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# Evaluating the Integration of Chlorine Dioxide into a Coagulation, Sedimentation, and Filtration Process Treating Surface Water

Martin Coleman
*University of Central Florida*

EVALUATING THE INTEGRATION OF CHLORINE DIOXIDE INTO A COAGULATION, SEDIMENTATION, AND FILTRATION PROCESS TREATING SURFACE WATER

by

MARTIN D. COLEMAN, E.I.
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# ABSTRACT

Methods of optimizing the coagulation, flocculation, sedimentation, and filtration (CSF) process at a conventional surface water treatment plant (WTP) were conducted to investigate opportunities for the reduction of disinfection by-product (DBP) precursor material. The research had two primary components: (1) optimize coagulant dosage and associated operating pH and (2) investigate pretreatment oxidation with chlorine dioxide ($ClO_2$) and potassium permanganate ($KMnO_4$). To accomplish the first component, jar tests were conducted at various pH and aluminum sulfate (alum) dosages to model current and potential treatment conditions during the CSF process at a WTP. Isopleths were developed to examine the removal efficiencies of turbidity and natural organic matter (NOM). NOM is a DBP precursor material and was represented by non-purgeable dissolved organic carbon (DOC) throughout the research. Isopleths indicated that at pH 6.2 and a corresponding alum dosage of 20 mg/L (control condition), turbidity and DOC were reduced by 90 and 35 percent, respectively. However, at pH 5.5 and 30 mg/L alum dosage, turbidity removal decreased to 80 percent whereas, DOC removal improved to 50 percent. Jar testing was conducted to evaluate differences in the use of $KMnO_4$ and $ClO_2$ as a pretreatment chemical to observe the reduction of DBP precursor material (i.e., NOM), dissolved iron, and dissolved manganese. Addition of $ClO_2$ was able to reduce total trihalomethanes and haloacetic acid formation potentials (168-hours) up to 40 percent and 15 percent, respectively, and was dependent on chlorine dioxide generation method, dosage, and raw water characteristics. Chlorine dioxide also was shown to remove iron and manganese at levels greater than 99 percent.

This thesis would not have been possible without the love and support of the Coleman family:

Jeffrey, Vonnie, Margarita, Chelsea, Rebecca, and Angel

*Many hands make light work.*

# ACKNOWLEDGMENTS

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# LIST OF ACRONYMS AND OTHER ABBREVIATIONS

%R                      percent recovery

°C                      degrees Celsius

µg/L                    micrograms per liter

µL                      microliters

µS/cm                   microSiemens per centimeter

AEL                     American Environmental Laboratory

Alum                    aluminum sulfate

Authority               Butts County et al. Water & Sewer Authority

AWWA                    American Water Works Association

Burford WTP             Emerson L. Burford Water Treatment Plant

$Ca(OCl)_2$             calcium hypochlorite

$CaCO_3$                calcium carbonate

CECE                    Department of Civil, Environmental, and Construction Engineering

CSF                     coagulation, flocculation, sedimentation, and filtration

$CHBr_3$                bromoform

$CHBrCl_2$              bromodichloromethane

| | |
|---|---|
| $CHCl_3$ | chloroform |
| $Cl^-$ | chloride ion |
| CL | control limit |
| $Cl_2$ | free chlorine |
| $ClO_2$ | chlorine dioxide |
| $ClO_2^-$ | chlorite |
| $ClO_3^-$ | chlorate |
| cm | centimeters |
| D/DBP Rule | Disinfectants and Disinfection Byproducts Rule |
| DBPFP | disinfection by-product formation potential |
| DBPs | disinfection by-products |
| DOC | dissolved organic carbon |
| EDA | ethylenediamine |
| Fe | iron |
| FP | formation potential |
| ft | feet |
| GAC | granulated activated carbon |

| | |
|---|---|
| HAA5 | total haloacetic acids |
| HCl | hydrochloric acid |
| HOCl | hypochlorous acid |
| IDSE | initial distribution system evaluation |
| I-stat | industrial statistic |
| $KMnO_4$ | potassium permanganate |
| L | liter |
| LCL | lower control limit |
| LRAA | locational running annual average |
| LWL | lower warning limit |
| MCL | maximum contaminant level |
| MDL | minimum detection limit |
| mg/L | milligram per liter |
| MGD | million gallons per day |
| mL | milliliters |
| Mn | manganese |
| MRDL | maximum residual disinfectant level |

| MRDLG | maximum residual disinfectant level goal |
|-------|------------------------------------------|
| MRL | minimum residual level |
| MTBE | methyl tertiary-butyl ether |
| $Na_2SO_3$ | sodium sulfite |
| $NaClO_2$ | sodium chlorite |
| NaOCl | sodium hypochlorite |
| $NH_4Cl$ | ammonium chloride |
| NOM | natural organic mater |
| NPDOC | non-purgeable dissolved organic carbon |
| NTU | Nephelometric Turbidity Unit |
| $OCl^-$ | hypochlorous ion |
| $OH^-$ | hydroxyl ions |
| PAC | powder activated carbon |
| POE | point-of-entry |
| Pt-Co | platinum cobalt units |
| RAA | running annual average |
| RPD | relative percent difference |

| | |
|---|---|
| rpm | rotations per minute |
| SCU | ClariCone® solids contact unit |
| SM | Standard Methods |
| soda ash | sodium carbonate |
| TOC | total organic carbon |
| TTHM | total trihalomethanes |
| TTHMFP | total trihalomethanes formation potential |
| UCF | University of Central Florida |
| UCL | upper control limit |
| USEPA | United States Environmental Protection Agency |
| UWL | upper warning limit |
| w.r.t. | with respect to |
| WL | warning limit |
| WTP | water treatment plant |

# CHAPTER 1 : INTRODUCTION

In Butts County, Georgia, public water supply is provided through a partnership that includes Butts County and the cities of Jackson, Jenkinsburg and Flovilla, referred to as the *Butts County, City of Flovilla, City of Jackson, and City of Jenkinsburg Water & Sewer Authority* (Authority). The primary treatment facility, Emerson L. Burford Water Treatment Plant (Burford WTP), conventionally treats surficial water taken from the Ocmulgee River. The Authority's conventional treatment includes raw water pre-treatment (i.e. oxidation), coagulation, flocculation, sedimentation, filtration, and disinfection. The Authority relies on the use of chlorine gas as both a primary and secondary disinfectant to inactivate pathogens and maintain a chlorine residual throughout the distribution system. However, disinfectants react with organic and inorganic matter in source water and distribution systems to form carcinogenic disinfection by-products (DBPs). Drinking water contaminants that can cause health effects after continuous long-term exposure at levels greater than the maximum contaminant level (MCL) are considered "chronic" contaminants. Chlorine, when used as a disinfectant, reacts with natural organic matter (NOM) to form chlorinated DBPs; many of these chlorinated DBPs are suspected carcinogens, hence, minimizing their concentration in distributed disinfected finished drinking water is in the best interest for the consuming public. The two regulated DBP groups of concern in the Authority's system include the total trihalomethanes (TTHMs) and haloacetic acids (HAA5). Within Authority's potable water distribution system, elevated levels of TTHMs have been recorded above the MCL of 80 µg/L as set at the locational running annual average by the United States Environmental Protection Agency (USEPA, 2006). To identify opportunities to reduce DBP formation within the Authority's water system, the existing coagulation, sedimentation and filtration (CSF) process was examined

for treatment performance to identify possible modifications that could be used to improve NOM removal. Methods employed for reducing the amount of DBP formation distributed throughout the Authority's water system could include reducing precursor quantities (e.g., use of enhanced coagulation, granular activated carbon, or membrane technologies), changing oxidant/disinfectant type or dosage (e.g. integration of ozone or chlorine dioxide), and reducing DBPs post formation (e.g., use of spray aeration technologies). Another option to achieve DBP reduction is to efficiently oxidize NOM content during pretreatment to alter reactivity. The Authority currently relies on potassium permanganate ($KMnO_4$) to treat for intermittent taste and odor and oxidize iron and manganese to allow the metals to precipitate and be removed by the CSF process. $KMnO_4$, a weak oxidant, does not typically impact DBP formation. However, the use of chlorine dioxide, a strong oxidant, oxidizes metals and, in part, total organic carbon (DBP precursors).

This research examined opportunities for alternative oxidation and modified coagulation process operations to achieve additional reduction of NOM within a conventional surface water treatment plant. Tasks were conducted to examine the coagulant dosage, operating pH within the contact basin, and pretreatment with potassium permanganate or chlorine dioxide. Hence, included in this work was the need to investigate the effectiveness of chlorine dioxide as compared to potassium permanganate for use as a pretreatment oxidant to treat Ocmulgee River water. To evaluate alternative oxidation pretreatment methods, two chlorine dioxide generation techniques were explored and used for the bench-scale oxidation pretreatment trials to compare against the existing permanganate method: (i) a traditional method based on mixing chlorine gas with sodium chlorite solutions (provided by Evoqua® Water Technologies), and (ii) an alternative method where two chemical powders are used to create chlorine dioxide (provided by TwinOxide®).

# CHAPTER 2 : LITERATURE REVIEW

## Conventional Treatment Overview

Public drinking water systems use various methods of water treatment to provide safe drinking water for their communities. Today, the more common steps in the treatment of surface water supplies used by community water systems include (CDC, 2015; Crittenden et al., 2012):

- **Coagulation and Flocculation**. Coagulation and flocculation are often the first steps in water treatment. Typically, chemicals with a positive charge such as metal salts or polymeric chemical(s), referred to as coagulants, are used to destabilize colloidal suspended particles. The positive charge of these chemicals neutralizes the negative charge dissolved particles and colloids in the water. The destabilized particles aggregate or bond together with interparticle bridging to form larger particles in a process called flocculation.

- **Sedimentation**. During sedimentation, the larger particles formed during flocculation (referred to as flocs) have sufficient specific gravities and settle with gravity or can be captured within a filter. The process of flocs settling in a contact basin is due to its weight and is defined at sedimentation.

- **Filtration**. Once the floc has settled in the sedimentation basin, water at the top of the structure (supernatant) flows over a weir and enters a gallery of filters where the water is filtered to remove finer particles that were not able to settle within the contact basin. Filtration can be completed using traditional sand, multimedia, cartridge, or membrane filtration. Many variables can be adjusted throughout this procedure to optimize the

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removal of specific compounds. Filtration removes the remaining dissolved particles that may have attached parasites, bacteria, and viruses from the water stream.

- **Disinfection**. After the water has been filtered, a disinfectant (chlorine in the case of this research) is added to inactivate any remaining parasites, bacteria, and viruses, and to protect the water from germs and other possible remaining microbiological contaminants when it is piped to the consuming public within the community.

- **Corrosion Control (Stabilization)**. Corrosion control treatment is a requirement of the EPA's 1991 Lead and Copper Rule (LCR). Stabilization is required to improve the aesthetics of the water and aid in compliance of the LCR. Corrosion inhibitors are used not only to control lead and copper release at the consumer tap, but also to prevent corrosion of iron pipe and other metals in the distribution system. The most common corrosion inhibitors used by water systems are phosphate-based chemicals.

One of the goals of conventional treatment is to remove DBP precursors, such as NOM, which is a heterogeneous mixture of multiple organic compounds with varying reactivity and functional properties (Chen et al., 2002). The composition of NOM varies widely according to water characteristics and environmental factors. For example, surface water is often higher in NOM compared to ground water sources and originates from various biological, geological, and hydrological cycles (Sillanpää et al., 2018). The results reported herein represent NOM as non-purgeable dissolved organic carbon (DOC). Often, DOC can contribute adversely to water's organoleptic properties (i.e., color, taste, and odor) and may serve as a facilitator for the enmeshment of toxic organic and inorganic pollutants (Sillanpää et al., 2018). Reduction of NOM

reduces undesirable characteristics of the treated water, with specific benefit to minimizing DBP formation, and is as such regulated as a treatment technique as a part of the United States Environmental Protection Agency's (USEPA) Stage 1 Disinfectants and Disinfection Byproducts (D/DBP) Rule in terms of total organic carbon (TOC) (USEPA, 1998).

*Modeling Coagulation, Flocculation, Sedimentation, and Filtration by Simulation*

Modeling of systems through simulation allows better understanding of the physical and chemical mechanisms occurring within the treatment processes (Heddam et al., 2011). Current methods of modeling conventional treatment include computer simulations and more traditional jar testing. An example of a computer model used to estimate optimal operating parameters during coagulation is the Adaptive Neuro-Fuzzy Inference System (ANFIS) (Heddam et al., 2011). While computer models are less time consuming once in operation, the physical and chemical reactions taking place during coagulation and flocculation are difficult to simulate within a mathematically derived model. This study has opted to utilize jar testing to model conventional treatment because of the complexity of site-specific water qualities.

Jar testing is a historically proven technique used to model conventional treatment within a bench-scale apparatus. Jar testing allows the user to conditionally test with the same chemicals and raw water used during full-scale treatment without the uncertainty of correctly defining input chemical characteristics within a computer model. Physical modeling with jar tests also accounts for minute chemical reactions that take place during full-scale treatment that may be ignored within a computer model. Yonge and colleagues (2012) used jar testing to compared iron and aluminum coagulants and their respected reduction of turbidity, color, and NOM for raw water originating

from an organic laden surface water source located near Sarasota, Florida. Jar test sequencing to simulate full-scale treatment was used with varying coagulants, coagulant dosage, and operating pH. Contour plots depicting the removal of a constituent to the coagulant dosage and pH were developed to map optimal operating zones. The results reported herein refer to these contour plots as isopleths.

*Coagulation with Aluminum Sulfate*

The most common coagulant used for water treatment is aluminum sulfate, or "alum" (Crittenden et al., 2012). Due to its common implementation, studies evaluating the use of alum have determined that optimum operating pH is approximately 6.0. When operating below a pH of 6.0, positively charged aluminum species form. When operating above a pH of 6.0, negative aluminum species concentrations increase (Yonge, 2012). NOM, primarily negatively charged particles, is removed most effectively in the presence of positively charged aluminum species (Crittenden et al., 2012; Yonge, 2012). Therefore, operating at a pH below 6.0 may yield to greater removal of NOM. Alkalinity adjustment chemicals can be expensive for a utility to depress the pH and then raise to stabilize the water after treatment. Thus, the removal of NOM must be balance with the need to change the raw water pH with the use of additional chemicals and operational costs.

Disinfection

Both primary and secondary disinfection is essential in providing potable water and has become mainstream in water treatment around the world. Disinfection mainly consists of the removal of pathogenic organisms by filtration or the inactivation of microorganisms using chemical oxidizers (Howe et al., 2012). Inactivation of microorganisms is completed by transforming the organisms

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in a way that inhibits the spread of disease (e.g., eliminating the ability to reproduce or damaging cell wall to promote lysing). Pretreatment using oxidants to control algae and other nuisance factors at raw water intakes typically encompasses the initial addition of an oxidizing agent. Primary disinfection is used to inactivate pathogens, while secondary disinfection carries a residual to further provide inactivation of pathogens and provide residual maintenance, which occurs in the distribution system. Chlorine disinfection, with either chlorine gas or sodium hypochlorite (aqueous), is commonly used to inactivate pathogens because of its rapid kinetics, availability, and low cost. When a chlorine comes in contact with NOM, DBPs form; chronic exposure to DBPs are suspected to pose epidemiological risks and are regulated accordingly (Richardson, 2005).

## Summary of Disinfectant By-Product (DBPs) Regulations

In 1979, the United States Environmental Protection Agency (USEPA) promulgated the first regulation concerning DBPs which set a limit on total trihalomethanes (TTHMs) (USEPA, 1979). TTHMs represent the sum of chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). The 1979 maximum contaminant level (MCL) on TTHMs was established at 100 micrograms per liter ($\mu g/L$) and was measured with a running annual average (RAA) of four samples taken from the distribution system each quarter. In 1998, USEPA passed the Stage 1 D/DBP Rule and reduced the TTHMs limit from 100 to 80 $\mu g/L$. Stage 1 also added MCLs for haloacetic acids (HAA5), bromate, and chlorite. HAA5 is the sum of monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid.

In addition to MCLs, Stage 1 D/DBP Rule established maximum residual disinfectant levels (MRDLs) and maximum residual disinfectant level goals (MRDLGs) for disinfection using chlorine, chloramines, and chlorine dioxide (USEPA, 1998). One method of mitigating DBP formation is to reduce DBP precursor material. TOC is a primary DBP precursor, thus Stage 1 D/DBP Rule mandated TOC reduction based on source water characteristics (TOC and alkalinity). Table 2-1 and Table 2-2 summarize the regulations within Stage 1 D/DBP Rule (USEPA, 1998). Maintaining a disinfectant residual above the minimum chlorine residual level of 0.2 mg/L as $Cl_2$ in the distribution system while also mitigating the formation of DBPs below regulated limits has become a challenge for many water purveyors.In an effort to further define DBP formation throughout the entire system, Stage 2 D/DBP Rule requires water utilities to perform an initial distribution system evaluation (IDSE) (USEPA, 2006). IDSE is used to identify the locations within the distribution system that have the highest DBPs concentrations. These compliance sites with the highest TTHMs and HAA5 concentrations are used to determine the locational running annual average (LRAA) on quarterly basis. The number of samples are based on the population served and source water type. System monitoring was also increased from every quarter (Stage 1) to every 90 days (Stage 2) (USEPA, 2006).

**Table 2-1: Stage 1 D/DBP Rule MCL and MRDL Summary**

| Disinfection By-Products | MCL (mg/L) | Disinfectant | MRDL (mg/L) |
| --- | --- | --- | --- |
| TTHM | 0.080 | Chlorine | 4.0 (as $Cl_2$) |
| HAA5 | 0.060 | Chloramines | 4.0 (as $Cl_2$) |
| Chlorite | 1.0 | Chlorine Dioxide | 0.8 (as $ClO_2$) |
| Bromate | 0.01 | - | - |

**Table 2-2: Stage 1 D/DBP Rule TOC Reduction Requirements**

| Source Water TOC (mg/L) | Minimum TOC Reduction (%) | | |
| --- | --- | --- | --- |
| | Source Water Alkalinity (mg/L as CaCO$_3$) | | |
| | 0 - 60 | 60 - 120 | > 120 |
| < 2.0 to 4.0 | 35% | 25% | 15% |
| 4.0 to 8.0 | 45% | 35% | 25% |
| > 8.0 | 50% | 40% | 30% |

Chemical Oxidation Overview

Conventional oxidation occurs between two chemicals when an electron is transferred. The compound donating the electron is said to be the reducing agent; the net positive change is said to oxidize the compound. The compound receiving the electron is the oxidizing agent and the negative change, imparted by the accepted electron, reduces the compound. The research herein compares chlorine dioxide and potassium permanganate. The tested oxidants can be used to oxidize undesired metals in source water. For example, iron (Fe) and manganese (Mn) are soluble in the Fe (II) and Mn (II) oxidation states. When oxidized to Fe (III) and Mn (III), they become insoluble and precipitate out of solution and are commonly captured by the treatment process (Howe et al., 2012). Pretreatment is not only used to precipitate metals out of solution, but can also partially consume DBP precursors (eg., NOM), reduce color in the water, and eliminate taste and odor compounds. Furthermore, oxidation will reduce toxic organics such as pesticides, benzene, trichloroethene, and methyl tertiary-butyl ether (MTBE) (Crittenden et al., 2012).

DBP Formation and Formation Potential

DBPs form from the interaction between a disinfectant (e.g., chlorine) and DBP precursors (e.g., NOM and inorganics found in source waters). NOM can be classified as either hydrophilic, transphilic, or hydrophobic, with hydrophobic being further classified into humic and fulvic compounds (Baribeau et al., 2006). Humic substances are less soluble while fulvic substances are more soluble in water. In general, humic acids generate more DBPs due to their higher aromatic content (Baribeau et al., 2006). TOC, dissolved organic carbon (DOC), and $UV_{254}$ are often used to measure NOM concentration in water. These carbon surrogates are described in Table 2-3.

