for chlorate exists at the federal level, the state of California limits it to 0.8 mg/L (800 µg/L) (Crittenden et al., 2012). The 1.1 mg/L ClO_2 dose used in these experiments produced a chlorite concentration of 65 µg/L and therefore did not exceed the chlorite MCL, as shown in Figure 5.4.

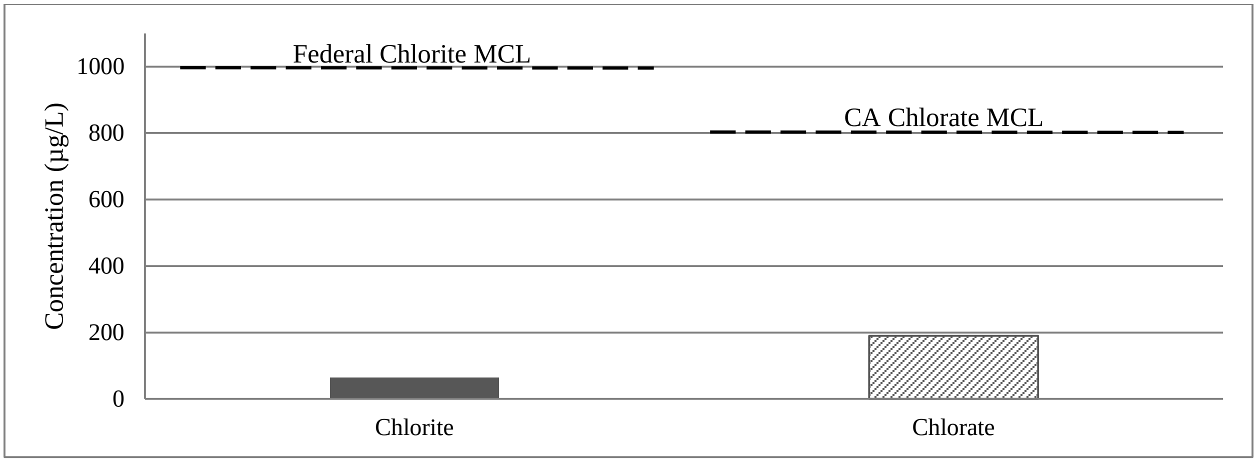


Figure 5.4
Average chlorite and chlorate concentrations for the 1.1 mg/L ClO_2 dose

During the DBP plan of study, it was determined that water samples would be collected from the Fena water system based on the normal operating practice of drawing Fena Lake supplies at the 12-ft depth. Due to the fact that deep-lake conditions did not represent actual practice, evaluations of water quality at Fena Lake depths greater than 20 feet were not performed. Furthermore, prior analysis (UCF, 2013) clearly delineated the effects of depth on finished water quality such that an additional study was not necessary. Appendix A, B, C, and D contain the TTHM, HAA5, chlorite and chlorate, and water quality depicting data that was collected during the duration of this study.

DBP Formation at the NWTP and Distribution System with and without Prechlorination

Due to the concern that the NWTP was in violation of the Stage 2 D/DBP Rule, the Navy ceased prechlorination on August 28, 2013. Results from the in-plant study to evaluate the TTHM and HAA5 concentrations at the NWTP clearwell before and after the Navy ceased prechlorination are displayed in Figure 5.5. TTHM and HAA5 concentrations were reduced by 73% and 87%, respectively after the Navy ceased prechlorination. Historical plant data from September of 2012 was used as a comparison to September 2013 so that the same time of year was used.

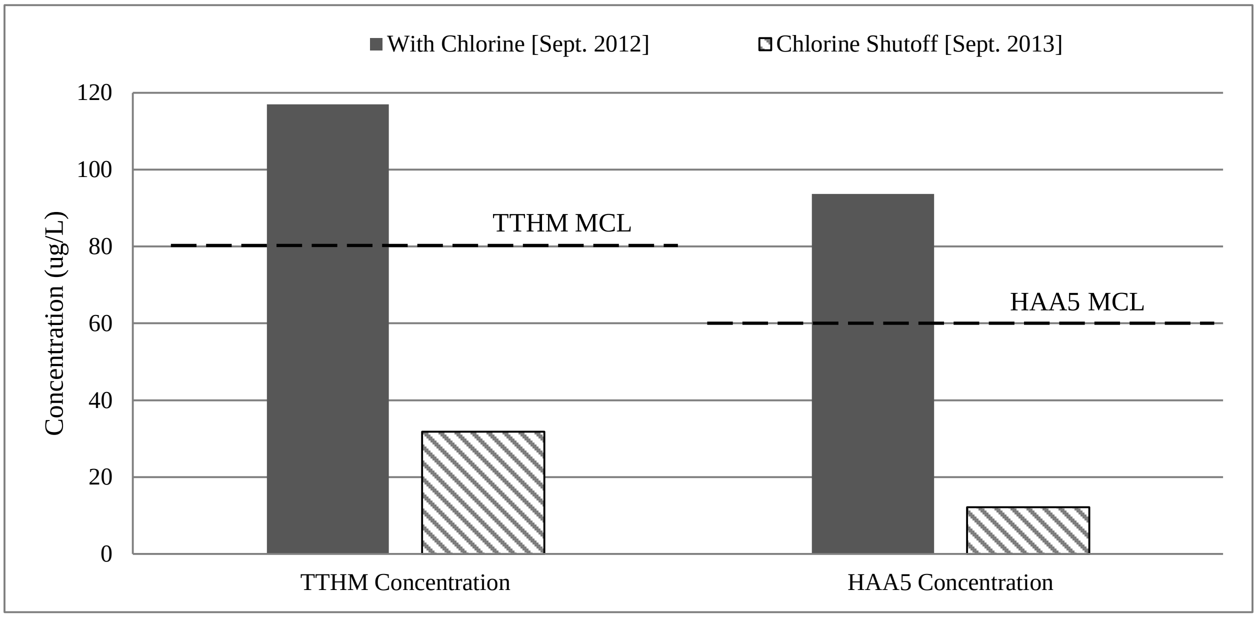


Figure 5.5
DBP concentrations at NWTP clearwell grab samples pre and post-chlorine shutoff

As previously stated, a review of water quality data by Brown and Caldwell (2014) demonstrated that numerous locations within the U.S. Navy water system regularly exceeded the MCLs for DBPs between 2009 and 2012. Four sampling locations within the U.S. Navy distribution system were used for comparison purposes to evaluate the TTHM and HAA5 concentrations before and after the prechlorination was turned off. The TTHM and HAA5 results are presented in Figure 5.6 and Figure 5.7, respectively. As shown in the figure, the four locations in the distribution exceeded the TTHM and HAA5 MCLs of 80 and 60 µg/L, respectively. However, after the Navy ceased prechlorination, the TTHMs and HAA5s were reduced by an average of 62% and 75%, respectively, and were significantly below the MCLs.

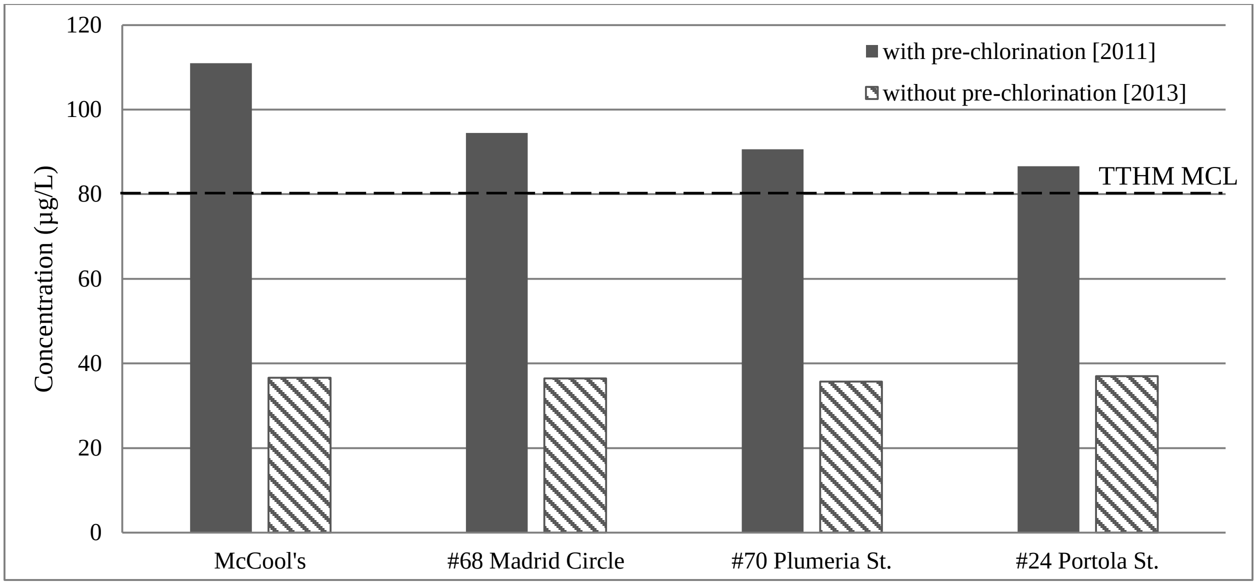


Figure 5.6
TTHM concentrations in the distribution system with and without prechlorination to illustrate the significant reduction in DBPs between 2011 and 2013

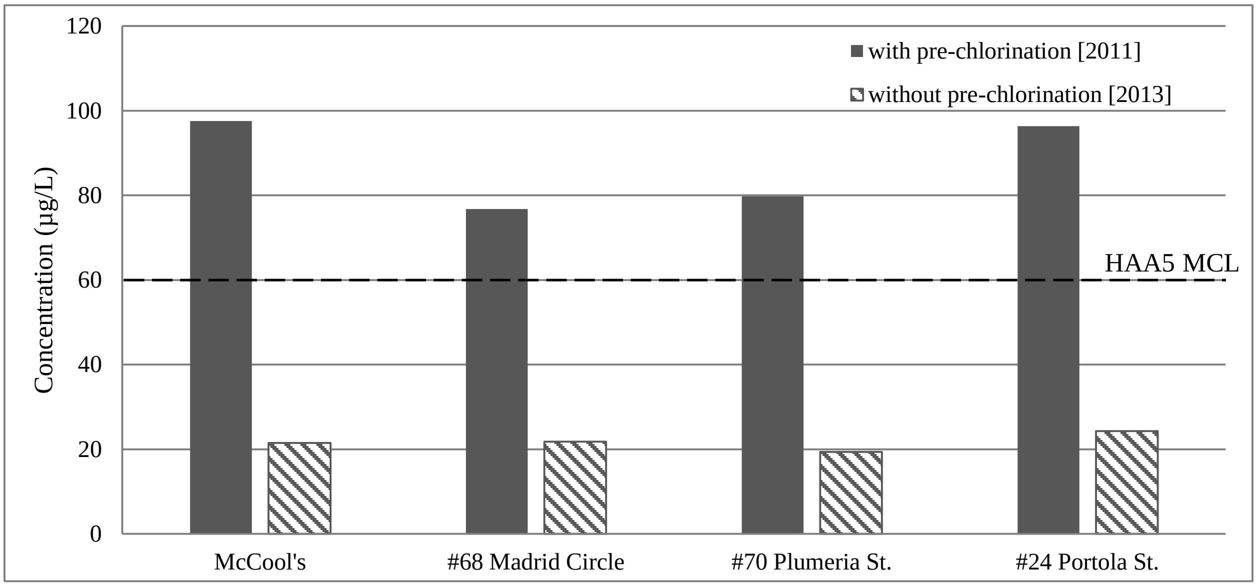


Figure 5.7
HAA5 concentrations in the distribution system with and without prechlorination to illustrate the significant reduction in DBPs between 2011 and 2013

<u>Fluoride Tracer Study Results</u>

The results from the fluoride tracer study that were used to confirm that the detention times varied within a small subdivision within the distribution system are displayed in Figure 5.8. It was discovered that the #8 Anae Lane, Apra View location was being fed by a dead-end pipeline at the back of the unit and had a ten-day detention time whereas the location across the street had a five-day detention time. The TTHM and HAA5 concentrations were also much higher for the #8 Anae Lane, Apra View compared to the house across the street. The pipeline valve was adjusted and as a result, the detention time was reduced from ten to five days and the DBP concentrations were similar to the sample location across the street.