**Table 2-3: Common Carbon Surrogate and Descriptions**

| Carbon Surrogate | Description | Significance |
|---|---|---|
| TOC | Summation of organic carbon present in sample | Indicator of potential DBP formation |
| DOC | TOC that passes through a 0.45 μm filter (dissolved) | Indicator of the reaction portion of the TOC |
| $UV_{254}$ | Used to identify light absorption of reactive humic components | Identifies the reactive portion of the DOC |
| SUVA | Ratio of $UV_{254}$ to DOC | Indicator of reaction portion of the TOC |

To predict the formation of DBPs in the system, disinfection by-product formation potential (DBPFP) is used to simulate the theoretical capability of DBPs to form within the distribution system with representative contact times. Water would be dosed with disinfectant and DBP formation would be measured over set time intervals (e.g., 1 hour, 4 hours, 12 hours, 24 hours, 48 hours, etc.). The measured DBP formation with respect to time would be plotted to generate a

DBPFP curve with the x-axis representing time and y-axis representing DBP concentration. DBPFP does not consider in situ variables encountered within the distribution system and is conducted within a controlled incubator with controlled pH and temperature. DBPs form when the oxidant attacks NOM, often at carbon-carbon double bonds, creating oxidized organic compounds. As the oxidation continues, the organic chains become more fragmented and simpler in structure (AWWA, 2011). The formation of DBPs from the oxidation of NOM and inorganics is summarized in Figure 2-1.
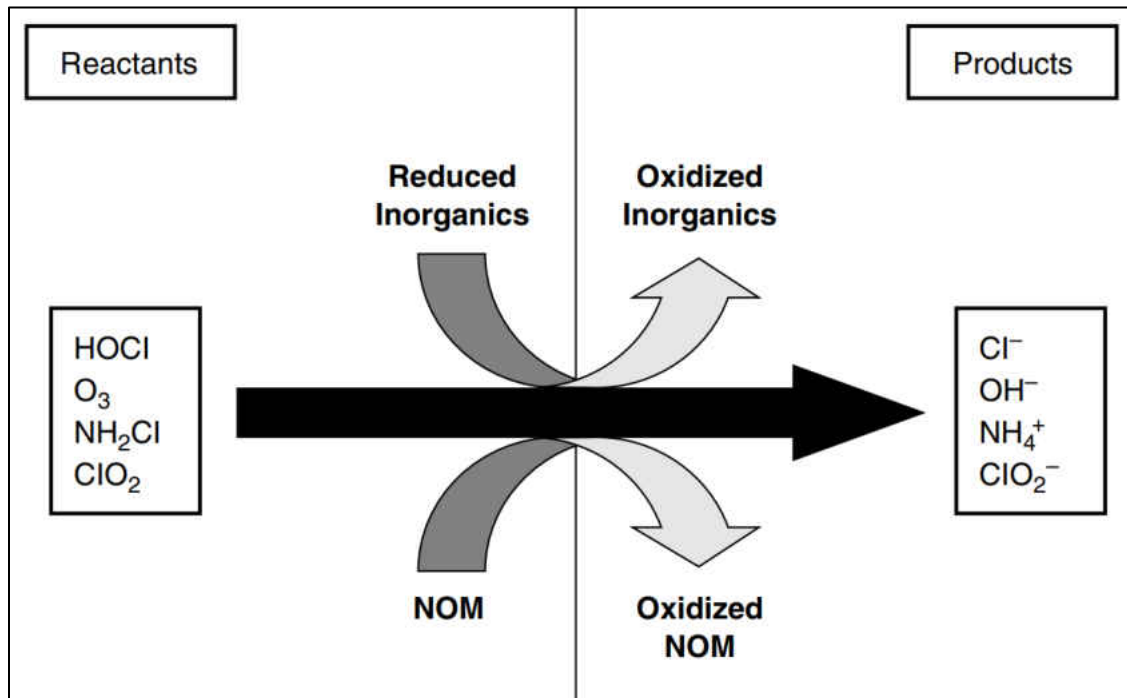


**Figure 2-1: Reactants and Products of Oxidation (AWWA, 2011)**

<u>Disinfectant Types and By-Products</u>

DBP formation depends on several water quality parameters as well as disinfection factors such as water temperature, pH, disinfectant (type, dosage, and residual), concentration of precursors (e.g., NOM and bromide), and contact time (LaBerge, 2014). There are numerous compounds formed from the reaction of an oxidant and NOM; only chlorine and chlorine dioxide by-products will be discussed in detail because they were the primary DBPs of the research. Potassium permanganate and chlorine dioxide solutions are compared in this research as pre-oxidants used for pretreatment. The dosage of an oxidant depends on whether the oxidant is being utilized for inactivation, residual maintenance, or both.

*Chlorine (Free Chlorine and Chloramines)*

Chlorine is the most common primary and secondary disinfectant used in water treatment and comes in gaseous phase (chlorine gas as $Cl_2$), aqueous phase (NaOCl), solid (calcium hypochlorite as $Ca(OCl)_2$) (Sadiq and Rodriguez, 2004). For the purpose of the research, chlorine is relied on for use as both a primary and secondary disinfectant used to supply the free chlorine residual in the distribution system. When ammonia is present in water dosed with chlorine, chloramines will form monochloramine (note: this research does not include study of monochloramine for DBP control at the request of the funding agency). When chlorine gas is diffused into water, hypochlorous acid (HOCl) and chloride ions ($Cl^-$) will form; the weak acid ($pK_a = 7.6$ at 20°C) can cause a depression of pH in water with insufficient alkalinity (Howe et al., 2012). When adding aqueous chlorine (NaOCl), it rapidly reacts with water to form HOCl and sodium hydroxide (AWWA, 2011). Oxidation of water is most effective at low pH values. The chemical reactions

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for gaseous and liquid chlorine addition is shown by Equation (2-1) and Equation (2-2) respectively. HOCl contributes the greatest oxidizing potential and will dissociate into hypochlorous ion (OCl⁻), as show in Equation (2-3). The sum of free chlorine ($Cl_2$), HOCl, and OCl⁻ is referred to as free available chlorine and is expressed as mg/L as $Cl_2$ (AWWA, 2011)

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{2-1}$$

$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^- \tag{2-2}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{2-3}$$

As the initial dosage of chlorine increases, the DBPFP tends to also increase. Thus, USEPA's Stage 1 D/DPB Rule sets the maximum chlorine residual disinfection level at 4.0 mg/L to achieve inactivation of pathogens while also minimizing DBP formation. Chlorine produces the greatest known variety of DBPs, including the primary DBPs of concern: TTHMs and HAA5. Despite TTHMs and HAA5 forming simultaneously, their ideal formation conditions differ. TTHM formation prefers alkaline conditions because hydroxyl ions (OH⁻) serve as catalysts for the reaction, while HAA5 formation is more rapid during acidic conditions (Kawamura, 2000). The pH of the dosed water heavily dictates the generation rate of DBPs and can be adjusted to favor either TTHM or HAA5 formation. Water containing elevated levels of bromide will form more brominated species (bromoform and dibromoacetic acid). Waters with low bromide concentration will favor formation of chloroform and di- and trichloroacetic acid. When moderate levels of bromide are present in the water, a mixture of brominated species will form (e.g., bromoform, bromodichloromethane and bromodichloroacetic acid) (AWWA, 2011).

*Chlorine Dioxide*

As DBP regulations become stricter and source waters decrease in either quality or quantity, the need for utilities to reduce TTHM formation both in the treatment plant and distribution system has become evident. Chlorine dioxide has increased in popularity because it produces significantly less halogenated by-products (e.g., chloroform) when compared to disinfection with chlorine gas and hypochlorite. Disinfection with chlorine dioxide is widely used in Europe, especially in Germany, Switzerland, and France (Howe et al., 2012), but is growing in popularity in other parts of the world. About 10 percent of utilities in the United States utilize chlorine dioxide (Howe et al., 2012). Caution must be exercised when handling chlorine dioxide because concentrated bulk solutions can be explosive when exposed to heat or sparks. For the safety of the operators and transportation, chlorine dioxide is not shipped in bulk, but generated on-site.

Chlorine dioxide is often used with low dosages as a pretreatment chemical to control iron, manganese, and taste and odor compounds (Hall, 2014). Chlorine dioxide does not hydrolyze in water and remains in its gaseous molecular form; thus, chlorine dioxide is more volatile compared to other disinfectants that hydrolyze in water (e.g., chlorine or potassium permanganate). Chlorine dioxide typically accepts an electron from readily available organics or inorganics (e.g., NOM, metals, or taste and odor compounds) to form chlorite ($ClO_2^-$), as shown in Equation (2-4). Chlorine dioxide will dissociate into both chlorite ($ClO_2^-$) and chlorate ($ClO_3^-$) ions in waters with elevated temperature and pH, as seen in Equation (2-5). Both of these by-products are undesirable in drinking water. The by-products can originate from the dosing chemical (made with the generation process) or by the decomposition of the chlorine dioxide after oxidizing. Chlorine dioxide's oxidation state is +4, intermediate between that of chlorite (+3) and chlorate (+5); with

the transfer of an electron, both by-products form. Werdehoff and Singer (1987) estimated the formation of chlorite varies between 50 to 70 percent of the initial chlorine dioxide dosage. This limits the amount of chlorine dioxide dosage to remain below the chlorite MCL (1.0 mg/L) (USEPA, 2006).

$$ClO_2 + e^- \rightarrow ClO_2^- \tag{2-4}$$

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \tag{2-5}$$

The main advantages with chlorine dioxide include (1) reduced formation of halogenated by-products (TTHMs and HAA5), (2) limited reactions with ammonia, thus lower dosing requirements when compared to chlorine, and (3) reduction of iron, manganese, and taste and odor constituents. Disadvantages include increased monitoring for chlorite and chlorate, handling concerns with concentrated bulk solutions, and the volatility of the dosing solution.

The most common type of chlorine dioxide generation for drinking water treatment involves the reaction between sodium chlorite ($NaClO_2$), chlorine gas ($Cl_2$), and either hypochlorous acid (HOCl) or hydrochloric acid (HCl). The reactions that occur in the chlorine dioxide generator are summarized by Equations (2-6), (2-7), and (2-8) (Jonnalagadda and Nadupalli, 2014).

$$2NaClO_2 + Cl_2(g) \rightarrow 2ClO_2(g) + 2NaCl \tag{2-6}$$

$$2NaClO_2 + HOCl \rightarrow NaCl + NaOH + 2ClO_2(g) \tag{2-7}$$

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2(g) + 2H_2O + 5NaCl \tag{2-8}$$
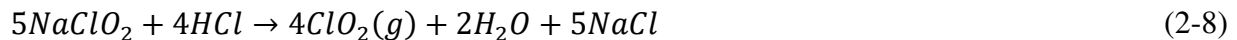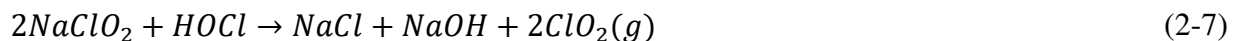
A second method for generating chlorine dioxide was used in the research. Two powders, provided by TwinOxide®, were combined with deionized water to form a 0.3 percent (3000 mg/L) solution of chlorine dioxide. The powders, components A and B, were primarily sodium chlorite and

sodium bisulfite, respectively. Information on reaction and kinetics was limited because of the proprietary nature of the TwinOxide® product. Complete formation of the 0.3 percent solution was complete after 3 hours of reaction time (TwinOxide, 2017).

*Potassium Permanganate*

Potassium permanganate ($KMnO_4$) is primarily used to oxidize iron and manganese and oxidize odor and taste compounds. Unlike chlorine and chlorine dioxide, $KMnO_4$ is a weak disinfectant which necessitates more time for the oxidation to occur (Crittenden et al., 2012). $KMnO_4$ can be added either as a solid or as a concentrated liquid solution. Caution should be taken when handling the solid form of $KMnO_4$ because of its flammable risks. According to Crittenden et al. (2012), $KMnO_4$ also sufficiently oxidizes sulfide and can control fishy/grassy odors produced by methyl sulfides. Over-dosing $KMnO_4$ in the 0.2 mg/L range can result in undesirable pink water; correct dosing is essential for optimal color. A contact time of at least 1 hour is recommended for oxidation with $KMnO_4$ depending on temperature and pH. Excessive use of $KMnO_4$ can cause elevated levels of manganese in the distribution system as well at the treatment plant leading to black or brown manganese dioxide deposits (Crittenden et al., 2012).

DBPs Control and Treatment

Studies have been performed for methods used to reduce the formation of DBPs, primarily TTHMs and HAA5. From these studies, the most effective methods included the (1) reduction of free-chlorine contact time, (2) use of an alternative disinfection chemical or dosage, (3) removal of DBP precursors, and (4) control of pH during disinfection. Concerning disinfection with chlorine, DBP formation can be minimized by adding chlorine at the end of the treatment, once precursor

material has been partially removed in the treatment process. Disinfectant residuals should be monitored both at the point of entry and throughout the distribution system after dosing (i.e., avoiding excessive dosing). Alternative disinfectants to chlorine include, but are not limited to, chlorine dioxide, ozone, and chloramines; these chemicals have historically shown reduced TTHM and HAA5 formations in respective system integration. Chlorine dioxide dissociates into chlorite and chlorate; chlorite is costly to remove after formation, thus the most effective method to reduce chlorite is to reduce the initial chlorine dioxide dosage.

The removal of DBP precursors can be achieved through different treatment processes including granulated activated carbon (GAC) or powdered activated carbon (PAC), membrane filtration, and anion exchange (AWWA, 2011). These treatment alternatives focus on the removal of NOM to minimize the number of precursors (organics) that could react with free chlorine to form DBPs. As aforementioned, pH highly dictates the formation speciation of DBPs. For example, the formation potential of TTHMs is higher in alkaline conditions because hydroxide ions serve as catalysts to speed up the reaction between NOM and free chlorine. In contrast, HAA5 form more rapidly in acidic conditions (AWWA, 2011). Optimizing the pH during disinfection can be used to promote the formation of specific DBPs and reduce the theoretical formation of others.

# CHAPTER 3 : BACKGROUND AND EXISTING CONDITIONS

Located approximately 60 miles south of Atlanta, Georgia, Butts County sprawls across 188 square miles of rural Georgia. The County's public water supply is provided through a partnership that includes Butts County and the Jackson, Jenkinsburg and Flovilla municipalities, referred to as the *Butts County, City of Flovilla, City of Jackson and City of Jenkinsburg Water & Sewer Authority* (Authority). The Authority provides roughly 800 million gallons of drinking water every year to its consuming public. The Authority utilizes two surface water treatment plants for supply to the system. The primary plant (about 90% of system supply), Emerson L. Burford conventional water treatment plant (WTP), is located along the Ocmulgee River in east central region of Butts County. Emerson L. Burford WTP currently has a maximum treatment capacity of 4.0 million gallons per day (MGD). A second, smaller source of supply is the Gerald L. Stewart WTP, located on the Towaliga River with a capacity of 1.0 MGD.

## Surficial Source Waters

Both source rivers are a part of the Upper Ocmulgee watershed, which encompasses portions of 20 Georgia counties, including a portion of metropolitan Atlanta. The watershed consists of the Alcovy, Yellow, and South Rivers, which drain the eastern and southeastern metropolitan Atlanta region and converge at Jackson Lake. Emerson L. Burford WTP raw water intake is located roughly 0.7 miles downstream of Jackson Lake dam on the Ocmulgee River in east Butts County. The Towaliga River, part of the Towaliga Watershed, forms from smaller streams in southern Henry County and eastern Spalding County. This watershed has been impounded in several areas upstream from Jackson's intake for Henry County's water supply. Water from the Towaliga River

is treated at the Gerald L. Stewart plant; owned by the City of Jackson and operated by the Authority. Customers in the far southwest corner of Butts County on Chappell Mill Road, Fenner Road, and in the Brushy Creek subdivision receive their water supply via purchase from the City of Griffin. The raw water source locations are shown in Figure 3-1.
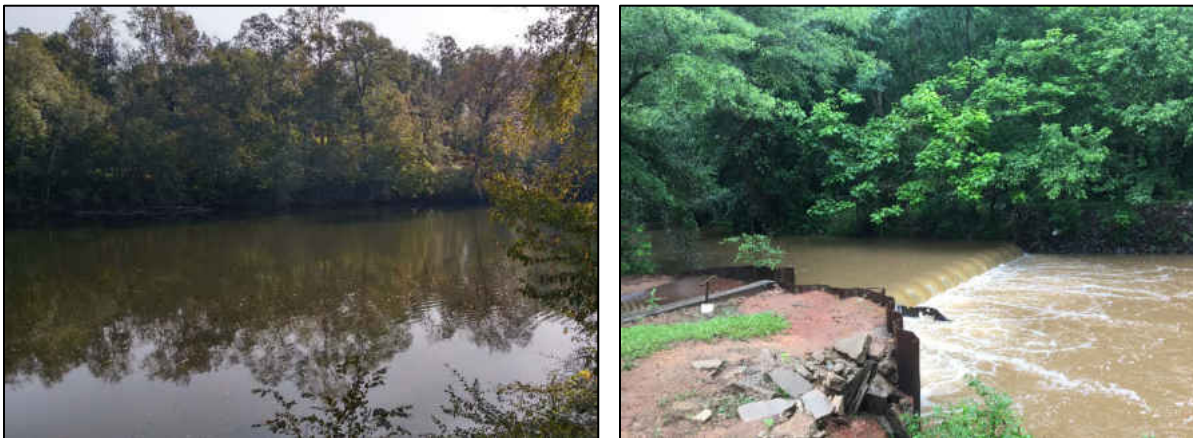


**Figure 3-1: Ocmulgee River (left) and Towaliga River (right)**

Treatment Process

Both of the Authority's WTPs utilize conventional surface water treatment with aluminum sulfate (alum) coagulation. Located near the intake structure, raw water for the Emerson L. Burford WTP is pretreated with an annual average dosage of about 0.23 milligrams per liter (mg/L) of potassium permanganate. Pretreatment is largely used to oxidize metals to allow precipitation and settling in a settling basin. Another benefit of oxidation pretreatment includes the elimination of taste and odor compounds. After potassium permanganate addition, the water flows roughly 1800 feet (ft) where alum, powder activated carbon (PAC), and sodium carbonate (soda ash) are dosed and mixed using a static mixer. The coagulant-dosed water enters a flocculation head tower where flocculant aids (polymers) are added to the water prior to entering into a ClariCone® (Chicago

Bridge and Iron, Chicago, Illinois) solids contact unit, pictured in Figure 3-2. Minute amounts of chlorine gas are diffused into the ClariCone® for algae control. After settling, the supernatant flows into a secondary conventional package plant. The water is dosed with approximately 1.0 mg/L alum and enters an up-flow media contact settling basin. Settled water then passes through a multimedia sand filter. Upon exit from the filter, it is post treated with chlorine gas, fluoride, and soda ash for pH adjustment. After post treatment, finished water is stored in a 1.0-million gallons ground storage tank to achieve adequate chlorine contact time prior to entering the distribution system (point of entry). An overview of Emerson L. Burford WTP's treatment and process flow is provided in Figure 3-3.



**Figure 3-2: ClariCone® Solids Contact Unit Located At Emerson L. Burford WTP**
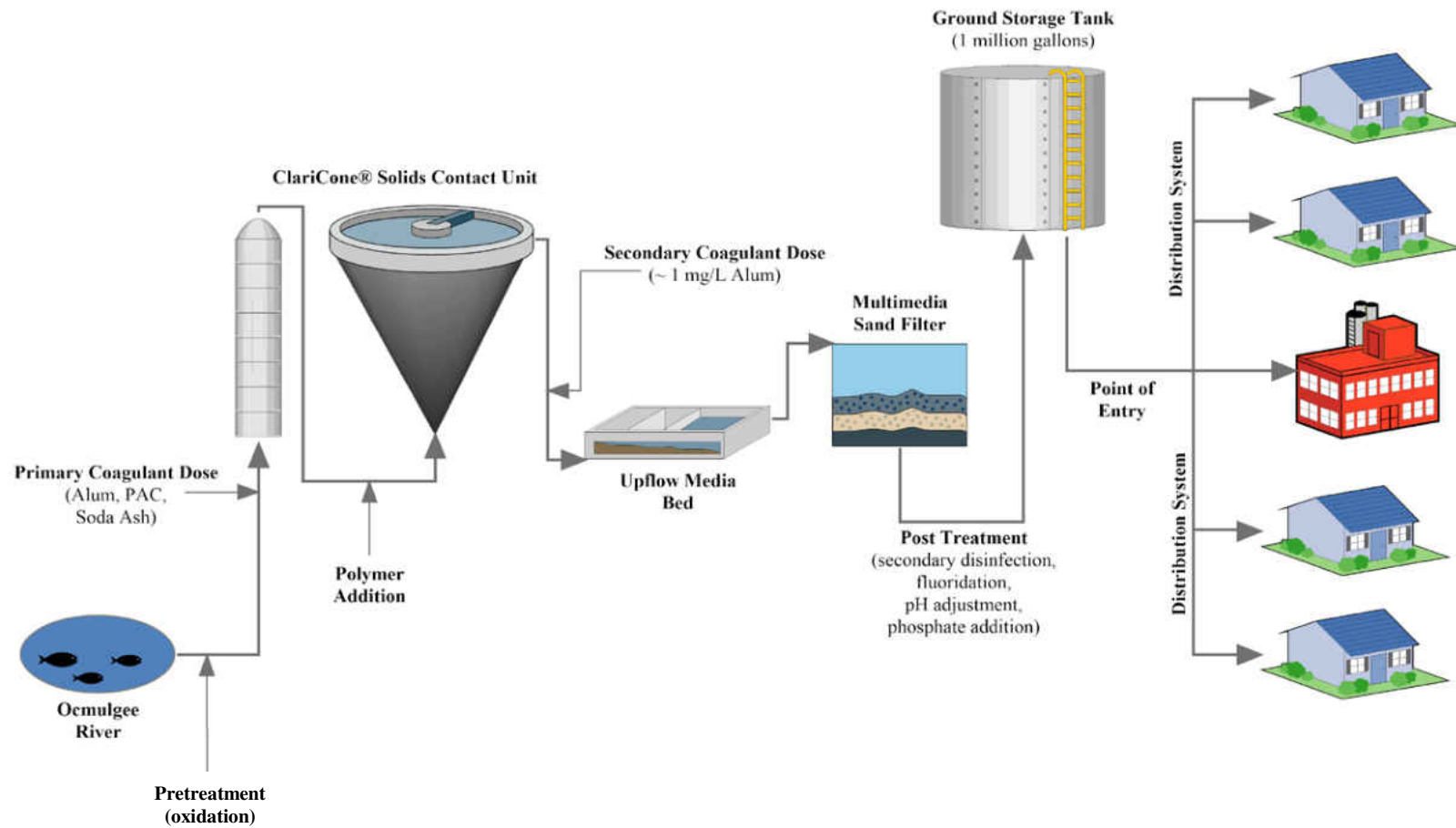
**Figure 3-3: Emerson L. Burford WTP's Process Flow Diagram**

# CHAPTER 4 : METHODS AND MATERIALS

This chapter includes a summary of the experimental plan as well as a detailed description of the methods and materials used during data collection. Initial efforts were conducted to further characterize the raw water supply quality to develop a more robust understanding of the chemistries that could impact the Authority's coagulation, flocculation, sedimentation, and filtration (CSF) process. Methods primarily included jar tests and chlorine disinfection to simulate disinfection by-product (DBP) formation in the distribution system. One of the components of the study was to determine the optimal coagulant dosage and operating pH for non-purgeable dissolved organic carbon (DOC) and turbidity reduction. Reduction of DOC (DBP precursor) leads to a reduction of DBP formation potential, thus optimizing DOC reduction is a key treatment strategy for reducing both total trihalomethanes (TTHMs) and haloacetic acids (HAA5). Another component of research scrutinized pretreatment by comparing potassium permanganate ($KMnO_4$) to chlorine dioxide ($ClO_2$). Water quality parameters used to compare oxidants included turbidity, iron and manganese reduction, as well as DOC and DBP formation potential reduction.

## Summary of Experimental Plan

Raw surficial water taken from the Ocmulgee River (Jackson, GA) was transported to the University of Central Florida's (UCF) laboratories for analysis and experimentation. Between January 2017 and January 2018 a total of nine bulk water sampling events were performed at the Authority's facilities to support the development of water quality data for background purposes in addition to plant profiles. A plant profile is defined as the collection of water quality after each unit operation or process within the treatment process.

Preliminary jar tests without pretreatment were conducted to determine optimal coagulant dosages based on DOC and turbidity removal. These preliminary jar tests produced isopleths, or contour plots that relate coagulant dosage (aluminum sulfate or alum), pH, and either DOC or turbidity removal. Isopleths provided a tool for operators to change dosing and pH requirements in an effort to optimize DOC removal. DOC is a primary DBP precursor material and its reduction is a key component in reducing DBP formation after disinfection with chlorine gas. After determining optimal alum dosage based on average raw water characteristics, jar tests were performed to compare pretreatment oxidation with potassium permanganate and chlorine dioxide.

Two types of chlorine dioxide solutions were tested and reported herein. The first chlorine dioxide solution was provided by TwinOxide[®] and the second was provided by Evoqua[®]. Chlorate and chlorite formation was measured in response to both chlorine dioxide solutions using ion chromatography. The formation of chlorite set a threshold for chlorine dioxide dosing to remain under the United States Environmental Protection Agency's (USEPA) maximum contaminant level (MCL) of 1.0 mg/L (USEPA, 2006). Water quality parameters collected during jar testing included metal concentrations, turbidity, true color, pH, temperature, and DOC. Parameters were measured prior to and after jar testing to track the impacts of operational variables. After sedimentation, jar tested water was filtered using a 0.45 µm pore membrane and dosed with sodium hypochlorite to simulate disinfection. Samples were stabilized to a pH of 7.5 and placed in an incubator at 30°C for 168 hours to allow chlorine residual decay and DBPs formation. This incubation period simulated DBP formation in the distribution system during summer conditions. DBP formation potential was compared between full-scale treated water (control) and simulated treatment with potassium permanganate and chlorine dioxide as preoxidants.

## Methods, Equipment, and Reagents

UCF relied on several chemical reagents and instrumentation to perform the experiments reported herein. The chemicals used were laboratory grade approved, and analytical procedures employed followed *Standard  Methods for the Examination of Water and Wastewater* (Baird et al., 2017). Table 4-1 provides a summary of the methods of analytical tests conducted during the research. Table 4-2 summarizes the chemical reagents used throughout the research.

**Table 4-1: List of Methods and Equipment for Water Quality Analysis**

| Test | Test Location | Method | Equipment Description | Minimum Reporting Level | Preservation Technique |
|------|---------------|--------|----------------------|------------------------|------------------------|
| pH | UCF Laboratory/field | SM: 4500-H+ B. Electrometric Method | Hach HQ40D pH and temperature probe | 0.1 pH units | Analyze immediately |
| Temperature | UCF Laboratory/field | SM: 2550 B. Laboratory and Field Methods | Hach HQ40D pH and temperature probe | 0.1 °C | Analyze immediately |
| Free Chlorine | UCF Laboratory | HACH Method 8021 | HACH Spectrophotometer DR5000 | 0.02 mg/L as $Cl_2$ | Analyze immediately |
| Chlorine Dioxide ($ClO_2$) | UCF Laboratory | Hach Method 10126 | HACH Spectrophotometer DR5000 | 0.04 mg/L as ClO2 | Analyze immediately |
| Chlorite | UCF Laboratory | EPA Method 300.1: Ion chromatograph | Dionex ICS-1100 with AS40 Automated Sampler | 0.2 mg/L | 50 mg/L EDA |
| Chlorate | UCF Laboratory | EPA Method 300.1: Ion chromatograph | Dionex ICS-1100 with AS40 Automated Sampler | 0.2 mg/L | 50 mg/L EDA |
| HAA5 | Advanced Environmental Laboratory (AEL) | SM:5710C | Agilent 6890N Network Gas Chromatograph | 3 µg/L | Ammonium chloride 4 °C in the dark |
| TTHM | UCF Laboratory | SM: 6232 B: Liquid-Liquid Extraction Gas Chromatographic | Perkin Elmer Clarus 580 Gas Chromatographer | 5.0 µg/L TTHM | Sodium sulfate, 4 °C in the dark |
| Alkalinity | UCF Laboratory | SM: 2320 B. Titration Method | Sulfuric Acid Burette Titration | 5.0 mg/L as $CaCO_3$ | Analyze immediately |
| Color (True) | UCF Laboratory | SM: 2120 C. Spectrophotometric- Single-Wavelength Method | HACH Spectrophotometer DR5000 | 1.0 PCU | Analyze immediately |
| Conductivity | UCF Laboratory/field | SM: 2510 B. Laboratory Method | Hach HQ40D conductivity probe | 0.01 µS/cm | Analyze immediately |
| Turbidity | UCF Laboratory/field | SM: 2130 B. Nephelometric Method | HACH 2100N Laboratory Turbidity Meter | 0.01 NTU | Analyze immediately |
| Iron | UCF Laboratory | SM: 3120 B. Inductively Coupled Plasma (ICP) Method | Perkin Elmer Optima 2100 DV | 0.01 mg/L | 2% Nitric Acid |
| Manganese | UCF Laboratory | SM: 3120 B. Inductively Coupled Plasma (ICP) Method | Perkin Elmer Optima 2100 DV | 0.001 mg/L | 2% Nitric Acid |
| DOC | UCF Laboratory | SM: 5310 C. Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method | Teledyne Tekmar Total Organic Carbon Fusion UV/Persulfate Analyzer | 0.1 mg/L | 2% Phosphoric Acid |

SM = Standard Methods    EDA = ethylenediamine    TTHM = total trihalomethanes    HAA5 = haloacetic acids

**Table 4-2: Summary of Chemical Reagents**

| Chemical | Description |
|---|---|
| Aluminum sulfate (alum) | Coagulant, SG = 1.34, stock ≈ 646,000 mg/L alum |
| Potassium permanganate | ACS grade – powder |
| TwinOxide® chlorine dioxide solution | Component A and B powders – form 0.3% chlorine dioxide solution when combined |
| Evoqua® chlorine dioxide solution | Approximately 500 mg/L chlorine dioxide |
| Powder Activated Carbon (PAC) | Aqua NUCHAR®, activated carbon used in full-scale and jar testing |
| Praestol™ Polymer 2500 and 2540 | Flocculation aids used in full-scale and jar testing |
| Sodium carbonate (soda ash) | ACS grade (98%) – used for pH adjustment |
| Sulfuric acid | 0.02 N – used for pH adjustment and alkalinity analysis |
| EDA, ethylenediamine | Chlorite and chlorate preservation |
| Hexane | ACS grade – used for TTHM analysis |
| TTHM calibration mixture | 100,000 mg/L stock (4-8047 Supelco) |
| Sodium sulfite | ACS grade – solid, used for TTHM preservation |
| Ammonium chloride | ACS grade – solid, used for HAA5 preservation |
| pH buffer solutions | 4,7, and 10 pH buffers |
| Sodium hypochlorite | ACS grade – used for disinfection |
| Organic carbon stock | Ricca Chemical, 1000 mg/L |
| Turbidity solution | Solution made from clay/sandy soil taken from Ocmulgee River, stock estimated at 60,000 NTU |
| Manganese ICP standard | 1000 ppm – used for ICP standards and spikes |
| Iron ICP standard | 1000 ppm – used for ICP standards and spikes |

ACS = American Chemical Society          SG = specific gravity

## Chemical Reagent Preparation

Three chemical oxidants were used throughout the jar testing procedure to evaluate their potential for pretreatment: potassium permanganate and two varieties of chlorine dioxide solutions. Other chemicals including sodium carbonate (soda ash), powder activated carbon (PAC), and two flocculation aids (polymers) were added to jars to simulate full-scale treatment. To test multiple raw water conditions, jar tests were performed using bulk raw water (representing average conditions) collected form Ocmulgee River and simulated "peak" raw water. The "peak" condition was defined as the highest historical recordings for turbidity, iron, and manganese as provided by the Authority staff and were 125 nephelometric turbidity unit (NTU), 1.15 milligrams per liter (mg/L), and 1.25 mg/L, respectively. Average conditions were defined as water with turbidity, iron, and manganese concentrations of approximately 10 NTU, 0.2 mg/L, and 0.02 mg/L, respectively.

### *Potassium Permanganate*

To prepare the potassium permanganate stock solution, 0.2 grams of potassium permanganate crystals were placed in a 200 milliliter (mL) volumetric flask and filled with deionized water. The flask was sealed with Parafilm® and mixed to dissolve the potassium permanganate crystals. The final solution was dark purple in color and approximately 1000 mg/L. To achieve a dosage of 0.23 mg/L in a 2-L jar, 460 microliters (µL) of the potassium permanganate solution were dosed into jars. The mixture was prepared on a monthly basis and stored in a dark cool location to match operation guidelines provided by Authority.

*Chlorine Dioxide*

The research included the use of two chlorine dioxide solutions. The first solution was formed based on the reaction of two powders provided by TwinOxide® (International B.V., The Netherlands), component A and B. To make a 1-L sample of chlorine dioxide solution, 20 grams of each component was added into deionized water. As per mixing instructions provided by TwinOxide®, component B was added to the water first and immediately followed by component A into an amber glass bottle. The powders, components A and B, were primarily sodium chlorite and sodium bisulfite, respectively. The sample was mixed by gently inverting the amber glass bottle three times. Sample was left in a dark cool location for at least three hours prior to use to allow full reaction and generation of chlorine dioxide.

Information on reactions and kinetics were limited because of the proprietary nature of the TwinOxide® product. After the required reaction time, solutions ranged from 3000 to 4000 mg/L of $ClO_2$, or 0.3 to 0.4 percent, respectively. The stock solution was sensitive to ultraviolet light and naturally decayed over time. TwinOxide® advertised the solution would hold for up to 30 days (TwinOxide, 2017). However, samples generated in UCF's laboratory generally decayed to half its original strength within that time. A decay curve of TwinOxide® chlorine dioxide solution is provided in Figure 4-1.
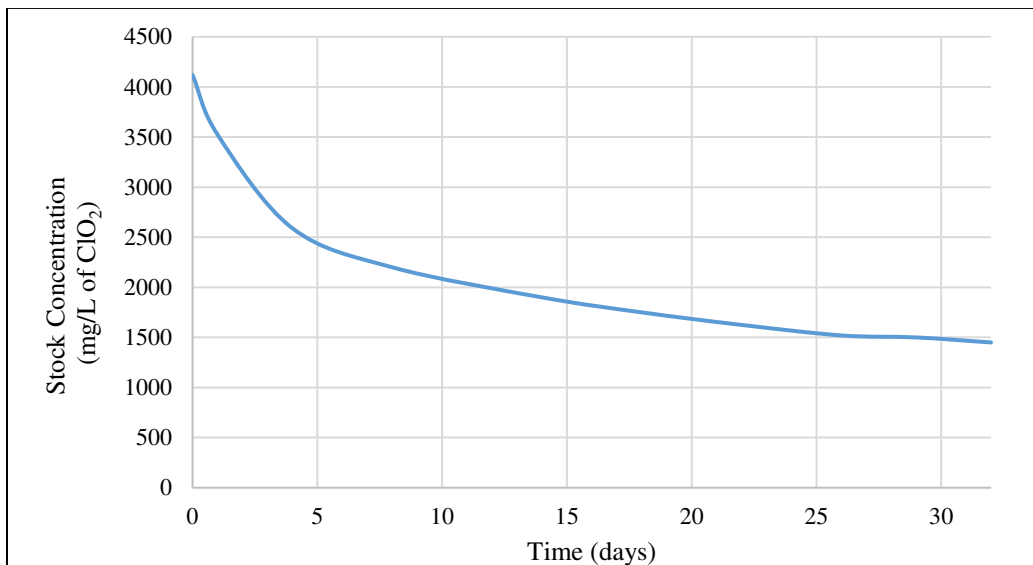
**Figure 4-1: TwinOxide® Stock ClO₂ Concentration Decay**

The second chlorine dioxide solution was generated by equipment provided by Evoqua® Water Technologies (Boston, MA) located at Harry Simmons Water treatment Plant (WTP) in Griffin, GA (approximately 20 minutes west of study area). Figure 4-2 displays the $ClO_2$ generator used at Harry Simmons WTP in Griffin, GA. This type of chlorine dioxide generation is more common in drinking water treatment and involves the reaction between sodium chlorite ($NaClO_2$) and chlorine gas ($Cl_2$) as chemical inputs. The initial solution was stored in amber glassware and was approximately 500 mg/L of $ClO_2$, but quickly decayed to half its original strength within 168 hours. The Evoqua® chlorine dioxide solution was stored at 4°C and storage container was wrapped in aluminum foil to reduce exposure to light.

**Figure 4-2: Evoqua® ClO₂ Generator (Harry Simmons WTP, Griffin, GA)**

*Sodium Carbonate, PAC, and Flocculation Aids*

Sodium carbonate (soda ash) was provided to UCF in powder form. To prepare a 36,000 mg/L solution of soda ash, 3.6 grams was placed in a 100-mL volumetric flask and filled with deionized water. The sample was agitated by inverting the volumetric flask until solid particles had dissolved. Powder activated carbon (PAC) was mixed into deionized water to form an aqueous slurry to allow easier dosing for jar testing. PAC does not dissolve in water and will remain in suspension. To make a solution of 4,000 mg/L, 0.8 grams of PAC was added to 200 mL of deionized water. The solution was shaken prior to dosing to promote homogeneous particle distribution.

Both flocculation aids, Praestol$^{TM}$ Polymer 2500 and 2540, were delivered as a powder. A 120 mg/L solution of each polymer was made by adding 60 milligrams (mg) into a flask with 500 mL of deionized water. Each polymer solution was mixed using a magnetic stirring bar for at least one hour to promote dissolution of the solid into the aqueous solution.

*Turbidity Solution*

To simulate a disruption in the Ocmulgee River or turnover in Jackson Lake, a turbidity solution was produced and dosed into the raw water for jar testing. Based on historical observations by the Authority staff, peak levels of turbidity have been recorded up to 125 NTU. Average turbidity in the raw water sourced from the Ocmulgee River ranged from 5 to 40 NTU with an average of approximately 10 NTU depending on seasonal conditions. Soil samples were taken from the banks of the Ocmulgee River. The soils were collected by the Authority staff and comprised mostly of natural organics (e.g., leaves and sticks), clay, and sand. As received, the moist soil samples are displayed in Figure 4-3. Soil samples were dried at 180°C for 12 hours and granulated using a

mortar and pestle. The samples were individually passed through a No. 45 sieve to remove large particles with diameters greater than 355 µm. Approximately 20 grams of dried sieved clay sample and 20 grams of dried sieved sand sample were combined and mixed into 200 mL of raw Ocmulgee River water. The resulting solution had a turbidity estimated at 60,000 NTU.

To simulate the worst historical case as of January 2018, 5 mL of the turbidity stock solution were added to each two liter (L) jar prior to addition of dosing chemicals as shown in Figure 4-4. This resulted in a raw turbidity of approximately 120 to 130 NTU. Figure 4-5 displays a visual comparison between typical raw water used and simulated "peak" raw water. During the dosing of the turbidity stock, the stock was continuously mixed with a magnetic stirring bar to keep homogeneous particle distribution to promote turbidity dosing consistency.