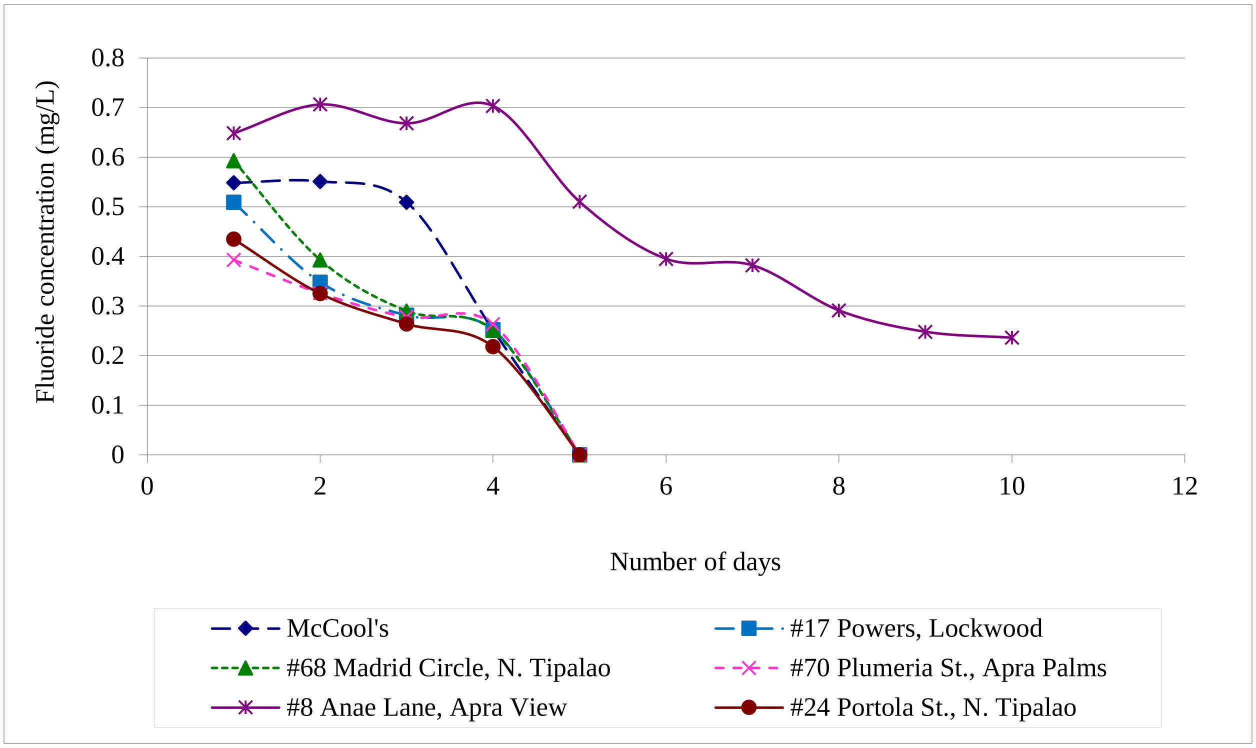


Figure 5.8
Fluoride tracer study [8/30 – 9/8/2013]

Ballasted Floc Clarifier In-Series

Table 5.2 presents the TTHM and HAA5 data from when the NWTP operated the BFC in-series with the conventional system under severe weather conditions. The TTHM and HAA5 concentrations were below 39 and 28 µg/L, respectively. The data shows that BFC in-series is a practical option for the plant during severe weather.

Table 5.2
DBPs by location when running BFC in-series [10/09/2013]

Analyte	Sample location					
	McCool's	#17 Powers, Lockwood	#9 Anae Lane, Apra View	#68 Madrid Circle, N. Tipalao	#70 Plumeria St., Apra Palms	#24 Portola St., N. Tipalao
TTHM (ug/L)	29.9	30.5	38.7	36.2	31.0	29.3
HAA5 (ug/L)	20.6	23.3	28.0	24.1	17.2	21.2

Quality Control Results

A quality control chart based on percent recovery was plotted for accuracy and is presented in Figure 5.9. There was one percent recovery value that exceeded the UCL. The precision quality control chart, displayed in Figure 5.10, was based on the I-statistic values. There was one I-statistic value that violated the UCL and one value that violated the UWL. The errors shown in both quality control charts were most likely due to human error or contamination. The values in violation of the UCL and UWL were not included in the TTHM analysis and final results.

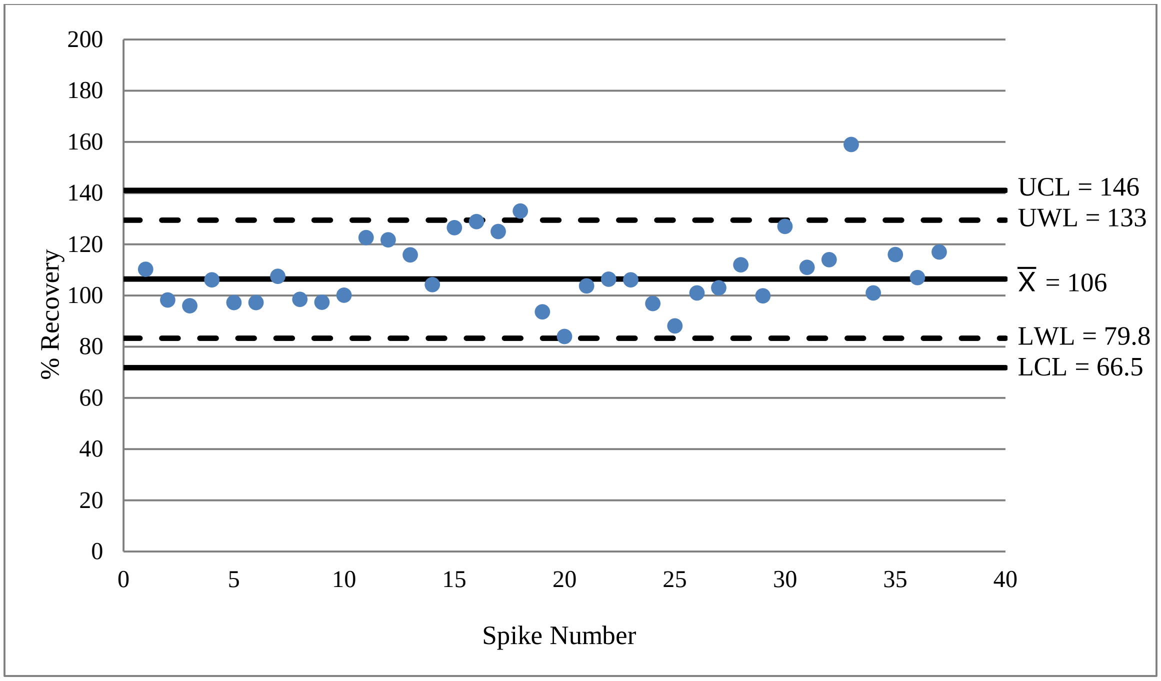


Figure 5.9
Control chart for TTHM accuracy

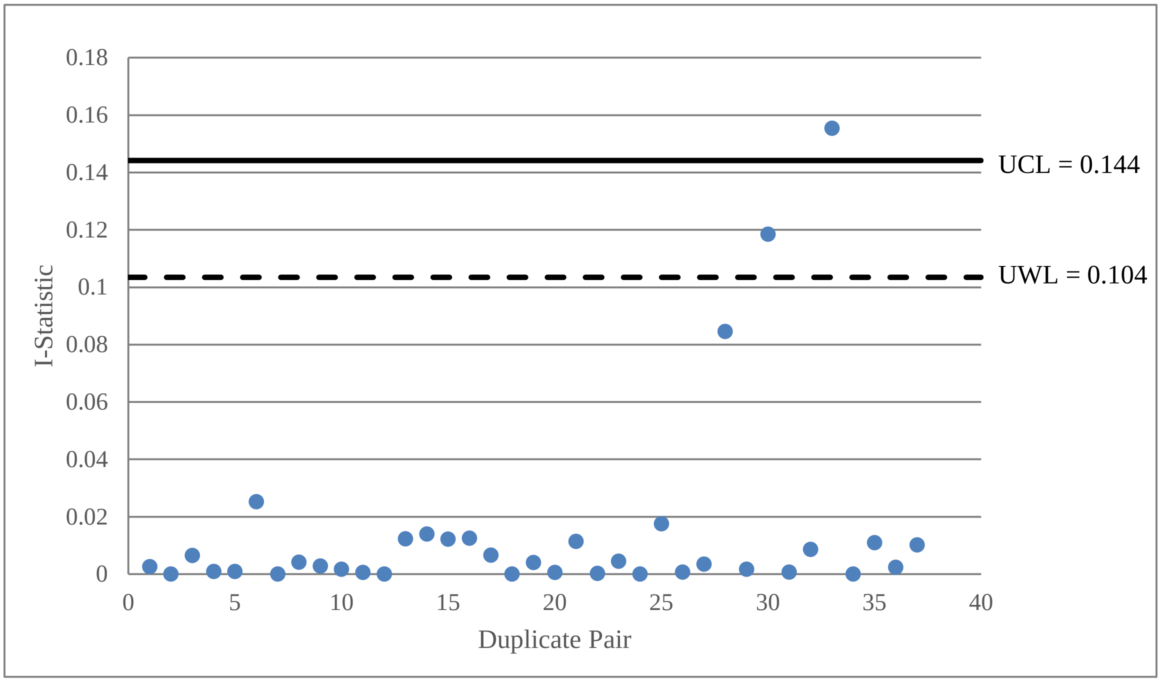


Figure 5.10
Control chart for TTHM precision

6. CONCLUSIONS & RECOMMENDATIONS

Conclusions

- Eliminating prechlorination at Fena Lake reduced DBPs in the NWTP and PWS. Based on the results obtained from grab samples drawn at the NWTP in Guam, the TTHM and HAA5 concentrations at the clearwell were reduced by 72.8% and 87.0%, respectively, when prechlorination ceased at Fena Lake. Also, the TTHM and HAA5 concentrations throughout the distribution system were reduced by an average of 61.6% and 75.0%, respectively.
- Treating Fena Lake raw water with chlorine dioxide resulted in significant DBP reduction. Based on the formation potential studies performed in UCF drinking water laboratories comparing alternative pre-oxidant treatments (chlorine, potassium permanganate, chlorine dioxide, and no pre-oxidant), chlorine dioxide resulted in the highest TTHM and HAA5 reduction at 34.4% and 53.3%, respectively. No pre-oxidant at Fena Lake resulted in 22.8% reduction and 37.3 % reduction for TTHM and HAA5 formation, respectively in the formation potential studies.
- A chlorine dioxide dose of 1.1 mg/L on raw Fena Lake water did not produce chlorite in excess of the chlorite MCL. The Stage 1 D/DBP Rule set the MCL for chlorite in water at 1 mg/L (1,000 µg/L) and the 1.1 mg/L ClO_2 dose used in the UCF laboratory experiments resulted in a chlorite concentration of 65 µg/L, significantly below the MCL.
- Treating Fena Lake raw water with potassium permanganate resulted in slight DBP reduction compared to historical prechlorination conditions. Based on the studies performed in UCF drinking water laboratories comparing alternative pre-oxidant treatments (chlorine, potassium permanganate, chlorine dioxide, and no pre-oxidant), potassium permanganate resulted in