**Figure 4-3: Ocmulgee River Bank Clay (left) and Sand (right) Samples**

**Figure 4-4: Turbidity Stock Dosing**



**Figure 4-5: Typical Ocmulgee Water (left) and Simulated Peak Turbidity Water (right)**

## Bulk Water Sampling

During monthly site visits by UCF conducted January 2017 through January 2018, 15-gallon drums were filled with raw Ocmulgee River water from the sampling tap located on the pumping structure at Emerson L. Burford Water Treatment Plant (Burford WTP) near Jackson, GA. An example of a 15-gallon drum used for collection is displayed in Figure 4-6. Turbidity, conductivity, temperature, and pH of the raw water was recorded at the time of the bulk collection within the field; alkalinity, UV254, true color, DOC, and metals analysis were performed after samples were brought to UCF for laboratory analysis. The quality of the data produced was dependent upon the integrity of the raw samples provided to the laboratory. Consequently, precautionary measures were taken to avoid sample contamination and deterioration during bulk sample collection. The specific measures employed during this study component included the use of method specific sample containers, and analytical grade reagents and preservatives. Sample were kept in a clean environment (including work areas and transportation vehicles). When not in use, raw water and plant samples were kept in cool dark places (4°C refrigerator). Prior to bulk collection, each sampling container was primed at least twice with source water.

**Figure 4-6: Storage Drum (15-gallons) for Ocmulgee River Bulk Water Collection**

Preliminary Trials

Preliminary titrations were conducted on raw water with varying alum dosages to determine the amount of soda ash and sulfuric acid dosage required for pH adjustment. Jar test trials varied pH between 4.5 and 8.0 along with alum dosages between 10 and 100 mg/L. Titrations were completed with 100 mL of samples and scaled up to the 2-L jar volume. The response on pH with respect to alum dosage is displayed in Figure 4-7. Alum dosage was kept constant for each trial with pH being the test variable. 2-L jars were primed and then filled with raw Ocmulgee River water. During the setup procedure, bulk raw water was continuously mixed using a magnetic stirring bar to keep particles suspended and promote homogeneity throughout the jars. The mixing setup is displayed in Figure 4-8. Jar testing trials were completed with varying paddle speed and times. Finished jar tested water quality was compared to full-scale finished water quality and experimental parameters were adjusted until jar scale and full-scale water quality were congruent.

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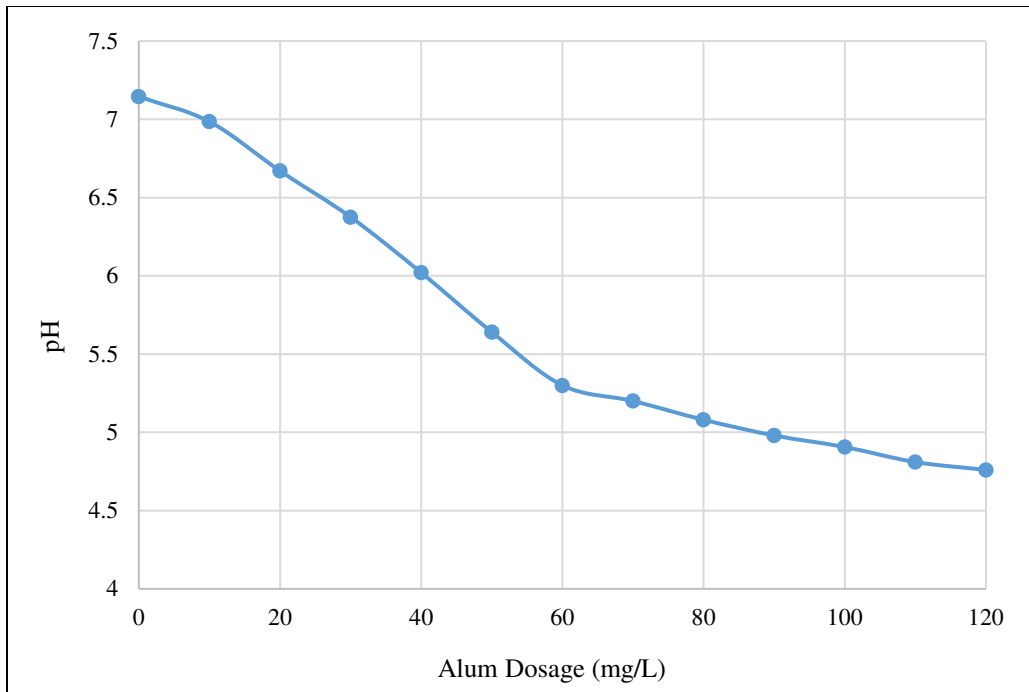
**Figure 4-7: Alum Dosage and pH Response Curve**



**Figure 4-8: Raw Water Mixing Setup**

Jar Testing Procedure

Phipps & Bird jar testing equipment was used to model the CSF process. Water quality parameters collected from prior plant audits were used to adjust jar test parameters to match Burford WTP conditions. Operating parameters (e.g., coagulant dosage, mixing energy, filtration rate, or operating pH) were modified to determine their impact on finished water quality produced from the full-scale treatment. The first step to prepare a jar test was to remove collected and stored raw water from UCF's 4°C refrigerator to allow the bulk sample to reach room temperature prior to testing. This was typically performed overnight to allow adequate time for the sample to approach approximately 20°C. A total of ten jars were utilized per test. Each 2-L square acrylic B-KER2® testing jar included a stainless-steel one inch by three inches paddle and sampling port. Paddles where lowered into the jar to their maximum depth of nine inches. Paddles could be rotated at different speeds to model several mixing regimes.

The jar tester was programed to model pretreatment, rapid mix and coagulation, flocculation, and sedimentation sequences during the CSF process. At the full-scale plant, raw Ocmulgee River (Burford WTP source) water is currently dosed with potassium permanganate near the intake structure then flows to the ClariCone® solids contact unit (SCU). During average flow conditions, the hydraulic time for the water to flow from the intake structure to the SCU is approximately 15 - 20 minutes. Thus, pretreatment was simulated in the jar tests for 15 minutes with paddles set to 200 rotations per minute (rpm) to simulate pipe flow mixing conditions. During simulated pretreatment with chlorine dioxide, jars were partially sealed with Parafilm® to reduce the volatilization of chlorine during mixing regimes. A photo of sealed jars is provided in Figure 4-9. The rapid mix sequence was programed to simulate the static mixer installed under the SCU

structure (30 seconds of mixing at 300 rpm). Flocculation was divided into two sequences. The first (10 minutes at 25 rpm) was used to simulate the flow through the head tank located adjacent to the SCU. The second flocculation sequence (5 minutes at 10 rpm) modeled the lower portion of the SCU where mixing and centrifugal force aid floc formation. The final sequence modeled sedimentation for one hour and 30 minutes. During sedimentation, the paddles were removed from the jars to avoid settling disruption and interception. The pH of each jar was recorded during the flocculation phases. Figure 4-10 displays the first six jars after the flocculation phase with raised paddles.



**Figure 4-9: Chlorine Dioxide Trial in Parafilm® Sealed Jars**



**Figure 4-10: Phipps and Bird Jar Testing Equipment**

After settling for one hour and 30 minutes, the jar outlet tubing was flushed and the first 100 mL were wasted. Using the flushed outlet tubing, 400 mL of settled water was placed in flasks and read for turbidity. An example of the data collection sheet used for the study is given in Appendix A. Approximately 400 mL of settled sample from each jar was filtered through a mixed cellulose 0.45 µm pore size membrane using a glass vacuum filtering apparatus. Filtered water was prepared and analyzed for non-purgeable dissolved organic carbon (DOC). Jar testing was an iterative process with variable alum dosage ranging between 10 and 100 mg/L. The raw data collected from the jar tests are presented in Appendix B.

## DBPs Formation Potentials

Jar tests were performed to simulate current conditions at Burford WTP with raw water pretreatment with potassium permanganate ($KMnO_4$) and test conditions (chlorine dioxide solutions). Both TwinOxide® and Evoqua® chlorine dioxide solutions were tested to measure variability between generation methods. After filtering settled jar test water with a 0.45 μm filter, water was dosed with sodium hypochlorite at 4 mg/L of free chlorine ($Cl_2$) to retain a residual of about 2 mg/L as $Cl_2$ after 15 minutes. Samples were adjusted to a pH of approximately 7.5 using sodium carbonate (soda ash) to match full-scale chemical addition. Water dosed with chlorine was stored in an incubator at 30°C to simulate summer conditions for up to 168 hours. As a control, finished water from Burford WTP without post treatment (i.e., disinfection and pH adjustment with soda ash) was also pH adjusted and dosed with sodium hypochlorite at 4 mg/L of $Cl_2$ to quantify a control condition formation potential. The formation potential of TTHMs were measured at the following time intervals: 10 minutes, 48 hours, 72 hours, and 168 hours detention times. HAA5 168-hr formation was also analyzed independently. TTHMs and chlorine residual

samples were contained within 60 mL amber glass bottles. HAA5 samples were held in 250 mL amber glass bottles. Bottles were sealed to minimize aeration and air contact. Aerating and allowing bubbles within sampling bottles would allow partial loss of TTHMs due to their volatility.

Samples were removed from the 30°C incubator, chlorine residual read, and TTHM bottles were quenched at specific time intervals. HAA5 samples were quenched at the 168-hr time interval. TTHM samples were quenched with sodium sulfite ($Na_2SO_3$) and HAA5 samples were quenched with ammonium chloride ($NH_4Cl$). After quenching, both TTHMs and HAA5 samples were stored at 4°C until chemical analysis could be conducted in accordance to *Standard Methods for the Examination of Water and Wastewater* (SM) 5710 B, Total Trihalomethanes Formation Potential and 5710 D, Formation of Other Disinfection By-Products (Baird et al., 2017). TTHMs were analyzed using SM 6232 B, Liquid-Liquid Extraction Gas Chromatographic Method (Baird et al., 2017). For the safety of UCF student researchers, HAA5 analysis was performed by Advanced Environmental Laboratories (AEL), a certified lab located in Orlando, Florida.

Multiple trials of TTHM formation potential using different raw water characteristics were conducted. The surficial raw water characteristics fluctuated with respect to time and seasonal conditions. The fluctuation in raw water quality made identical replication of TTHM formation potential difficult. Average values for formation are presented in the Results and Discussion. Multiple in situ trials for TTHM formation at various temperatures simulating winter and summer conditions were also examined.

# CHAPTER 5 : RESULTS AND DISCUSSIONS

This chapter reports on the results of bench-scale testing of coagulation, flocculation, sedimentation, and filtration (CSF) using aluminum sulfate (alum) coagulant with and without a pretreatment oxidant. Pretreatment with potassium permanagante or chlorine dioxide was explored and disinfection by-product (DBPs) formation response compared. Oxidation of iron and managanese, removal of turbidity, and reduction of color were also examined for test conditions.

## Description of Raw Water

UCF conducted a total of nine plant profiles between January 26, 2017 and January 6, 2018. A plant profile was defined as the collection of water quality after each unit operation or process within the treatment train. A summary of raw water quality for Burford WTP is provided in Table 5-1. Finished water quality produced by Burford WTP is summarized in Table 5-2.

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**Table 5-1: Burford WTP Raw Water Quality**

| Date | 1/26/17 | 3/14/17 | 4/12/17 | 5/11/17 | 6/6/17 | 7/24/17 | 9/17/17 | 10/21/17 | 1/5/18 | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|
| **Turbidity (NTU)** | 32 | 3 | 23 | 6 | 5 | 9 | 13 | 3 | 8 | 11 |
| **pH** | 6.7 | 7.2 | 6.8 | 7.0 | 6.6 | 6.6 | 6.8 | 7.0 | 7.2 | 6.9 |
| **Temperature (°C)** | 14 | 14 | 17 | 23 | 25 | 28 | 26 | 22 | 9 | 20 |
| **Conductivity (μS/cm)** | 97 | 125 | 81 | 118 | 107 | 97 | 88 | 126 | 117 | 106 |
| **DO (mg/L)** | 9 | 9 | 8 | 6 | 7 | 8 | 9 | 6 | 10 | 8 |
| **UV 254 (cm$^{-1}$)** | 0.15 | 0.07 | 0.18 | 0.09 | 0.09 | 0.11 | 0.12 | 0.09 | 0.08 | 0.11 |
| **True Color (Pt-Co)** | 39 | 12 | 63 | 15 | 17 | 20 | 26 | 5 | 18 | 24 |
| **Alkalinity (mg/L CaCO$_3$)** | 24 | 27 | 20 | 29 | 28 | 25 | 22 | 34 | 29 | 26 |
| **DOC (mg/L)** | 3.8 | 2.4 | 4.0 | 2.9 | 2.7 | 2.7 | 3.3 | 2.8 | 2.8 | 3 |
| **Fe (mg/L)** | 0.20 | 0.08 | 0.32 | 0.16 | 0.12 | 0.15 | 0.21 | 0.10 | < 0.01 | 0.15 |
| **Mn (mg/L)** | < 0.005 | < 0.005 | 0.01 | < 0.002 | <0 .002 | < 0.001 | 0.001 | < 0.001 | 0.03 | 0.006 |

**Table 5-2: Burford WTP POE Water Quality**

| Date | 1/26/17 | 3/14/17 | 4/12/17 | 5/11/17 | 6/6/17 | 7/24/17 | 9/17/17 | 10/21/17 | 1/5/18 | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|
| **Turbidity (NTU)** | 0.08 | 0.08 | 0.09 | 0.18 | 0.08 | 0.13 | 0.12 | 0.12 | 0.13 | 0.11 |
| **pH** | 7.5 | 8.0 | 8.2 | 7.7 | 8.1 | 7.4 | 7.3 | 7.4 | 7.6 | 7.7 |
| **Temperature (°C)** | 15 | 15 | 18 | 22 | 24 | 28 | 24 | 22 | 10 | 20 |
| **Conductivity (µS/cm)** | 176 | 195 | 171 | 200 | 201 | 185 | 159 | 209 | 187 | 187 |
| **DO (mg/L)** | 9 | 10 | 9 | 8 | 8 | 8 | 8 | 8 | 11 | 9 |
| **Free Chlorine (mg/L)** | 1.6 | 1.8 | 1.6 | 1.6 | 1.7 | 1.6 | 1.7 | 1.7 | 1.6 | 1.7 |
| **UV 254 (cm$^{-1}$)** | 0.02 | 0.02 | 0.03 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| **True Color (Pt-Co)** | 4 | 3 | < 1 | < 1 | 2 | 2 | < 1 | < 1 | < 1 | 3 |
| **Alkalinity (mg/L CaCO$_3$)** | 42 | 46 | 51 | 57 | 60 | 54 | 40 | 56 | 46 | 50 |
| **DOC (mg/L)** | 1.6 | 1.2 | 1.8 | 1.5 | 1.2 | 1.3 | 1.3 | 1.5 | 1.5 | 1.4 |
| **Fe (mg/L)** | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| **Mn (mg/L)** | 0.01 | 0.008 | 0.02 | 0.01 | 0.007 | 0.004 | 0.004 | 0.003 | 0.022 | 0.010 |

## Alum Isopleths

One objective of the study was to quantify how the existing coagulation process was performing relative to turbidity and non-purgeable dissolved organic carbon (DOC) removal, and evaluate other dosage and conditions where additional treatment could be obtained. One method of displaying data collected from jar tests is to summarize visually in a contour plot called isopleths. Within an isopleth, the y-axis represents the dosage of the coagulant (10 to 100 mg/L alum), the x-axis represents the operating pH (4.5 to 8 pH), and the z-axis corresponds to the removal percentage of a test constituent. Isopleths comparing turbidity and DOC removal were used to model the CSF and are reported herein. The isopleths have an optimum operation zone and the current operating points are labeled on the corresponding isopleth. The isopleth illustrated in Figure 5-1 presents turbidity removal while the isopleth in Figure 5-2 illustrates DOC removal.
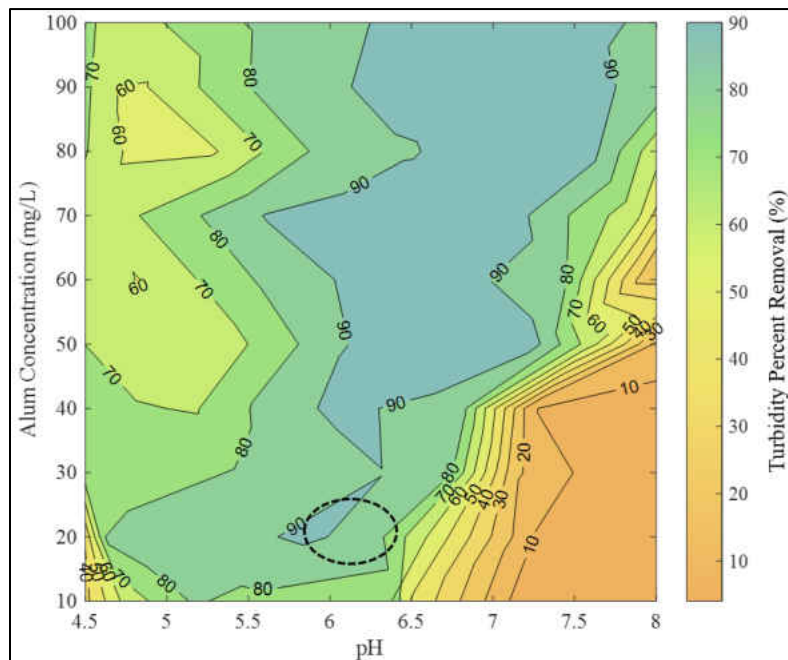


**Figure 5-1: Turbidity Removal Isopleth with Current Operating Zone**
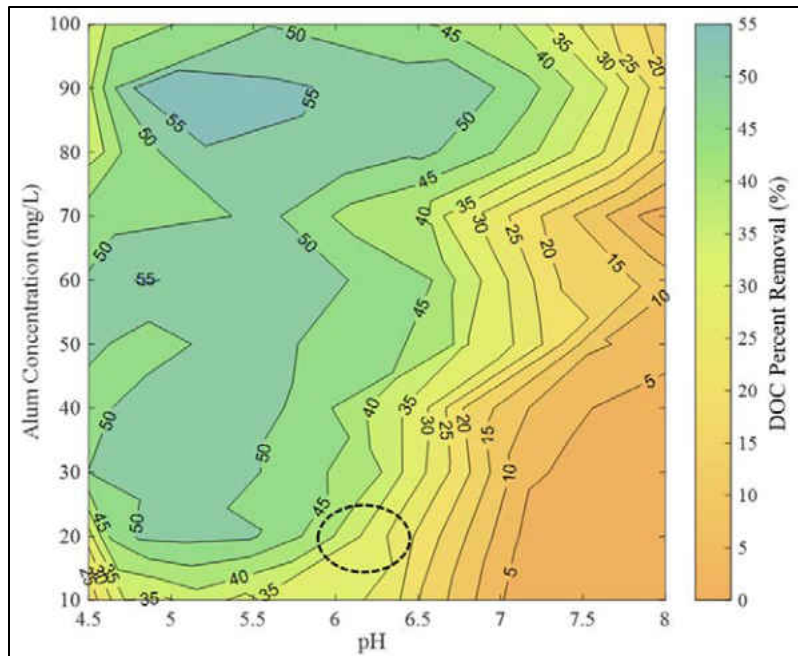
**Figure 5-2: DOC Removal Isopleth with Current Operating Zone**

To isolate the coagulation efficiency, Figure 5-1 does not take into account turbidity removal due to filtration. The Authority operates with an average alum dosage of 20 mg/L at a target operating pH approximately between 6.0 to 6.2 units, depending on raw water characteristics. This condition, represented with a dotted circle on each isopleth presented herein, results in approximately 90 percent turbidity removal and about 35 percent removal of DOC, where DOC represents dissolved natural organic matter (NOM) found in the raw water supply. When NOM reacts with a disinfectant (i.e., chlorine), disinfection by-products (DBPs) can form, such as total trihalomethanes (TTHMs) and haloacetic acids (HAA5). As regulated by the United States Environmental Protection Agency (USEPA), TTHMs and HAA5 are suspected carcinogens with a maximum contaminant level (MCL) of 80 and 60 µg/L, respectively (USEPA, 1998). By optimizing the reduction of DOC in the treatment process, formation of DBPs should also be reduced. Thus, the optimization of DOC removal is a crucial step for reducing DBPs in the system.

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Currently, the Authority meets or exceeds regulatory target removals for total organic carbon (TOC). However, DOC isopleth evaluation results suggest that it is possible to remove additional NOM using a higher dosage of alum at a lower pH without significantly compromising turbidity reduction at the Burford WTP after filtration. Isopleth results indicated that the current system is optimized for turbidity removal. The plant must balance turbidity reduction with removal of DOC in an effort to reduce DBP formation out in the distribution system. The Authority currently utilizes spray aeration within their distribution system for the reduction of TTHMs. While the aeration system is able to reduce TTHMs by about 50 percent, this only benefits consumers downstream of the aeration system. DBP precursor reduction is the preferred method for controlling the formation of DBPs because reduction of the precursor material within the treatment plant will allow the consuming public to benefit throughout the entire distribution system and not solely after an aeration unit.

## Disinfection By-products Analysis

After simulating pretreatment with chlorine dioxide and potassium permanganate, formation potential for TTHMs and HAA5 were collected. Two solutions of chlorine dioxide were tested, chemically formed TwinOxide® and a sodium chlorite and chlorine gas generated Evoqua® solution. A control condition was used to measure the difference between the full-scale treatment and jar tested (simulated) water with potassium permanganate. The control water was finished water from the full-scale WTP without disinfection or pH stabilization; disinfection was provided to the test conditions by dosing with sodium hypochlorite at 4 mg/L as $Cl_2$.

Figure 5-3 graphs the TTHM formation potential (TTHMFP) over time for the control condition and simulated pretreatment with potassium permanganate, TwinOxide® chlorine dioxide solution, and Evoqua® chlorine dioxide solution. When examining TTHMFPs between the 1.0 and 1.5 mg/L $ClO_2$, there was not sufficient evidence to support a significant difference in the TTHM formation reduction. Thus, the formation with respect to a dose of 1.5 mg/L has been omitted. Water dosed with TwinOxide® chlorine dioxide as the pretreatment oxidant (1.0 mg/L $ClO_2$) resulted in 23 percent reduction when compared with the simulated pretreatment with potassium permanganate over the 168-hr formation test period. Water pretreated with Evoqua® chlorine dioxide (1.0 mg/L $ClO_2$) resulted in 37 percent reduction when compared with water simulating pretreatment with potassium permanganate. From the trials conducted, Evoqua® chlorine dioxide was able to depress the formation of TTHMs more effectively than TwinOxide® chlorine dioxide. The control condition violated the TTHM MCL at approximately 70 hours. TwinOxide® chlorine dioxide was estimated to violate the MCL around 168 hours of formation. Evoqua® chlorine dioxide did not reach the MCL within the testing period and would take greater than a week to form over 80 µg/L TTHMs.

The difference in TTHMFP between the two chlorine dioxide solutions may be caused by variability in raw water; surficial water taken from the Ocmulgee River has shown variability to DOC and other parameters with respect to seasonal conditions. Overall, pretreatment with chlorine dioxide depressed TTHMFP an average of 20 to 40 percent depending on raw water characteristics, chlorine dioxide generation methods, and chlorine dioxide dosage. These measurements were collected within a laboratory with controlled temperature and adjusted pH. Testing with surficial water sources come with inevitable variability that originate from field conditions. Differences in

bench-scale simulation with jar tests and the control water taken prior to disinfection at the full-scale plant were observed. These differences in similitude could be caused by factors that are modeled during jar testing procedure, but could not be fully scaled down into bench or laboratory-scale conditions (e.g., enhanced coagulation with additional alum dosage post settling, upflow sludge blanked filtration, or multi-phase flocculation). Full-scale installation of chlorine dioxide pretreatment may yield slightly different results compared to the bench-scale trials reported herein.

To illustrate the TTHM reduction by speciation, Figure 5-4 shows the concentrations of each TTHM species (i.e., chloroform, bromodichloromethane, dibromochloromethane, and bromoform). Historically, chlorine dioxide is most effective at reducing chlorinated byproducts. From the results, $ClO_2$ does not provide much reduction of brominated species. However, the lack of bromide in the raw water could introduce bias. HAA5 analysis was performed on samples after 168 hours of reaction time within the 30°C incubator. Pretreatment with potassium permanganate produced 54 µg/L HAA5 after incubation for 168 hours. Water dosed with 1.0 mg/L of TwinOxide® $ClO_2$ generated 48 µg/L and water dosed with 1.0 mg/L Evoqua® $ClO_2$ generated 45 µg/L HAA5 over a week. These results are graphed in Figure 5-5.
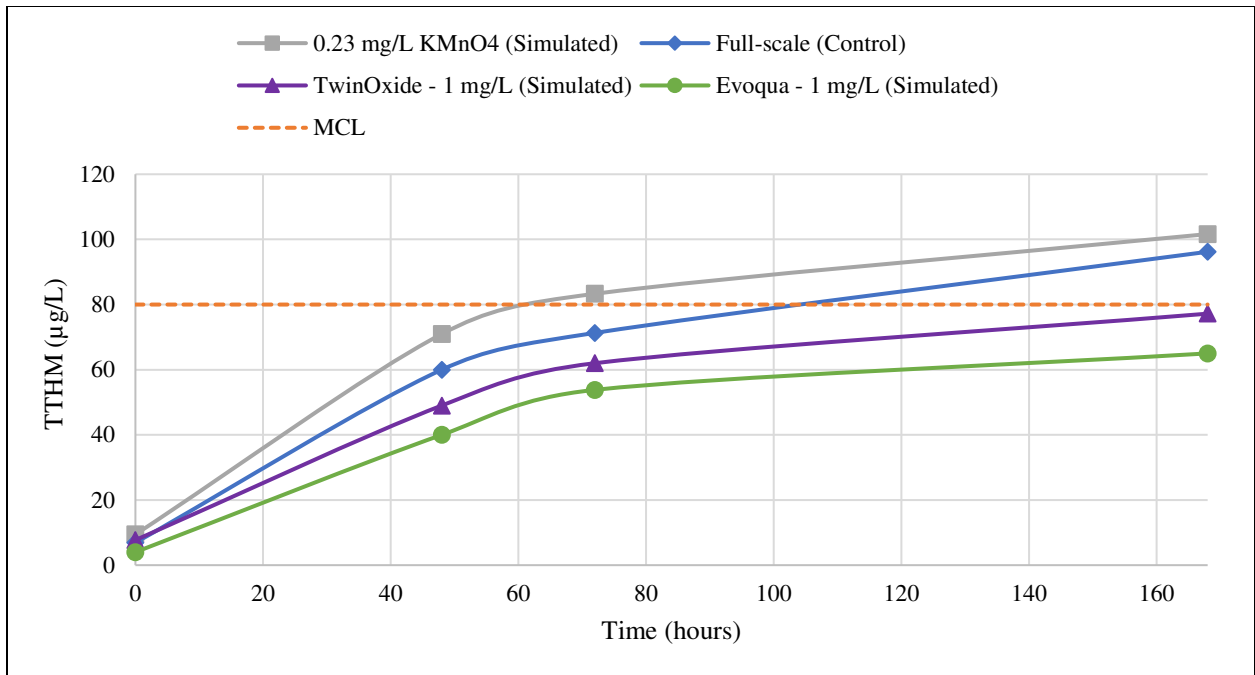
**Figure 5-3: TTHMFP Trials Comparison**
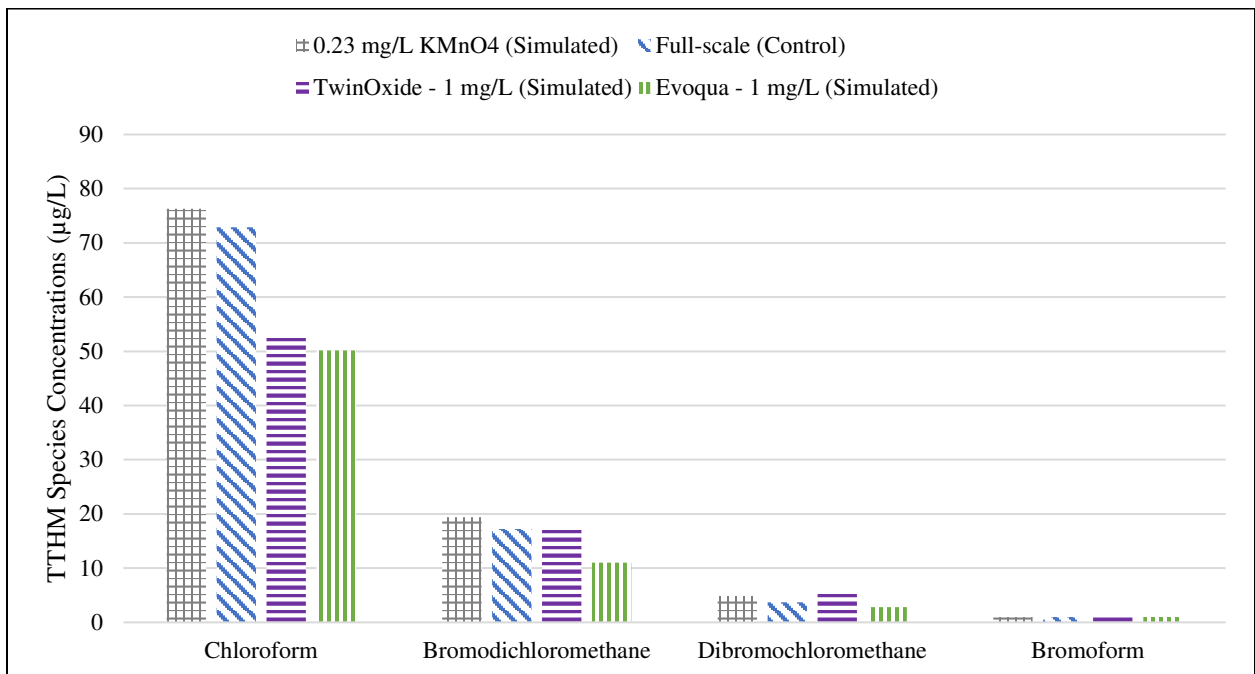


**Figure 5-4: TTHM Species (168-hr) Formation Comparison**

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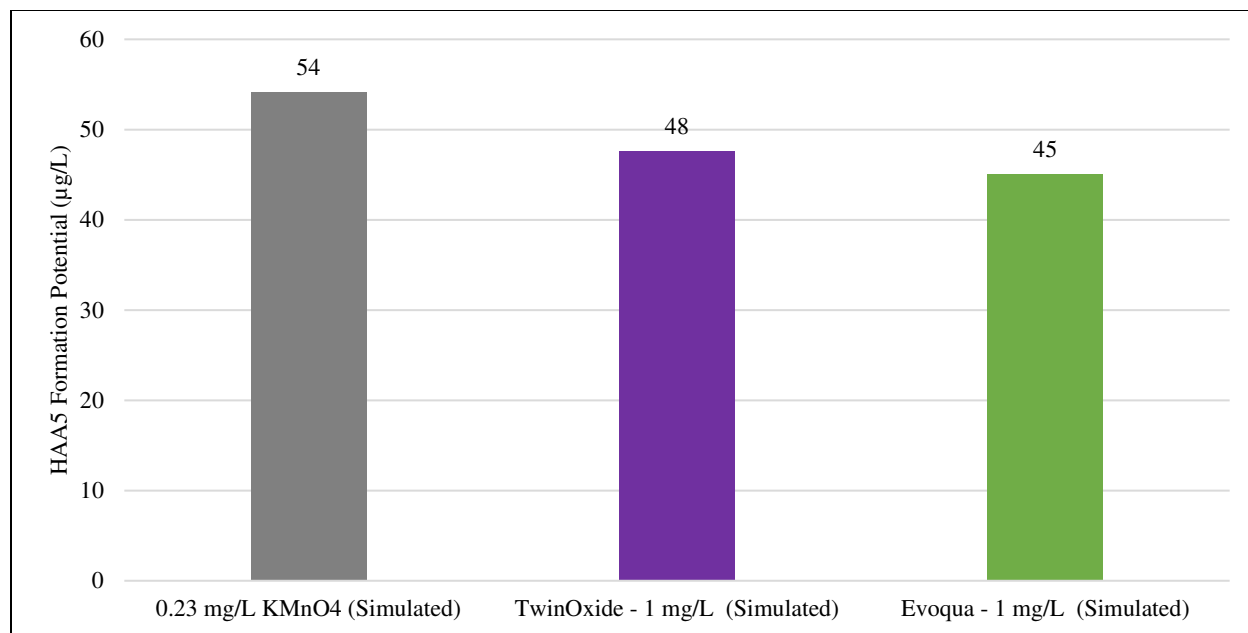
**Figure 5-5: Average HAA5 (168-hr) Formation Potential Comparison**

*Chlorite and Chlorate Formation Considerations*

Initially, the TwinOxide® solution contained about 4000 mg/L and over a month the solution decayed to 1500 mg/L of $ClO_2$. The half-life of the solution was estimated at 10 days. Both TwinOxide® and Evoqua® chlorine dioxide solutions dissociated into chlorite ($ClO_2^-$) and chlorate ($ClO_3^-$) ions over time in waters with elevated temperature and pH. Chlorite is currently regulated with a MCL of 1.0 mg/L (USEPA, 2006). Werdehoff and Singer (1987) estimated the formation of chlorite varies between 50 to 70 percent of the initial chlorine dioxide dosage. This limits the amount of chlorine dioxide dosage to remain below the chlorite MCL. To determine general formation of chlorite and chlorate, data from both TwinOxide® and Evoqua® chlorine dioxide solutions were combined. Figure 5-6 and Figure 5-7 display the chlorite and chlorate formation, respectively. From the best fit linear trendline, chlorite and chlorate formed at approximately 68 percent and 5 percent of the initial chlorine dioxide dosage, respectively.

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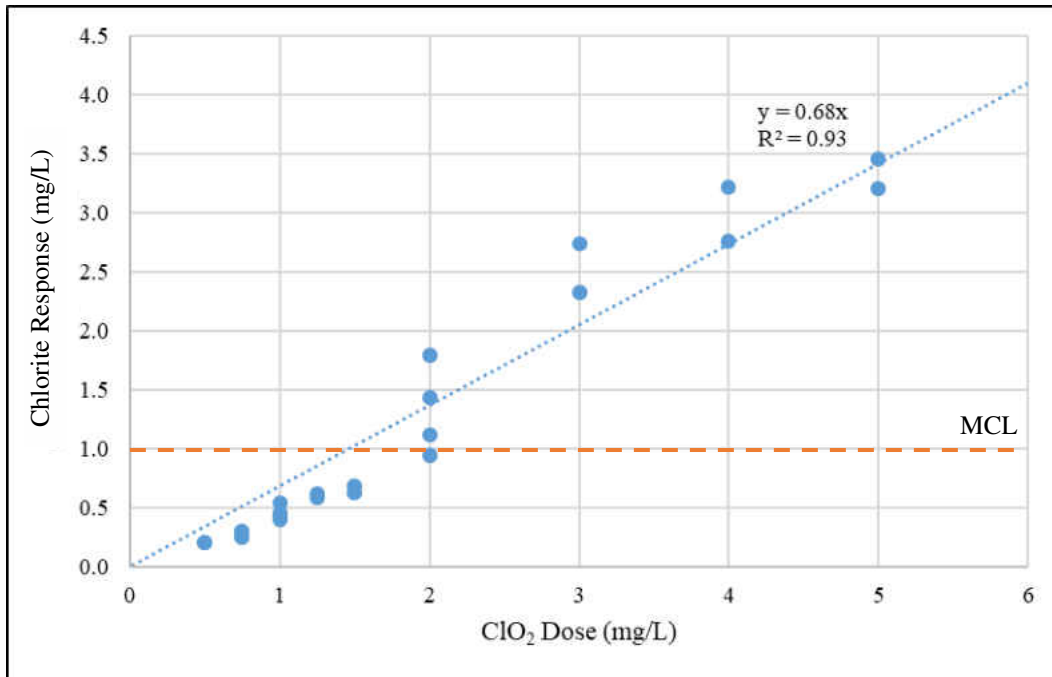
**Figure 5-6: Formation of Chlorite w.r.t. ClO$_2$ Dosage**
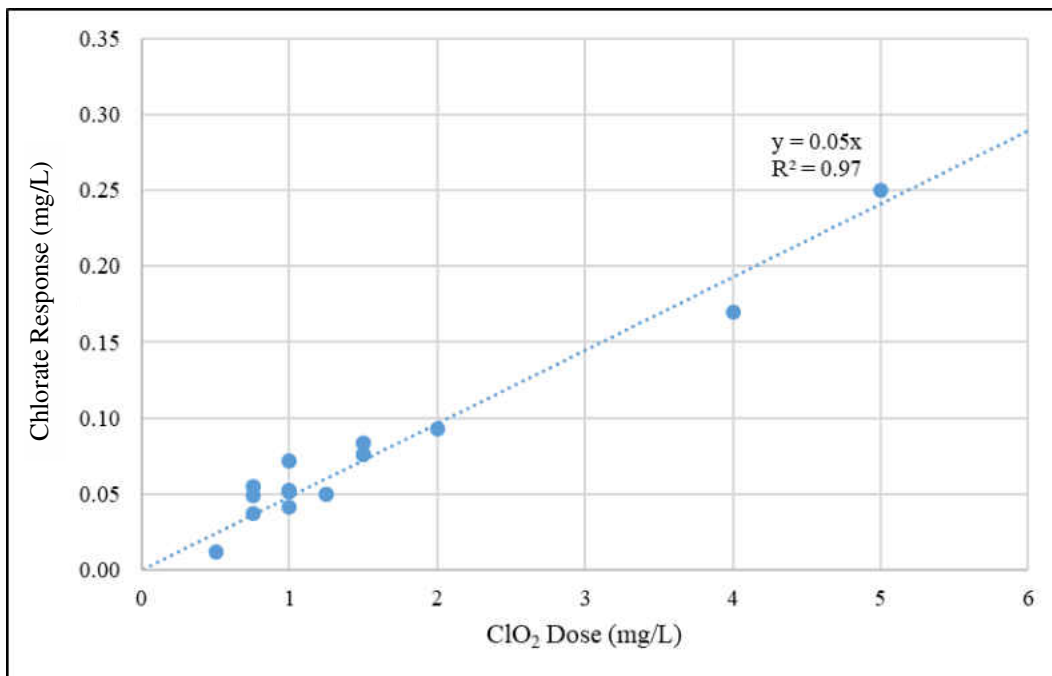


**Figure 5-7: Formation of Chlorate w.r.t. ClO$_2$ Dosage**

Chlorine dioxide's effect on free chlorine residual after disinfection was also examined. In general, pretreatment with chlorine dioxide experimentally held a higher residual throughout the 168-hr test duration. The USEPA set a minimum residual level (MRL) for chlorine at 0.2 mg/L as $Cl_2$. During distribution system screenings, free chlorine readings below the MRL occurred at several points. Assuming the chlorine type and dosage during disinfection remained constant, the use of chlorine dioxide as a pretreatment oxidant could aid in free chlorine residuals in the distribution system. Results of the simulated chlorine residual decay is plotted on Figure 5-8.
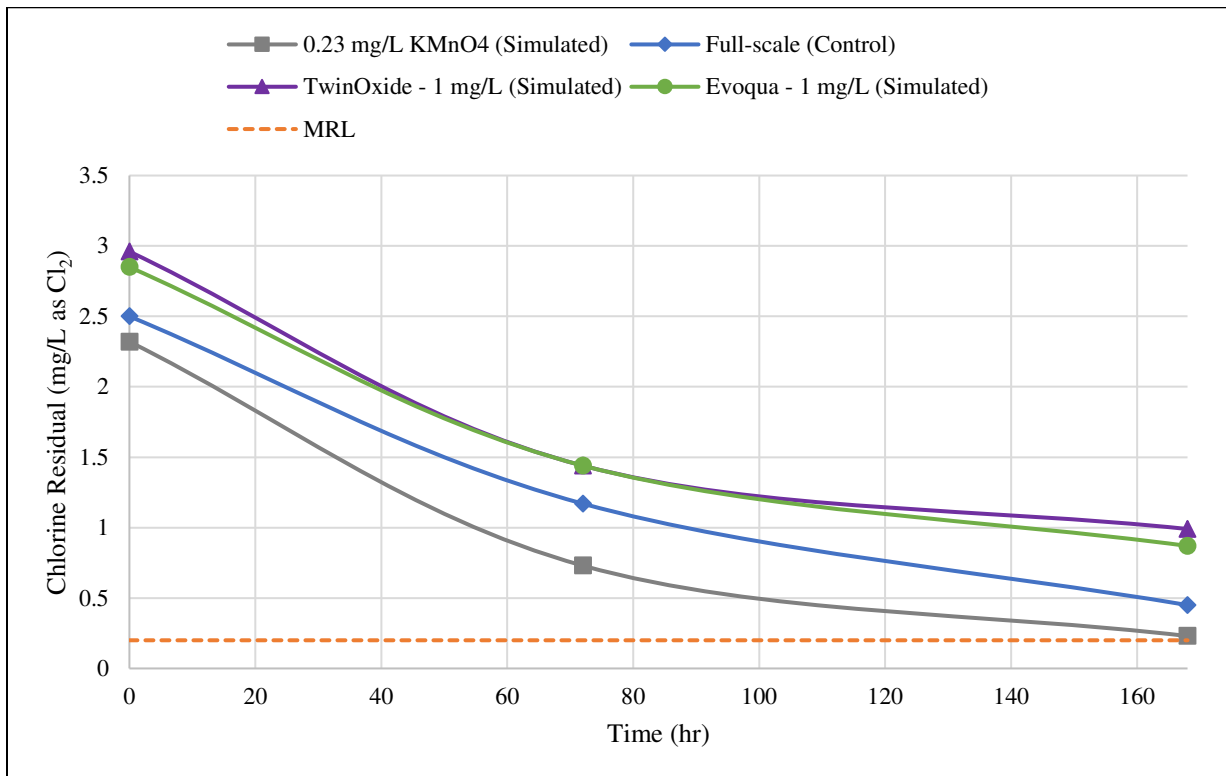


**Figure 5-8: Chlorine Residual Decay Curves ($ClO_2$, $KMnO_4$, and Control Conditions)**

## Turbidity, Color, Iron, and Manganese Removal Considerations

Chlorine dioxide was compared directly with potassium permanganate for turbidity, color, iron, and manganese removal. To test multiple raw water conditions, jar tests were performed using average raw water collected form Ocmulgee River and simulated "peak" raw water. The "peak" condition was defined at the peak historical recordings for turbidity, iron, and manganese as provided by the Authority staff and were 125 NTU, 1.15 mg/L, and 1.25 mg/L, respectively. Average conditions were defined as water with turbidity, iron, and manganese concentrations of approximately 10 NTU, 0.2 mg/L, and 0.02 mg/L, respectively.