TTHM and HAA5 percent reductions of 5.70% and 22.7%, respectively, when compared to prechlorination that was historically implemented at Fena Lake. Although Colthurst and Singer (1982) found that $KMnO_4$ absorbs THM precursors that can then be removed in sedimentation and filtration, the increase in DBPs with $KMnO_4$ pretreatment relative to no pretreatment may be due to the additional primary disinfectant added downstream or because the dissolved organic carbon was less amendable to coagulation. The use of potassium permanganate may also present operation challenges related to chemical feed containment, handling and dosing control that could compromise its use and not having accurate control of the permanganate dosages will result in pink water formation as demonstrated by Hall (2014).

- An analysis of fluoride tracer data confirmed excessive detention times existed within the PWS. Variable hydraulic detention times existed within Apra View Housing ranging from 5 to 10 days. It was determined that the housing complex was being fed by a dead-end pipeline. The information was used to take corrective management actions.
- A BFC placed in-series with the CSF clarifier was effective in controlling DBP formation during severe weather conditions. Based on the results obtained, the TTHM and HAA5 concentrations taken throughout the distribution system were below 39 µg/L and 29 µg/L, respectively, when the NWTP ran BFC in-series with the conventional system and the prechlorination process was off-line at Fena Lake. Should the plant experience severe weather in the future, a BFC-CSF clarifier in-series approach is a practical option recommended for application in the NWTP.

Recommendations

- Additional studies to evaluate DBP formation throughout the distribution system when using various blends of Fena Lake, Bona Spring, and Almagosa Spring are recommended. One option the US Navy should consider to study further is related to the qualitative observation that would indicate that the spring-lake blends produce less DBP formation than that of Fena Lake itself. Consequently, if proven, this would allow the Navy to increase spring flows and reduce Fena Lake flows during peak DBP events (should they occur). Consequently, should higher levels of DBPs be observed, then the flow of the springs could be increased (if available) in proportion to the Fena Lake flows, thereby further reducing DBP formation within the Navy distribution system. However, secondary impacts of this decision could mean intermittent red water complaints or corrosion impacts as the Springs' water is a different quality than Fena Lake. Thus it is not a long-term solution, but would be able to be implemented quickly at low cost until other options have been fully vetted. Consequently a study that further investigates this observed trend may be of benefit to the Navy's operations.
- Prechlorination should remain off-line at Fena Lake to avoid excessive DBP formation within the NWTP and PWS. Based on the results of this study, to avoid excessive DBP formation in the PWS, it is recommended that prechlorination remain off-line. However, it is further recommended that an alternative pretreatment system be identified to either enhance or replace prechlorination in the event a taste and odor event occur in Fena Lake.
- Additional chlorine dioxide engineering evaluations to include pilot testing are required to pursue an alternative option to the continued use of chlorination pretreatment. It is recommended that pilot testing of chlorine dioxide pretreatment be performed for a minimum

of eight months to capture seasonal impacts prior to engineering studies and design activities commencing for this pretreatment option. The use of chlorine dioxide would aid in operation of the facility with respect to iron and manganese control, taste and odor (based on analogous water industry research), as well as aid in reducing formation of regulated DBPs. Public outreach and education would be a necessary component of these additional studies and evaluations should this option be pursued.

APPENDIX A. UCF TTHM DATA

Table A.1

October 16, 2013 THM FP concentrations - Cl_2 vs. $KMnO_4$

Pre-oxidant	Number of Hours After Dose	Chloroform (µg/L)	Bromo-dichloromethane (µg/L)	Dibromo-chloromethane (µg/L)	Bromoform (µg/L)	TTHM (µg/L)
Control	0	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	2	15.7	6.28	< 1.00	< 1.00	23.9
	6	22.5	8.59	1.31	< 1.00	33.4
	24	35.4	11.9	1.94	< 1.00	50.2
	96	60.1	16.4	2.63	< 1.00	80.2
	168	74.5	18.1	2.85	< 1.00	96.5
Cl_2	B1285	12.7	< 1.00	< 1.00	< 1.00	15.7
	Rapid Mix	20.0	1.49	< 1.00	< 1.00	23.5
	0	24.2	2.40	< 1.00	< 1.00	28.6
	2	33.3	3.44	< 1.00	< 1.00	38.7
	6	40.7	4.35	< 1.00	< 1.00	47.0
	24	61.8	6.34	< 1.00	< 1.00	70.1
	96	96.5	9.06	< 1.00	< 1.00	107
	168	115	10.0	< 1.00	< 1.00	127
$KMnO_4$	B1285	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	Rapid Mix	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	0	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	2	20.2	7.56	1.05	< 1.00	29.8
	6	26.1	9.44	1.41	< 1.00	38.0
	24	40.9	12.9	1.94	< 1.00	56.8
	96	71.4	17.8	2.56	< 1.00	92.8
	168	91.1	19.9	2.82	< 1.00	114

Table A.2

October 28, 2013 THM FP concentrations - Cl_2 vs. $KMnO_4$

Pre-oxidant	Number of Hours After Dose	Chloroform (µg/L)	Bromo-dichloromethane (µg/L)	Dibromo-chloromethane (µg/L)	Bromoform (µg/L)	TTHM (µg/L)
Control	0	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	2	13.7	4.66	< 1.00	< 1.00	20.3
	6	19.4	7.07	< 1.00	< 1.00	28.5
	24	30.9	10.2	1.16	< 1.00	43.3
	96	52.2	14.5	1.96	< 1.00	69.7
	168	66.3	16.4	2.07	1.39	89.2
Cl_2	B1285	12.9	< 1.00	< 1.00	< 1.00	15.9
	Rapid Mix	23.0	1.28	< 1.00	< 1.00	26.3
	0	28.0	2.72	< 1.00	< 1.00	32.7
	2	34.1	3.82	< 1.00	< 1.00	39.9
	6	42.7	5.14	< 1.00	< 1.00	49.8
	24	58.6	6.78	< 1.00	< 1.00	67.4
	96	83.5	8.92	< 1.00	< 1.00	94.4
	168	98.5	9.13	< 1.00	< 1.00	109.6
$KMnO_4$	B1285	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	Rapid Mix	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	0	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	2	14.7	5.42	< 1.00	1.24	22.3
	6	20.9	7.61	< 1.00	1.29	30.5
	24	32.4	10.4	1.11	1.79	45.7
	96	58.6	16.2	2.09	1.80	77.9
	168	73.2	18.3	2.42	1.79	95.0

Table A.3

January 21, 2014 THM FP concentrations - Cl_2 vs. $KMnO_4$

Pre-oxidant	Number of Hours After Dose	Chloroform (µg/L)	Bromo-dichloromethane (µg/L)	Dibromo-chloromethane (µg/L)	Bromoform (µg/L)	TTHM (µg/L)
Control	0	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	2	8.16	3.68	< 1.00	< 1.00	13.8
	6	14.0	6.70	< 1.00	< 1.00	22.7
	24	29.7	13.2	1.33	< 1.00	45.2
	96	51.3	18.6	2.47	< 1.00	73.4
	168	61.5	20.7	2.79	< 1.00	86.1
Cl_2	0	20.4	2.92	< 1.00	< 1.00	25.4
	2	25.6	3.57	< 1.00	< 1.00	31.2
	6	32.7	5.30	< 1.00	< 1.00	40.0
	24	51.0	11.6	< 1.00	< 1.00	64.7
	72	71.0	11.4	< 1.00	< 1.00	84.5
	168	97.7	17.3	1.80	< 1.00	117
$KMnO_4$	0	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	2	13.3	5.35	1.40	< 1.00	21.0
	6	19.4	12.0	1.61	< 1.00	34.0
	24	37.7	14.7	3.91	< 1.00	57.4
	72	57.9	19.3	4.56	< 1.00	82.8
	168	80.8	23.0	5.53	< 1.00	110

Table A.4

June 17, 2014 THM FP concentrations - Cl_2 vs. ClO_2

Pre-oxidant	Number of Hours After Dose	Chloroform (µg/L)	Bromo-dichloromethane (µg/L)	Dibromo-chloromethane (µg/L)	Bromoform (µg/L)	TTHM (µg/L)
Control	0	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	48	38.8	14.6	4.77	< 1.00	59.2
	168	55.6	20.0	6.34	< 1.00	83.0
Cl_2	0	19.7	5.05	1.76	< 1.00	27.5
	48	51.5	12.5	3.58	< 1.00	68.7
	168	87.9	18.2	4.47	< 1.00	111
ClO_2	0	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	48	21.1	12.4	6.00	< 1.00	40.5
	168	34.2	17.5	8.00	< 1.00	60.8

Table A.5

July 7, 2014 THM FP concentrations - Cl_2 vs. ClO_2

Pre-oxidant	Number of Hours After Dose	Chloroform (µg/L)	Bromo-dichloromethane (µg/L)	Dibromo-chloromethane (µg/L)	Bromoform (µg/L)	TTHM (µg/L)
Cl_2	0	14.3	4.31	1.44	< 1.00	21.1
	2	21.9	6.82	2.18	< 1.00	31.9
	6	28.5	8.61	2.71	< 1.00	40.8
	24	41.8	12.4	3.57	< 1.00	58.9
	96	70.0	17.8	4.46	< 1.00	93.4
	168	86.8	20.2	4.83	< 1.00	112
ClO_2	0	< 5.00	< 1.00	< 1.00	< 1.00	< 8.00
	2	8.22	7.66	4.83	1.20	21.9
	6	12.7	10.6	6.08	1.34	30.8
	24	21.9	14.9	8.16	1.50	46.5
	96	35.9	19.4	9.35	1.60	66.3
	168	41.8	20.3	9.24	1.58	73.0

Table A.6

July 7, 2014 THM FP concentrations - Cl_2 vs. $KMnO_4$ vs. ClO_2

Pre-oxidant	Number of Hours After Dose	Chloroform (µg/L)	Bromo-dichloromethane (µg/L)	Dibromo-chloromethane (µg/L)	Bromoform (µg/L)	TTHM (µg/L)
Control	0	4.68	0.83	0.56	< 0.45	5.51
	48	38.3	7.67	6.05	< 0.45	52.0
	168	51.9	18.8	6.43	< 0.45	77.2
Cl_2	0	12.2	3.67	1.01	< 0.45	16.9
	48	52.3	12.8	0.56	< 0.45	65.2
	168	81.6	15.1	3.23	< 0.45	100
$KMnO_4$	0	4.46	0.79	0.56	< 0.45	5.25
	48	39.0	16.2	5.46	< 0.45	60.8
	168	66.3	21.3	6.63	< 0.45	94.3
ClO_2	0	1.58	0.61	0.56	< 0.45	2.19
	48	21.2	13.1	6.60	< 0.45	40.9
	168	39.0	17.9	8.04	0.52	65.5