Overall, both chlorine dioxide solutions (TwinOxide® and Evoqua®) matched or outperformed simulated treatment with potassium permanganate. Turbidity removal examined for average and peak conditions is provided in Figure 5-9. Under peak and average conditions, true color reduction is depicted in Figure 5-10. Throughout the study, jars supplied with tested oxidants for pretreatment removed detectable iron for both average and peak conditions. Under average conditions, detectable manganese was removed, assuming potassium permanganate was dosed using stoichiometric ratios. Stoichiometric addition of potassium permanganate was vital to avoid over-dosing; over-dosing allowed excess manganese supplied by potassium permanganate to be read in finished water. For peak conditions, 3.2 mg/L of potassium permanganate was required to achieve the maximum removal of iron and manganese (greater than 99%). For chlorine dioxide, 4.0 mg/L (as $ClO_2$) of either TwinOxide® or Evoqua® chlorine dioxide solution was required to remove (greater than 99%) detectable iron and manganese.
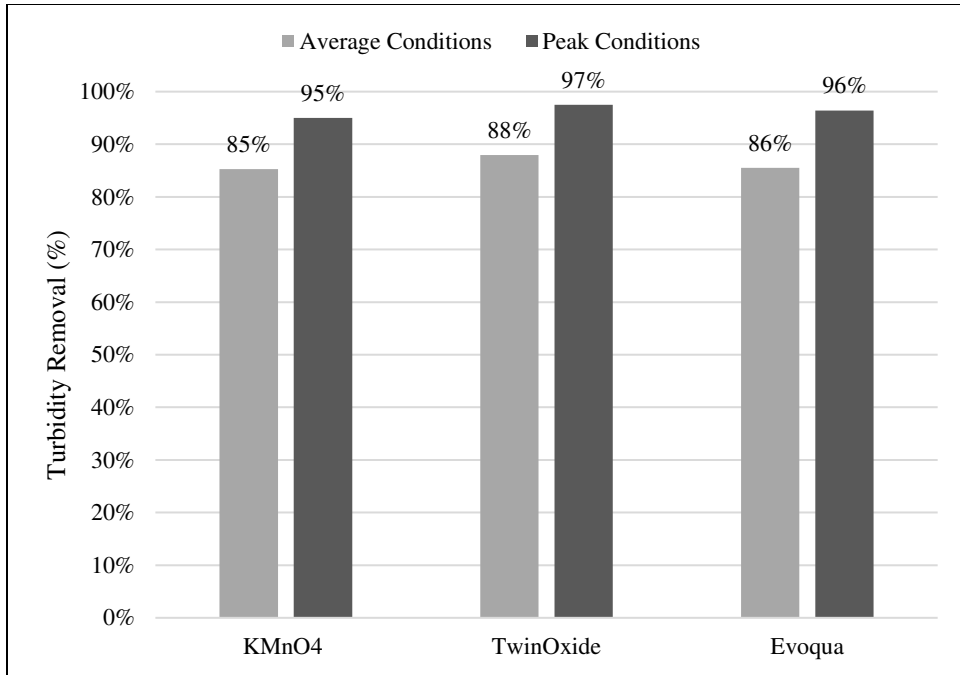
**Figure 5-9: Average and Peak Conditions Turbidity Removal**
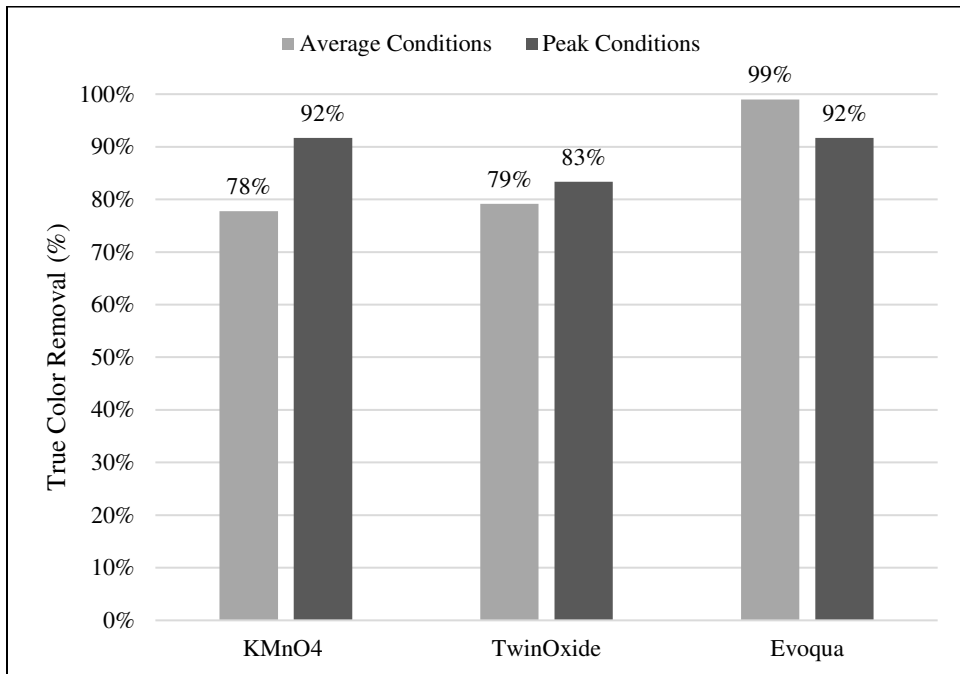


**Figure 5-10: Average and Peak Conditions True Color Removal**

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## Field and Laboratory Quality Control

Both field and laboratory water collection and analysis were completed in strict accordance with Standard Methods (Baird et al., 2017) and the USEPA's *Methods for Chemical Analysis of Water and Wastewater* (Kopp and McKee, 1983). Prior to final collection, bottles and caps were primed with the sample to avoid contaminating samples with residue from the cleaning procedure or other contaminants. For consistent priming, roughly a quarter of the sampling container was filled, capped, and inverted to allow sample to prime interior surfaces including the cap. Samples containing volatile compounds (e.g., TTHMs) were filled to eliminate headspace to avoid aeration or constituent volatilization using appropriate sample containers and collection methods. TTHMs samples were inverted and agitated to check if any air gap or bubbles were present. If present, recapping would occur to best reduce the excess air.

Samples were analyzed within appropriate holding times in accordance to Standard Methods and USEPA guidelines. Procedures for sample collection, storage, preservation, and transportation were established based on the recommendations found in Standard Methods. Methods for analytical testing of water samples were supplied by the appropriate portions of USEPA's *Handbook of Analytical Quality Control in Water and Wastewater Laboratories* (USEPA, 1979a) and Standard Methods. Where applicable, precision and accuracy measurements were made with TTHMs, DOC, and turbidity analysis to constantly and routinely monitor and assess the quality of the data collected throughout the study.

*Accuracy*

Accuracy evaluation encompasses the use of spikes or known reference samples. A minimum of 20 percent of the samples, or at least one sample per day (whichever is greater) were spiked for the analytes being tested. Percent recovery (%R) measured the accuracy of a machine to detect the response of the spike and is calculated using Equation (5-1):

$$\%R = \frac{A-B}{C} \times 100$$ (5-1)

Where:     *%R* = percent recovery (%)

               *A* = response of spiked sample (mg/L)

               *B* = response of unspiked sample (mg/L)

               *C* = amount of known spike (mg/L)

Accuracy was assessed by plotting each spike response on the y-axis of the accuracy control chart. In addition to the percent recovery obtained for each individual spike, the warning and control limits were plotted for the same time period. These are abbreviated in the table's legend as UWL and UCL (for upper warning limit and upper control limit, respectively) and LWL and LCL (for lower warning limit, and lower control unit, respectively). Warning limits are set at two standard deviations above and below the expected value or average of the first 20 points. Control limits are set at three standard deviations above and below the average, again for the first 20 points. The calculations for warning limits and control limits are shown in Equations (5-2) and (5-3), respectively. Figure 5-11 displays the accuracy control chart for DOC (SM: 5310 C). The accuracy control chart for TTHMs analysis (SM: 6232 B) is presented as Figure 5-12.

$$WL = \bar{R} \mp 2S \tag{5-2}$$

$$CL = \bar{R} \mp 3S \tag{5-3}$$

Where:        $WL$ = warning limit

                    $CL$ = control limit

                    $\bar{R}$ = average recovery of the first 20 points

                    $S$ = standard deviation

A violation of accuracy control occurs if the UCL or LCL is surpassed, two successive points are outside of the warning limits, systematic trend over time is observed, or seven successive points land above or below the expected value or mean. As seen in Figure 5-11, the UCL and LCL were not surpassed. However, one data point was outside of the warning limit. Including this single point, seven points where below the expected value. This suggests that in the beginning stages of the study possible bias was observed. This bias likely originated from aging or contaminated organic carbon stock solution used for the creation of standards and spiking solutions. If organic carbon stock became contaminated with an oxidizing agent, the standard will degrade over time. New standard was purchased to correct the issue and succeeding data points remained within accuracy control.

For TTHMs analysis, accuracy control was maintained throughout the study and upper control and lower control limits (UCL and LCL) were not surpassed. Two data points were outside of warning limits, but this was not considered a control violation because succeeding points returned to the expected value.
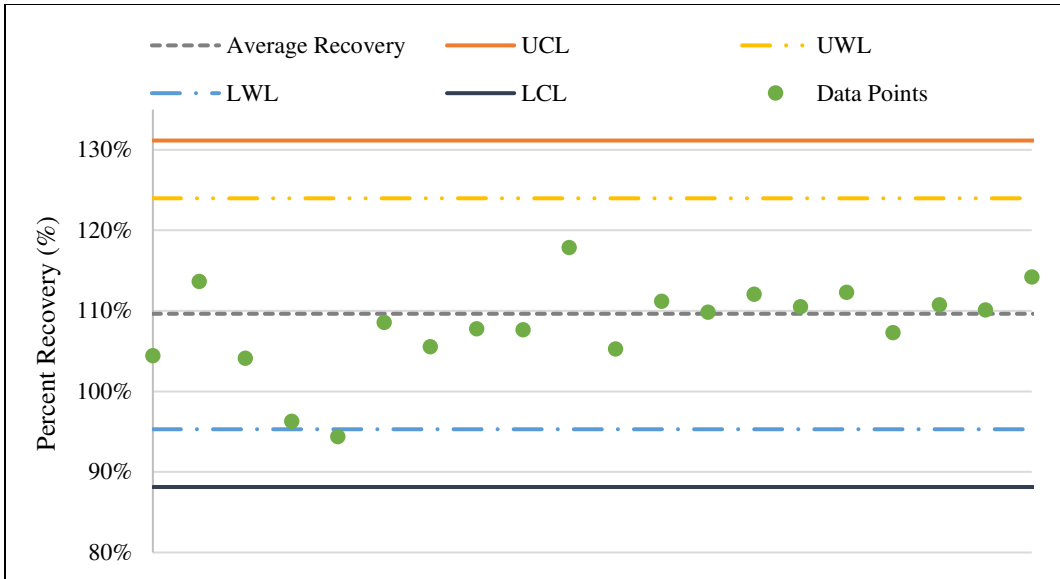
**Figure 5-11: Accuracy Control Chart for DOC**
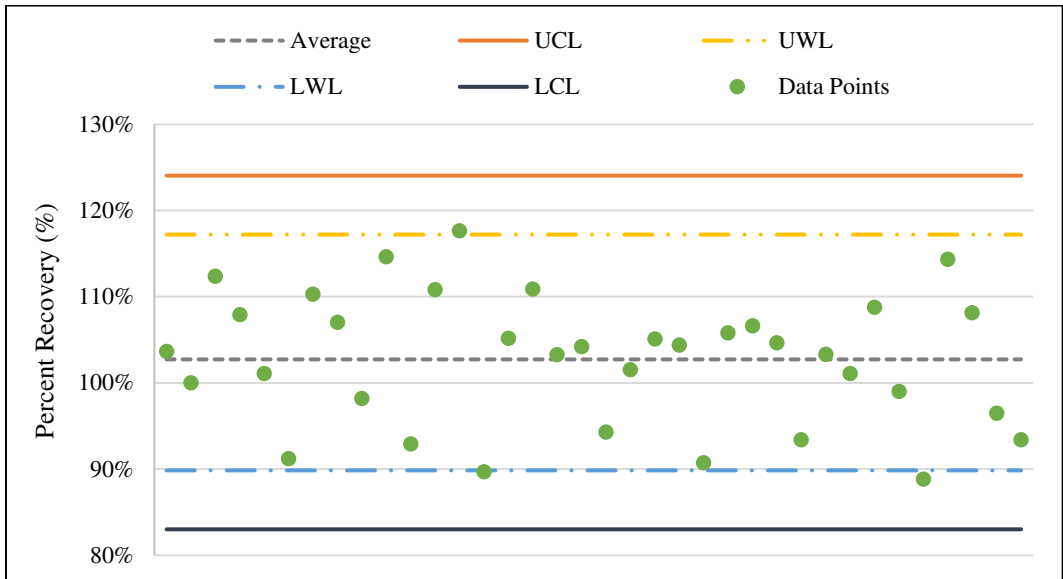


**Figure 5-12: Accuracy Control Chart for TTHMs**

*Precision*

Precision is assessed by measuring the reproducibility observed between duplicate analyses. Duplicates are two determinations of the same analyte for the same sample made by repeating the analytical procedure in its entirety. Precision can also measure the amount of variability in the sample during collection with respect to time. Precision is expressed either as relative percent difference (RPD) or the industrial statistic (I-stat) for each pair of analyses and is calculated by Equations (5-4) and (5-5), respectively. Both RPD and I-stat are presented herein and are measured with regard to the warning and control limits. Precision control charts of RPD and I-stat versus sample number (chronologically) are to be used to aid the interpretation. Figure 5-13 displays the precision control chart for DOC in terms of RPD. Figure 5-14 and Figure 5-15 presents the precision control charts for turbidity in terms of RPD and I-stat, respectively. The precision control chart for TTHMs analysis using Standard Method 6232 B: Liquid-Liquid Extraction Gas Chromatographic is presented as Figure 5-16.

$$RPD = \frac{|S_o - S_D|}{\left(\frac{S_o + S_D}{2}\right)} \times 100 \tag{5-4}$$

$$I\text{-}stat = \left|\frac{S_o - S_D}{S_o + S_D}\right| \tag{5-5}$$

Where:     $RPD$ = relative percent difference (%)

$S_o$ = sample concentration (mg/L)

$S_D$ = duplicated sample

Violations of precision control occurs if a single data point surpasses the CL, two successive points violate the WL, or if a systematic trend over time is observed. For DOC and turbidity, the CL was not surpassed. As seen in Figure 5-13, two successive points violated the WL. Thus, a precision control violation occurred. Following the control violation, data points remained under the WL and did not appear to follow a systematic trend. Thus, DOC returned to precision control after the only violation observed. This precision control violation was likely caused by random error either during collection, jar testing, or DOC analysis. Figure 5-14 and Figure 5-15 illustrate the precision control charts for turbidity using RPD and I-stat, respectively. No precision control violations were observed in either control chart. Thus, precision control was maintained for DOC and turbidity analysis. Concerning TTHM precision control, the CL was not surpassed. As seen in Figure 5-16, a single point surpassed the warning limit. However, successive points returned to the expected value, thus TTHMs precision control was maintained throughout the duration of the study.
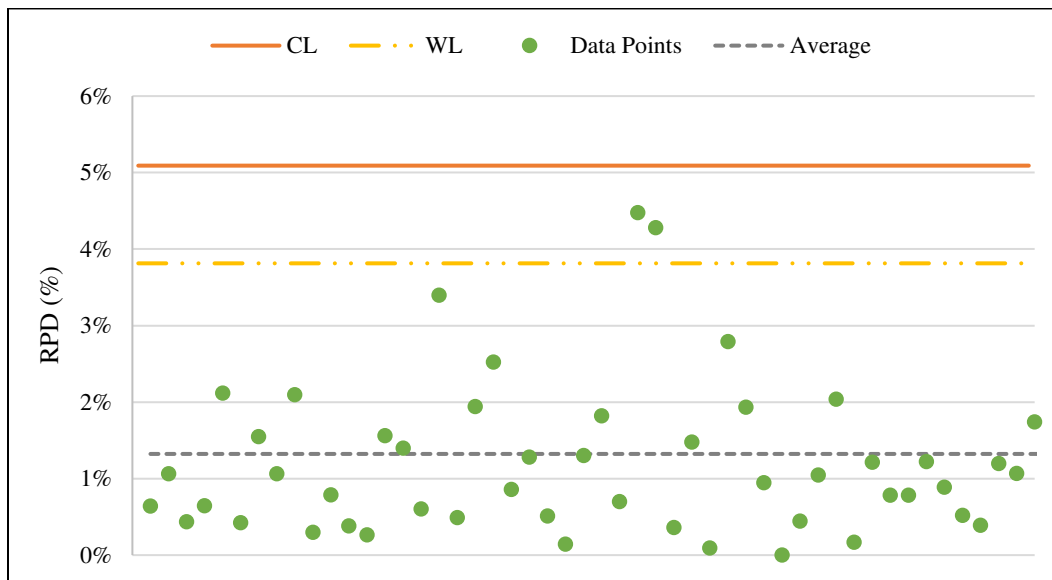