APPENDIX B. UCF HAA5 DATA

Table B.1

June 16, 2014 HAA5 concentrations: Cl_2 vs. $KMnO_4$ vs. ClO_2

Pre-oxidant	Number of Hours After Dose	Bromoacetic Acid (µg/L)	Chloroacetic Acid (µg/L)	Dibromoacetic Acid (µg/L)	Dichloroacetic Acid (µg/L)	Trichloroacetic Acid (µg/L)	HAA5 (µg/L)
Control	0	0.54	0.200	0.540	4.21	2.47	6.68
	48	0.90	0.240	0.900	19.0	16.4	37.5
	168	0.68	4.84	1.13	26.6	15.5	48.8
Cl_2	0	0.63	2.98	0.540	13.3	7.71	24.6
	48	0.77	4.76	0.870	29.1	20.4	55.9
	168	0.65	7.41	1.00	40.1	24.5	73.1
$KMnO_4$	0	0.54	0.200	0.540	4.53	2.66	7.19
	48	0.75	4.12	0.770	21.6	18.0	45.3
	168	0.60	4.91	1.18	32.1	21.6	60.5
ClO_2	0	0.54	0.200	0.540	2.91	1.17	4.08
	48	0.83	3.97	1.09	13.2	8.09	27.2
	168	0.94	5.29	1.37	21.1	10.0	38.8

Table B.2

June 30, 2014 HAA5 concentrations: Cl_2 vs. $KMnO_4$ vs. ClO_2

Pre-oxidant	Number of Hours After Dose	Bromoacetic Acid (µg/L)	Chloroacetic Acid (µg/L)	Dibromoacetic Acid (µg/L)	Dichloroacetic Acid (µg/L)	Trichloroacetic Acid (µg/L)	HAA5 (µg/L)
Control	0	0.54	1.16	0.540	3.91	2.12	7.19
	48	0.85	0.200	0.840	22.0	17.3	41.0
	168	0.71	5.17	1.38	36.0	23.2	66.5
Cl_2	0	0.54	2.84	0.540	16.9	12.4	32.2
	48	0.78	4.36	0.910	34.2	26.1	66.4
	168	0.65	7.57	1.29	52.0	33.6	95.2
$KMnO_4$	0	0.54	1.47	0.540	4.08	2.16	7.71
	48	0.81	0.200	0.960	21.9	19.0	42.7
	168	0.67	5.23	1.38	34.3	24.7	66.3
ClO_2	0	0.54	0.200	0.650	2.40	0.910	2.40
	48	0.82	0.200	1.47	13.0	6.22	21.5
	168	0.86	0.200	1.73	20.3	7.17	30.1

Table B.3

July 7, 2014 HAA5 concentrations: Cl_2 vs. $KMnO_4$ vs. ClO_2

Pre-oxidant	Number of Hours After Dose	Bromoacetic Acid (µg/L)	Chloroacetic Acid (µg/L)	Dibromoacetic Acid (µg/L)	Dichloroacetic Acid (µg/L)	Trichloroacetic Acid (µg/L)	HAA5 (µg/L)
Control	0	0.54	1.48	0.540	3.41	1.72	6.61
	48	0.83	0.200	0.910	17.6	14.7	34.1
	168	0.92	5.30	0.830	24.1	15.7	46.9
Cl_2	0	0.54	0.200	0.540	13.4	8.75	22.2
	48	0.82	4.89	0.810	27.2	20.7	54.5
	168	0.91	6.93	0.880	40.3	28.4	77.5
$KMnO_4$	0	0.54	2.00	0.540	3.97	2.17	8.14
	48	0.89	4.97	0.790	20.1	11.8	38.5
	168	1.04	5.37	1.25	35.2	16.1	56.1
ClO_2	0	0.54	0.200	0.540	2.47	0.91	2.47
	48	1.11	0.200	1.63	11.9	4.11	18.8
	168	1.28	4.79	1.44	18.6	5.07	31.2

Table B.4

August 4, 2014 HAA5 concentrations: Cl_2 vs. $KMnO_4$ vs. ClO_2

Pre-oxidant	Number of Hours After Dose	Bromoacetic Acid (µg/L)	Chloroacetic Acid (µg/L)	Dibromoacetic Acid (µg/L)	Dichloroacetic Acid (µg/L)	Trichloroacetic Acid (µg/L)	HAA5 (µg/L)
Control	168	0.86	3.96	1.35	24.9	15.3	46.4
Cl_2	168	0.75	5.73	0.94	42.7	25.0	75.2
$KMnO_4$	168	0.84	4.35	1.34	31.0	20.8	58.4
ClO_2	168	0.93	3.58	2.05	21.0	8.18	35.7

APPENDIX C. CHLORITE AND CHLORATE DATA

Table C.1

Chlorate and chlorite concentrations for 1.1 mg/L ClO_2 pre-oxidant dose

Experiment #	Chlorate Concentration (µg/L)	Chlorite Concentration (µg/L)
4	< 190	< 65
5	-	-
6	< 190	< 65