**Figure 5-13: Precision Control Chart (RPD) for DOC**
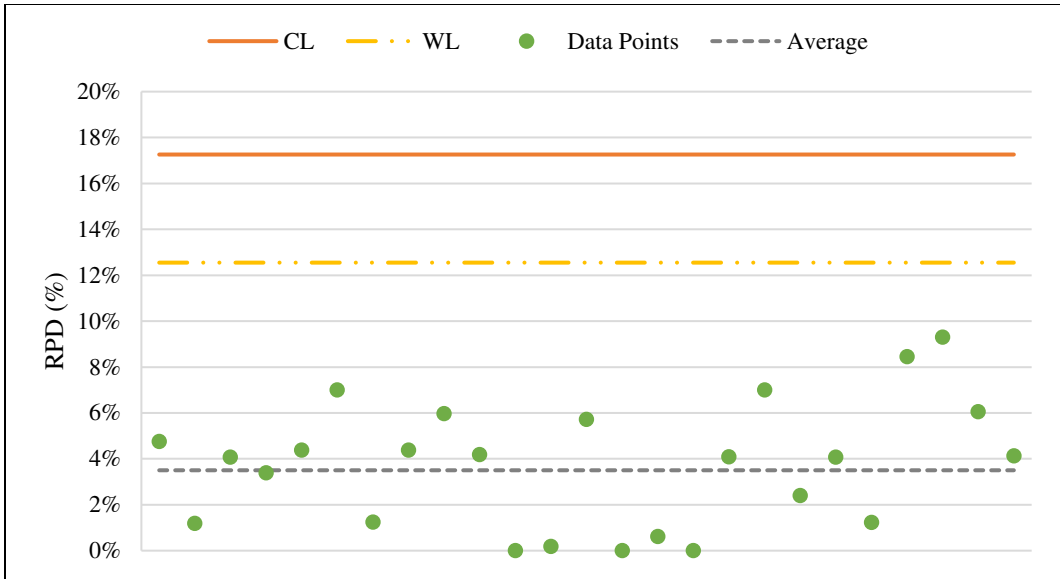
**Figure 5-14: Precision Control Chart (RPD) for Turbidity**



**Figure 5-15: Precision Control Chart (I-stat) for Turbidity**
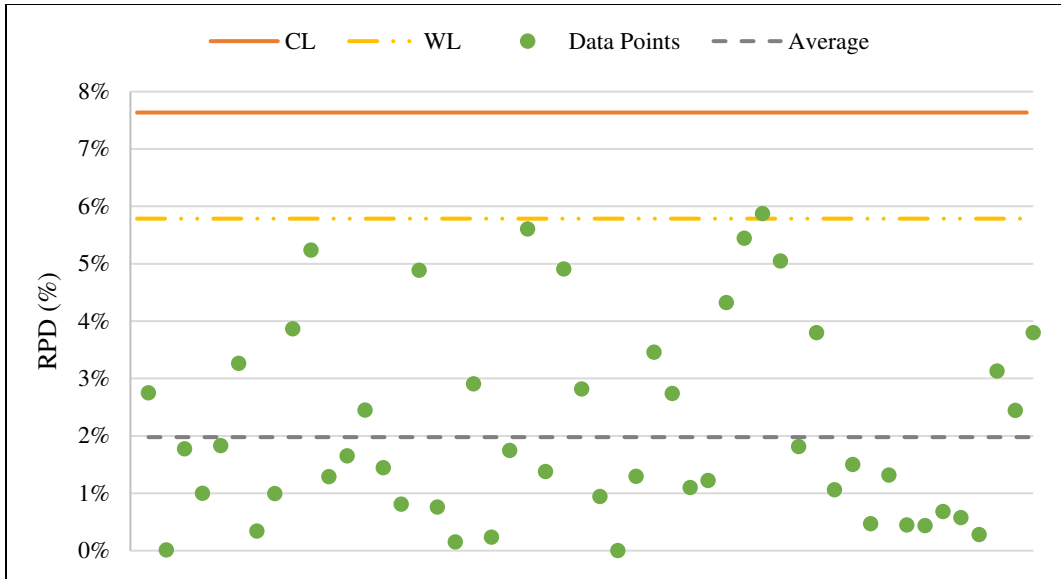
**Figure 5-16: Precision Control Chart for TTHMs**

# CHAPTER 6 : CONCLUSIONS AND SUMMARY

This research examined opportunities for alternative oxidation and modified coagulation process operations to achieve additional reduction of natural organic matter (NOM) within a conventional surface water treatment plant. Jar tests were performed to quantify the current removal of turbidity and organics within a 4.0 million gallon per day (MGD) conventional surficial water treatment plant (WTP). Chlorine dioxide ($ClO_2$) was compared against potassium permanganate for pretreatment. Treatment effectiveness was measured by comparing oxidation and the removal of iron and manganese and its potential to reduce disinfection by-products from forming in the distribution system. The conclusions listed herein are based on research conducted as reflected by the site conditions present at the time of sampling and experimentation:

- The Emerson L. Burford WTP is currently optimized for turbidity removal yet has an opportunity for greater non-purgeable dissolved organic carbon (DOC) removal. Based on the isopleth data reported herein, Burford WTP is currently operating with approximately 90 percent turbidity removal and 35 percent DOC reduction, respectively. Depressing pH towards 5.5 and dosing alum at 30 mg/L may yield up to 50 percent DOC removal while maintaining similar turbidity removal. Reducing or removing soda ash injection prior to ClariCone® solids contact unit could decrease the operating pH and provide greater DOC removal.

- Pretreatment with $ClO_2$ at Burford WTP provides an opportunity to enhance DBP reduction beyond that experienced by the Authority under existing conditions. Bench-scale experimentation with jar tests indicate 20 to 40 percent reduction of total trihalomethanes

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(TTHMs) using $ClO_2$ examined across a 168-hr formation period. The 168-hr formation of haloacetic acids (HAA5) was reduced 10 to 15 percent depending on raw water characteristics and $ClO_2$ type and dosage when compared to simulated pretreatment with potassium permanganate.

- Chlorine dioxide effectively oxidized iron and manganese without providing excess manganese supplied from over-dosing. Finished jar tested water quality produced by the $ClO_2$ matched or surpassed iron and manganese removal when compared to pretreatment with potassium permanganate. Iron and manganese were removed well below the secondary maximum contaminant levels (MCLs) of 0.3 and 0.05 mg/L, respectively.

- Potassium permanganate over-dosing resulted in excess manganese in the finished water and the distribution system. Current methods (i.e., incorrect filter pore size) of measuring iron and manganese provided an over-estimation for the potassium permanganate dosage. Jar testing trials performed by the Authority staff were not conducted with adequate time for the potassium permanganate to fully oxidize dissolved iron and manganese in the raw water. Over-dosing potassium permanganate resulted in an annual average of 0.01 mg/L of manganese in Burford finished water, greater than the annual average dissolved manganese in the raw water (0.006 mg/L).

- A $ClO_2$ dosage of 1.0 mg/L on raw Ocmulgee River water did not produce chlorite in excess of the MCL. Trials conducted with both chlorine dioxide solutions determined that chlorite formed at roughly 68 percent of the $ClO_2$ dosage. Chlorate formed at about 5 percent of the chlorine dioxide dosage. From these findings, it is recommended to maintain a dosage of below 1.4 mg/L of $ClO_2$ to prevent chlorite MCL exceedance.

- While jar testing with chlorine dioxide, jars should be sealed to prevent the loss of $ClO_2$. $ClO_2$ is naturally a gas and will be stripped from solution when aerated, or mixed within a jar testing apparatus. Preliminary trials with jar testing equipment found that about 20 percent of the $ClO_2$ was lost when jars were not sealed with Parafilm®, whereas less than 5 percent of the initial $ClO_2$ dosage was lost in sealed jars.

# CHAPTER 7 : RECOMMENDATIONS

This chapter will provide recommendations based on the findings of the research. Recommendations will be primarily comprises of: (1) coagulation, flocculation, sedimentation, and filtration treatment enhancements, (2) future treatment endeavors utilizing chlorine dioxide, and (3) optimizing current dosing of potassium permanganate.

## Coagulation, Flocculation, and Sedimentation Treatment Enhancements

As reported herein, the isopleths suggest the current coagulation, flocculation, sedimentation, and filtration (CSF) treatment is optimized towards turbidity removal. Total organics, represented herein as DOC, are removed roughly 35 percent by current treatment dosing conditions. Recommendations for modifications on full-scale treatment include:

1. Reduced use of sodium carbonate (soda ash) during coagulation could provide improved pH conditions for enhanced coagulant effectiveness (aluminum sulfate, or alum). Future endeavors should explore the impact of pH on pretreatment with both potassium permanganate and chlorine dioxide prior to full-scale system changes. The effects of pH during post treatment should also be explored with respect to DBP formation and corrosion impacts.

2. Isopleths suggest increased removal of DOC could be obtained with elevated dosing of alum. From the isopleth data, jars that received 30 mg/L of alum at pH of 5.5 were able to remove 50 percent of the raw DOC. This reduction could prove beneficial for reducing TTHM formation after disinfection.

## Treatment with Chlorine Dioxide

As per the methods reported herein, UCF examined the use of chlorine dioxide for pretreatment potential replacement of the Authority's current use of potassium permanganate. The findings favor the conversion from potassium permanganate to chlorine dioxide for TTHM formation potential reduction. Chlorine dioxide was able to reduce TTHM 168-hr formation potential by 20 to 40 percent, depending on raw water characteristics and chlorine dioxide type and dosage. TTHM formation reduction was provided by chlorine dioxide's potential to oxidize organics (DBP precursor material) prior to disinfection with chlorine gas. Potassium permanganate has a limiting effect on organics that form disinfection by-products (DBPs). This technique of reducing the DBP precursors is a key treatment strategy for reducing TTHMs and haloacetic acids (HAA5). Chlorine dioxide was also able to match potassium permanganate's removal of turbidity, color, iron, and manganese for both average and peak contaminant conditions. Recommendations made to accurately dose chlorine dioxide for future full-scale treatment include:

1. Chlorine dioxide dosage calculations should be done using soluble (dissolved) iron and manganese concentrations. Soluble iron and manganese can be measured with Hach method 8008, or equivalent, after filtering with a 0.45 µm filter.

2. Chlorine dioxide stoichiometric ratios are as follows (Crittenden et al., 2012):

   a. 1 mg/L soluble iron requires 1.2 mg/L of chlorine dioxide

   b. 1 mg/L soluble manganese requires 2.5 mg/L of chlorine dioxide

   The use of Equation (7-1) is recommended to determine chlorine dioxide dosage:

$$\left(\frac{mg}{L} soluble\ Fe\right) 1.2 + \left(\frac{mg}{L} soluble\ Mn\right) 2.5 = ClO_2\ dose\ in\ \frac{mg}{L} \qquad (7\text{-}1)$$

## Optimized Treatment with Potassium Permanganate

When examining the metal content within Burford WTP's process, finished water consistently had greater levels of manganese than the raw water. Raw water was often below manganese's detection limit (< 0.001 mg/L) while Burford's point-of-entry (POE) annual average manganese was 0.01 mg/L. This observation is likely from over-dosing potassium permanganate. Recommendations towards accurately dosing potassium permanganate within the current treatment process are presented in this section.

1. Similar to calculating the dosage for chlorine dioxide, dosage calculations should be done using soluble iron and manganese concentrations.

2. Stoichiometric ratios for dosing calculations include (Crittenden et al., 2012):

   a. 1 mg/L soluble iron requires 0.94 mg/L of potassium permanganate

   b. 1 mg/L soluble manganese requires 1.92 mg/L of potassium permanganate

   The use of Equation (7-2) is recommended to determine potassium permanganate dosage:

$$\left(\frac{mg}{L} \, soluble \, Fe\right) 0.94 + \left(\frac{mg}{L} \, soluble \, Mn\right) 1.92 = KMnO_4 \, dose \, in \, mg/L \qquad \text{(7-2)}$$

3. When performing jar tests with potassium permanganate, adequate time must be given for the reagent to work. It is best practice to simulate the average hydraulic detention times of the full-scale system during jar testing.

4. Table 7-1 provides the mixing sequence for the jar tests conducted by UCF to simulate the full-scale Burford WTP.

**Table 7-1: Jar Testing Mixing Sequence**

| Process Stage | Mixing Speed and Duration | Chemical Addition |
|---|---|---|
| Pretreatment (oxidation) | 200 rpm for 15 minutes | $KMnO_4$ |
| Rapid Chemical Mix | 300 rpm for 30 seconds | Alum, PAC, pH adjustment (if used) |
| "Head Tank" Flocculation | 25 rpm for 10 minutes | None |
| "Base of Cone" Flocculation | 10 rpm for 5 minutes | Polymers |
| Sedimentation | 0 rpm for 1 hour and 30 minutes | None |

# APPENDIX A: DATA LOG SHEETS AND CHAIN OF CUSTODY

**Table A - 1: Burford WTP Field Data Collection Data Sheet**

| Location at WTP | Raw | Raw w/KMnO4 | Pre Cone Full Dose | Post Cone | Filter A | Filter Comb | POE |
|---|---|---|---|---|---|---|---|
| Sample ID | B1 | B2 | B3 | B4 | B5 | B6 | B7 |
| Sampling Time | | | | | | | |
| Turbidity (NTU) | | | | | | | |
| Turbidity Dupe | | | | | | | |
| pH | | | | | | | |
| pH Dupe | | | | | | | |
| Temp (°C) | | | | | | | |
| Temp Dupe | | | | | | | |
| Conductivity (µS/cm) | | | | | | | |
| Conductivity Dupe | | | | | | | |
| DO (mg/L) | | | | | | | |
| DO Dupe | | | | | | | |
| Free Chlorine (mg/L) | | | | | | | |
| Free Chlorine Dupe | | | | | | | |

**Table A - 2: Stewart WTP Field Data Collection Data Sheet**

| Location at WTP | Raw | Settled Pond | Settled w/KMnO4 | Full Dose | Filter Comb | POE |
|---|---|---|---|---|---|---|
| Sample ID | S1 | S2 | S3 | S4 | S5 | S6 |
| Sampling Time | | | | | | |
| Turbidity (NTU) | | | | | | |
| Turbidity Dupe | | | | | | |
| pH | | | | | | |
| pH Dupe | | | | | | |
| Temp (°C) | | | | | | |
| Temp Dupe | | | | | | |
| Conductivity (µS/cm) | | | | | | |
| Conductivity Dupe | | | | | | |
| DO (mg/L) | | | | | | |
| DO Dupe | | | | | | |
| Free Chlorine (mg/L) | | | | | | |
| Free Chlorine Dupe | | | | | | |

**Table A - 3: System Screening Data Collection Sheet**

## Water Quality Field Data Sheet

| Location | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sampling Time | | | | | | | | |
| Turbidity (NTU) | | | | | | | | |
| Turbidity Dupe | | | | | | | | |
| pH | | | | | | | | |
| pH Dupe | | | | | | | | |
| Temp | | | | | | | | |
| Temp Dupe | | | | | | | | |
| Conductivity | | | | | | | | |
| Conductivity Dupe | | | | | | | | |
| DO (mg/L) | | | | | | | | |
| DO Dupe | | | | | | | | |
| Free Chlorine (mg/L) | | | | | | | | |
| Chlorine Dupe | | | | | | | | |
| TTHM Check | | | | | | | | |
| TTHM Dupe | | | | | | | | |
| HAA Check | | | | | | | | |
| 1 L Check | | | | | | | | |

**Table A - 4: Jar Tests Data Collection Sheet**

| Test/Jar ID | Chemical Dosages (mg/L or volume) | | | | | | pH | Temp (C) | Turbidity (NTU) | True Color (PtCo) |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Oxidant (KMnO₄ – 1,000 mg/L ClO₂ – 3000 mg/L) | | Alum (stock = 645,960 mg/L) | Sulfuric Acid (stock = 0.2 N) | Polymer 2500 (stock = 120 mg/L) | Polymer 2540 (stock = 120 mg/L) | PAC (stock = 4,000 mg/L) | | | | |
| A1 | | | | | | | | | | | |
| A2 | | | | | | | | | | | |
| A3 | | | | | | | | | | | |
| A4 | | | | | | | | | | | |
| A5 | | | | | | | | | | | |
| A6 | | | | | | | | | | | |
| B1 | | | | | | | | | | | |
| B2 | | | | | | | | | | | |
| B3 | | | | | | | | | | | |
| B4 | | | | | | | | | | | |
| RAW | NA | NA | NA | NA | NA | NA | NA | | | | |

# Mixing Times/RPM

| | |
| --- | --- |
| Oxidation: | 15 mins/200 rpm |
| Rapid Mix: | 30 sec/300 rpm |
| Flocculation: | 10 mins/25 rpm and 5 mins/10 rpm |
| Sedimentation: | 1 hour and 30 mins |

**Table A - 5: UCF Drinking Water Research Chain of Custody**

| UNIVERSITY OF CENTRAL FLORIDA — DRINKING WATER RESEARCH | 12800 Pegasus Dr. Eng 2 Suite 211, Orlando, FL 32816 | CHAIN OF CUSTODY RECORD | Page 1 of 1 |
|---|---|---|---|

| PROJECT REFERENCE | PROJECT NO. | PROJECT LOCATION (STATE) | Reason for Request: |
|---|---|---|---|
| P.O. NUMBER | CLIENT PHONE | CLIENT FAX | |
| CLIENT NAME | | CLIENT EMAIL | |

CLIENT ADDRESS

| COMPANY CONTRACTING THIS WORK | SAMPLER'S SIGNATURE |
|---|---|

| SAMPLE | | SAMPLE IDENTIFICATION (If membrane please include model, position and S/N) | SAMPLE TYPE | | | | REQUIRED SERVICE (if applicable) | REMARKS (Specify any preservatives used) |
|---|---|---|---|---|---|---|---|---|
| DATE | TIME | | Chemical Reagent | Water | Filter | Other: | | |
| | | | | | | | | |
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| | | | | | | | | |
| | | | | | | | | |

| RELINQUISHED BY: (SIGNATURE) | DATE | TIME | REMARKS: |
|---|---|---|---|
| RECEIVED BY: (SIGNATURE) | DATE | TIME | REMARKS: |

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**Table A - 6: Preliminary Titrations Data Collection Sheet**

**Trial 1:**

| Water Source/Date | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Dose | | | | | | | | | | | | | | |
| Initial pH | | | | | | | | | | | | | | |
| Base (Soda Ash) Volume Added | | | | | | | | | | | | | | |
| Acid (Sulfuric Acid) Volume Added | | | | | | | | | | | | | | |
| pH adjustment | | | | | | | | | | | | | | |

**Trial 2:**

| Water Source/Date | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Dose | | | | | | | | | | | | | | |
| Initial pH | | | | | | | | | | | | | | |
| Base (Soda Ash) Volume Added | | | | | | | | | | | | | | |
| Acid (Sulfuric Acid) Volume Added | | | | | | | | | | | | | | |
| pH adjustment | | | | | | | | | | | | | | |

# APPENDIX B: JAR TEST DATA

**Table B - 1: Isopleth Jar Test Data (MATLAB Input)**

| Jar No. | Alum Dosage (mg/L) | pH | Turbidity (NTU) | Turbidity Rem (%) | DOC (mg/L) | DOC Rem (%) |
|---|---|---|---|---|---|---|
| 1 | 10 | 4.3 | 4.8 | 16 | 2.6 | 10 |
| 2 | 10 | 4.7 | 2.3 | 61 | 1.9 | 35 |
| 3 | 10 | 5 | 1.5 | 75 | 1.9 | 34 |
| 4 | 10 | 5.2 | 1.1 | 81 | 1.8 | 38 |
| 5 | 10 | 5.5 | 1.3 | 78 | 1.9 | 33 |
| 6 | 10 | 5.5 | 1.3 | 78 | 1.9 | 35 |
| 7 | 10 | 6.5 | 1.4 | 75 | 2.1 | 28 |
| 8 | 10 | 6.4 | 2.4 | 58 | 2.2 | 24 |
| 9 | 10 | 7.2 | 5.5 | 4 | 3.1 | 0 |
| 10 | 10 | 8.3 | 5.1 | 11 | 3.1 | 0 |
| 11 | Raw Water | 6.9 | 5.7 | NA | 2.9 | NA |
| 12 | 20 | 4.4 | 4.7 | 18 | 2.2 | 25 |
| 13 | 20 | 4.6 | 1 | 83 | 1.6 | 46 |
| 14 | 20 | 4.8 | 0.9 | 85 | 1.4 | 51 |
| 15 | 20 | 5.1 | 0.8 | 85 | 1.4 | 51 |
| 16 | 20 | 5.5 | 0.7 | 88 | 1.4 | 51 |
| 17 | 20 | 5.9 | 0.5 | 92 | 1.7 | 43 |
| 18 | 20 | 6.3 | 0.8 | 85 | 2.0 | 32 |
| 19 | 20 | 7.3 | 5.2 | 9 | 2.9 | 0 |
| 20 | 20 | 8.2 | 5.2 | 8 | 3.0 | 0 |
| 21 | 20 | 8.2 | 5.2 | 8 | 3.0 | 0 |
| 22 | Raw Water | 6.9 | 5.7 | NA | 2.9 | NA |
| 23 | 30 | 4.5 | 1.5 | 76 | 1.5 | 50 |
| 24 | 30 | 5 | 1.5 | 76 | 1.4 | 54 |
| 25 | 30 | 5.4 | 1.2 | 81 | 1.5 | 51 |
| 26 | 30 | 5.7 | 1 | 83 | 1.5 | 48 |
| 27 | 30 | 6.3 | 0.7 | 89 | 1.8 | 41 |
| 28 | 30 | 6.3 | 0.6 | 90 | 1.9 | 37 |
| 29 | 30 | 6.7 | 1 | 83 | 2.3 | 24 |
| 30 | 30 | 7.1 | 4.8 | 21 | 2.8 | 7 |
| 31 | 30 | 7.6 | 5.7 | 7 | 2.9 | 2 |
| 32 | 30 | 8 | 4.8 | 10 | 3.0 | 1 |
| 33 | Raw Water | 6.5 | 6.2 | NA | 3.0 | NA |
| 34 | 40 | 4.5 | 1.5 | 76 | 1.6 | 47 |
| 35 | 40 | 4.8 | 1.8 | 71 | 1.4 | 53 |
| 36 | 40 | 5.2 | 1.9 | 69 | 1.4 | 53 |

**Table B – 1 (continued)**

| Jar No. | Alum Dosage (mg/L) | pH | Turbidity (NTU) | Turbidity Rem (%) | DOC (mg/L) | DOC Rem (%) |
|---|---|---|---|---|---|---|
| 37 | 40 | 5.5 | 1.3 | 79 | 1.4 | 52 |
| 38 | 40 | 5.9 | 0.6 | 90 | 1.5 | 48 |
| 39 | 40 | 6 | 0.5 | 92 | 1.6 | 45 |
| 40 | 40 | 6.5 | 0.7 | 89 | 2.0 | 33 |
| 41 | 40 | 6.8 | 0.9 | 86 | 2.4 | 19 |
| 42 | 40 | 7.3 | 5.5 | 10 | 2.7 | 8 |
| 43 | 40 | 8 | 5.9 | 4 | 3.0 | 1 |
| 44 | Raw Water | 6.4 | 6.2 | NA | 3.0 | NA |
| 45 | 50 | 4.5 | 1.9 | 70 | 1.6 | 51 |
| 46 | 50 | 4.9 | 2.4 | 62 | 1.8 | 47 |
| 47 | 50 | 5.3 | 2.2 | 65 | 1.6 | 53 |
| 48 | 50 | 6.2 | 0.5 | 93 | 1.8 | 47 |
| 49 | 50 | 6.7 | 0.4 | 93 | 1.9 | 43 |
| 50 | 50 | 6.8 | 0.5 | 92 | 2.2 | 34 |
| 51 | 50 | 7.1 | 0.4 | 93 | 2.4 | 29 |
| 52 | 50 | 7.3 | 0.6 | 91 | 2.5 | 24 |
| 53 | 50 | 7.6 | 2.1 | 66 | 3.0 | 10 |
| 54 | 50 | 8 | 5.1 | 18 | 3.0 | 9 |
| 55 | Raw Water | 6.5 | 6.2 | NA | 3.3 | NA |
| 56 | 60 | 4.5 | 1.9 | 70 | 1.6 | 51 |
| 57 | 60 | 4.8 | 2.5 | 60 | 1.5 | 56 |
| 58 | 60 | 5.6 | 1.1 | 82 | 1.6 | 51 |
| 59 | 60 | 6.1 | 0.5 | 92 | 1.7 | 50 |
| 60 | 60 | 6.6 | 0.4 | 93 | 1.8 | 45 |
| 61 | 60 | 6.7 | 0.4 | 94 | 1.9 | 42 |
| 62 | 60 | 7.4 | 0.9 | 85 | 2.7 | 18 |
| 63 | 60 | 7.9 | 4.5 | 26 | 2.9 | 14 |
| 64 | 60 | 8.4 | 4.5 | 26 | 3.2 | 5 |
| 65 | 60 | 8.6 | 4.9 | 20 | 3.0 | 8 |
| 66 | Raw Water | 6.5 | 6.1 | NA | 3.3 | NA |
| 67 | 70 | 4.1 | 1.4 | 77 | 1.8 | 40 |
| 68 | 70 | 4.6 | 2.2 | 64 | 1.5 | 48 |
| 69 | 70 | 5.6 | 0.5 | 91 | 1.5 | 51 |
| 70 | 70 | 6.1 | 0.5 | 92 | 1.7 | 43 |
| 71 | 70 | 6.6 | 0.3 | 95 | 1.8 | 39 |
| 72 | 70 | 6.6 | 0.4 | 94 | 1.9 | 36 |
| 73 | 70 | 7.1 | 0.4 | 93 | 2.3 | 23 |
| 74 | 70 | 7.9 | 2.2 | 63 | 2.8 | 4 |
| 75 | 70 | 8.3 | 5.1 | 14 | 2.9 | 1 |

**Table B – 1 (continued)**

| Jar No. | Alum Dosage (mg/L) | pH | Turbidity (NTU) | Turbidity Rem (%) | DOC (mg/L) | DOC Rem (%) |
|---|---|---|---|---|---|---|
| 76 | 70 | 8.5 | 5.1 | 14 | 3.0 | 0 |
| 77 | Raw Water | 6.8 | 5.9 | NA | 3.0 | NA |
| 78 | 80 | 4.5 | 3.1 | 71 | 2.2 | 39 |
| 79 | 80 | 4.8 | 4.4 | 59 | 1.8 | 50 |
| 80 | 80 | 5.3 | 4.5 | 58 | 1.5 | 57 |
| 81 | 80 | 6 | 1.6 | 85 | 1.6 | 56 |
| 82 | 80 | 6.4 | 1.2 | 89 | 1.7 | 53 |
| 83 | 80 | 6.5 | 1.1 | 90 | 1.6 | 54 |
| 84 | 80 | 7.1 | 0.6 | 95 | 1.9 | 46 |
| 85 | 80 | 7.6 | 0.5 | 95 | 2.3 | 35 |
| 86 | 80 | 8.1 | 4.9 | 54 | 2.9 | 17 |
| 87 | 80 | 8.4 | 7.2 | 33 | 3.1 | 12 |
| 88 | Raw Water | 7 | 10.7 | NA | 3.6 | NA |
| 89 | 90 | 4.5 | 2.8 | 73 | 2.0 | 42 |
| 90 | 90 | 4.7 | 4 | 61 | 1.6 | 51 |
| 91 | 90 | 4.8 | 4.3 | 58 | 1.5 | 55 |
| 92 | 90 | 5.6 | 1.7 | 84 | 1.3 | 61 |
| 93 | 90 | 6.3 | 0.8 | 92 | 1.4 | 59 |
| 94 | 90 | 6.7 | 0.7 | 93 | 1.6 | 52 |
| 95 | 90 | 7.2 | 0.5 | 95 | 2.2 | 36 |
| 96 | 90 | 7.7 | 0.7 | 93 | 2.6 | 24 |
| 97 | 90 | 8.1 | 2 | 80 | 2.9 | 14 |
| 98 | 90 | 8.4 | 4.8 | 53 | 3.1 | 8 |
| 99 | Raw Water | 7 | 10.3 | NA | 3.4 | NA |
| 100 | 100 | 4.5 | 2.5 | 76 | 2.3 | 35 |
| 101 | 100 | 4.6 | 3.8 | 63 | 2.0 | 42 |
| 102 | 100 | 5.6 | 1.8 | 83 | 1.7 | 50 |
| 103 | 100 | 5.6 | 1.8 | 83 | 1.7 | 50 |
| 104 | 100 | 6.6 | 0.6 | 94 | 1.9 | 45 |
| 105 | 100 | 6.6 | 0.6 | 94 | 1.9 | 45 |
| 106 | 100 | 7 | 0.4 | 96 | 2.0 | 41 |
| 107 | 100 | 7.5 | 0.4 | 96 | 2.4 | 30 |
| 108 | 100 | 7.5 | 0.4 | 96 | 2.4 | 30 |
| 109 | 100 | 8 | 1.4 | 87 | 2.9 | 17 |
| 110 | Raw Water | 7 | 10.3 | NA | 3.4 | NA |
| 111 | 20 | 6 | 1.4 | 89 | 2.1 | 39 |
| 112 | 40 | 5.3 | 4.4 | 65 | 1.8 | 47 |
| 113 | 40 | 5.3 | 2.5 | 80 | 1.7 | 50 |
| 114 | Raw Water | 7 | 12.7 | NA | 3.4 | NA |

**Table B - 2: Turbidity, True Color, and DOC Data from Jar Testing**

| Sample ID | Water Quality Parameter | | |
|---|---|---|---|
| | Turbidity (NTU) | True Color (Pt-Co) | DOC (mg/L) |
| Raw Ocmulgee River | 3.1 | 6 | 2.8 |
| Raw - Rep 1 | 2.9 | 3 | 3.2 |
| Raw - Rep 2 | 20 | 12 | 2.5 |
| Raw - Rep 3 | 4.8 | 17 | 2.7 |
| **Raw - Average** | **7.7** | **9.5** | **2.8** |
| $KMnO_4$ (0.23 mg/L) | 0.4 | 1 | 1.7 |
| $KMnO_4$ (0.23 mg/L) - Rep 1 | 0.4 | 1 | 1.6 |
| $KMnO_4$ (0.23 mg/L) - Rep 2 | 0.5 | 2 | 1.7 |
| **$KMnO_4$ (0.23 mg/L) - Average** | **0.5** | **1.3** | **1.7** |
| Control | 0.5 | 2.4 | 1.3 |
| Control - Rep 1 | 1.0 | < 1 | 1.9 |
| Control - Rep 2 | 0.4 | < 1 | 1.5 |
| Control - Rep 3 | 0.2 | < 1 | 1.4 |
| **Control - Average** | **0.5** | **1.4** | **1.5** |
| TwinOxide (1 mg/L) | 0.4 | 1 | 1.6 |
| TwinOxide (1 mg/L) - Rep 1 | 0.3 | 2 | 1.6 |
| TwinOxide (1 mg/L) - Rep 2 | 0.3 | 1 | 1.6 |
| TwinOxide (1 mg/L) - Rep 3 | 0.5 | 1 | - |
| **TwinOxide (1 mg/L) - Average** | **0.4** | **1.3** | **1.6** |
| Evoqua (1 mg/L) | 0.3 | < 1 | 1.9 |
| Evoqua (1 mg/L) - Rep 1 | 0.4 | < 1 | 2.0 |
| Evoqua (1 mg/L) - Rep 2 | 0.5 | < 1 | 2.1 |
| Evoqua (1 mg/L) - Rep 3 | 0.4 | < 1 | - |
| **Evoqua (1 mg/L) - Average** | **0.4** | **< 1** | **2.0** |

**Table B - 3: Iron and Manganese (Average Condition) Data from Jar Testing**

| Sample ID | Average Conditions | |
|---|---|---|
| | Fe (mg/L) | Mn (mg/L) |
| Raw | 0.1 | < 0.001 |
| Raw - Rep 1 | 0.21 | 0.001 |
| Raw - Rep 2 | 0.15 | < 0.001 |
| Raw - Rep 3 | 0.12 | < 0.002 |
| **Raw - Average** | **0.15** | **0.001** |
| KMnO4 (0.23 mg/L) | < 0.01 | 0.003 |
| KMnO4 (0.23 mg/L) - Rep 1 | < 0.01 | 0.005 |
| KMnO4 (0.23 mg/L) - Rep 2 | < 0.01 | 0.004 |
| **KMnO4 (0.23 mg/L) - Average** | **< 0.01** | **0.004** |
| Control | < 0.01 | 0.020 |
| Control - Rep 1 | < 0.01 | 0.011 |
| Control - Rep 2 | < 0.01 | 0.024 |
| Control - Rep 3 | < 0.01 | 0.016 |
| **Control - Average** | **< 0.01** | **0.018** |
| TwinOxide (1 mg/L) | < 0.01 | < 0.001 |
| TwinOxide (1 mg/L) - Rep 1 | < 0.01 | < 0.001 |
| TwinOxide (1 mg/L) - Rep 2 | < 0.01 | < 0.001 |
| TwinOxide (1 mg/L) - Rep 3 | < 0.01 | < 0.001 |
| **TwinOxide (1 mg/L) - Average** | **< 0.01** | **< 0.001** |
| Evoqua (1 mg/L) | < 0.01 | < 0.001 |
| Evoqua (1 mg/L) - Rep 1 | < 0.01 | < 0.001 |
| Evoqua (1 mg/L) - Rep 2 | < 0.01 | < 0.001 |
| Evoqua (1 mg/L) - Rep 3 | < 0.01 | < 0.001 |
| **Evoqua (1 mg/L) - Average** | **< 0.01** | **< 0.001** |

**Table B - 4: Iron and Manganese (Peak Condition) Data from Jar Testing**

| Sample ID | Peak Conditions | |
|---|---|---|
| | Fe (mg/L) | Mn (mg/L) |
| Simulated Raw (Spiked) | 1 | 1.2 |
| KMnO4 (3.48 mg/L) | < 0.01 | 0.005 |
| KMnO4 (3.48 mg/L) - Rep 1 | < 0.01 | 0.004 |
| KMnO4 (3.48 mg/L) - Average | < 0.01 | 0.004 |
| KMnO4 (3.19 mg/L) | < 0.01 | 0.003 |
| KMnO4 (3.19 mg/L) - Rep 1 | < 0.01 | 0.002 |
| KMnO4 (3.19 mg/L) - Average | < 0.01 | 0.003 |
| TwinOxide (4.0 mg/L) | < 0.01 | < 0.001 |
| Evoqua (4.0 mg/L) | < 0.01 | < 0.001 |

# APPENDIX C: DISINFECTION BY-PRODUCTS DATA (TTHM, HAA5, CHLORITE, AND CHLORATE)

**Table C - 1: Free Chlorine Residual Decay and TTHMs Formation Data**

| Pre-oxidant | Hours After Disinfection | Chlorine Residual (mg/L as Cl2) | Chloroform (µg/L) | Bromodichloro-methane (µg/L) | Dibromochloro-methane (µg/L) | Bromoform (µg/L) | TTHM. (µg/L) |
|---|---|---|---|---|---|---|---|
| KMnO$_4$ 0.23 mg/L | 0 | 2.3 | 7.2 | 0.5 | < 1 | < 1 | 9.2 |
| | 72 | 0.7 | 62.6 | 15.8 | 3.9 | < 1 | 83.3 |
| | 168 | 0.2 | 78.4 | 19.4 | 4.4 | < 1 | 103 |
| Control | 0 | 2.5 | 5.0 | 0.4 | < 1 | < 1 | 6.9 |
| | 72 | 1.2 | 52.7 | 14.2 | 3.4 | < 1 | 71.3 |
| | 168 | 0.5 | 72.9 | 17.2 | 3.7 | < 1 | 97.6 |
| TwinOxide 1.0 mg/L | 0 | 3.0 | 5.0 | 1.4 | < 1 | < 1 | 7.7 |
| | 48 | - | 33.7 | 14.2 | 5.2 | < 1 | 54.1 |
| | 72 | 1.7 | - | - | - | - | - |
| | 168 | 1.1 | 53.0 | 17.4 | 5.8 | < 1 | 77.2 |
| Evoqua 1.0 mg/L | 0 | 2.9 | 2.0 | 0.5 | < 1 | < 1 | 4.0 |
| | 72 | 1.4 | 39.5 | 10.3 | 3.0 | < 1 | 53.8 |
| | 168 | 0.9 | 50.2 | 11.0 | 2.8 | < 1 | 65.0 |
| TwinOxide 1.5 mg/L | 0 | 2.7 | 5.0 | 1.5 | 0.3 | < 1 | 7.8 |
| | 48 | 1.4 | 30.1 | 12.7 | 5.1 | < 1 | 48.9 |
| | 168 | 0.6 | 51.3 | 17.3 | 6.3 | < 1 | 75.9 |
| Evoqua 1.5 mg/L | 0 | 2.9 | 2.0 | 0.5 | < 1 | < 1 | 4.0 |
| | 72 | 1.7 | 38.8 | 7.7 | 2.0 | < 1 | 49.5 |
| | 168 | 0.9 | 56.1 | 10.8 | 2.5 | < 1 | 70.4 |

**Table C - 2: Total Haloacetic Acids (HAA5) Data**

| Pre-oxidant | Bromoacetic Acid (µg/L) | Chloroacetic Acid (µg/L) | Dibromoacetic Acid (µg/L) | Dichloroacetic Acid (µg/L) | Trichloroacetic Acid (µg/L) | HAA5 (µg/L) |
|---|---|---|---|---|---|---|
| KMnO₄ 0.23 mg/L | 0.55 | 5.7 | 1.2 | 29.2 | 18.1 | 54.7 |
| | 0.54 | 5.2 | 1.2 | 28.4 | 18.2 | 53.0 |
| TwinOxide 1.0 mg/L | 0.54 | 5.7 | 1.7 | 25.5 | 13.1 | 45.9 |
| | 0.54 | 6.0 | 1.8 | 28.8 | 12.7 | 49.3 |
| Evoqua 1.0 mg/L | 1.21 | 3.6 | 1.5 | 26.8 | 13.7 | 45.1 |
| TwinOxide 1.5 mg/L | 0.54 | 5.6 | 2.0 | 24.3 | 10.6 | 42.4 |
| | 0.56 | 3.6 | 2.2 | 25.5 | 9.9 | 41.8 |
| Evoqua 1.5 mg/L | 0.74 | 3.6 | 1.9 | 31.1 | 12.0 | 51.0 |

**Table C - 3: Chlorite and Chlorate Formation w.r.t. $ClO_2$ Dosage**

| $ClO_2$ Solution Provider | Chlorine Dioxide Dosage | Average Chlorite (mg/L) | Average Chlorate (mg/L) |
|---|---|---|---|
| | 0.50 | 0.20 | 0.01 |
| | 0.75 | 0.28 | 0.05 |
| | 0.75 | 0.27 | 0.05 |
| | 1.0 | 0.50 | 0.06 |
| | 1.0 | 0.42 | 0.05 |
| | 1.25 | 0.60 | 0.05 |
| TwinOxide® | 1.5 | 0.65 | 0.08 |
| | 2.0 | 1.0 | 0.09 |
| | 2.0 | 1.8 | - |
| | 3.0 | 2.7 | - |
| | 4.0 | 3.2 | - |
| | 5.0 | 3.5 | - |
| | 2.0 | 1.4 | - |
| | 3.0 | 2.3 | - |
| Evoqua® | 4.0 | 2.8 | 0.17 |
| | 5.0 | 3.2 | 0.25 |

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