Federal chlorite MCL = 1000 µg/L, California chlorate MCL = 800 µg/L

APPENDIX D. WATER QUALITY DATA

Table D.1

Water quality data

Experiment	Date	Sample ID	Parameter					
			pH (Std Units)	Temp (°C)	Conductivity (uS/cm)	Turbidity (NTU)	TOC (mg/L)	UV254 (1/cm)
Part 1 Trial 1	10/16/2013	Raw	7.62	21.5	155	2.31	NC	NC
		Cl_2	7.02	22.5	169	1.28	NC	NC
		No pretreatment	7.04	22.5	154	1.46	NC	NC
		$KMnO_4$	7.01	22.5	158	1.08	NC	NC
		Raw Filtered	7.52	23.4	157	0.03	NC	NC
		Cl_2 Filtered	7.25	23.2	173	0.08	NC	NC
		No pretreatment Filtered	7.23	23.2	157	0.06	NC	NC
		$KMnO_4$ Filtered	7.25	23.1	157	0.07	NC	NC
Part 1 Trial 2	10/28/2013	Raw	7.56	21.5	144	2.90	NC	NC
		Cl_2	7.05	21.6	171	2.91	NC	NC
		No pretreatment	7.01	21.6	153	2.85	NC	NC
		$KMnO_4$	6.97	21.5	158	2.83	NC	NC
		Raw Filtered	7.49	22.3	156	0.03	NC	NC
		Cl_2 Filtered	6.92	22.5	173	0.09	NC	NC
		No pretreatment Filtered	6.88	22.5	163	0.07	NC	NC
		$KMnO_4$ Filtered	6.91	22.5	162	0.04	NC	NC
Part 1 Trial 3	1/21/2014	Raw	8.03	20.3	194	2.12	NC	NC
		Cl_2	7.07	20.3	211	2.19	NC	NC
		No pretreatment	7.08	20.3	201	2.11	NC	NC
		$KMnO_4$	7.13	20.3	201	2.04	NC	NC
		Raw Filtered	8.01	22.4	154	0.04	NC	NC
		Cl_2 Filtered	7.02	22.5	169	0.10	NC	NC
		No pretreatment Filtered	6.97	22.3	162	0.08	NC	NC
		$KMnO_4$ Filtered	6.92	22.5	159	0.07	NC	NC

NC = not collected

(continued)

Table D.1 (Continued)

Water quality data

Experiment	Date	Sample ID	Parameter					
			pH (Std Units)	Temp (°C)	Conductivity (uS/cm)	Turbidity (NTU)	TOC (mg/L)	UV254 (1/cm)
Part 2 Trial 4	6/17/2014	Raw	8.58	22.3	215	1.67	3.52	NC
		Cl_2	7.11	23.5	238	1.71	3.71	NC
		No Pretreatment	7.13	23.2	227	1.64	3.65	NC
		$KMnO_4$	7.04	22.0	224	1.69	3.62	NC
		ClO_2	6.80	21.9	241	1.73	3.59	NC
		Raw Filtered	7.32	22.5	214	0.03	2.69	NC
		Cl2 Filtered	7.12	22.4	222	0.21	NC	NC
		No Pretreatment Filtered	7.10	22.4	219	0.16	NC	NC
		KMnO4 Filtered	7.08	22.5	221	0.13	NC	NC
		ClO_2 Filtered	7	22.5	235	0.15	NC	NC
Part 2 Trial 3	7/7/2014	Raw	8.15	22.5	263	1.40	3.57	0.040
		Cl_2	7.11	22.0	280	2.35	3.72	0.050
		No Pretreatment	7.11	22.0	270	2.56	3.65	0.061
		$KMnO_4$	7.04	22.5	273	2.47	3.63	0.064
		ClO_2	6.78	22.6	294	1.59	3.13	0.045
		Raw Filtered	7.88	22.5	262	0.03	3.32	0.039
		Cl2 Filtered	7.43	22.6	281	0.19	2.52	0.023
		No Pretreatment Filtered	7.37	22.6	274	0.16	2.37	0.028
		KMnO4 Filtered	7.34	22.7	275	0.15	2.29	0.028
		ClO_2 Filtered	7.00	22.9	296	0.16	2.16	0.023
Part 2 Trial 4	8/4/2014	Raw	7.99	21.8	249	1.58	3.43	0.005
		Cl_2	7.91	22.0	254	1.82	3.80	0.042
		No Pretreatment	7.92	21.9	247	1.52	3.53	0.051
		$KMnO_4$	7.96	21.8	248	1.71	3.58	0.052
		ClO_2	6.95	22.0	272	1.91	3.78	0.047
		Cl2 Filtered	7.16	22.9	274	0.10	2.53	0.016
		No Pretreatment Filtered	6.99	22.3	262	0.13	1.98	0.019
		KMnO4 Filtered	6.99	22.5	264	0.09	2.00	0.023
		ClO_2 Filtered	7.10	22.4	295	0.08	1.85	0.021

APPENDIX E. SYSTEM MANAGEMENT DBP DATA

Table E.1
Clearwell DBP data

Date	Condition	TTHM (ug/L)	HAA5 (ug/L)	% Reduction	
				TTHM	HAA
Sept. 2012	with prechlorination	117	93.7	-	-
Sept. 2013	without prechlorination	31.8	12.2	72.8%	87.0%

Table E.2
Distribution system DBP data

Sample Location	**2011**		**2013**	
	TTHM	**HAA5**	**TTHM**	**HAA5**
McCool's	111	97.6	36.6	21.5
#68 Madrid Circle, N. Tipalao	94.5	76.8	36.5	21.8
#70 Plumeria St., Apra Palms	90.6	79.8	35.7	19.4
#24 Portola St., N. Tipalao	86.6	96.4	37	24.3

Table E.3
Fluoride tracer study

Number of Days / Location	Fluoride Concentration (mg/L)						Date Sampled
	McCool's	#17 Powers, Lockwood	#68 Madrid Circle, N. Tipalao	#70 Plumeria St., Apra Palms	#8 Anae Lane, Apra View	#24 Portola St., N. Tipalao	
1	0.548	0.509	0.593	0.393	0.648	0.435	8/30/2013
2	0.551	0.348	0.393	0.326	0.706	0.325	8/31/2013
3	0.509	0.281	0.290	0.278	0.668	0.264	9/1/2013
4	0.251	0.252	0.251	0.263	0.703	0.218	9/2/2013
5	<mdl	<mdl	<mdl	<mdl	0.510	<mdl	9/3/2013
6					0.395		9/4/2013
7					0.382		9/5/2013
8					0.291		9/6/2013
9					0.248		9/7/2013
10					0.236		9/8/2013
11					<mdl		9/9/2013

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